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DEDICATION

The progress of the North Dakota Academy of Science has been guided by many prominent men and women in the area of science. It is by the dedicated efforts of these people that the Academy today has reached a position of recognition in the scientific community. It is therefore proper that this edition of the Proceedings shall be dedicated to the memory of two gentlemen whose scholarly achievements and administrative abilities have advanced the cause of our Academy. Dr. Ralph E. Dunbar and Dr. A. Rodger Denison will always be remembered for their friendliness and their untiring and unselfish efforts in the tasks to be performed.

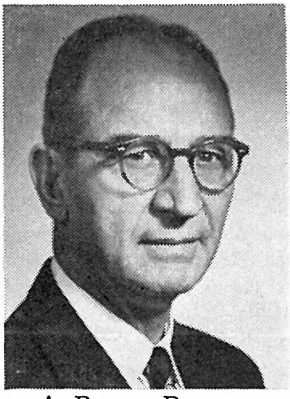
Dr. Ralph E. Dunbar was Dean of the School of Chemical Technology, North Dakota State University, Fargo, North Dakota at the time of his death. He is survived by his wife and two daughters. He received his B.S. from Dakota Wesleyan University, 1921; M.A., Columbia University, 1926; Ph.D., University of Wisconsin, 1934. Dr. Dunbar began his career as an educator in high school chemistry teaching 1921-1925; advanced to college teaching, Dakota Wesleyan University 1925-1936, Iowa State University 1936-1937, North Dakota State University, professor of chemistry 1937-1943, Dean 1943-1961.

RALPH E. DUNBAR
(1895-1960)

His research activities included studies in acetals, dehydrogenations, catalysis, reaction mechanisms and chemistry of plastics. He has published 147 scientific articles and authored six text books. He held membership in many scientific, professional and local societies and clubs. He was honored by being listed with many of the groups such as "Who's Who in America, American Men of Science, Who's Who in North Dakota, Blue Book, etc." As a true friend and inspiring lecturer, he was esteemed and admired by his students and colleagues. The Dunbar Award established by the Academy in honor of Dr. Dunbar is an award that is given annually to a talented North Dakota high school student who is doing outstanding work in an area of science. The student is selected at the North Dakota Science Fair and presents his paper at the annual meeting of the Academy.

Dr. A. Rodger Denison, world prominent petroleum geologist, and his wife were among the fatalities resulting from an airliner crash at Honolulu airport on July 22, 1962. They are survived by a son and a daughter. Dr. Denison received his B.S. degree in Geology from the University of Oklahoma in 1921. He taught one year at his alma mater before entering the services of Amerado Petroleum

Corporation as a geologist. In 1925 he took a leave of absence to continue his graduate work and was awarded a M.S. in Geology that spring from the University of Oklahoma. He returned to Amerado as District Geologist. In 1927 he was appointed Division Geologist and in 1937 Chief Geologist. He was elected Vice-Presdent in 1950. The South Dakota School of Mines and Technology awarded his an honorary degree of Doctor of Science in 1952 in view of his impressive contributions to the science of geology in education as well as in application to industry. He has authored 16 publications on the geological problems of oil production. He received many distinguished honors, was a member of many honorary societies and served the government on committees and panels pertaining to the petroleum industry. His interest in the Williston Basin with the ultimate discovery of oil in North Dakota brought him into association with the North Dakota Academy of Science.



A. RODGER DENISON
(1897-1962)

As a member of this organization, and because of his interest in promoting its growth and achievements, he established the Denison Awards as a means of stimulating student interest and participation in research. These awards are given to three college students who present the best papers on scientific research at the Academy's annual meeting. The Academy membership is indeed grateful to Dr. Denison for his inspiring influence. Likewise, the industry is deeply appreciative of his years of notable service, and the geological profession has been enriched by his contributions.

It is gratifying that continued support for these awards for succeeding years has been assured. The Dunbar Award is financed by contributions from a member of the Academy. Funds for continuation of the Denison Awards were secured from the E. I. Dupont de Nemours Company and the Red River Valley Section of the American Chemical Society. The Academy extends sincere thanks to this individual and these organizations for their kind cooperation. It is through such effort that the progress and achievements of the Academy can be maintained. This is evidenced by the number and the high standard of the papers appearing in the Proceedings.

Respectfully,

C. A. Wardner

C. A. Wardner
President 1962-1963

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GAS CHROMATOGRAPH MOLECULAR WEIGHT DETERMINATION ERRORS

Kenneth W. Lau and Virgil I. Stenberg

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First Place Winner, A. Rodger Denison, Student Research Competition

Gas chromatography has developed into a useful tool for the separation of complex mixtures of organic substances. The process is relatively new, being developed mainly within the last decade. It has been known for several years that there is a fair correlation between the molecular weight of a compound and its retention time on the gas chromatograph. Limitations are also realized. If the structures are altered, i.e., isomers, and if polar groups are introduced, the retention times vary. In other words, molecular weight is only one of the factors determining the retention time of a sample.

Nevertheless if one compares the unknown sample to a set of structurally similar compounds of known retention times, the molecular weight can be determined quite accurately. Examples of this have been reported.[1]

The work to be described concerns our efforts to generalize this procedure to unknowns with (a) nothing known of their structures, (b) their approximate relative polarity known, and (c) compounds of known functional groups. The investigations thus far have consisted of (1) recording the retention times of various molecules with different functional groups and plotting these retention times against their respective molecular weights, and (2) evaluating the maximum error in the prediction of molecular weights from a determined retention time.

Figure 1 summarizes the data from various homologous series. The gas chromatograph conditions have been standardized to have an elution flow of 65 ml/min and the temperature of 70 degrees. Upon scrutiny of this table one can see that, in general, the non-polar compounds have smaller retention times than the polar compounds and that certain compounds which have an excessive weight of inorganic substituents give abnormally short retention times. For the present study the latter group will be excluded. If one had no preconceived ideas about the structure of the unknown, it is seen in figure 2 that the maximum error in a prediction of the unknown's molecular weight would be 48%; therefore dimeric forms could easily be distinguished. It is further seen that the greatest error occurs with

[1]Robert L. Pecsok, Editor; "Principles and Practice of Gas Chromatography"; John Wiley & Sons, Inc., 1959.

retention times around 200 seconds, on the inflection part of the curve, while the least error occurs with retention times around 1,200 seconds.

If one were to estimate the polarity of the unknown, the accuracy is measurably increased. In the case of a highly polar unknown, the maximum error in the molecular weight would be 31%. Again, the greatest error occurs on the inflection part of the curve although, in the polar compounds, the error is seen (figure 2) to go through a minimum of approximately 14% between 800-900 seconds and then rise again to 22% at 2000 seconds. That the retention times for the highly polar compounds are longer than they should be for their respective molecular weights is accounted for by their increased solubility in the adsorbent of the column, n-decyl phthalate, and by the hydrogen bonding of these molecules which, in effect, increases their molecular weight. As would be expected, the greatest deviation is found in the acids because of the known dimerization of the acids.

In the case of a less polar unknown, the maximum error is only 13%. Again, there is a slight increase in the error on the inflection part of the curve. From figure 1 it is obvious that the greatest devia-

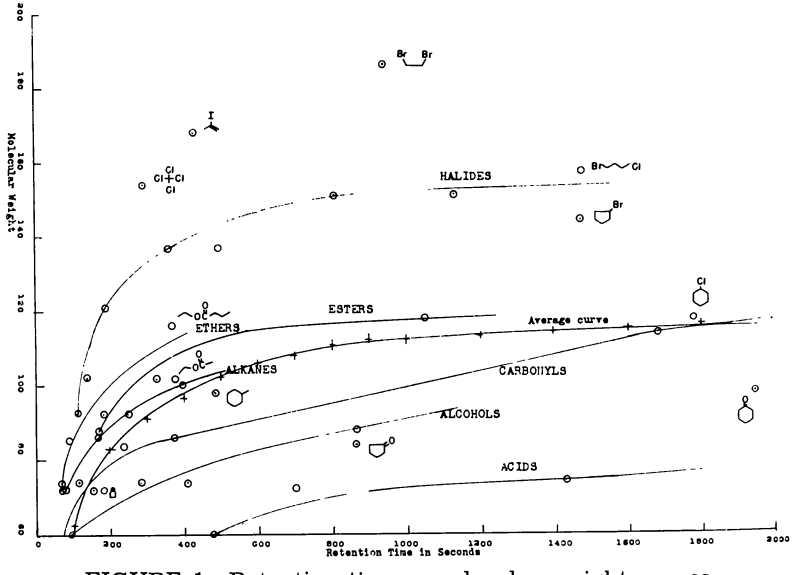

FIGURE 1—Retention time - molecular weight curves.

tion is in the halogen series. This is accounted for by the nature of the polar-covalent bond of halides which would make them less soluble in the adsorbent and force them into the vapor phase. With the equilibrium shifted to the vapor phase, the compound is swept

through the column faster, giving a molecular weight which is lower than the actual molecular weight.

If the unknown was found to contain a single functional group, and that functional group determined, the normal error would be approximately 5%. Although in the case of irregular structures, the error can range up to 27% (cyclohexyl chloride).

While the maximum errors cited in this study will hold for most compounds, there are a few structures with abnormal retention

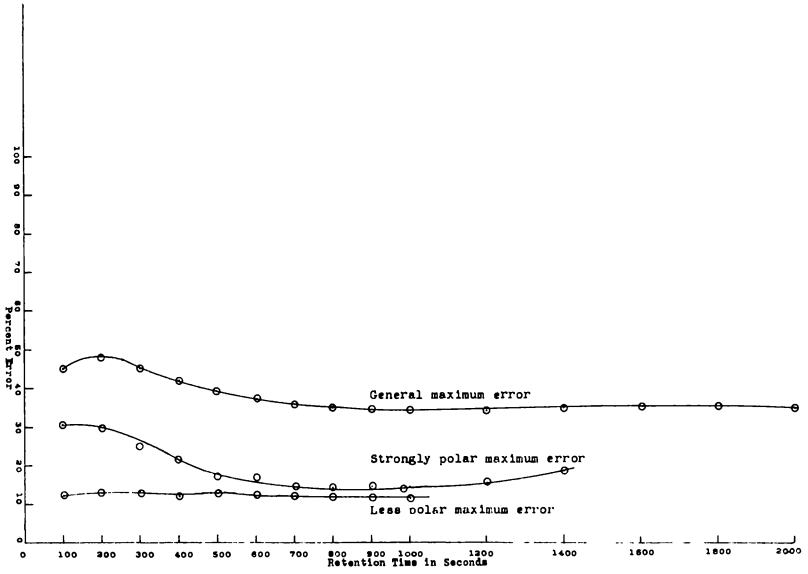

FIGURE 2 — Maximum error curves

times that would give rise to greater error. Examples of these are labeled in figure 1. The abnormal retention times are accounted for by an increased polar-covalency of their bonds, making them only slightly soluble in the adsorbent. This decreased solubility will enable them to be swept through the column even more rapidly and produce erroneous molecular weights. The cyclic structures also give erroneous molecular weights. The reason for this is not yet clear although it is noted that the smaller the ring, the closer it conforms to the normal series. Further elucidation of this anomaly awaits more data.

Although no samples of poly-functional compounds with groups such as -OH or -COOH have been investigated in this study, we expect abnormally long retention times. The main reason for this speculation is that compounds with these polar groups have longer retention times than average. One might reasonably expect that by

putting several of these groups on the same molecule, their retention would be accentuated.

This work has been done with the gas chromatograph at a constant temperature of 70 degrees. In order to make this work more complete the studies should be extended to include different column temperatures. It is not known now whether errors will be effected by changing the column temperature.

TABLE I
RETENTION TIME DATA

Compound	Retention time, Sec.	Compound	Retention time, Sec.
Acids		*Alcohols*	
acetic	475	ethyl	68
acrylic	700	isopropyl	94
propionic	1425	n-butyl	404
n-butyric	3393	isobutyl	281
isobutyric	4210	t-butyl	115
Alkanes		n-amyl	862
pentane	81	*Ethers*	
cyclohexane	241	vinyl ethyl	73
hexane	175	tetrahydrofuran	188
methylcyclohexane	490	diethyl	77
heptane	395	p-dioxane	388
Halides		n-propyl	330
methylene chloride	89	isopropyl	140
n-butyl chloride	253	*Carbonyls*	
sec-butyl chloride	185	acetaldehyde	45
t-butyl chloride	114	acetone	68
cyclohexyl chloride	1780	n-butyraldehyde	153
allyl bromide	188	cyclopentanone	863
n-butyl bromide	498	3-pentanone	378
sec-butyl bromide	360	cyclohexanone	1952
bromocyclopentane	1473	3-heptanone	1686
n-pentyl bromide	1125	4-heptanone	2760
isopentyl bromide	810	2-octanone	3760
carbon tetrachloride	293	*Esters*	
1-bromo-3-chloropropane	1480	ethyl acetate	169
2-allyl iodide	431	ethyl propionate	385
ethylene bromide	943	ethyl butyrate	377
		ethyl lactate	1052

CONCLUSIONS

1. The maximum error for a typical compound about which nothing is known ranges from 48% to 34%.
2. The error in prediction of a molecular weight is dependent upon the retention time. The least error occurs with a high retention time, i.e., in the flat part of the curve and the greatest error occurs with a low retention time, i.e., in the inflection part of the curve.

3. The error is dependent upon the functional group that the molecule contains, with the highly polar compounds giving a high molecular weight, and the less polar compounds giving a low molecular weight.

The authors wish to thank Richard Olson and Richard Ode, students in the Department of Chemistry at the Universtiy of North Dakota, for their assistance in this investigation.

EXPERIMENTAL

The instrument used in this study was a Beckman GC-2 gas chromatograph. The liquid phase of the column was n-decyl phthalate adsorbed on fire brick. The carrier gas (helium) pressure was maintained at 30 psi with an elution flow of 65 ml/min. The filament current and the column temperature were maintained at 250 ma and 70°C, respectively. The samples employed were commercial grade. The data for figure 1 are presented in table I.

DISTRIBUTION OF FISH IN THE FOREST RIVER OF NORTH DAKOTA

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Second Place Winner, A. Rodger Denison, Student Research Competition

INTRODUCTION

During the spring and fall of 1962, a study was undertaken of the fish of the Forest River, in Walsh and Grand Forks Counties, North Dakota. Specimens were obtained from several environments in nine localities along the Forest River and its tributaries. The fish were identified and a species list was drawn up noting geographic and ecologic distributions. The purpose of this work, then, was to compile as complete a list as possible of the fish inhabiting the Forest River as well as to study possible limiting effects of the Pleistocene geology of the area on the distribution of the fish in the stream.

Prior to the present study, the most comprehensive published work on the fish in this area was that of Hankinson (1929). His work was a compilation of all available data regarding distribution of fish in North Dakota. Of the 57 species he reports from North Dakota, only six, *Rhinichthys cataractae, Notropis deliciosus missouriensis, N. blennius, N. cornutus, Hadropterus maculatus,* and

Eucalia inconstans, were reported from the Forest River. Twenty-nine species were taken from the Red River, of which the Forest River is a tributary. Regarding tributaries of the Red River, adjacent to the Forest River, thirteen species were reported from the Park River, while the Turtle River was not sampled.

Subsequent work by the North Dakota Game and Fish Department has been summarized by Carufel (1958). He lists 99 species positively reported from the state, but does not deal with their distribution. In brief, no known published studies since Hankinson (1929) deal with the Forest River.

The present collection in the Biology Department of the University of North Dakota contains not only those specimens collected as part of this study but also material collected over the past several years. In many cases the localities are not listed so that their only value in this study is to increase the number of specimens available for compilation of the species list. The material from this collection for which locations have been adequately described has been incorporated into the study.

The seining equipment was made available by Dr. Robert Seabloom, Assistant Professor of Biology, University of North Dakota. Collecting techniques were demonstrated by Mr. Oscar Kalin, who also assisted greatly in identification of some of the fish, while Messrs. Kalin, Ted James, and Robert Sigsby assisted in the use of the seine.

PROCEDURE

During the initial series of collecting trips in May, 1962, collecting localities were determined primarily by degree of flooding. Downstream from the town of Forest River, Sec. 28, T. 155 N, R. 53 W., flooding was so severe that access to the stream could be gained in only three places. Above Forest River, an attempt was made to sample every area that had different stream characteristics. Seining in the fall was concentrated near the mouth of the stream.

The collections were made using a 4′ x 12′ minnow seine, sampling the entire stream width. Dip nets were also used along the banks, in weedy areas, and in areas of rapids. The material collected was identified using Eddy and Surber (1947) and Eddy (1957).

Comments on the geology of the area are primarily taken from personal observation, employing reference material only where necessary to present a more complete picture.

SURFICIAL GEOLOGIC SETTING

The Forest River flows over two distinctly different geologic units which affect the characteristics of the stream (fig. 1). All of the deposits that crop out at the surface along the river are glacial in origin, having been deposited during the most recent, or Pleistocene Epoch. From the center of Township 56 West to the western border of the study area the river flows over an area of ground

moraine composed of glacial till. Although no mechanical analyses have been made in the immediate vicinity of the Forest River, Laird (1944, p. 19) reports till predominately composed of blue clay with pebbles of limestone, shale, and igneous and metamorphic rocks in the area near Emerado, North Dakota. This material is relatively impermeable.

East of this area, the stream flows over sediments deposited in glacial Lake Agassiz. The surface material is of two types, silt and laminated clay. The silt varies from true silt to sandy silt. This material probably covers most of the area indicated as lake sediments on the index map (fig. 1). Laminated clay lies disconformably beneath the silt (Laird, 1944, p. 21). In areas where the silt has been eroded, the clay may crop out at the surface. From the standpoint of this study, however, the two materials may be considered as a single homogeneous unit composed of fine-grained, impermeable sediment.

Trending almost north-south through the area of lacustrine sediments is a series of gravel ridges, the Lake Agassiz beaches. They were first described and named by Upham (1859) in his monographic study of Lake Agassiz. The beaches are anomalous to the general picture in that they are the only units which are permeable and, indeed, most of the shallow wells in the lake basin are drilled in beach gravels (Laird, 1944, p. 32). They not only provide some of the water for the Forest River but also affect the bottom conditions where the stream intersects the ridges.

In T. 154 N., R. 55 W., the stream crosses an end moraine trending in the same general direction as the beach ridges (fig. 1). It is composed of material similar to that of the ground moraine to the west but can be distinguished by the fact that it stands out as a ridge of low hills.

Outwash along the length of the river modifies the effects of the various lithologies on the stream channel. The outwash deposits are direct derivatives of the adjacent material but, through the process of winnowing, appear to be coarser grained. The general tendency is to remove the finer fraction and leave the coarser material as a lag, thereby reducing the range of grain size. That this process is in action may be demonstrated by the fact that near the branching of the river, where coarser material predominates, the water tends to be clear while where the river flows over the lake basin the water is clouded by fine material being carried in suspension.

Since the retreat of the ice and the diminution of Lake Agassiz the general land surface has changed little. The brief span of time since the retreat of the ice combined with the gentle slope of the land has resulted in very slight amounts of stream erosion. The general meandering character of the Forest River is suggestive of mature and old age streams; however, the fact that it flows in a

narrow valley and possesses a very narrow floodplain is proof that it is youthful, as is the entire area.

LOCALITIES COLLECTED

Eleven localities along the Forest River were investigated during the course of the field work, nine of which produced fish. The localities are shown in Figure 1. Data collected at each of the localities is listed below.

Locality 1. NE¼ Sec. 28, T. 156 N., R. 51 W., Walsh County, North Dakota, October, 1962. The stream level was low enough that the entire width of the stream could be sampled. The bottom was muddy and the water turbid. No vegetation was noted on the stream bottom. Eleven species were taken from this locality.

Locality 2. NE¼ Sec. 6, T. 155 N., R. 51 W., Walsh County, North Dakota, May, 1962. Flood conditions made sampling of the main channel impossible. The stream width was approximately 30 feet. Due to the flooding, the water was very turbid. Bottom conditions were not noted in the actual stream channel; however, the bottom in the areas sampled was muddy. Material that had been deposited by the flood waters was black and fine grained, containing a large amount of organic matter. This condition is probably true in the main channel also. Two species of fish were collected.

Locality 3. SE¼ Sec. 11, T. 155N., R. 52 W., Walsh County, North Dakota, October, 1962. As at Locality 1, the bottom was composed of organic mud and the water was extremely cloudy. Plants were noted growing in the stream. Seven species of fish were collected.

Locality 4. SW¼ Sec. 31, T. 156 N., R. 52 W., Walsh County, North Dakota, May, 1962. At this locality the stream was confined to a rather narrow course. This factor combined with a flood level of about ¾ feet made access to the stream impossible; therefore, it was not sampled. The water was turbid and the bottom appeared to be muddy.

Locality 5. C. Sec. 11, T. 155 N., R. 53 W., Walsh County, North Dakota, May 1962. Flooding in this area again made seining impossible; however, dip nets were employed along the bank. The bottom was more firm at this stop than at the previous localities although the water was still cloudy. No fish were taken but several crayfish and innumerable insect larvae were collected.

Locality 6. NE¼ Sec. 31, T. 155 N., R. 53 W., Walsh County, North Dakota, May, 1962. At this point on the stream flooding was reduced and it was possible to collect the entire stream width. The bottom was covered with sand and pebbles. There was virtually no vegetation on the bottom. The only area accessible for effective sampling was a 75 foot section of rapids and the areas immediately above and below the rapids. Only one species of fish was collected.

Locality 7. S½, SW¼ Sec. 11, T. 154 N., R. 55 W., Grand Forks

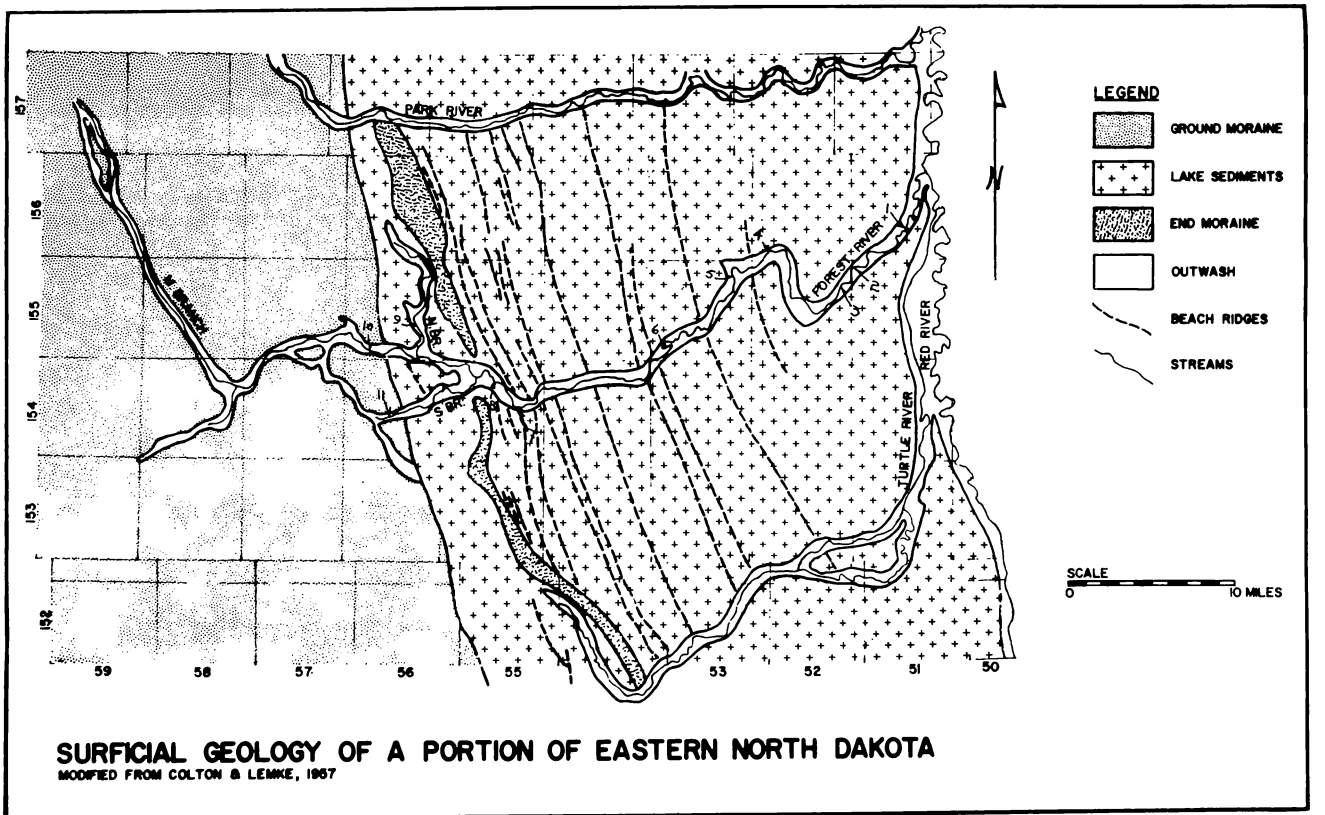

FIGURE 1—Surficial geologic map of Forest River area showing fish-collecting localities by numbers.

County, North Dakota, May, 1962. This locality is in the University of North Dakota Biology Area and encompasses a beaver dam on a tributary stream as well as areas of rapids and sand bottomed pools. A large collection of fish have been taken here over a period of ten years. No collections were made at this locality by the writer. The stream conditions are similar to those described for Locality 8.

Locality 8. Sec. 16, T. 154 N., R. 55 W., Grand Forks County, North Dakota, April, 1962. The area sampled was just below the rapids in the biology area. Although the bottom was sandy, flooding had caused the river to be very cloudy. There was very little bottom vegetation. Six species of fish and several insect larvae were collected.

Locality 9. C. Sec. 26, T. 155 N., R. 56 W., Walsh County, North Dakota, May, 1962. The North Branch of the Forest River at this locality is not significantly smaller than the main river. The characteristics of the stream are not markedly different from those of the main channel; the bottom consists of fine sands and mud. Reeds and grasses grow along the banks. Above the highway bridge on ND 81, approximately 200 yards, is a man-made dam with a fall of 5-6 feet. Although seining was performed, no fish were taken above the dam. Five species of fish, insect larvae, pelecypods, and gastropods were collected from the areas adjacent the shore below the dam. No fish were taken from the sandy areas. This was the only locality on the river where people were fishing.

Locality 10. SW¼ Sec. 28, and SE¼ Sec. 29, T. 155 N., R. 56 W., Walsh County, North Dakota, May, 1962. The Middle Branch of the Forest River is extremely small. The area sampled had a gravel bottom and no vegetation. No fish were taken at this locality, possibly because the river freezes solid and the fish had not yet moved back into the area.

Locality 11. SW¼ Sec. 16, and SE¼ Sec. 17, T. 154 N., R. 56 W., Grand Forks County, North Dakota, May, 1962. The South Branch of the Forest River is a sand and gravel bottomed stream with very clear water and spotty vegetation. Three species of fish were collected in abundant quantities.

FAUNAL LIST

All fish collected were sorted according to species and locality. Table I is a systematic list of the species encountered in the study.

DISTRIBUTION OF FISH

The Forest River and its tributaries can be subdivided into two general units on the basis of environment. The environments, in turn, are a reflection of the Pleistocene geology. The river, although youthful, has the general appearance of a mature, low gradient river. This results from being confined primarily to the Glacial Lake Agassiz plain. Most of the river can be characterized as having a

TABLE I

SYSTEMATIC LIST OF FISH COLLECTED IN THE FOREST RIVER

Family	Species
Catostomidae	
	Catostomus commersonni (Lacepede)
	Carpiodes cyprinus (LeSueur)
Cyprinidae	
	Cyprinus carpio Linnaeus
	Campostoma anomalum (Agassiz)
	**Rhinichthys cataractae* (Valenciennes)
	Rhinichthys atratulus Agassiz
	Hybopsis biguttata (Kirtland)
	Semotilus atromaculatus (Mitchill)
	Pimephales promelas Rafinesque
	Pimephales notatus (Rafinesque)
	**Notropis cornutus* (Agassiz)
	***Notropis deliciosus missouriensis* (Girard)
	***Notropis blennius* (Girard)
Ictaluridae	
	Ictalurus nebulosus (LeSueur)
	Ictalurus melas (Rafinesque)
	Noturus gyrinus (Mitchill)
Esocidae	
	Esox lucius Linnaeus
Percopsidae	
	Percopsis omiscomaycus (Walbaum)
Percidae	
	Perca flavescens (Mitchill)
	Stizostedion vitreum (Mitchill)
	Etheostoma nigrum Rafinesque
	**Percina maculata* (Girard)
Centrarchidae	
	Ambloplites rupestris (Rafinesque)
	Pomoxis nigromaculatus (LeSueur)
Gasterosteidae	
	**Eucalia inconstans* (Kirtland)

*Fish found in this study that are listed in Hankinson (1929).
**Fish listed in Hankinson (1929) and not found is this study.

bottom of reworked Lake Agassiz silt and clay and being slow moving and turbid. The bottom sediment is rich in organic material. Flooding increased the turbidity during the time of initial sampling; however, observations during the fall indicate that the water does not clear up significantly during the remainder of the year.

The second general environment, sampled at localities 7, 8, 10, and 11, is that of more rapidly moving water, sand and gravel bottom,

sparse bottom vegetation, and relatively clear water. These conditions prevail where the stream flows over Lake Agassiz beaches as well as on the till plain to the west. The stream is clearer due to the lack of fine bottom material to be stirred up and has a steeper gradient because the beaches are small ridges through which the river must cut. Table II shows the relationship of fish species to collection localities and general environment.

TABLE II

DISTRIBUTION OF FISH COLLECTED SHOWING OCCURRENCE OF SPECIES VERSUS COLLECTING LOCALITY AND GENERAL ENVIRONMENT

Species	Locality											Environment	
	1	2	3	4	5	6	7	8	9	10	11	Sand	Mud
Catostomus commersonni			X				X					1	1
Carpiodes cyprinus	X												1
Cyprinus carpio	X		X										2
Campostoma anomalum							X					1	
Rhinichthys cataractae							X					1	
Rhinichthys atratulus									X				1
Hybopsis biguttata							X	X				2	
Semotilus atromaculatus							X	X				2	
Pimephales promelas		X									X	1	1
Pimephales notatus							X	X				2	
Notropis cornutus	X		X			X	X	X			X	4	2
Ictalurus nebulosus									X		X	1	1
Ictalurus melas	X		X										2
Noturus gyrinus							X		X			1	1
Esox lucius	X		X										2
Percopsis omiscomaycus	X												1
Perca flavescens	X												1
Stizostedion vitreum	X		X										2
Etheostoma nigrum							X	X	X			2	1
Percina maculata							X					1	
Ambloplites rupestris	X		X				X					1	2
Pomoxis nigromaculatus	X												1
Eucalia inconstans	X	X					X	X	X			2	3

As illustrated in Table II, six of the twenty-three species were collected only in the general environment characterized by a sandy bottom, clear water, and rapids. Nine species were collected in areas of muddy bottom conditions, while the remainder appeared to show no preference. In several cases, however, a given species was collected at only one locality so inadequacy of sampling must be considered before conclusions can be made.

CONCLUSIONS

On the basis of the data collected one can conclude that fifteen of the twenty-three species collected show a preference for one of the two general environments outlined. Nothing can be said about the limiting factor, or factors, within these environments until studies of water chemistry, temperature, food availability, and current are undertaken. The general environments resulting from the Pleistocene history of the area are, however, well defined and appear to characterize the stream adequately.

BIBLIOGRAPHY

Carufel, L. H., 1958, Tentative check list for fishes of North Dakota: North Dakota Outdoors, v. 21, no. 5, p. 10-11.

Colton, R. B., and R. W Lemke, 1957, Glacial map of North Dakota: U S. Geol. Survey.

Eddy, Samuel, 1957, How to know the freshwater fishes: Wm. C. Brown Co., Dubuque, Iowa, 253 p.

————, and Thaddeus Surber, 1947, Northern fishes: Charles T. Branford Co., Newton Center, Mass., 276 p.

Hankinson, T. L., 1929, Fishes of North Dakota: Papers Mich. Acad. Sci., Arts, Letters, v, 10, p. 439-460.

Laird, W. M., 1944, The geology and ground water resources of the Emerado Quadrangle: North Dakota Geol. Survey, Bull. 17, 35 p.

Upham, Warren, 1895, The glacial Lake Agassiz: U. S. Geol. Survey, Mon. 25, 658 p.

A CUMULATIVE REPORT ON WINTER BIRD POPULATION STUDIES IN EIGHT DECIDUOUS SHELTERBELTS OF THE RED RIVER VALLEY, NORTH DAKOTA[1]

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Third Place Winner, A. Rodger Denison, Student Research Competition

Although shelterbelts have been common for the last thirty years, very little data with regard to the influence on attraction of winter fauna has been recorded. During the past ten years studies

[1]Studies supported in 1960 by North Dakota Institute for Regional Studies, and in 1962 and 1963 by N.S.F. Undergraduate Research Participation Grant.

[2]Senior student.

have been conducted on the populations of breeding birds and winter birds in the deciduous flood plain forest, on the breeding birds of certain shelterbelts and tree claims, and on a summary of the previous records of the winter birds in the state as recorded in the Audubon Christmas Census. Up until 1960, however, little attention had been paid to the effect of shelterbelts on bird populations, especially in winter.

This particular census study was carried out over a period of three years and this report is a summary of data acquired during the winter months of 1960, 1962 and 1963. January and February were the months in which data were obtained; because during these months the late fall migrants would not be so readily represented, and early spring migrants would, equally, be left out.

The censusing was done entirely on foot, and during 1960 and 1962 with the aid of snowshoes. Counts were made almost entirely by sight, but occasionally a singing bird was recorded. About four hours were required per trip to include all eight belts. The time varied only slightly from trip to trip depending on snow depth and weather conditions. During January and February of the three years, nearly all types of winter weather conditions were experienced. The winter of 1960 produced rather heavy snow cover with drifts in some belts of 3 to 4 feet. In 1962, there was also much snow with drifts in some belts up to 6 feet deep. In contrast, during January and February 1963, very little snow was encountered; but the temperature was quite low (a maximum low of -27° F).

On the days censused a record was kept of all birds sighted, and after the yearly studies were made the density per hundred acres was calculated using this formula:

$$\frac{\text{Total number of one species} \times 100 \text{ acres(A)}}{\text{Number of trips} \times \text{area in acres}} = \text{Density/100 A}$$

and, Density/100 A = Average number per species/100 A

Because of the low density of most species, the average density per actual area was not calculated. The relative density (in terms of birds per 100 A.) of the various species is indicated in the graphs.

The right belts (see map in figure 1) can be classified into two general categories:

1. The belts closely adjacent to some river bottoms; that is, within probable, easy flying distance to these bottoms. This type of habitat provides a relatively unisolated habitat for the birds enabling them to move from the bottoms up into the belts and back.
2. Belts isolated from any bottom lands. This includes the typical shelterbelt of the open prairie and a farmstead isolated from a river bottomland.

The belts used in this study are numbered 3, 4, 5, 7, 6, 8, 9, 10. They are numbered in this manner for uniformity with past studies. A description of each belt is listed below and the number in parenthesis refers to the map in figure 1.

Yunker's Belt (#3) is ½ mile north of Fargo. The 8 rows are planted in a north-south direction for a distance of 1,220 feet and a total area of 2.5 acres. The dominant plants are green ash, hackberry, American elm, and along each edge, caragana. The main species of birds were the Bohemian waxwing and ring-neck pheasant. This belt is 13 years old.

Stockman's Belt (#4) is located 3 miles north of Fargo. The nine rows run in a north-south direction for a distance of 2,340 feet and

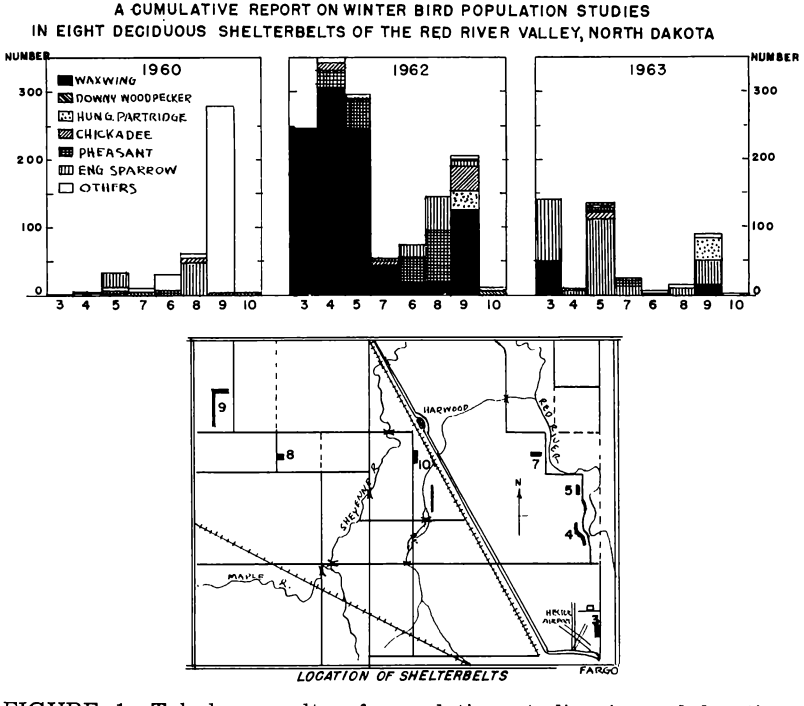

FIGURE 1—Tabular results of population studies in and locations of eight deciduous shelterbelts

an area of 5.9 acres. This 15-year-old belt provided a count of 100 Bohemian waxwings on one day during the 1962 census. This illustrates the unstable character of the density of this species with respect to any small area. From the graph it also can be seen what the occasional visit of a large flock of wandering birds does to popu-

lation statistics. Also observed, though infrequently, were pheasants, chickadees and downy woodpeckers.

Harris's Belt (#5) is located 4 miles north of Fargo; this 18-year-old belt has nine rows running north and south for a distance of 1,140 feet for an area of approximately 2.8 acres. During 1962, this belt also produced many waxwings; and during 1963, a flock of sparrows from the farm across the road invaded the belt.

Barker's Belt (#7) is located 4½ miles northwest of Fargo; this belt is 180 by 820 feet and is composed of 19 rows for an area of approximately 3.4 acres. This belt may have been a tree claim and is thought to date back to 1914. The dominant trees here are cottonwood, willow and boxelder. This belt was not frequented by many species nor numbers; however, those most frequently seen were the pheasant and waxwing, as well as several common redpoll in 1960.

Ellenson's Belt (#6), a 25-year-old belt, runs in a north-south direction and is composed of 8 rows. The belt is 6 miles northwest of Fargo. This belt is approximately 4,700 feet long and 80 feet wide for an area of about 9.2 acres. Due to a corn field and a nearby farm, this belt contained the highest population of pheasants. Also waxwings were seen as rather infrequent visitors in 1962 and 1963.

Farmstead Belt (Krogh) (#8) is an abandoned farmstead with trees planted in rows. There are two stands of trees, one on each side of the demolished farm site. The dominant trees are boxelder, green ash, cottonwood and scattered willow, which make up most of the 3.9 acres. In 1960 this belt contained an unused granary and consequently a large population of sparrows. In 1962, however, the granary was gone and thus a decrease in the sparrow population. Pheasants frequented the belt in 1962 but were rarely seen in 1960 and 1963.

Nygard's Belt (#9) is the more typical open prairie type of belt. This belt is essentially composed of two belts; the longer of the two has six rows running in a north-south direction for 4,750 feet. The other belt forms an L shape at the north end of the first, has six rows, and runs east from it for 1,600 feet. The total acreage is approximately 8.3 acres. This belt provided the greatest variety of species; a total of seven different birds were seen in 1962. Waxwings were the most abundant, while Hungarian partridge were seen exclusively in this belt. Chickadees were seen in pairs or in threes nearly every trip in 1960 and 1962, but none was seen in 1963.

Anderson Tree Claim (#10) is the 14 acres remaining of a tree claim probably made in the 1880's. It is approximately ½ mile south of Harwood, North Dakota. This is the oldest belt and is predominantly green ash and American elm, with some boxelder and hackberry. The west side of the belt is a dense thicket with underbrush such as chokecherry, buckbrush, gooseberry and wildrose. Although this belt seems the most suitable for providing heavy cover, it was

utilized the least of the eight belts. Downy woodpeckers and great horned owls were seen only infrequently during the three years censused.

The numbers and different species seen (see figure 1) in the different types of belts does not indicate that amount of cover is a prerequisite for bird utilization because the greatest populations of birds were seen in the less dense belts.

During days of blowing snow there was a marked increase in numbers of birds present in the sheltered areas. On clear, cold days or clear warm days with no wind, the belts were relatively void of life. During a snowstorm (1962) the greatest variety of birds was seen. The shelterbelt and tree claim areas seem to be used sometimes as places of refuge during bad weather or serve as stopping places for birds during calmer weather.

The total number of species seen was 17. This is in keeping with Cassel's records in a study of an area along the Red River. With a small number of birds seen over a period of only ten trips it is often impossible to reflect the true situation by merely assessing the data which is recorded. Annual variations in the density of certain species and their effect upon the total population can be seen in the case of both the Bohemian waxwings and pheasants in 1962.

It will take many years of censusing shelterbelts to record a true picture of the utilization trends of the different species of birds.

Thanks are given for the assistance by Dr. J. Frank Cassel of the Zoology Department of North Dakota State University of Agriculture and Applied Science. Dr. Cassel provided the initial information and material to make this study possible. Also I am grateful to Daniel W. Anderson who did the census work in 1960, and to Bruce A. Renhowe who assisted me in the field in 1962 and 1963. Appreciation also should be expressed to the owners upon whose property this study was carried out.

THEORETICAL PREDICTION OF THE PROPERTIES OF COMPOUNDS. PART IX. FURTHER DISCUSSION ON THE STABILITY RULES FOR PLANAR CONJUGATED SYSTEMS

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In 1959 Manatt and Roberts (1) tabulated the ΔDE values for a number of cyclobutadiene systems. The ΔDE was defined as the increases in DE values between substituted and unsubstituted systems such as cyclobutadiene, benzocyclobutadiene and dimethylenecyclobutene. This work, however, has not been able to contribute any

means of predicting the stability of these strained ring systems. First, the ΔDE so defined does not correlate to the stability of the substituted systems. Second, it is unable to predict the stability of the unsubstituted systems, e.g., cyclobutenedione, 1,2-dimethylenebenzocyclobutene, 1-keto-2-methylenebenzocyclobutene, benzocyclobutenedione, and the three unsubstituted compounds mentioned above.

In 1960, shortly after the isolations of di-(2,3-naphtho)-cyclobutadiene (I), di-(1,2-naphtho)-cyclobutadiene (II) and dibenzocyclobutadiene were reported, Ali and Coulson (2) explained the relative stability of these three compounds on the basis of MO calculations of DE values and bond orders. They indicated that I is far more stable than II in agreement with the difference in DE values. They also mentioned that the sequence of increase of the degree of double-bond fixation corresponds exactly with the sequence of decrease of stability of these molecules; the greater the degree of bond fixation, the extent of conjugation is less with the consequence of lower stability. However, it must be pointed out that the DE value or the degree of double bond fixation alone is unable to predict the stability of compounds. These have been discussed in Part I (3) of this series, but will be further elucidated in the present paper.

In Part I of this series, the author proposed seven stability rules, which can be applied to any planar conjugated ring or chain systems. These rules are not only able to correlate the calculated DE value to the stability of a system but are also able to predict the stability and some of the properties of the system. The recent report of the isolation of dimethylenebenzocyclobutene by Cava and co-workers (4) and tetraphenylcyclobutadiene dication by Freedman and Frantz (5) has advanced the applicability of these rules. In order to clarify the set of rules in Part I, the seven rules are restated. In addition to the seven rules, three more stability rules will be stated in this paper.

The stability rules for planar conjugated systems may be stated as follows:

RULE I

The more delocalization energy a system has, the more stable the system will be, provided this system is not greatly destabilized by one or more of the instability factors such as:

(1) large angular strain
(2) zero DE or small DE
(3) high free valence index
(4) non-singlet ground state
(5) steric hindrance arising from interior hydrogens
(6) small energy difference between the highest occupied molecular orbital and the lowest empty molecular orbital.
(7) all bonding molecular orbitals have not been completely occupied or have electrons in antibonding molecular orbitals

(8) high degree of double bond fixation for bonds involving a highly strained ring.

RULE II

For "synthesis"[1] of system B from system A by increasing the extent of conjugation, either by increasing the number of conjugated carbon atoms (one C-C at a time) or by adding additional bonds (one at a time) to the same conjugated system,

$$A \rightarrow B$$

the "synthesis energy" $(\Delta E)_{BA}$ is defined as

$$(\Delta E)_{BA} = (DE)_B - (DE)_A$$

A "synthetic" route is said to be a "stable synthetic" route if the value of "synthesis energy" in every step of this route is positive, otherwise the "synthetic" route is said to be an "unstable synthetic" route.

A system "synthesized" via a "stable synthetic" route is called a "synthesizable" system and is said to be "synthesizable". A system "synthesized" via an "unstable synthetic' route is called an "unsynthesizable" system and is said to be "unsynthesizable". In a "synthesis" diagram, some systems might appear to be "synthesizable" (e. g. benzene), other systems might appear to be "unsynthesizable" (e.g. cyclobutadiene), and still other systems might appear to be both "synthesizable" and "unsynthesizable" (e. g., benzocyclobutadiene, biphenylene). An example is given as figure 1.

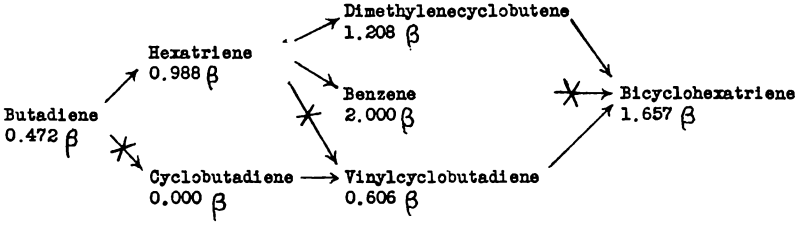

FIGURE 1—"Synthesis" diagram for bicyclohexatriene

RULE III

If a system is not "synthesizable" from any one of the possible "synthesizable" systems, then this system can be predicted to be incapable of existence. These unstable systems dimerize or polymerize in order to reduce the high degree of angular strain of the strained ring (e. g., cyclobutadiene, benzocyclobutadiene, bicyclo- (e. g., bicyclohexatriene).

RULE IV

If a system can be "synthesized" only from "unsynthesizable" systems, then this system can be predicted to be incapable of existence (e. g., trifulvalene).

[1]One should note that the word "synthesis" used here does not imply any actual experimental method of preparation.

RULE V

If a system is "formed" by fusion of two or more "unsynthesizable" systems such that the resulting molecule involves no stable part, then this system can be predicted to be not capable of existence (e. g., bicyclohexatriene).

RULE VI

If a system is "synthesizable" from all possible "synthesizable" systems, then the capability of existence of this system depends on the degree of influence of the instability factors stated in rule I.

RULE VII

Bicyclic systems with a four-membered ring and a ring with $4n+2$ π-electrons are predicted to be incapable of existence if $n \leqq 1$ (with exception of the cation of a compound containing a seven-membered ring with $n = 1$). If $n > 1$, however, these systems are predicted to be stable provided these molecules are not greatly destabilized by the instability factors stated in rule I.

RULE VIII

Bicyclic systems containing one four-membered ring, "formed" by adding additional bonds to monocyclic systems which have $4n+2$ π-electrons, are predicted to be incapable of existence.

RULE IX

Tricyclic systems with a central four-membered ring, in general, are predicted not to be stable enough to exist if $2 \geqq m > 0$, $n > 0$, where m and n are the number of π-nuclei, excluding the "fused" carbon atoms, at each side of the central four-membered ring. If $m > 2$ and $n > 2$, however, these systems are predicted to be stable provided that these substances are not greatly destabilized by the instability factors stated in rule I.

RULE X

All atoms in a molecule, jointed directly or indirectly, mutually interact with one another. Each atom in a molecule has a definite chemical interaction with the others, and hence each part of the molecule affects the rest of the molecule. The influence of interaction among the atoms in a molecule reaches a certain equilibrium. In a planar conjugated system, there exists a large delocalized π-bond through which the stable part of the molecule affects and hence stabilizes the unstable part of the molecule. A system, therefore, formed by fusion of one or more unstable systems and one or more stable systems can be predicted to be capable of existence provided that it has large enough stabilization energy, does not violate rule III and is not greatly destabilized by the instability factors stated in rule I. The stabilization energy ΔE_S is defined as follows:

$$\Delta E_S = \frac{(DE)_{\text{system}} - (DE)_{\text{stable part(s)}}}{\text{Number of 4-membered rings}}$$

The minimum required stabilization energy for each carbon atom of an unstable four-membered ring, of which all four carbon atoms are sp^2, is assigned to be 0.114 β. Compounds containing one or more unstable rings, therefore, are capable of existence if they have the required minimum stabilization energy, do not violate rule III, and are not greatly destabilized by the instability factors.

It must be pointed out that:

a. a stable part (conjugated part) or parts should be taken out from the considered molecule such that the DE of this stable part or the sum of the DE of these stable parts is largest
b. a stable part must have two and only two "fused" carbon atoms from the same four-membered ring
c. a stable part must not be an odd-membered system, unless this odd-membered system is a monocyclic ring with $4n+2$ π-electrons or a polycyclic system with a $4n+2$ perimeter
d. if a carbon atom of an unstable four-membered ring is involved also in another highly strained ring, such as four- or three-membered ring, the minimum required stabilization energy for this carbon atom is very much larger than 0.114β.

In order to elucidate rule X, predictions of the stability of some compounds by this rule are tabulated in Table I. MO calculations of

TABLE I
DE AND ΔE_s VALUES

Cyclobutadiene,	DE (β)	Conjugated Pt,	DE (β)	ΔE_s (β)	Stability
1. unsubstituted	0.000	ethylene	0.000	0.000	unstable
2. phenyl-	2.527	styrene	2.424	0.103	unstable
3. vinyl-	0.606	butadiene	0.472	0.134	unstable
4. 9, 10-phenanthrene-	5.693	phenanthrene	5.448	0.245	unstable
5. benzo-	2.381	benzene	2.000	0.381	unstable
6. 2, 3-naphtho-	4.200	naphthalene	3.683	0.517	stable
7. 2, 3-anthra-	5.881	anthracene	5.314	0.567	stable
8. di-(9, 10-phenanthrene)-	11.276	phenanthrene	5.448	0.380	unstable
9. di-(1,2-naphtho)-	7.820	naphthalene	3.683	0.454	stable
10. dibenzo-	4.505	benzene	2.000	0.505	stable
11. di-(2,3-naphtho)-	7.980	naphthalene	3.683	0.614	stable
12. di-(2,3-anthra)-	11.275	anthracene	5.314	0.647	stable
13. dimethylene-	1.208	butadiene	0.472	0.736	stable (reactive)
14. 1,2-dimethylenebenzo-	3.153	benzene butadiene	2.000 0.472	0.680	stable (reactive)
15. 1,2-diketo-	1.319	glyoxal	0.356	0.963	stable
16. 1,2-diketobenzo-	3.222	benzene glyoxal	2.000 0.356	0.866	stable
17. dication, tetraphenyl-	12.060	1,2-diphenylethylene cation	5.374	1.312	stable
18. 1,2-divinylbenzo-	3.449	benzene hexatriene	2.000 0.988	0.461	unstable
19. tetra-(1-butadienyl)-	4.607	decapentaene	2.053	0.501	unstable
20. tetraketo-	1.369	glyoxal	0.356	0.657	stable (dianion)

compounds 18 and 19 were reported in Part VI (6) of this series. These two hydrocarbons do not violate rule III and have moderate ΔE_s values provided all carbon atoms lie in a plane. The isolation

of these two systems is predicted to be unlikely because not all of the π-nuclei of these two compounds, particularly the π-nuclei of the side chains, need lie in a plane. This argument may be applied to the incapability of the isolation of 1,2-diphenylbenzocyclobutadiene, 1,2-dicarboxybenzocyclobutadiene and 1-carboxy-2-phenylbenzocyclobutadiene.

It is noteworthy that the stability of compounds containing four-membered rings is firmly related to the stabilization energy. For example, the stabilization energy (ΔE_S) decreases in the following sequence: 11, 10, 9 and 5 (cf. table I). This corresponds exactly with the sequence of the stability of these compounds. If the DE per π-electron is used as the criterion, a sequence which is different from that of the stability of the above four compounds is obtained. If one inserts unknown compounds 8 and 4 into these sequences, the incorrectness of using DE per π-electron as the criterion is most obvious.

A high degree of double bond fixation can be considered as an instability factor for bonds involving a highly strained ring, as stated in rule I. However, it must be pointed out that bond fixation alone can not be used for prediction of the stability of compounds containing highly strained rings. For example, the degree of double bond fixation decreases in the following sequence: 4, 8, 5, 9, 10, 11, 3, 2 and 1. This sequence implies that compounds 1, 2 and 3 are more stable than compounds 11, 10 and 9. According to stability rule X, it is predicted that compounds 1, 2 and 3 are incapable of existence, whereas compounds 11, 10 and 9 are relatively stable substances.

REFERENCES

1. S. L. Manatt and J. D. Roberts, J. Org. Chem., 24, 1336 (1959).
2. M. A. Ali and C. A. Coulson, Tetrahedron, 10, 41 (1960).
3. H. S. Lee, Proc. N. Dak. Acad. Sci., 16, 27 (1962).
4. M. P. Cava, M. J. Mitchell, and R. J. Pohl, Tetrahedron Letters, 18, 825 (1962).
5. H. H. Freedman and A. M. Frantz, Jr., J. Am. Chem. Soc., 84, 4165 (1962).
6. H. S. Lee, Chemistry, No. 2, 55-58 (1963).

A REPORT ON COLLECTING, PREPARING, AND MOUNTING TARDIGRADES FROM CENTRAL EASTERN NORTH DAKOTA

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INTRODUCTION

The purposes of this report are: (1) to describe the tardigrade fauna of central eastern North Dakota, (2) to point out the environ-

ments and collecting localities in which tardigrades are found, (3) to describe the techniques used in mounting tardigrades. The occurrence of tardigrades in North Dakota has apparently not been previously reported.

I express my sincere thanks to Dr. G. C. Wheeler for suggesting this problem, and to him and Dr. J. N. Wheeler for their interest and guidance throughout my course of study.

COLLECTING LOCALITIES AND ENVIRONMENTS

Collections of mosses and lichens containing tardigrades were made at the following localities: Lincoln Park, Grand Forks; Turtle River State Park, near Arvilla; along the Forest River near North Dakota Highway 18, north of Inkster; on the roofs of the Biology Building and Babcock Hall on the campus of the University of North Dakota. All of the preceeding localities are in Grand Forks County, North Dakota. The mosses from the roofs of the Biology Building and Babcock Hall were the only samples in which *Milnesium tardigradum* was found. All samples contained *Macrobiotus* sp.

Macrobiotus and *Milnesium tardigradum* are both aquatic and semiaquatic according to Pennak (1). All of the tardigrades that I have collected are of the semiaquatic type. The improbable situation of semiaquatic animals living on terrestrial plants is easily explained when more of the nature of the tardigrade is known. *Macrobiotus* and *Milnesium tardigradum* have the unusual ability to assume an inactive or anabiotic state when the plants with which they are associated become dried out. According to Pennak (1) "Metabolic processes proceed very slowly, but the length of time a specimen can remain in continuous anabiosis depends on the amount of stored food in the body." Tardigrades will return to an acitve state as soon as moisture is added to their environment. When moistened by dew, rain, melting snow, or water splashed from a stream, plants are nearly covered by a thin water layer or many droplets of water. In reality, these tiny layers and droplets of water constitute a semiaquatic environment for the minute tardigrade.

PREPARATION FOR MOUNTING

The mosses and lichens were soaked for several days to return the tardigrades to the active state. After soaking the plant material was thoroughly washed and the washings were examined for tardigrades. The tardigrades were then removed from the washings with a micropipette, placed on a deep well slide, and covered with a vaseline-sealed cover slip in order to induce a state of asphyxia. In asphyxia in tardigrades the body swells slightly and becomes turgid and rigid. The inducement of this condition before killng and fixing yields especially fine specimens.

Canada balsam and polyvinyl alcohol were used as mounting mediums with the specific purpose of determining which of the two media was best suited for tardigrades. The use of Canada balsam

involves the drop by drop change of solutions from water to a low percentage alcohol solution, to a higher percentage alcohol and finally to 95 percent alcohol. A drop by drop change of solution from 95 percent alcohol to carbol xylol to xylol is then necessary before Canada balsam can be added. The technique also requires that the specimens be pierced so that the various solutions can invade them completely. The use of this technique results in a high rate of specimen loss because of disfiguration due to piercing and because of specimen collapse due to the reaction between solutions.

The technique involved in using polyvinyl alcohol is relatively simple. A clearing solution of phenol and lactic acid may be added to the polyvinyl alcohol so that killing, fixing, clearing, and mounting of the tardigrade may be accomplished in one step. This process consists of placing a drop or two of prepared solution on the slide,

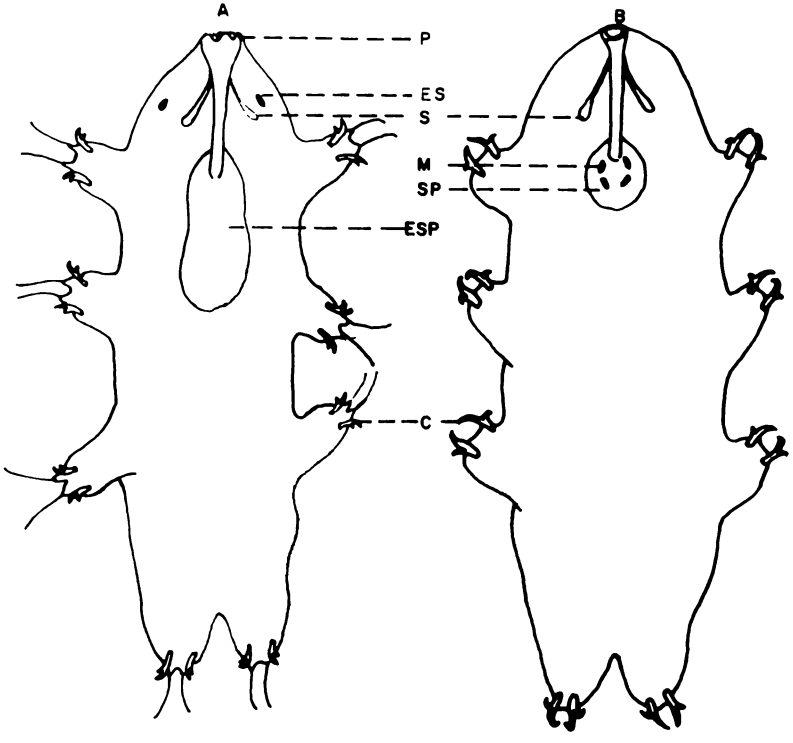

FIGURE 1 — Semidiagrammatic ventral view of *Milnesium tardigradum* and *Macrobiotus* sp. A, *Milnesium tardigradum*: P, oral papillae; ES, eyespot; S, stylet; ESP, elongated sucking pharynx; C, claws. B, *Macrobiotus* sp.: S, stylet; M, macroplacoids; SP, sucking pharynx; C, claws.

setting the specimen in the solution alcohol and covering the preparation with a cover slip. No collapsed specimens were observed when this technique was used.

The high percentage of specimen loss and the difficulties of the involved Canada balsam technique when compared to the ease with which tardigrades may be mounted in polyvinyl alcohol and clearing solution indicates that the latter is the preferred mounting technique.

SYSTEMATIC DESCRIPTIONS

Phylum TARDIGRADA

Class EUTARDIGRADA

Order MACROBIOTOIDEA

Family MACROBIOTIDAE

Genus MACROBIOTUS Shultz, 1834

MACROBIOTUS sp.

Macrobiotus (figure 1B) exhibits a sucking pharynx with macroplacoids, a smooth cuticle and two double claws on each leg. The two double claws on each leg are similar in shape and each double claw consists of a large claw and a small claw. The two larger claws of each leg more or less face toward each other while the two smaller claws more or less face away from each other. The animal is generally about 0.07 centimeters long.

Family ARTISCIDAE

Genus MILNESIUM Doyère, 1840

Milnesium tardigradum Doyère, 1840

Milnesium tardigradum (figure 1A) is characterized by an elongated sucking pharynx without macroplacoids, eye spots, six prominent papillae around the mouth, and two pairs of claws on each leg. Each leg exhibits a pair of long slender claws and a pair of short stout claws. The animal is generally about 0.08 centimeters long.

REFERENCES

1. Pennak, R.W., Fresh water invertebrates of the United States, New York, The Ronald Press Co., pp. 240-255, 1953.

METHYLENE INSERTION REACTIONS IN METAL HALIDES

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Diazomethane reacts with zinc chloride to form bis-chloromethylzinc. This compound was reacted with ethanol with formation of zinc ethoxide. The quantity of ethanol released from the ethoxide

upon fusion with benzoic acid has been used for a quantitative determination of the extent of reaction of diazomethane with the metal halide. This technique has been applied to other metal halides which, up to now, had not been known to react with diazomethane.

The halides with yield of methylene insertion products are:

$ZnCl_2$	68.8%	$CdCl_2$	10.9%
$CaCl_2$	45.5%	$SrCl_2$	5.3%
$MgCl_2$	38.9%	KCl	no reaction
LiCl	29.0%	NaCl	no reaction

[1]This investigation was supported in part by a Public Health Service fellowship (No. 15.094) from the Division of Research Grants, Public Health Service.

LATE PLEISTOCENE FISH FROM LAKE SEDIMENTS IN SHERIDAN COUNTY, NORTH DAKOTA[1]

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INTRODUCTION

During the summer of 1962, while mapping the glacial geology of western Sheridan County, North Dakota, samples of fresh-water mollusk shells from ice contact lake sediments were collected. These sediments were found on a dump pile of a recently dug stock pond located on top of the Prophets Mountains in Sheridan County. At a later date the Pleistocene fish fossils discussed below were found and collected by Dr. John R. Reid, Assistant Professor of Geology, University of North Dakota and Mr. Thomas C. Gustavson and me, graduate students in geology at the University of North Dakota.

SUMMARY OF THE GLACIAL GEOLOGY OF THE PROPHETS MOUNTAINS AREA

The Prophets Mountains lie within the Missouri Coteau District which, according to Fenneman (8), is in the Missouri Plateau (Glaciated) Section of the Great Plains Province. These hills are a topographically prominent part of the Lincoln Valley moraine, standing 300 feet above the surrounding area. The Lincoln Valley moraine has partly overriden and truncated the Streeter moraine. The Streeter moraine is a prominent feature that can be traced from McIntosh County, near the South Dakota border, to its truncation by the Lincoln Valley moraine in western Sheridan County.

[1]Published by permission of State Geologist, North Dakota Geological Survey.

According to Frye and Willman (9), the last stages of the Pleistocene Epoch are divided into the Wisconsinan Stage which began 70,000 to 50,000 radiocarbon years ago and ended approximately 5,000 radiocarbon years ago and the Recent Stage which began 5,000 radiocarbon years ago. The Wisconsinan Stage has been subdivided by Frye and Willman (10) into the Altonian Substage (50-70,000 - 28,000 radiocarbon years B.P.), the Farmdalian Substage (28,000 - 22,000 radiocarbon years B.P.), the Twocreekan Substage (12,500 - 11,000 radiocarbon years B.P.) and the Valderan Substage (11,500 - 5,000 radiocarbon years B.P.).

Mollusk shells and spruce wood in the Burnstad Drift, of which the Streeter moraine is a part, have been dated in Kidder, Stutsman, Logan and McIntosh Counties and have been found to be 9,000± 300 to 11,650± 310 radiocarbon years old. According to Clayton (2) the 11,650± 310 date is "from clam shells found in Burnstad lake sediment in a ridge (push ridge?) of the Streeter moraine." If Clayton's tentative interpretation of the geology of the site in which the clams were found is correct, then the glacier which deposited the Streeter moraine was active after 11,650± 310 radiocarbon years B.P. The Streeter moraine would then be less than 11,650± 310 radiocarbon years old. Since the Lincoln Valley moraine truncates the Streeter moraine, it must be younger than the Streeter moraine; therefore it is also less than 11,650 ± 310 radiocarbon years old.

The Lincoln Valley moraine, though younger than the Streeter moraine, does not represent a significant glacial advance; outwash, formed at the front of the Lincoln Valley moraine, is collapsed in the Burnstad Drift that is associated with the Streeter moraine, indicating that a mass of stagnant ice existed in front of the Lincoln Valley moraine at the time of its deposition. Futhermore the Lincoln Valley moraine and its associated drift and the Streeter moraine and its drift are similar in lithology and topography. For these reasons the Lincoln Valley Drift is considered to be part of the Burnstad Drift.

The glacier that deposited the Lincoln Valley moraine untimately stagnated and superglacial lakes insulated from the ice by ablation drift were formed. It was in these lakes that the mollusks and fish reported here lived. Meltwater channels also present during this time flowed down to the terminus of the ice.

DESCRIPTION OF THE PROPHETS SITE

Location—The sediments in which the mollusk shells and fish remains were found were located on the dump pile of a recently dug stock pond. The pond is located in a depression between two linear parallel ridges of the Lincoln Valley moraine, 0.2 mile south and 0.2 mile east of NE cor., sec. 29, T. 147 N., R. 78 W., Sheridan County, North Dakota.

Lithology — The sediments in which the fish were found are composed of a grey calcareous silty clay. Much of the sediment ap-

pears to be rhythmically bedded and they may possibly be glacial varves.

Fauna — Species of the white sucker, *Catostomus commersoni* (Lacépède, creek chub, *Semotilus atromaculatus* (Mitchill), and finescale dace, *Chrosomus neogaeus* (Cope), were found at the Prophets site. The fish have been only tentatively identifed. These fish are common varieties found living today and, according to Carufel (1), occurrences of all but the finescale dace have been reported in North Dakota.

According to Eddy (4) and Eddy and Surber (6), the white sucker is very common east of the Rockies from southern Canada south to Colorado, Missouri and Georgia. It is abundant in all the waters of Minnesota, Wisconsin and nearby states. The white sucker occurs in enormous numbers in the headwaters of tributaries to the Mississippi and in the streams and lakes of the Superior, Rainy, and Red River drainages.

Eddy and Surber (7) note that the chub is found from Montana to eastern Canada and south to the Gulf Coast. It is common in all parts of Wisconsin and attains wide distribution over Minnesota. The chubs prefer small rivers and large creeks, but they are occasionally found in lakes.

According to Eddy (5), the finescale dace is found from northwest Canada to New England and south to northern Minnesota, Wisconsin, and Michigan. Isolated populations are found in western Nebraska and in the Black Hills.

The species of mollusks found at the Prophets sits were identified by Mr. Samuel J. Tuthill, graduate student at the University of North Dakota, and he states (personal communication):

> "The 15 specimens of mollusks which were includede in the sediment sample from the Prophets site are too few to warrant much speculation as to the ecologic conditions of the body of water in which they lived. The following organisms were identified:

Mollusca:	Pelecypoda;	5 *Pisidium* sp. valves
	Gastropoda;	1 *Armiger crista* (Linne), 1758
		2 *Gyraulus parvus* (Say), 1817
		3 *Lymnaea humilis* (Say), 1822
		4 *Lymnaea* sp. cf. *L. palustris* (Miller)
Arthopoda:	Ostracoda;	6 valves of freshwater ostracodes

Algae:	several oögonia of calcareous algae, probably of the genus *Chara*

This assemblage suggests the existence of seasonally temperate body water. Because algae require light for photosynthesis, the oögonia indicate that the water was clear. The gastropods are all pulmonate forms and could have withstood seasonal drying of the environment, but the presence of fish remains weakens this line of logic at least for the time during which fish occupied the body of water. The mollusks are all typical of quiet water bodies, but this alone does not prove that the body of water was a lake, as many streams possess aquatic habitats quite similar to lakes. Aquatic and marginal vegetation was probably abundant.

The fossil mollusks are not indices for geologic age of the sediments, as they are conspecific with the present molluscan fauna of the Missouri Coteau district in North Dakota. However, if a sufficient quantity of shell material was obtained from future collections it could be dated by the radiocarbon method; the present collection is too small for this purpose."

DISCUSSION

The finding of these fish marks the first known discovery of Pleistocene fish remains in North Dakota. It was previously thought by Clayton (2) and Tuthill and others (11) that fish existed in the ice contact lakes of the Missouri Coteau during the Upper Wisconsinan becausenaiads, whose glochidia are parasitic on fish, have been found in many localities in the Missouri Coteau district.

The evidence for the upper Wisconsinan age of the fish remains is strong, though not conclusive. The only feasible way in which Recent age fish could have reached the top of the Prophets Mountains would be in the beaks of pelicans or other birds which prey on fish. The large number of fish specimens found would tend to reduce this possibility, but not disprove it.

The fish probably reached the area of the Prophets Mountains during the period when drift-covered stagnant ice existed in front of and on the Lincoln Valley moraine. The fish could then have easily swum up drift-insulated meltwater streams from beyond the terminus of the ice and established successful populations in the ice contact lakes that existed in the area of the Prophets site at that time.

The only other possible explanation for the topographically isolated occurrence of these fish remains is that they were displaced from their original site of deposition by glacial shearing during the formation of the Lincoln Valley moraine. This is improbable because the fish remains are well preserved and are not contorted. Deforma-

tion of the soft clay sediments, fish remains, and the mollusk shells would be expected if they were carried in shear planes in the ice.

SUMMARY

This preliminary investigation of the Prophets site indicates that there are three possibilities for the occurrence of the topographically-isolated fish remains: they may have been carried in sediments by terminal glacial shearing, they may have been carried by pelicans or other birds that prey on fish, or they may have swum up melt-water channels in the drift-covered stagnant ice. The evidence seems to indicate that the latter hypothesis is the most feasible. It is hoped that future studies of the Prophets site will reveal more evidence to support the late Wisconsinan age of the fish remains.

ACKNOWLEDGMENTS

I wish to thank Dr. Teruya Uyeno at the Museum of Zoology, University of Michigan for his tentative identification of the fish remains and Dr. F. D. Holland, Jr., Associate Professor at the University of North Dakota for his personal assistance in arranging for the identification. Mr. S. J. Tuthill kindly identified the molluskan fauna, and Dr. John R. Reid and Mr. Thomas C. Gustavson helped in collecting the specimens studied. The initial investigation was made possible through the financial assistance of the North Dakota Geological Survey under the direction of Dr. Wilson M. Laird, State Geologist.

BIBLIOGRAPHY

1. Carufel, L. H., Tentative check list for fishes of North Dakota, North Dakota Outdoors, p. 10-11, Nov. 1958.
2. Clayton, Lee, Late Wisconsin Mollusca from ice contact deposits in Logan County, North Dakota, North Dakota Acad. Sci. Proc., v. 15, p. 17, 1961.
3. ————, Glacial geology of Logan and McIntosh Counties, North Dakota, North Dakota Geol. Survey Bull. 37, p. 68, 1962.
4. Eddy, S., How to know the freshwater fishes, Wm. C. Brown Co., Dubuque, Iowa, p. 76, 1957.
5. *Ibid.*, p. 91.
6. Eddy, S., and Surber, T., Northern fishes, University of Minnesota Press, Minneapolis, p. 128, 1943.
7. *Ibid.*, p. 153.
8. Fenneman, N. M., Physiographic divisions of the United States, U. S. Geol. Survey (map), 1946.
9. Frye, J. C., and William, H. B., Classification of the Wisconsinan Stage in the Lake Michigan lobe, Illinois Geol. Survey, Circ. 285, p. 2, fig 1, 1960.
10. *Ibid.*, fig. 1.
11. Tuthill, S. J., Clayton, Lee, and Laird, W. M., A comparison of a fossil Pleistocene molluscan fauna from North Dakota with a Recent molluscan fauna from Minnesota, Amer. Midl. Naturalist (in press).

N-ACYL MIGRATION BY ULTRAVIOLET LIGHT

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ABSTRACT

Phenyl esters are known to undergo rearrangement to both o- and *p*-hydroxyphenylketones with Lewis acid catalysts and under the influence of ultraviolet light. We now wish to report that an analogous reaction can be effected with ultraviolet light upon anilides. Thus irradiation of ethanol solutions of acetanilide and propionanilide induces isomerization to *o*- and *p*-aminophenylketones according to figure 1. In addition aniline was obtained as a cleavage product.

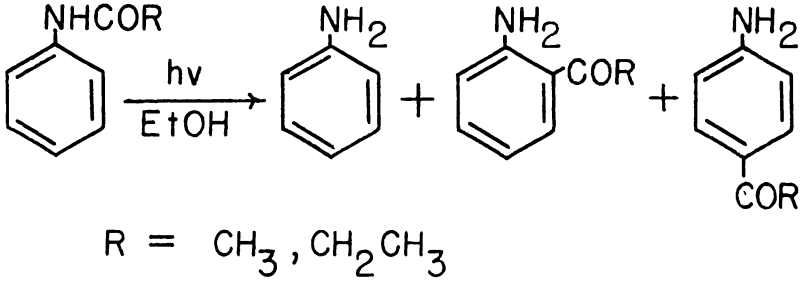

FIGURE 1—General reaction.

In contrast, benzanilide yields only ethyl benzoate, benzoic acid and aniline. Significantly no rearranged products were obtained. Although the mechanism of the reaction remains unestablished, a radical-solvent cage mechanism appears to be reasonable based on the analogy of the photo-decomposition of acetone and from the nature of the products. The appearance of benzoic acid, an unexpected product is explained by the oxidation of benzaldehyde, an expected product.

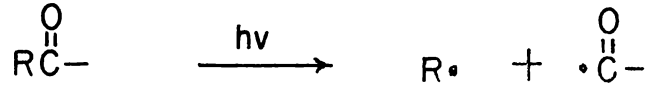

FIGURE 2—General initiating step.

The present reaction appears to be one more example of a general type as illustrated in figure 2 where R is now known to be the methyl group (alkyl), phenoxy, vinyl ether and an aniline group.

ACKNOWLEDGMENT

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THE ESTABLISHMENT AND DEVELOPMENT OF VALLEY CITY, NORTH DAKOTA

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INTRODUCTION

The urban settlement, be it city, village or hamlet, is regarded by the geographer as a man-made habitat on the earth's surface. Unlike the parts of the settlement pattern that are devoted to crop raising, grazing or forestry, these urban agglomerations serve commercial, cultural or administrative functions, or combinations thereof.

Two important concepts in urban geography are those of 'site' and 'situation.' Site can be defined as the precise features of the terrain on which the settlement began and over which it has spread. It includes such items as relief, geology, vegetative cover and water supply. Situation is usually taken to mean the relation of the place under study to other places, for we regard the settlement pattern as an interrelated whole. Site and situation must be taken together in the study of the development and present status of the settlement.

In North Dakota, an outstanding group of urban places is the system of trading centers which serve the large rural agricultural area. It is the purpose of this study to illustrate the establishment of one of these trading centers and its growth through the first important period of expansion in North Dakota—the great Dakota Boom of 1879 to 1886.

In 1871, when the Northern Pacific Railroad reached the Red River of the North at the present site of Fargo, northern Dakota Territory was a vast rolling prairie inhabited by a few Indians and fewer trappers, traders and soldiers. Little land had been put under cultivation; indeed, soldiers returning east in the 1860's reported the land as worthless for any agricultural purposes.

FIRST TOWNSITE

The Northern Pacific extended its tracks west to the James River Valley during 1872, and in September the first train crossed

the Sheyenne River. A siding laid in the valley west of the river gave the locality its first official name, Fifth Siding.

During that summer of 1872 a party of townsite speculators representing the Lake Superior and Puget Sound Company, a Northern Pacific subsidiary, passed through the valley and selected a quarter section of land on the river bank as a future townsite. The embryo village was given the more romantic name of Wahpeton, a Sioux word meaning "village of the leaves."

It soon became apparent that the party had blundered in its selection. The Northern Pacific's land grant gave it title to only the odd-numbered sections, while the land chosen lay within an even-numbered one. This was public land open to settlement by anyone who cared to choose it.

A year later a Canadian, John Morrison, filed a pre-emption on that exact same quarter section. Subsequent attempts to evict him from the land failed and the first townsite venture in the Sheyenne Valley ended unsuccessfully.

THE WORTHINGTON-MARSH TOWNSITE

In December, 1873, two men from Wisconsin, George Worthington and L. D. Marsh, settled in the valley having purchased a section of railroad land some miles south of the railroad crossing. Two months later the pair, under the name of the Dakota Land Improvement Company, signed an agreement with the railroad reserving every other odd-numbered section in townships 139 and 140, range 58, to be sold to incoming settlers by the company at mutual profit.

One of the provisions called for the establishment of a townsite on a quarter section of land in the section just west of the ill-fated Wahpeton townsite of 1872. The new site was given the name of Worthington in honor of one of the founders of the Dakota Land Improvement Co.

This speculation also failed largely from the lack of new settlers. This lack is not surprising. In the fall of 1873, shortly after the line had been completed to the Missouri, the Northern Pacific failed; this precipitated a nationwide financial panic. The period from 1873 to 1878 was one of pronounced economic depression throughout the country. This, along with several other factors, retarded immigration to northern Dakota. From 1874 to 1876 enormous swarms of grasshoppers ate their way across the prairies. In addition, the winter of 1874-75 was exceedingly severe and this, followed by several dry years, served to deter most potential immigrants.

THE NORTHERN PACIFIC TOWNSITE

Immigration picked up in 1877 and the following summer the Northern Pacific platted its own townsite at the Sheyenne crossing on the same quarter section named in the 1874 Dakota Land Improvement Co. agreement. By the end of that year, during which a

popular vote changed the locality's name to Valley City, the settlements consisted of 30 to 50 inhabitants.

The year 1879 marked the beginning of the Dakota Boom during which much of the Territory was settled. There were a number of influences that produced the boom. Rainfall was a primary factor. During the boom period rainfall was ample and came at such times as to permit good crops. During the winter of 1880-81, heavy snows fell while the ground was practically unfrozen and because of great

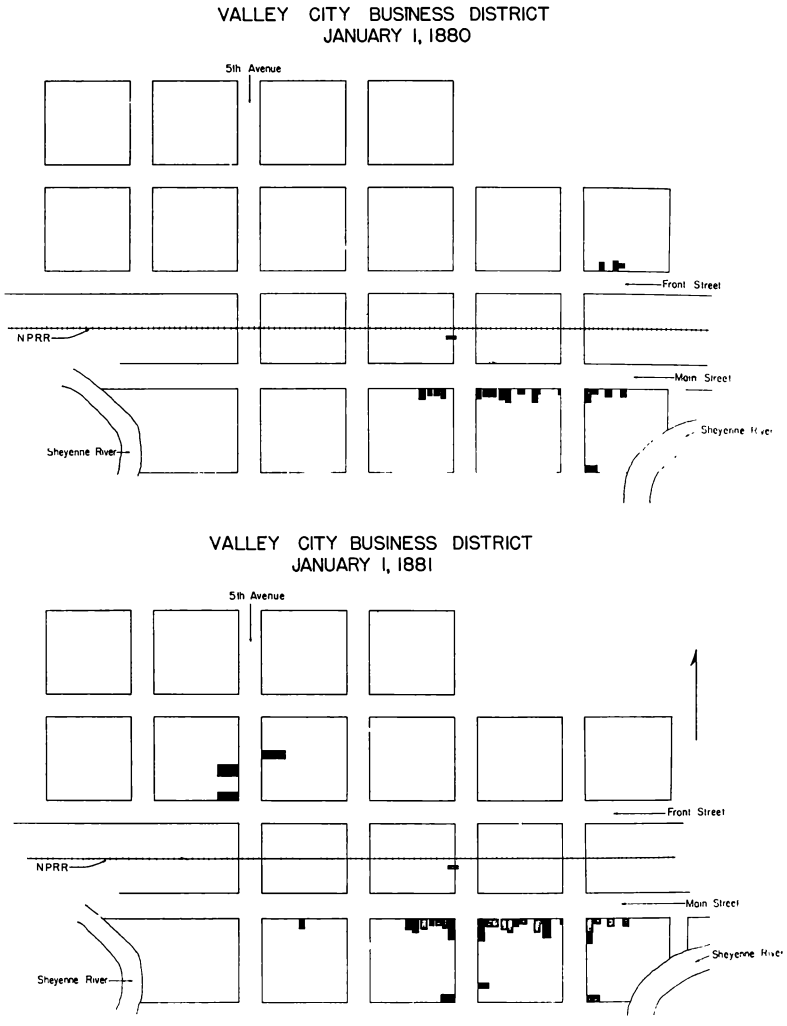

FIGURE 1—Valley City business district January 1880 and 1881.

snow depths the earth remained only slightly frozen during the winter. When the snow melted in the spring it saturated the soil and subsoil with water and promoted good crop conditions for several years.

The extension of railroads throughout most of northern Dakota was another important factor. A cheap means of transportation was thus provided to move the area's products to the east and bring in the numerous materials needed by the settlers. Without the railroad to bring timber into a treeless Dakota, a building boom could never have started.

In addition, most of the desirable farmland to the east had been occupied by 1879 causing a general rise in price and taxes. Dakota's free, or at least cheaper, farmland was the object of a large number of settlers. These included many who had lost everything in the 1873-78 depression as well as the great numbers of foreign immigrants flocking into the country. The success of the bonanza farms also served to promote immigration.

At this time the country was in its most prosperous condition since 1873. The considerable amounts of capital required to construct railroads and buildings, break sod and raise crops became more easily available as credit conditions improved.

BUSINESS DISTRICT OF 1880

By January 1, 1880, Valley City had grown considerably. Its business district had taken on the characteristics seen in many of the pioneer towns laid out by the railroad in that the business buildings tended to face toward the tracks on both sides of the right of way with the depot in the center. The sole deviation lay in the fact that only one side of the right of way was fully occupied. (See figure 1).

In order to alter this established pattern it would take the introduction of some new element into the environment. There are two potential cases present here.

First, to the northeast are two new buildings housing a newspaper office and a harness shop. This might be dismissed as the beginning of development on the opposite side of the right of way.

However, to the south there is an element that might have considerable influence on the growth of the business district. In 1879 Hiram Walker built a small water-powered flour mill on the Sheyenne River at the south edge of town. At the same time a small hotel, the Valley City House, was built along the street connecting the business district and the mill. Here there is a distinct possibility of future business expansion since in those days business and industrial development tended to grow toward each other.

During 1880 a new force made itself felt, as the map of expansion shows. North of the tracks and several blocks to the west three large new buildings were erected—a brick bank building and a general store and a livery stable, both of wood frame construction.

This new outgrowth came about through the efforts of a group of land speculators, all employees of the Northern Pacific's Land Examining Department. They were Charles F. Kindred, chief clerk at the Brainerd headquarters and owner of a large amount of Barnes County farmland; Edward Kopper, a surveyor who laid out the original plat of the town in 1878; Charles Thompson and John Holmes. These men found that most of the lots in the vicinity of the business district had already been purchased by other speculators. (See figure 1). They gained control of a large number of lots to the north and northwest of the existing business district, and attempted to create a new business district, thus raising land values to their eventual profit. With Kindred's financing the town's first bank opened. Holmes and Thompson built the new general store and George Getchell, a prominent Barnes County farmer, the livery stable.

The earlier movement to the northeast that began in 1879 ceased abruptly. The newspaper, purchased by Kindred, was moved to the bank building. The harness shop moved to a new building in the old business district.

The movement in the direction of the mill also died under the effects of the new speculation. The older district continued to grow, several large new buildings being constructed during 1880. Most important of all, several merchants built additions to their structures, indicating a confidence in the future of the town. It is at this point that Valley City can be said to have passed from its boom town era to that of a permanently established area.

1881-82 BUILDING BOOM

The summer of 1881 ushered in a business building boom in Valley City. That year and the one following saw the conflict between the two competing business districts reach its high point, resulting in a gradual decline of the older area as a center of retail business activity. This result, although inevitable, did not show itself strongly until the end of the Dakota Boom years.

The building race between the two districts waxed hot and heavy during the summer of 1881. Then, in September, a local land promoter, B. W. Benson, under the direction and financing of Kindred, began work on a three-story brick hotel building, a facility which the community badly needed. The following year the structure was completed by Thomas Adams, of the Adams Chewing Gum family, an easterner lured to Dakota Territory by Kindred. The hotel was named in Kindred's honor when it was completed in 1882. Late in 1881, George Getchell, who had already doubled the size of his livery stable, added a third story and a mansard roof to the structure and gave Valley City its first Opera House. (See figure 2).

The importance of these structures cannot be under emphasized. With their completion the newer business district had the financial and cultural centers of the community in addition to its largest and

finest hotel. In addition, a number of merchants who had rented space in buildings in the older business district moved to the newer area during this period and built substantial structures of their own. Among these were the town's pioneer druggist and harnessmaker.

Even so, the 1881-82 building boom saw several large new buildings go up in the older business district. The Parkhouse and Sayles general store and Darby O'Malley's Dakota House were erected on its western edge. But it was a case of too little too late. Finally, in

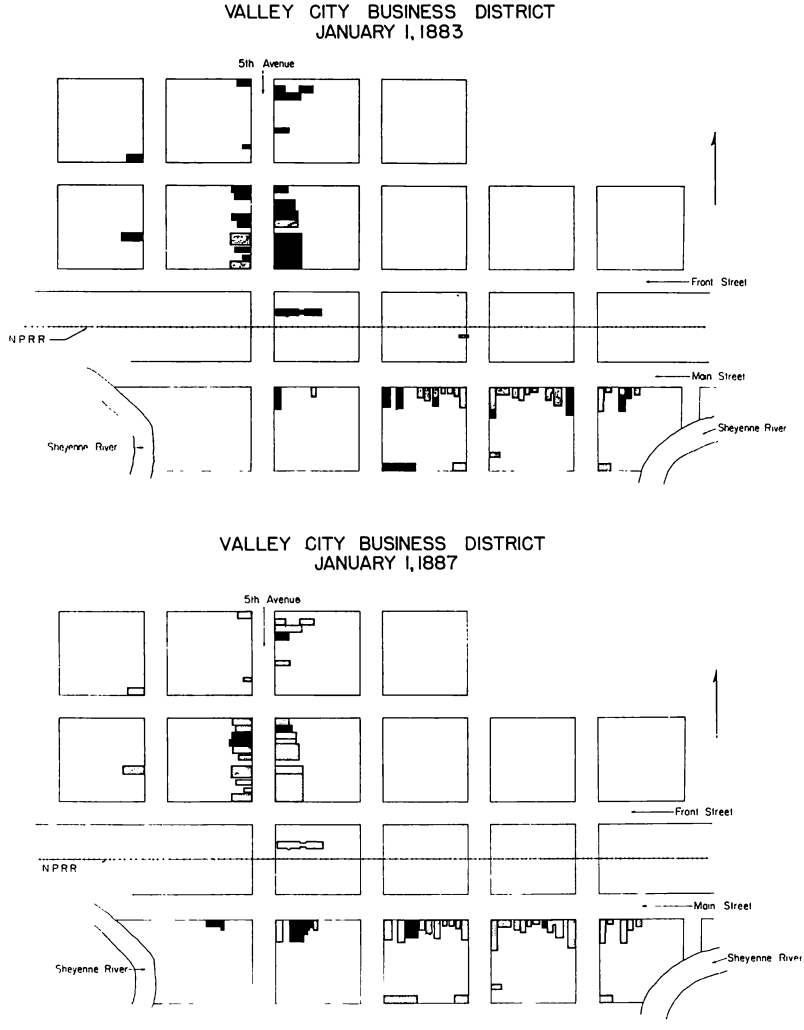

FIGURE 2—Valley City business district, January 1883 and 1887.

the summer of 1882, the railroad built a new depot just south of the Kindred Hotel, as if in recognition of the fact that the center of business activity had indeed moved west.

END OF THE BOOM

The Valley City business building boom came to a rather abrupt end in the fall of 1882. There are several possible reasons for this. Charles Kindred, who had spent so much in promoting a new business district in Valley City, virtually bankrupted himself in a losing attempt at being elected to the House of Representatives from Minnesota's newly-formed Fifth District.

Some accounts set his elections expeditures at well over $150,000. Considering that the purchasing power of the dollar of 1882 was equal to about three times that of today's dollar, a present day figure of close to half a million dollars emerges, a lot of money to be spent on any state election! Although existing records show no direct connection, the loss of Kindred's capital coincides closely enough with the end of the building boom to give the impression that the two incidents were related.

Another factor to be considered was that the boom was already moving west of Valley City. By the fall of 1882 most of the public and railroad lands had been taken up east of the Missouri and many of the settlers merely passed through on their way to the land still unselected in western Dakota and Montana.

From the end of 1882 to the end of the Dakota Boom in 1886, business building construction fell off sharply in comparison to the earlier years. However, there was an outgrowth of the earlier business district toward the west, which in effect, served to connect the two competing areas. The newer buildings in this area were built mainly of brick which helped to place the connecting link on a more solid foundation. In the older district, Darby O'Malley built a two-story brick addition to the Dakota House, but it still had neither size or accommodations to compare with the Kindred Hotel.

By 1887 widespread drought conditions had brought on the complete collapse of the Dakota Boom. A general depression spread across the territory resulting in a large number of business failures. Hundreds of settlers, harrassed by the drought and disappointed in business and land speculations, left the Dakotas. Valley City was hit as hard by the changing conditions as any other Dakota town. Stores that had been doing a bustling business in 1882 and 1883 stood empty in 1887. (See figure 2).

Fires, in the end, spelled finish to the older business district. A blaze in February, 1890, wiped out the heart of the area. Two years later the brick addition to the Dakota House was destroyed. The burned-over lots stood empty for the most part until after the turn of the century.

Strangely enough, the foundations which Kindred and his group of speculators had laid have remained to this day the core of Valley City's modern central business district. However, all members of the group, with the exception of John Holmes, dissappeared from the Dakotas before the end of the boom. Holmes continued to operate his general store until his death in the early 1900's.

SUMMARY AND CONCLUSION

This study of the establishment of a Dakota trading center and the early development of its retail business district is not only a study in urban geography but a study in pioneer settlement as well. Within broad limits, there are a number of characteristics in the establishment and growth of Valley City which would apply to pioneer settlements by Europeans in different parts of the world in the last century, particularly in regard to land policies and railroad development.

In the case of Valley City it can be seen that the point where the Northern Pacific tracks crossed the Sheyenne Valley was a probable location for a settlement. Had the railroad crossed ten miles north or ten miles south, a similar settlement most surely would have sprung up. Thus the intersection of these two lines, one natural and the other man-made, greatly influenced the site of the settlement.

The effect of situation can be noted in both local and nationwide conditions. Although the site had been determined in 1872, economic depression throughout the United States postponed growth of any consequence for nearly eight years. Only when the favorable climatic and economic conditions that led to the Dakota Boom of 1879 arose did Valley City show any signs of expansion.

When the locality did begin to grow it did so along the lines of a typical railroad town, two lines of business buildings facing each other across the railroad tracks. It was only when a new, strong, outside force made itself felt that there was a deviation from the established lines of development. In this case, that new force was land speculation and the large amounts of capital spent to promote it. Although in the past the term land speculation has been chiefly identified with hasty and unscrupulous attempts to artificially inflate land values, its effects are not necessarily destructive.

The Valley City business district of the late 1880's forms the core of today's modern central business district. The fact that it fits well into its own peculiar site and situation 80 years after its initial development was borne out recently by a newspaper statement by a modern-day Valley City real estate promoter. Asked why he was building shopping centers in Jamestown and other communities rather than his home town, he replied that his surveys had shown that Valley City's central business district is well adequate to efficiently serve its trade area for present and will be for some years to come.

ACKNOWLEDGMENTS

This study could never have been completed had it not been for the numerous Valley City residents who cheerfully donated their time, memories and family historical materials.

The archives of the North Dakota Institute of Regional Studies at Fargo and the help of the Archivist, Dr. William C. Hunter, were important in making available primary source material.

A special note of thanks is due Dr. Warren D. Kress of the Geography Department at the North Dakota State University of Agriculture and Applied Science. Without his unflagging enthusiasm and lavishly donated knowledge and experience the author would probably have given up.

BIBLIOGRAPHY

Baker, James H. Lives of the Governors of Minnesota. St. Paul Minnesota Historical Society. 1908.

Barnes County, North Dakota, Register of Deeds. Deed Books. Manuscript materials on file at the Barnes County Court House, Valley City, N. Dak.

Briggs, Harold E. Frontiers of the Northwest. New York. Peter Smith. 1950.

Glimpses of Valley City, North Dakota (Booklet of photogravures by Fisher and Company, Valley City, photographers). Brooklyn. The Albertype Co. 1903.

Hard, Herbert A. Soil and Geological Survey of North Dakota, 1911-1912. Fargo. Agricultural College Survey. 1912.

Hibbard, Benjamin H. A History of the Public Land Policies. New York. The MacMillan Co. 1924.

Lounsberry, Col. Clement A. Early History of North Dakota. Washington, D. C. Liberty Press. 1919.

Mayer, Harold M., and Kohn, Clyde F. (editors). Readings in Urban Geography. Chicago. University of Chicago Press. 1959. (pages 10-26, 110-21, 210-17, 331-45).

North Dakota, a Guide to the Northern Prairie State. Federal Writer's Project. New York. Oxford University Press. 1950.

North Dakota Illustrated. (Collection of photographs). Fargo. United Commercial Travelers of America. 1911.

Northern Pacific Times. Valley City, N. Dak. Various issues, 1879-1880.

Orfield, Matthias N. Federal Land Grants to the States with Special Reference to Minnesota. Minneapolis. Bulletin of the University of Minnesota. March, 1915.

Powers, James B. Correspondence as General Agent for the Northern Pacific Land Examining Department, and other related correspondence for the period 1873-1887. Manuscripts in archives of the North Dakota Institute of Regional Studies, Fargo, N. Dak.

Valley City Directory. Fargo. Pettibone Directory Co. Volumes for 1908, 1920 and 1927.

Robinson, Elwyn B. The Themes of North Dakota History. Revision of address read on November 6, 1958, at the 75th Anniversary Conference of the University. Grand Forks.
Second Crossing of the Sheyenne. Historical pamphlet published for the Valley City Diamond Jubilee Celebration in June, 1958.
Smalley, Eugene V. History of the Northern Pacific Railroad. New York. G. P. Putman's Sons. 1883.
Trinka, Zena I. North Dakota of Today. St. Paul. Louis F. Dow Co. 1920.
Valley City, North Dakota. The Record. April, 1898. Pages 177-196. (Published at Fargo by C. A. Lounsberry).
Valley City Times. Valley City, N. Dak. Various issues, 1880-1887.
Valley City Times-Record. Valley City, N. Dak. Various issues, 1889-1899.
Williams, Mary Ann Barnes. Origins of North Dakota Place Names, Cass and Barnes Counties. Washburn, N. Dak. 1958.
Winser, Henry J. The Great Northwest. St. Paul. Northern News Co. 1888.

DERIVATIVES OF 5-METHYL-3-PHENYLISOXAZOLE-4-CARBOXYLIC ACID[1]

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Quilico and Fusco (1) found that an isoxazole ring compound may be prepared by the condensation of 1'-chlorobenzaldoxime with the sodium salt of ethyl acetoacetate.

The purpose of the work reported here was to prepare different 5-methyl-3-phenylisoxazole-4-carboxylic acid hydrazides and amides for pharmacological investigations as to their anti-bacterial activity. Interest in this topic is shown after it was discovered that a reaction between 5-methyl-3-phenylisoxazole-4-carboxylic acid and 6-amino-penicillanic acid produced a very effective penicillin-like material.

Further work is planned and several more derivatives will be prepared.

EXPERIMENTAL

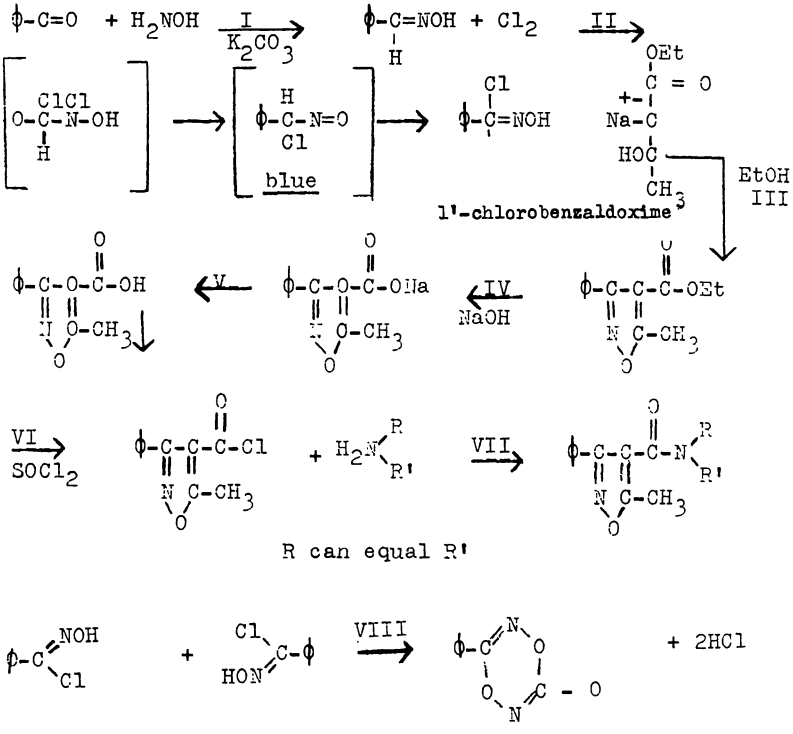
Benzaldoxime was prepared in the usual manner by reacting hydroxylamine hydrochloride with benzaldehyde in an aqueous potassium carbonate solution.

[1]This work was partially supported by the Mead Johnson Co., Evansville, Indiana.

[2]Visiting Professor of Organic Chemistry, University of Saigon, Saigon, Viet Nam.

1'-Chlorobenzaldoxime.-Benzaldoxime (0.4 mole or 48.4g) was dissolved in 200 ml of absolute ether and placed in an ice bath. Dry, HCl free Cl_2, generated from calculated amounts of $KMnO_4$ and HCl, was bubbled through the benzaldehyde solution (cf. reaction II). Color changes of yellow to green to blue-green to yellow were noted. The green blue-green is thought to be due to the formation of the nitroso-intermediate. The ether was removed and the product filtered giving a crude yield of about 62 grams or 98%. This product appears to be quite unstable and is very corrosive in solution. At more than 40°, it apparently decomposes giving off very strong vapors, perhaps according to equation VIII.

Ethyl 5-Methyl-3-Phenyl-Isoxazole-4-Carboxylate.-1'-Chlorobenzaldoxime (0.07 mole or 15.5 g) was dissolved in CCl_4. A sodium ethyl



acetoacetate solution (prepared by dissolving 0.10 mole or 2.3 g Na in an excess of absolute ethanol and refluxing with 13.0 g or 0.16 mole ethylacetoacetate for 30 minutes) was added to the flask containing the 1'-chlorobenzaldoxime with shaking while being cooled in an ice bath. Upon the addition of 1'-chlorobenzaldoxime, sodium chloride precipitated out immediately while the solution turned to a brownish-orange color.

The sodium chloride was removed by filtering the material through a mat of celite on a Buechner funnel. The carbon tetrachloride and excess ethanol were removed, and ether and water were added to the residue. The etheral solution was washed with a 4% NaOH solution and evaporated down. The final residue was then vacuum distilled. The fraction coming over from 176-190° was collected. This solidified upon standing. The resulting material was recrystallized several times from petroleum ether, b.p. 30-60°C. This was a white crystalline material, m.p. 47.5-48°; the yield was 4.2 g (18.25%).

5-Methyl-3-Phenyl-Isoxazole-4-Carboxylic Acid.-The ethyl ester (4.0 g or 0.0173 moles) obtained in the previous step was placed in a flask with 100 milliliters of methanol an excess amount of NaOH and refluxed on a steam bath for 4 hours. Hydrochloric acid was added until it was below a pH of 6. At the end of this time, the

TABLE I

MELTING POINTS OF PREPARED COMPOUNDS

Derivative of 5-methyl-3-phenylisoxazole-4-carboxylate acid	m.p. °C.
1. parent acid	189 (189 Lit.)
2. ethyl ester (A)	47.5-48 (48 Lit.)
3. 2,5-dichlorophenylhydrazide	175-176
4. 1,1-diphenylhydrazide	199.5-200
5. methyl ester	74-74.5
6. 2,4,6-trichlorophenylhydrazide	215-216
7. p-nitrophenylhydrazide	204
8. dicyclohexylamide	74-76
9. N-ethyl-N-naphthylamide	72-73.5
10. benzylamide	139-139.8
11. N-methylanilide	88.3-89
12. butylamide	95-96
13. o-nitroanilide	132.5-133.5
14. p-N, N-dimethylaminoanilide	162.5-163.5
15. diethylamide	75
16. 4-chlorophenylhydrazide	151.4-152

SPOT ANALYSIS OF ABOVE

	Calculated	Found
3.	C. 56.52% H 3.35% N 11.64%	C. 56.31% H 3.67% N 11.56%
6.	C. 51.47 H 3.05 N 10.60	C. 51.16% H 3.16% N 10.63%

contents of the flask was emptied into a beaker of ice. A white fluffy precipitate came out. The precipitate, m.p. 188-189°, was removed and recrystallized from benzene. The yield was 3.64 g (91%).

Isoxazole Acid Chloride.-Six grams (0.0295 moles) of the acid was placed in a flask with an excess of thionyl chloride and re-

fluxed for one hour. The excess thionyl chloride was distilled off. The resulting product was a yellowish liquid at room temperature. The yield was 3.68 g (92%).

Preparation of 2,5-Dichlorophenylhydrazide, a Typical Procedure.-Two grams (0.009 m) acid chloride and (.009 m) 2,5-dichlorophenylhydrazine were ground together in a beaker and allowed to stand. The material, m.p. 175-6°, was recrystallized from aqueous methanol. The yield was 2 g (61%).

The compounds listed in Table I are believed to contain the above structure.

REFERENCE

1. A. Quilico and R. Fusco, Chem. Abst., 67, 589-603 (1937).

PHOTOINDUCED AUTOXIDATION OF ETHERS

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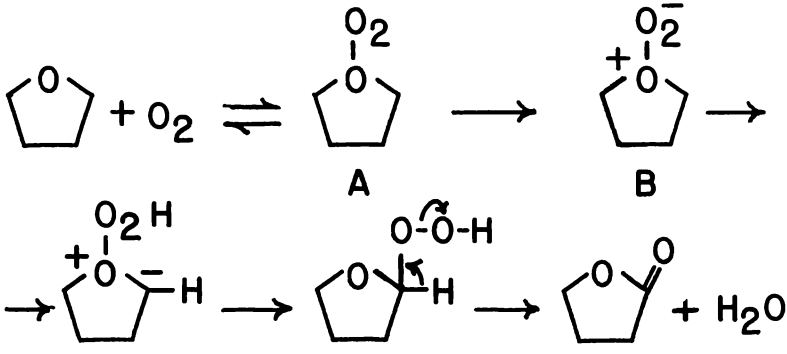
ABSTRACT

The oxidation of cyclic ethers to lactones and acids is known, but the conditions of the oxidation are vigorous.[1,2,3] Photochemical oxidation is a topic of a paper by Schenck *et al.*[1] in which they obtained hydroperoxides as products.

Irradiation of tetrahydrofuran with ultraviolet light produced butyrolactone, irradiation of n-propyl ether produced n-propyl pro-



pionate, and irradiation of dioxane gave uncharacterized carbonyl compounds. However, none of these were the cyclic ethylene glycol ester of oxalic acid. On the other hand, anisole remained unchanged.

We would like to suggest that the reaction proceeds via a mo-

lecular charge transfer complex between the ethereal oxygen and molecular oxygen. This is in contrast to the radical process of Schenck *et al.*[1] These complexes are known and their presence in the reaction mixtures is upheld by ultraviolet spectral data. It is believed that this complex is the species absorbing the ultraviolet light and reacting.[5]

The charge transfer complex is a hybrid of a non-bonded (A) and charge separated or "dative" bond (B) structure. The excited complex has its highest contribution from the dative bonded structure (B), the oxygen of which can abstract an α-hydrogen and then undergo intramolecular rearrangement to form the product.

We gratefully acknowledge that this research was supported in part by a Chester Fritz Fellowship (R.D.O.), a Research Corporation Grant and a University of North Dakota Faculty Grant.

REFERENCES

1. Cass, O. W., Ind. Eng. Chem., 40, 216-219 (1948).
2. C. A., 43, 2224e, 3029f, 4687f (1949).
3. Takayama, Y. and Mizuno, S., J. Electrochem. Japan, 18, 298-301 (1950).
4. Schenck, G. O., Becker, H., Schulte-Elte, K. and Krauch, C. H., Chem. Ber., 96, 509-516 (1963).
5. Mulliken, R. S., J. Am. Chem. Soc., 72, 600 (1950).

INVESTIGATIONS OF THE FRUIT FLY

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Winner, Ralph E. Dunbar Award, North Dakota High School Science Competition

INTRODUCTION

Drosophila melanogaster is commonly called the fruit fly. It is a member of the insect order, Diptera. This means that the fruit fly undergoes complete metamorphosis. This metamorphosis takes about fourteen days at a temperature of 22°C. At cooler temperatures, this time is longer.

Male fruit flies have five visible segments on the abdomen. The abdomen is also more rounded in the male than the female. The male has a sex comb composed of a number of bristles on the first set of legs. A female has seven visible segments on the abdomen. Also, the abdomen becomes greatly enlarged on an older female because of maturing eggs.

TEMPERATURE AND INSECTICIDE TOXICITY

It was assumed that the toxicity of an organic insecticide varies with the temperature. To determine the toxicity of selected insecticides, tests with fruit flies were made. In the experiments that follow, fruit flies were placed in test tubes that had a twenty-five cubic centimeter capacity. Then one drop of chemical was carefully measured and placed on the cotton in the mouth of the test tube. Once this had been done, the flies were bumped onto the cotton to make sure that each fly had come in contact with the insecticide. Flies that could not right themselves after being placed on their backs were considered dead. Two minutes was allowed a given fly to right itself.

This procedure was repeated with various chemicals at 60°F, 70°F, and 80°F. In the first experiment DDT diluted to a strength of 1:1,000 was used; in the second, Cygon at 1:10,000; and in the third, Dieldrin at a strength of 1:1,000 was employed. The results of these experiments are shown in Tables I-III. It can be seen from these tables that the toxicity of DDT and Cygon varies directly with the temperature, but that the toxicity of Dieldrin varies inversely with the temperature.

Thus, from the experiments, one can tell at what temperatures the insecticide is most toxic to fruit flies. In this way less insecticide can be used for an effective kill.

P_1: DDT Female and Wild Male Cross

F_1:		Female	
		X'	X'
Male	X	X'X	X'X
	Y	X'Y	X'Y

F_2:		Female	
		X'	X
Male	X'	X'X'	X'X
	Y	X'Y	X Y

P_1: Wild Female and DDT Male Cross

F_1:		Female	
		X	X
Male	X'	X'X	X'X
	Y	X Y	X Y

F_2:		Female	
		X'	X
Male	X	X'X	X X
	Y	X'Y	X Y

FIGURE 1—Cross predictions for a recessive, sex-linked gene.

DDT RESISTANCE IN FRUIT FLIES

Some fruit flies have a natural resistance to DDT. However, these resistant fruit flies comprise a small percentage of the total number of fruit flies.

Experiment 4 was the development of a procedure for obtaining a strain of DDT-resistant fruit flies. A drop of DDT, diluted 1:200,000 with water, was placed at 72°F on a cotton plug in the mouth of a

25 cc test tube in the presence of first generation (P_1) fruit flies. After a short time, many of the fruit flies were dead. In this way, one can isolate the flies which are most immune to DDT. The amount of DDT and the length of the exposure were changed in succeeding generations. This resulted in a type of selection known as "line breeding" or "inbreeding". Results of the experiment are shown in Table IV. These are interpreted as indicating that fruit flies can acquire a resistance to DDT through line breeding.

Experiments 5 and 6 were test crosses made to determine if the trait of resistance of DDT is dominant or recessive and whether it is sex-linked. In Experiment 5 DDT-resistant females were mated with wild-type males and their offspring counted. The results of this experiment as shown in Table 5. These data, when diagrammed, follow the predictions for a sex-linked cross as shown in figure 1.

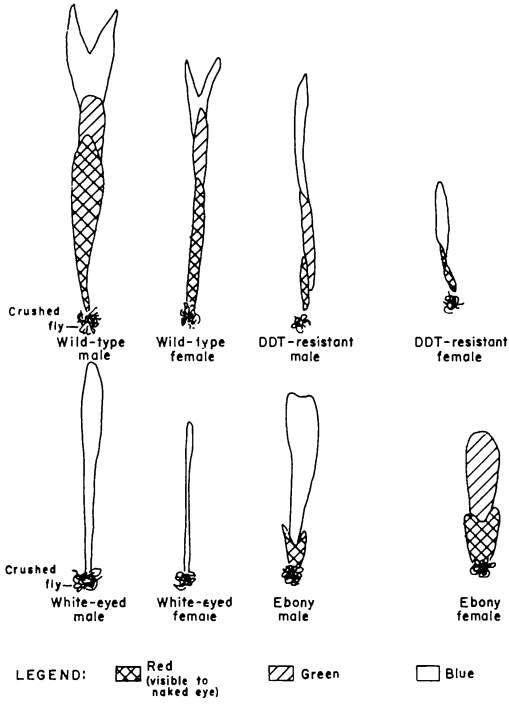

FIGURE 2—Chromatograms of fruit flies.

Experiment 6 was made as a check on Experiment 5. In the reciprocal cross, Experiment 6, just the opposite of Experiment 5 was done. The same traits were crossed, but the sexes of the flies in the P_1 generation were reversed; DDT-resistant males were mated with

wild-type females, and their offspring counted and recorded in the same manner as Experiment 5 and shown in Table VI.

These two experiments indicate that the DDT-resistant character is carried on the X-chromosome and is recessive and sex-linked.

CHROMATOGRAPHY

While it is possible to detect certain substances by the more conventional forms of analysis used in the laboratory, amino acids, sugars and the like are most easily detected by chromatography.

In making chromatograms for Experiment 7, five fruit flies were crushed at the lower end of a strip of #1 filter paper. Wild-type, DDT-resistant, white-eyed and ebony males and females were used. The filter paper was placed in a solvent. The solvent was composed of two parts (by volume) of distilled water, one part of ammonium hydroxide (NH_4OH), and one part isopropyl alcohol.

Some filter papers were left in the solvent for longer times than others. The ones which had been left in the solvent for 2½ hours are shown in figure 2.

Only certain pigments show up to the naked eye. The red, shown on the wild-type chromatogram for instance, is quite visible to the naked eye. The red must come only from the eye since the red is totally absent in the white-eyed fruit fly chromatogram. Under ultraviolet light, different colors appear. Evidently, each of these patches of color represents a different chemical. From this one can conclude that each sex, genotype, and phenotype of fruit fly has its own particular pattern on the chromatogram under ultraviolet light, and, if one has an unknown type of fruit fly, one can determine the genetic make-up of the fruit fly by chromatography.

In Experiment 8 chromatography was used to detect reducing sugars in the fruit fly. The reducing sugar, if it is contained in the fruit fly can be detected by chemical methods on the chromatogram of the fruit fly.

The chromatograms of the wild-type male were cut into one-half inch segments. A solution of 0.1 N silver nitrate was sprayed on the strips followed by an application of 5N ammonium hydroxide. Then the strips were heated in a 225°F oven. A check strip of fresh #1 filter paper was also made. From this exposure to heat, the strips of the chromatogram turned brown, indicating a reducing sugar was present. The check strip remained its original white color. On a chromatogram run for 2½ hours, the sugar didn't isolate itself at any particular level. In conclusion it appears that simple reducing sugar is present in the fruit fly which can be detected by chromatography.

TABLE I

TEMPERATURE-TOXICITY RELATIONSHIPS OF DDT

Temperature 60° F. (15.5° C.)					
Hours:	1	2	3	4	5
Total:	19	19	19	19	19
Live:	19	19	19	18	16
%:	100%	100%	100%	95%	85%
Dead:	0	0	0	1	3
%:	0%	0%	0%	5%	15%
Temperature of 70° F. (21° C.)					
Hours:	1	2	3	4	5
Total:	25	25	25	25	25
Live:	24	23	17	13	9
%:	96%	92%	68%	52%	36%
Dead:	1	2	8	12	16
%:	4%	8%	32%	48%	64%
Temperature of 80° F. (26.7° C.)					
Hours:	1	2	3	4	5
Total:	25	25	25	25	25
Live:	24	22	21	12	5
%:	96%	88%	84%	48%	20%
Dead:	1	3	4	13	20
%:	4%	12%	16%	52%	80%

TABLE II

TEMPERATURE-TOXICITY RELATIONSHIPS OF CYGON

Temperature of 60° F.					
Hours:	1	2	3	4	5
Total:	29	29	29	29	29
Live:	29	29	29	29	29
%:	100%	100%	100%	100%	100%
Dead:	0	0	0	0	0
%:	0%	0%	0%	0%	0%
Temperature of 70°F.					
Hours:	1	2	3	4	5
Total:	32	32	32	32	32
Live:	31	12	11	11	11
%:	97%	38%	34%	34%	34%
Dead:	1	20	21	21	21
%:	3%	62%	65%	65%	65%
Temperature of 80° F.					
Hours:	1	2	3	4	5
Total:	33	33	33	33	33
Live:	18	15	13	8	0
%:	55%	45%	39%	24%	0%
Dead:	15	18	20	25	33
%:	45%	55%	61%	76%	100%

TABLE III

TEMPERATURE-TOXICITY RELATIONSHIPS OF DIELDRIN

Temperature of 60° F.					
Hours:	1	2	3	4	5
Total:	27	27	27	27	27
Live:	11	11	8	7	4
%:	41%	41%	30%	26%	15%
Dead:	16	16	19	20	23
%:	59%	59%	70%	74%	85%
Temperature of 70° F.					
Hours:	1	2	3	4	5
Total:	35	35	35	35	35
Live:	22	19	16	14	12
%:	65%	55%	45%	40%	35%
Dead:	13	16	19	21	23
%:	35%	45%	55%	60%	65%
Temperature of 80° F.					
Hours:	1	2	3	4	5
Total:	36	36	36	36	36
Live:	36	21	20	19	7
%:	100%	59%	55%	53%	20%
Dead:	0	15	16	17	29
%:	0%	41%	45%	47%	80%

TABLE IV

DATA FROM EXPERIMENT 4

P_1:	Date:	Jan. 10		
	Total:	100		
	Hours:	11		
	Alive:	95		
	% alive:	95%		
	Dead:	5		
	% dead:	5%		
F_1:	Date:	Feb. 12		Feb. 8
	Ratio:	1:200,000		1: 1,000
	Total:	37		100
	Hours:	15		13
	Alive:	37		92
	% alive:	100%		92%
	Dead:	0		8
	% dead:	0%		8%
				Wild-type flies
F_2:	Date:	Mar. 1	Feb. 26	Feb. 24
	Ratio:	1: 1,000	Full Str.	1: 1,000
	Hours:	12	¼	¼
	Total:	20	150	80

Live:	20	75	0
%:	100%	50%	0%
Dead:	0	75	80
%:	0%	50%	100%

TABLE V

DDT RESISTANCE IN OFFSPRING OF RESISTANT FEMALE

P_1: DDT Female[1] and Wild Male Cross

	Date	Progeny DDT Females	Progeny Non-DDT Females	Progeny DDT Males	Progeny Non-DDT Males
F_1:	3/12/63	0	8	5	0
	3/15/63	0	8	8	0
	Total	0	16	13	0
F_2:	3/30/63	2	3	5	2
	3/31/63	14	10	10	13
	Total	16	13	15	15

[1]DDT fly is one which has resistance to the insecticide and a Non-DDT fly is one whch is not.

TABLE VI

DDT RESISTANCE IN OFFSPRING OF RESISTANT MALE

P_1: Wild Female and DDT Male Cross

F'_1: Date

		Progeny DDT Females	Progeny Non-DDT Females	Progeny DDT Males	Progeny Non-DDT Males
F_1:	3/12/63	0	4	0	4
	3/15/63	0	8	0	8
	Total	0	12	0	12
F_2:	3/30/63	0	11	3	5
	3/31/63	0	7	14	15
	Total	0	18	17	20

IMPROVEMENTS IN THE PROCESSING OF POTATO AND VEGETABLE PRODUCTS

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Invited Paper for the 55th Annual Meeting of the North Dakota Academy of Science, at Grand Forks, North Dakota, May 3-4, 1963.

Dehydrated and processed vegetables with a variety of brand names on the shelves of supermarkets over the country are ample evidence of the consumer acceptance of dehydrated foods. Not many years ago dehydrated foods in quantity were utilized only in emergency conditions by soldiers; it was imperative that perishable items be made stable and decreased in weight for transportation reasons. Dehydrated potatoes, onions, carrots and beets were used in fairly large quantities during World War II and improvements in these items due to the research programs instituted by the Army Quartermaster Corps in the Universities and Governmental departments during and after the War are largely responsible for the improvements which have resulted in the quality of these foods.

Processed vegetable products in the Red River Valley are largely limited to potatoes. A potential exists for pumpkin, squash, peas, and beans. Three plants produce potato flakes and slices, two plants produce potato flakes, two produce frozen French fried potatoes and two produce potato chips. These plants exclusive of potato chips accounted for 1,263,826 hundredweight of potatoes during the 1961-62 crop year. The consumer acceptance of dehydrated vegetables has resulted in the growth of an industry which has considerable future promise to us in the Red River Valley. A short history of the changes and improvements in processing together with an enumeration of the unsolved problems should give us an idea of what future developments might bring.

During World War II, it was necessary for logistic reasons to dehydrate a number of vegetable foods for use in the various theaters of war around the world. Dehydrated potatoes were produced in Grafton, Grand Forks and in East Grand Forks. These consisted of two types. The first was a cooked potato dried in shred form and the second type was a ⅜" × ⅜" × ⅜" dice form which was only cooked sufficiently long to inactivate the enzymes before drying. The first type was used for mashed potatoes and the second type was used for hash browns and for addition to canned beef stews and soups. During this period there was considerable variation in the quality of the products made due to lack of knowledge. Processors learned by experience, and quite often the experiences were painful

and costly. Processing equipment was difficult to procure and was designed and built by people who had no previous experience in this technology.

The production of good quality dehydrated food was no guarantee that the food would be in good condition when it was consumed. The policy in the Army of using the older stocks of food first and of procuring large quantities kept foods in storage long enough for significant deterioration. It was not realized at first that dehydrated foods were perishable and the extent to which dehydrated foods changed with adverse storage conditions. Dehydrated potatoes stored in tins covered with canvas reached daytime temperatures above 140° F. in the South Pacific. Under these conditions the potatoes browned, lost their capacity to reabsorb moisture, and became inedible because of their poor flavor.

Several studies initiated by the Army Quartermaster Corps resulted in improvements and a new knowledge of dehydration procedures. It had been known that reducing sugars accumulated in potatoes under conditions of cold storage and that these could be dispersed to some extent by warm storage of potatoes. Reducing sugars and amino acids combine to form a brown reaction product which is responsible for the bitter unwanted flavor in potatoes and potato chips. It was commonly thought that if the reducing sugar content was low enough so that browning did not take place during the drying step that the product would be satisfacory. Storage of the product in hot countries and its rapid deterioration pointed to the need for further study.

The Western Regional Laboratories of the U. S. Department of Agriculture made a thorough study of variables affecting storage life and determined that the rate of the browning reaction was a function of the moisture content in addition to the reducing sugar content. Very low moisture contents practically stopped the reaction. The addition of sulphur dioxide also inhibited the reaction. The storage problem was not solved, however. At very low moisture contents, the small amount of unsaturated fats in potatoes becomes rancid and unwanted flavors develop. Antioxidants postpone to some extent the development of rancidity, but this is still one of the unsolved problems of potato processing.

Because of the fact that two of the plants processing potatoes in the Red River Valley were located in Grand Forks and there were problems in which help was needed, our experiences began early. Dr. C. A. Wardner, Prof. B. G. Gustafson and I, all of the University of North Dakota, were quite closely connected with dehydration during the war years and have followed the industry actively since. Our first research project at the University of North Dakota was the effect of storage conditions of the raw potatoes upon the quality of the dehydrated product.

Potatoes stored at various temperatures were dehydrated, and accelerated storage tests were run on the product. This work showed that potatoes stored under warm conditions processed to a better dehydrated product, but the potatoes under these warm conditions broke dormancy; and after sprouting began, the dehydration qualities quickly deteriorated. When potatoes sprouted, the starch distribution in the tuber changed, leaving areas low in starch. These dehydrated to a glassy product which would not reabsorb water readily when reconstituted. Sprout inhibiting agents were not effective during these years.

At the end of World War II, dehydration of vegetables declined. The civilian market would not accept the product. Moderate amounts of dehydrated diced potatoes were still made for use in canned stews and soups, but most of the processors closed their plants or entered other lines.

It was during this period that a new product, first made in England, was introduced in this country. This product was called "potato granules," and it consisted of a powder of intact potato cells. The Army was greatly interested in this product because of the fact that feedings for 100 men could be packed in a number 10 can. A second advantage was that the product was free-flowing in the dry state and could be mixed with water in volume ratios to obtain a consistent texture. Two manufacturing plants were set up in this country for the manufacture of granules. Neither could produce a consistantly good product, and Army Quartermaster contracts for work on the improvement of this process were given to Kansas State University, the University of North Dakota and the Western Regional Laboratories (Albany, California) of the U. S. Department of Agriculture.

The process consisted of mixing dry potato powder (or granules) with freshly cooked potato in amounts such that the overall moisture content was 30% to 40%. At these moisture contents the damp mix was not sticky and could be dispersed in a heated air stream for rapid drying. The process was very difficult on a commercial basis because of the fact that a very large amount of potato had to be recirculated as add back in subsequent cycles to keep the process going. The material which was removed in each cycle as product had recirculated so many times it was very apt to be heat damaged and the mechanical attrition quite often ruined the texture.

The work done here demonstrated that a good product could be produced from Red River Valley potatoes and also the rates of drying of granules in air were determined. Before the work was begun here it was thought that dehydrated granules could only be made from Idaho potatoes. Dr. D. E. Severson of our Department and I (1) also published the first use of mono- and diglycerides as additives for improving the texture of dehydrated mashed potatoes.

In the preparation steps for dehydration, breakage of potato cells in greater or lesser amounts is unavoidable. The starch which is freed causes pastiness in proportion to the amount of free starch present. Careful procedures can minimize the amount of cell breakage, but some free starch is always present.

Schoch (2) in fractionating starch, stated that when a starch sol is treated with polar organic substances containing a hydrophilic group (such as hydroxyl or carboxyl) attached to a hydrophobic residue, the starch A-fraction absorbs this material by polar attraction for the hydrophilic group. The resulting complex is insoluble by reason of its hydrophobic loading and consequently separates from solution. This procedure was used by Schoch for separation of the starch fractions but the principle may also be used to render free gelatinized starch non-sticky.

Several materials may be used including glyceryl mono-oleate, monostearate, monolaurate and monopalmitate. Monolaurate was found to be the most effective; and approximately 0.25 percent by weight, based on the potato dry substance, added as an emulsion before drying, improved the texture very markedly. The addition of these materials to dehydrated potatoes intended for mashed potatoes is practiced in present commercial production.

Potato granules had severe storage deficiencies, and several research agencies worked on direct process products which would not depend upon the recirculation of part of the product. The most successful product was potato flakes made by drying mashed potato on a steam heated drum. This process is the same process as that used for potato flour, with one important modification of the process.

Reeve (3) found that the texture of mashed potatoes could be changed by modification of the cooking procedure. Potatoes are normally classified into two types, waxy and mealy. The waxy types usually do not make good mashed potatoes, but Reeve found that their texture could be modified and made mealy by a precook in water at 150° to 170° F. followed by cooling and then a final cook in boiling water or steam. The texture, depending upon the time and temperature during the precook step, could be changed through a smooth texture to mealy and even to a gritty texture.

The precooking process developed at the Eastern Regional Laboratories (Philadelphia) of USDA was very important to the sections of the country depending upon natural rainfall for their potato crop, in that the dehydrated product could be made quite consistent no matter what the crop conditions. As a result of this process, potato flake processing plants were established in many locations in the United States and in Canada. Prior to this, the industry had concentrated in Idaho.

The Borden Company, Pillsbury Company and Polar Potato Company supported the University of North Dakota in experimental

and developmental work on this process and set up a pilot plant on our campus. Cooperative work with the horticulture departments of the University of Minnesota and North Dakota State University is being done to determine the dehydration characteristics of new potato varieties.

Potatoes which are stored under controlled conditions by the USDA Research Center in East Grand Forks are also being dehydrated. The first year's tests were very encouraging, and they showed that potatoes could be processed satisfactorily when stored at 50° F. with C.I.P.C. sprout inhibitor up to the first week in August. This could result in a much longer processing season than is practiced now. Most plants are shut down before June 1.

Various addition agents have been tested for their effects on the processing and on the quality of the product. The following materials have been used successfully for prevention of graying of reconstituted potatoes: calcium acetate, sodium acid pyrophosphate and ethylenediaminetetraacetic acid.

Antioxidants formerly used consisted of butylated hydroxyanisole and butylated hydroxytoluene in a vegetable oil carrier. This formulation was added as a water emulsion to the cooked potato before drying. However, most of the active material is lost by steam distillation, and the antioxidant remaining might not be in contact with the unsaturated fatty acids of the potato. Our work with other formulations showed that alcohol solutions of the antioxidants were more effective; these addition agents merely postpone for a time the development of the rancid flavors, and a better solution to this problem is badly needed.

Further research is needed to produce dehydrated potatoes which are stable when stored and which will produce a reconstituted product comparable to freshly prepared potatoes. The fact that potatoes, immediately after dehydration, may be reconstituted to a product of good flavor and texture is encouraging. The changes in flavor take place mainly on storage of the dehydrated material.

Further problems needing solution are enumerated:

1. Nature, amount and location of fatty acids in potato varieties and the effect of cultural practices on these fatty acids.
2. The reducing sugar content of various potato varieties as a function of dry solids content, cultural practices, and storage conditions.
3. The amino acids in potatoes as a function of variety and cultural conditions.
4. Flavor-producing materials in various potato varieties and the changes of these during processing and storage.

These problems are basic and will require a great deal of analytical work. When problems of this type are solved, the industry can be put on a firm basis and its full potential will be realized.

REFERENCES

1. Severson, D. E. and Cooley, A. M. Food Technology, 1955, Volume 9, No. 5, Pages 223-227.
2. Schoch, T. J. "The Fractionation of Starch," from Advances in Carbohydrate Chemistry, 1945, Volume 1, Ed. by Pigman, W. W. and Wolfram, M. L., Academic Press, New York.
3. Reeve, R. M. 1954 Histological Survey of Conditions Influencing Texture in Potatoes. 1. Effects of Heat Treatment on Structure. Food Research, Volume 19, Pages 323-332.

POPULATION CAGES FOR *DROSOPHILA* STUDY

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ABSTRACT

This paper describes the construction of a new design of population cage for the fruit fly, *Drosophila melanogaster,* and some uses of this apparatus in teaching and research. The cages are constructed from readily available materials (plastic freezer boxes — 5" x 3" x 2½", #12 corks, fine wire screen, and ¾ ounce creamer bottles) and have proven to be satisfactory for maintenance of stocks for teaching or for analysis of population competiton.

Wild type stock exhibited a mean generation time (eggs laid to adults) of sixteen days at twenty degrees Centigrade. Population numbers remained relatively constant when one new food bottle was added each week, e.g., wild stock varied between 300 and 410 adult flies from February 27 to March 24, 1963. Detailed description of cage construction, general procedures and research potentials of this and similar apparatus were presented.

COVARIATION OF SOME MERISTIC CHARACTERS OF THE BROOK STICKLEBACK, *EUCALIA INCONSTANS,* FROM THE RED RIVER DRAINAGE[1]

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ABSTRACT

Meristic characters of fish, such as counts of fin rays and spines,

[1]The author wishes to acknowledge the assistance of Mr. Robert Freiburghause in the use of the computer laboratory of the University of North Dakota and in the analysis of these data.

have been used to compare subpopulations and as criteria for the description of species and subspecies. The present study is an evaluation of both variation and covariation observed in five samples of the brook stickleback, *Eucalia inconstans,* collected in Grand Forks County, North Dakota.

The fish were collected from (1) Freshwater and Saltwater Coulees, (2) English Coulee and (3) a beaver dam pond on a tributary of the Forest River. The following characters were measured by standard methods: dorsal spines, dorsal fin rays, caudal fin rays, pectoral fin rays, standard length and sex. Comparisons were made among the samples with regard to (1) mean counts for each character and (2) covariation among all combinations of characters. Inconsistencies in covariance of the meristic characters were observed. The statistical limitations, especially multivariate analysis, in problems of this nature were discussed.

PERSISTENCE OF ORGANOPHOSPHATE INSECTICIDES AND THEIR EFFECTS ON MICROFAUNA IN SOILS[1]

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ABSTRACT

Soil treatment with the organophosphate insecticides, malathion, Diazinon[3], demeton and phorate at 1, 5, 10 and 25 pounds per acre was carried out in 1961 and 1962. Using the fruit fly, *Drosophila melanogaster* for direct and indirect broassay of treated soil, no residues of malathion were detected in the top 8 inches of soil after 48 hours. Diazinon residues of 100 ppm. were recorded in the 0-4" layer after 48 hours; 10 ppm. were found in the 5-8" layer at the same period. No residues were found in either layer after 9 days. Demeton and phorate persisted in the soil for more than 23 days after application.

Very low populations of microfauna were found in the Fargo clay soil on which these tests were conducted. *Collembola* sp. and mites were found in insignificant numbers in the upper four inches of soil, but in increasing numbers in the succeeding four inches

[1] Support from the National Institutes of Health, Grant EF 210(C1) is gratefully acknowledged.
[2] Graduate assistant and associate entomologist, respectively.
[3] Registered trade name.

studied. All levels of application of phorate and demeton reduced *Collembola* sp. populations significantly. Malathion and diazinon, applied at 25 pounds per acre only, significantly reduced microfauna populations. Nine days after the applications, populations had been re-established.

RADIOISOTOPES AND THE DISTRIBUTION OF PRAIRIE ANT COLONIES

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ABSTRACT

The ant fauna of a lowland prairie community at The University of North Dakota Oakville Prairie Biology Research Area has been under study for the last five years. Six of the thirteen species known to inhabit this community live in large mounds of soil which rise 1 to 3 feet above the surface of the ground. The most common species in this community is *Lasius umbratus* (Nylander). The mounds of this hypogeic species are so numerous and so close to each other that it seemed possible that a single colony might occupy several adjacent mounds. Since the workers of this species do not normally appear above ground, it is necessary to use indirect means of detecting intercommunications between ants in different mounds. Radioactive phosphorus (P^{32}) was mixed with honey and placed in a mound. Ants feeding upon this mixture became radioactive. If these ants fed other members of the colony, the radioactivity would be spread throughout the colony. Therefore, the presence of radioactivity in ants of the same species in adjacent mounds is taken as an indication that all the mounds containing radioactive ants are part of the same social unit. By this process all the nests occupied by a single colony can be determined. In addition, it provides a means for making a census of the colonies in a given area.

Of approximately 1,000 mounds on this 10 acre section, 624 were known to be occupied by *L. umbratus* in September of 1962. During the summers of 1958-61 honey labelled with P^{32} was placed in 80 mounds and traced to 221 additional mounds. On this basis the mean number of mounds per colony is approximately 3.8.

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[1]This research has been supported by grants #5476 and 11299 from the National Science Foundation. In addition, undergraduate student research participation has been provided by National Science Foundation grant #12041.

STUDIES OF PHYTO-TOXIC PROPERTIES OF SOME EXTRACTS FROM WILD OAT SEEDS

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ABSTRACT

Aqueous extracts of wild oat seeds were found to inhibit seedling growth of a number of species including wild oats. The inhibitory principal was mostly water soluble, dialysiable, heat stable and non-volatile. Chromatographic tests indicated the presence of at least two inhibiting substances; one which remained at the origin when isopropanol: ammonia: water 80:5:15 (V/V) was used as the developing solvent and one or more at R_f 0.3-0.5 or 0.3-0.6. Since there was no fluorescence at R_f 0.4-0.6 the substances were probably not indoles. Ion exchange studies indicated the presence of a substance with a negative charge and another which was neutral.

OBSERVATIONS OF A MUSKRAT POPULATION DECLINE IN NORTH DAKOTA[1]

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During 1956 and 1957, a study was conducted of populations of the great plains muskrat (*Ondatra zibethica cinnamominus*) dwelling in four marshes in the drift prairie of northeastern North Dakota. The marshes were considered to be representative of the drift prairie west of the Red River Valley and east of the Missouri River Valley escarpment. The marshes were located in Sections 35 and 36, T. 157 N., R. 68 W., Towner County, North Dakota.

Three of the four marshes were quite small (fig. 1). Area 1 was 3.0 acres, and Areas 2 and 3 were 4.5 acres in size. The size of Area 4 was 47 acres. These marshes contained a variety of aquatic vegetation, the principal emergents including broadleaf cattail (*Typha latifolia*), bur reed (*Sparganium eurycarpum*), hardstem bulrush (*Scripus acutus*), river bulrush (*S. fluviatilis*), spike rush (*Eleo-*

[1]This study was supported by the North Dakota Game and Fish Department under project W-39-R.

[2]Dr. Beer is with the Department of Entomology, Fisheries and Wildlife, Unversity of Minnesota, St. Paul 1, Minnesota.

charis palustris), sedge (*Carex sp.*), arrowhead (*Sagittaria cuneata*), and water plantain (*Alisma sp.*).

The mean water depth for the marshes at the beginning of the study (July, 1956) was 27 (19-34) inches. Water levels declined to an overall depth of 11 (0-17) inches by freeze-up (November) of that year. Area 3 had become completely dry by October.

Snowfall during the following winter was extremely light. In March, 1957, the maximum snow depth was only four inches, as compared to 21 inches during that month in 1956. Rainfall during the summer of 1957 was the same as in 1956 (11.8 inches).

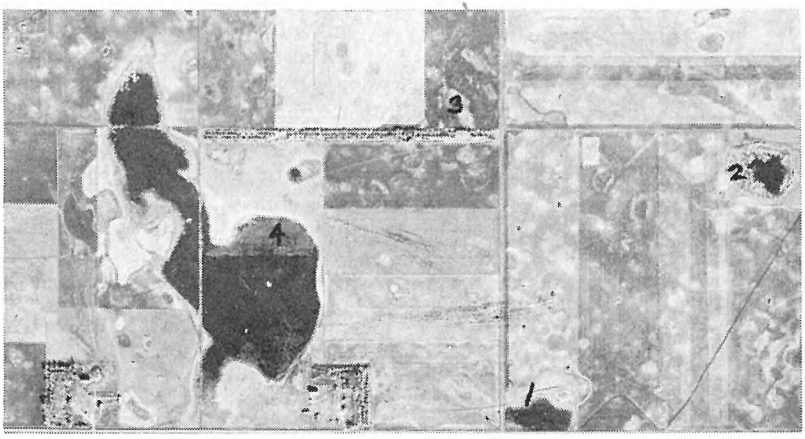

FIGURE 1—Aerial photograph of marshes in area studied.

Due to the lack of winter snow cover and the resulting small amount of spring run-off, the three small marshes became completely dry by the end of the summer in 1957. Area 4 still held 17 inches of water by the end of that summer.

POPULATION ESTIMATES

During the summer of 1956, intensive live-trapping resulted in the capture and release of 278 tagged muskrats on the four marshes.

TABLE I
POPULATION ESTIMATES (Fall, 1956)

Area	Total Tagged (N)	Total Recovered (H)	Tagged Recovered (R)	Population (P)	Confidence Interval (95%)
1	34	34	15	77	56- 94
2	19	18	13	26	22- 39
4	213	235	119	420	380-473

$$P = \frac{NH}{R}$$

Kill-trappng was conducted during the fall of that year, and population estimates were based upon the proportions of tagged to untagged recoveries according to the method of Lincoln (1930). These estimates are presented in Table I. No recoveries were made on Area 3. This marsh had become dry by fall and had probably been vacated. Twelve muskrats were tagged on Area 3 during the summer, and it is believed that this figure was close to the number of animals residing there.

Due to the lack of winter snow cover during the winter of 1956-57, ice formation was very heavy in the vicinity of the marshes in the study area. Over 30 inches of ice was measured in one of the adjacent roadside ditches. Local residents reported large numbers of road-killed muskrats in the vicinity during February of that year, many more than had been noted in recent years.

Only 12 muskrats were live-trapped in the marshes of the study area during the summer of 1957. Steel trapping during the following fall was completely unsuccessful. Here, then, was a situation where a winter drouth, was its associated heavy ice formation, resulted in the almost complete decimation of a local muskrat population.

This population decline occurred throughout the region as well as on the study area. Aerial counts of muskrat houses run by the North Dakota Game and Fish Department (unpublished) indicated an average of three houses per mile of transect in the vicinity of the study area marshes during the fall of 1956. This figure declined to zero in 1957. Similar declines in house counts occurred throughout the northern half of the state.

HOUSE CONSTRUCTION

Associated with the declining water levels on the study area marshes, there appeared to be a general abandonment of shallow water areas and bank dens in favor of house construction in deeper water. During the spring and summer of 1956, the study area residents were primarily bank-dwelling animals. No houses existed on the three small marshes, and only ten persisted on Area 4 during the summer months. Sixteen bank dens were known to be occupied on Area 4 during this period. Of these, only three remained active to the fall trapping season. Furthermore, recaptures of 16 tagged animals during the fall of that year indicated a general trend of fall movement into deeper water.

The bulk of the house construction on Area 4 in 1956 took place after September 14. Fifty houses were constructed on this marsh after that date. The fall population, therefore, consisted almost entirely of house-dwelling animals.

In 1957, the remnant population surviving the freeze-out was found dwelling in six houses throughout the summer. No bank dens were active on the marshes during that year.

POPULATION STRUCTURE

Analysis of muskrat population structure has indicated that there is generally an unbalanced sex ratio favor of the males (Beer and Truax, 1950). Average ratios for fall and winter populations were determined by Beer and Truax to be 125 males per 100 females (55.6%). These authors believed that indications of overpopulation included shifts in the adult sex ratio against the males and in the age ratio against the juveniles.

TABLE II

MUSKRAT POPULATION SEX RATIOS, 1956-1957

Area and Period	Adults			Juveniles		
	Males	Females	Per Cent Male	Males	Females	Per Cent Male
1956 (Summer)						
Study Area	28	24	53.8	119	108	52.5
1956 (Fall)						
Study Area	21	28	42.9	128	120	51.6
Regional	217	198	52.3	1400	1032	57.8
1957 (Fall)						
Regional	116	117	48.9	313	208	60.1

TABLE III

MUSKRAT POPULATION AGE RATIOS, 1956-1957

Area and Period	Juveniles	Adult Females	Juveniles per Adult Female
1956 (Summer)			
Study Area	227	24	9.5
1956 (Fall)			
Study Area	248	28	8.8
Regional	2432	198	12.3
1957 (Fall)			
Regional	521	117	4.4

The sex and age compositions of the study area and regional populations are presented in Tables II and III. The summer data for the study area are based upon live-trapped animals. while the fall data are based upon animals taken during the fall trapping season (November 1 - December 10). The regional data were obtained from samples of carcasses and pelts taken from the vicinity of each of the following towns: Leeds, Penn, Devils Lake, and Grand Forks. The regional data were therefore considered to be representative of the northeastern corner of the state.

The sex ratios (Table II) exhibited shifts in the proportions of males in the study area from summer to fall, during the fall between the study area and the region. and in the region from 1956 to 1957. However, these shifts did not vary significantly when subjected to statistical analysis ($P = .05$).

Juveniles per adult female (Table III) did not vary significantly in the study area from summer to fall, 1956, or between the study area and the region during the fall of 1956 ($P = .05$). A marked shift was noted in the regional age composition from 1956 to 1957. Juveniles per adult female declined from 12.3 to 4.4 during those two years. This shift was statistically significant ($P = .01$).

The exact cause of the drastically reduced reproductive success in 1957 is not known. It may have been due to small litter size, poor survival of young, or both. Adult females may have gone into the breeding season in poor reproductive condition following the severe winter. This may have resulted in small litter sizes. Furthermore, those few young produced may have been subjected to unusually high mortality during the dry summer and fall due to unsuccessful competition with adult animals for the few remaining suitable habitats.

SUMMARY

Lack of snow cover during the winter of 1956-57 resulted in heavy ice formation in four marshes in northeastern North Dakota. This caused a freeze-out and heavy mortality in the resident muskrat populations. This population decline appeared to be general throughout the region. Lack of spring run-off caused many marshes to dry up during the following summer, and forced the surviving muskrats into more unfavorable living situations. Receding water levels forced bank-dwelling animals to construct houses in open water. Shifts in population structure were noted: the most prominent was a reduction in the proportion of juveniles in the regional population from 1956 to 1957. Impaired reproductive activity of adults, poor survival of young, or both may have caused the shift in age ratios.

LITERATURE CITED

Beer, J. R., and W. Truax. 1950. Sex and age ratios in Wisconsin muskrats. J. Wildl. Mgmt. 14: 323-331.

Lincoln, F. C. 1930. Calculating waterfowl abundance on the basis of banding returns. U. S. Dept. Agr. Circ. 118. 4 p.

DEER AND ANTELOPE EPIZOOTIC IN THE NORTH DAKOTA BADLANDS

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Whitetail deer losses were first noted in the North Dakota Badlands on September 23, 1962. Subsequent investigations revealed that most areas draining the Little Missouri and Yellowstone Rivers west of Highway 85; the Killdeer Mountains; and the south bank of

the Missouri River from the Montana border to Newtown, North Dakota were involved. More than 200 dead whitetail deer, 18 mule deer and 11 antelope of all age and sex classes were examined.

In the deer, weakness, incoordination, labored breathing, diarrhea flecked with blood, and a frothy nasal discharge were the principal symptoms observed. The pathology included hyperemia, ulceration, hemorrhages, and erosions of the respiratory, gastrointestinal, and urogenital tracts. The spleen, liver, lungs, and pancreas were distended and engorged with blood. Petechial to eccymotic hemorrhages were also present on these organs. A severe edema was present in the brain. Corneal opacities were noted in one or both eyes.

In the antelope, the inflammation and hemorrhages were less severe but there was also a definite central nervous system involvement. Convulsions and "running fits" along with pronounced incoordination were noted in all animals. Death appeared to result from cardiac failure during a convulsion.

Specimens from sick and dead animals were checked and found to be negative for nitrate poisoning, pesticides, heavy metals, and poisonous plants. Traces of ergot were noted in a few animals. *Escherichia coli* was isolated from several deer in the Little Missouri River bottoms. Epidemic hemorrhagic disease virus was isolated from all of the specimens and is presumed to be the primary cause of the big game losses.

THE THEORY OF HYDROGEN ION EFFECTS ON HYDROLYTIC ENZYME ACTION

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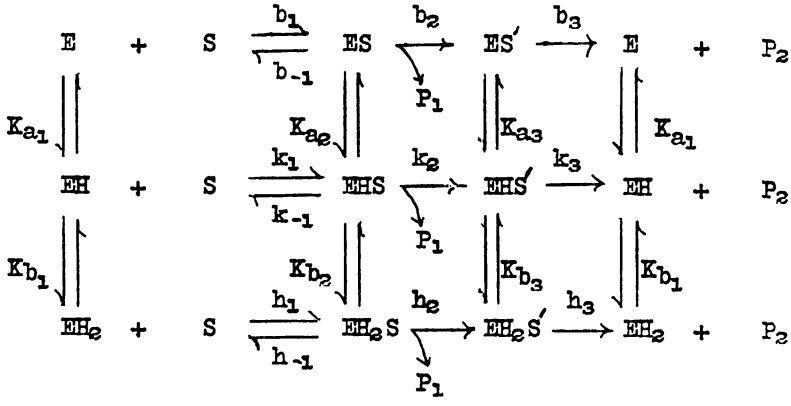
ABSTRACT

Kinetic schemes for hydrolytic enzyme action have been treated theoretically by Gutfreund and Sturtevant, Stewart and Ouellet, and recently Kezdy and Bender, for particular cases. The following general kinetic scheme, however, was worked out rigorously in this Laboratory and the theoretical treatment was carried out. The equations are applicable to the experimental conditions of excess substrate and excess enzyme. Under the first condition, the transient phase and steady-state equations were obtained subject to various assumptions. Under the second condition, only the transient phase equations were derived since the steady-state kinetics are nonexistent. This

[1]National Institutes of Health Predoctoral Fellow.

complete mathematical treatment has solved the long-standing puzzle of the pH dependency of rate constants in hydrolytic enzyme action. Without this treatment, kinetic results obtained in this Laboratory, as well as those tabulated in the literature, can not be fully explained. In addition to the usual rate constants, K_m, k_2 and k_3, this theory enables new rate constants to be evaluated for the first time. Experimental evidence in support of the following scheme was obtained.



EFFLUX OF AMINO ACIDS INTO THE INTESTINAL LUMEN[1]

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ABSTRACT

We have reported a measurable difference between the net and absolute absorption of tyrosine in the upper small intestine of the intact rat, using a recirculating perfusion system (J. Biol. Chem., *235*, 3224 (1960)). This implied that at least tyrosine could move back across the intestinal mucosa into the intestinal contents. In our investigations of the absorption of amino acid mixtures in the intestine *in situ* we found that several amino acids which we had not

[1] Guy and Bertha Ireland Research Laboratory, School of Medicine. These investigations were supported in part by a research grant from the National Institutes of Health, U.S.P.H.S. (No. AM-02023).

[2] Research Participant, National Science Foundation, Research Participation Program (NSF-G20987).

placed in the perfusate, appeared in this perfused solution after it had recirculated through the intestinal lumen. This efflux was stimulated by the presence of one or more amino acids carried in the perfusing solution and depressed by 2,4-dinitrophenol. Single-pass perfusion experiments, likewise, demonstrated that efflux occurred and that the presence of amino acids was indeed caused by secretion and not a "washed" residue from the intestinal wall. To show further an efflux, radioactive amino acids were injected intravenously and were found in the intestinal lumen in a matter of minutes; if they had to become a part of the cells of the villi and desquamated into the intestinal contents, it would have required a time interval equivalent the turnover time of these tissues (some 36 hours). The efflux of radioactive amino acids into the lumen was also found to occur even though there was a net absorption of water from the lumen.

RAT LIVER MICROSOMAL INORGANIC PYROPHOSPHATASES[1]

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ABSTRACT

Inorganic pyrophosphatase activity has been demonstrated (1) in rat liver microsomes, as well as in nuclei, mitochondria, and the soluble fraction. Activity-pH profiles indicate that such microsomes contain two and possibly more enzymes capable of hydrolyzing inorganic pyrophosphate (PP_i). $K_m(PP_i)$ was calculated as 1×10^{-4} *M* at pH 8.1 in the presence of Mg++ initially three times PP_i concentrations and 6.1×10^{-4} *M* at pH 5.0 without Mg++. On the basis of specific adenine nucleotide inhibition independent of Mg++-binding of a mitochondrial pyrophosphatase and partial reversal of F^- inhibition by these same nucleotides, it previously had been concluded (2) that PP_i hydrolysis and oxidative phosphorylation accompanying electron transport may involve common enzymes.

However, it now appears that microsomal inorganic pyrophosphatase inhibition by nucleotides is due entirely to chelation of MG++, since a) relatively high nucleotide/PP_i ratios are required, b) ATP inhibition is reversed by elevated Mg++ concentrations, c) GTP in-

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[1] Guy and Bertha Ireland Research Laboratory, School of Medicine. This work was supported in part by grants from the Hill Family and Smith, Kline, and French Foundations, and the National Institutes of Health, U. S. Public Health Service.

hibits as effectively as ATP, and d) AMP is without effect. F^- inhibition of microsomal pyrophosphatase activity is not reversed by ATP. PP_i-glucose phosphotransferase activity also was demonstrated in microsomes.

LITERATURE CITED

1. R. C. Nordlie and H. A. Lardy, Biochim. Biophys. Acta, *50*, 189 (1961).
2. R. C. Nordlie and H. A. Lardy, Biochim, Biophys. Acta, *53*, 309 (1961).

REACTION OF TITANIUM IV CHLORIDE WITH AMINES AND AMINE HYDROCHLORIDES

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ABSTRACT

A recent literature survey by Shiihara (1) indicates that there have been numerous studies made on the reaction of titanium IV chloride with various classes of organic compounds. Some work has been done in our laboratories concerning the reaction of titanium IV chloride with alcohols (2), carboxylic acids (3), ketones (4), and hydroxy-aromatic compounds (5). A limited amount of work is reported in the literature concerning the reaction of titanium IV chloride with amines (6) and amine salts (7).

Studies are in progress in our Laboratories on the reaction of titanium IV chloride with primary, secondary, and tertiary amines and amine salts, namely, amine hydrochlorides. Reaction of titanium IV chloride with isopropylamine hydrochloride, in a mole ratio of 2:1, yields a yellow solid (m. 55-62°) having an empirical formula, $(iso\text{-}Pr)_2 TiCl_4$. Similar results have been obtained with the secondary amine, diethyl amine hydrochloride. With tertiary amines, similar reactions yield dark colored complexes. In each case, the complexes and condensation products obtained depend on the concentration of the reacting amine.

LITERATURE CITED

1. Shiihara, I. Schwartz, W. T., and Post, H. W., Chem. Rev., *61*, 1-30 (1961)
2. Schwartz, D., Cross, W., Morgan, B. and Rheineck, A. E., Off. Dig.

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[1]Paint Research Institute Fellow

Federation Soc. Paint Technol. 35 No. 462, 645 (1963).
3. Unpubished work.
4. Schwartz, D. and Larson, B., J. Less-Common Metals (in press).
5. Schwartz, D. and Cross, W., J. Chem. Eng. Data (in press).
6. Trost, R. W., Can J. Chem. *30*, 835-41 (1952).
7. Caglioti, V., Chem. Abstr. 22, 2121 (1928).

EXTRACTION STUDIES ON THE $FeCl_3$-AQUEOUS HCl-TRI-N-OCTYLAMINE-NITROBENZENE SYSTEM[1]

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ABSTRACT

The complexing of metallic cations (Lewis acids) with inorganic ligands (Lewis bases) in aqueous solution often gives rise to complexes that are appreciably soluble in organic solvents not miscible with water. This occurs readily with Fe(III) and hydrochloric acid to form the species $HFeCl_4$ which is readily extracted by basic organic substances. In particular the extraction of this species by a long-chain tertiary amine such as tri-n-octylamine (TOA) from acid solution may be considered to occur via a mechanism analogous to that operating in anion exchange resin systems.(1) An unresolved difficulty is that amine concentration power-dependence studies indicate a different species than do limiting loading and spectrophotometric methods(2); these latter methods indicate the species $HFeCl_4$ (3).

During the course of studies, designed to help explain this anomaly, a study of the system $FeCl_3$-aqueous HCl-TOA-nitrobenzene has led to still more surprising results. Amine extraction systems reported in the literature have indicated that equilibrium is established rapidly, in most cases in a few minutes, in the slowest cases after a few hours of shaking the two phases together. This system requires several days before the distribution coefficent becomes constant. The coefficient appears to reach a constant value after about two hours, but this value begins to increase after several more hours of shaking. Data concerning the effect of acid strength and amine concentration on both equilibration time and the final value of the distribution coefficient is presented. Additional work, in progress, will be necessary to clarify the situation completely.

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[1]This work was supported by the Directorate of Chemical Sciences Air Force Office of Scientific Research under Grant-65-63.

REFERENCES

1. Moore, F. L. "Liquid-Liquid Extraction with High Molecular Weight Amines," National Academy of Sciences National Research Council Document No. 3101, December, 1960.
2. White, J. M., Kelly, D. and Li, N. C., J. Inorg. Nucl. Chem., *16*, 337 (1961).
3. Good, M.L. and Bryan, S. E., J. Am. Chem. Soc., 82, 5636 (1960).

HUMIC ACIDS FROM LEONARDITE; A SOIL CONDITIONER AND ORGANIC FERTILIZER

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INTRODUCTION

The term "humic acid" was first applied in 1826 by Sprengel (9) to that brown amorphous precipitate which is obtained by acidifying the alkali extract of decayed organic matter in soil. Since the inception of the term, humic acids have been extracted not only from soil but also from peat, brown coal, oxidized bituminous coal, and even from artificial materials obtained in the laboratory by action of inorganic acids or oxidizing agent on carbohydrates, proteins, and phenols. Odin (7) in 1922 redefined humic acids as yellow-brown to black-brown substances of unknown constitution, formed in nature by decomposition of organic materials under atmospheric influence or in the laboratory by chemical action. Humic acids can split off hydrogen ions and form typical salts with strong bases and usually are insoluble in water, soluble in alkali, and reprecipitated by acid. In general, humic acids are not chemically uniform substances, but are hydrophilic, reversible colloids with molecular weights varying from 300 to as high as 10,000 units. Their micelles carry a negative charge. The alkali solubility of humic acid is due to carboxyl and phenolic hydroxyl groups which account for about 22% of the weight of the molecule.

Humic acid is an essential part of soil. It is this material, present in good soil, that fixes nitrogen, makes available to the plant, through base exchange, the soil nutrients, and improves the physical structure of the soil. In recent years, much research has been conducted, particularly in India, Japan, Germany, Russia, and France, on replenishing the depleted humic acids of soils with the so-called "regenerated humic acids" obtained by oxidation of coal. These regenerated

acids, which closely resemble the natural humic acids, have either been added directly to the soil or first supplemented with plant nutrients. Greenhouse and field tests have shown that these humic acid preparations improve plant yields (3), decrease loss of moisture from the soil (6), and increase the workability of the soil (2).

As a convenient and commercial source of humic acids, extensive reserves of naturally oxidized lignite occur with virtually all lignite outcrops in North Dakota. The naturally oxidized material, which contains up to 86% humic acids on a moisture- and ash-free basis, has been given the name "leonardite," after A. G. Leonard, early director of the North Dakota Geological Survey, who did much of the early studies on these deposits (1). Leonardite is a coal-like substance similar in structure to lignite, but significantly different in its oxygen and ash contents. In Table I the ultimate analyses of lignite, leonardite, lignite oxidized with air in the laboratory at 150° C., and humic acid extracted from leonardite with 1N NaOH are compared. The ash content of leonardite varies from mine to mine but is usually between 15% and 30% on a moisture-free basis.

TABLE I
ANALYSES OF LIGNITE MATERIALS, PERCENT

	Leonardite	Lignite	Oxidized Lignite	Humic acid extracted from leonardite by 1N NaOH
Ash, moisture-free	18.7	10.0	10.7	3.9
Hydrogen, moisture- and ash-free	4.0	5.1	2.9	3.4
Carbon, moisture- and ash-free	65.2	72.8	65.4	63.5
Nitrogen, moisture- and ash-free	1.3	1.2	1.4	1.3
Oxygen, moisture- and ash-free	26.6	19.9	29.2	31.1
Sulfur, moisture- and ash-free	2.9	1.0	1.1	.7

AMMONIATION OF LEONARDITE

Nitrogen-enriched coal humic fertilizers have received much emphasis in the past few years. Recent investigations have indicated that these products perform well as conventional fertilizers and release nitrogen more slowly. The main problem in technology is to develop a product with sufficiently high nitrogen content (around 20%) which will still remain commercially competitive.

To determine if leonardite could be ammoniated to a product containing suficient nitrogen for use as an organic fertilizer, samples were prepared by three different methods: (1) Ammoniation in an aqueous slurry ;(2) ammoniation in a upward moving gas stream through a column of dried leonardite; and (3) ammoniation under

pressure of 2,000 p.s.i.g. at 200° C. The nitrogen analyses of these variously ammoniated leonardite samples and the analysis of an aqueously ammoniated humic acid extracted from leonardite appear in table 2. The increase of nitrogen content of leonardite, even under

TABLE II
NITROGEN ANALYSES OF VARIOUSLY AMMONIATED SAMPLES, MOISTURE-FREE BASIS PERCENT

Sample	Method of Ammoniation 1	2	3
Leonardite	3.87	2.82	11.15
Humic acid	8.13	——	——

radical conditions, is not sufficient for it to be used as an organic fertilizer. The nitrogen content of the ammoniated humic acid increased 2.5 times over that of the correspondingly ammoniated leonardite sample. The higher ash content, as well as the 15% non-humic carbonaceous material in the leonardite, accounts for the decreased reactivity with ammonia. Therefore, to prepare a high-nitrogen organic fertilizer, the humic acids would first have to be extracted from the leonardite.

RECOVERY OF HUMIC ACIDS FROM LEONARDITE

One part of the work at this laboratory was to find an inexpensive, rapid method for obtaining from leonardite bulk quantities of low-ash humic acids that could be used in preparing a soil conditioner and high-nitrogen-content organic fertilizer. The humic acids in leonardite are bound to the ash largely insoluble calcium salts. Therefore, to recover the humic acids requires not only a

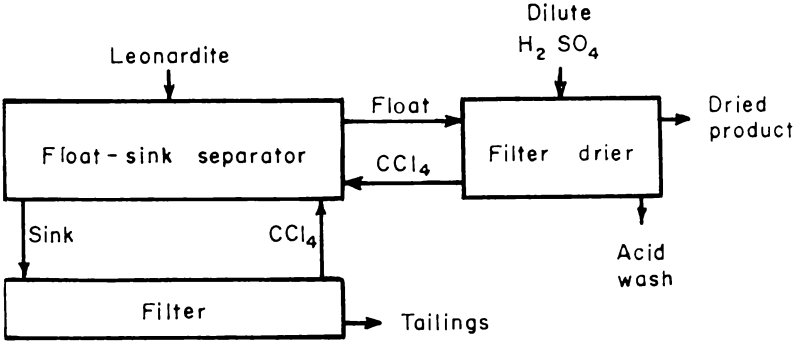

FIGURE 1—Float-sink separation.

physical means of removing the clay and sand, but also a chemical treatment to displace the calcium ion. In the past, alkali extraction of the humic acids with removal of the insolubles by centrifuging the humate solution was the standard procedure for obtaining low-

ash humic acids (5). The alkali extraction process, however, requires not only fresh alkali for each lot of humic acid prepared but also an equivalent amount of acid to set the humic acid free, both of which are used up in the process. The large volumes of water, which must be used to obtain a low-ash product, plus the unfilterable nature of the alkali humate solution and acid-precipitated humic acid, make the alkali extraction of humic acids unattractive. The problem of eliminating alkali extraction as the method of preparing low-ash humic acids was approached by two different routes: (1) Removing the ash physically and chemically from the leonardite, leaving a carbonaceous product containing around 85% humic acid; and (2) extracting the humic acid from the leonardite with an organic solvent that could be reclaimed for further extractions.

Float-Sink Process—

Figure 1 schematically represents the process that was used in our experiments. Partially-dried, pulverized leonardite was added to a separatory funnel containing CCl_4 as the dense medium. The float fraction containing the humic acids was transferred to a filter, and the CCl_4 was removed. The product was washed first with a dilute H_2SO_4 solution, then with warm water. The results of this

TABLE III

AN EXAMINATION OF THE FLOAT-SINK PROCESS, MOISTURE FREE BASIS, PERCENT

	Product			Tailings	
Ash	Yield	Ash	Humic acid	Yield	Ash
17.7	73.1	3.5	89.0	17.4	56.8

Note—Not included in data is loss of water-soluble material.

experiment appear in Table III. A $ZnCl_2$ solution was tried in place of CCl_4, but absorption of the solution on the carbonaceous material caused the latter to sink, resulting in a low yield of humic material.

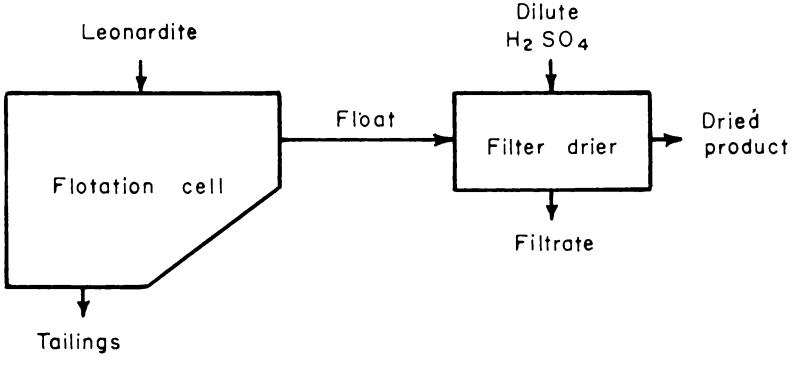

FIGURE 2 — Flotation process.

Flotation Process—

The flotation process for ash separation is schematically depicted in figure 2. The as-received, pulverized leonardite was added to the flotation cell, which contained a lignite-tar creosote fraction as a frothing agent. The froth was collected on a filter, and the filter cake was washed with dilute H_2SO_4 followed by warm water. Results of a typical experiment in this process appear in table 4.

TABLE IV
ANALYSIS OF THE FLOTATION PROCESS

Feed, Percent		Product, Percent		
Moisture	Ash, moisture-free	Moisture	Ash, moisture-free	Yield, moisture-free
9.5	18.2	6.0	11.3	13.6

Organic-Solvent Extraction Process—

The use of an organic solvent for extraction of humic acids would be most attractive if the solvent could be reclaimed by distillation and reused without reaction with or being absorbed on the humic acids. Polansky and Kinney (8) made an extensive survey of organic solvents and solvent mixtures regarding their ability to disperse humic acids from nitric acid-oxidized bituminous coal. They concluded that the most economical and most easily handled solvent for the commercial extraction of humic acids is a mixture of acetone and water. Fowkes and Frost (4) showed that an acetone-water solution would extract humic acids from leonardite provided the leonardite was pretreated with dilute mineral acid. The amount of humic acids extractable was directly proportional to the amount

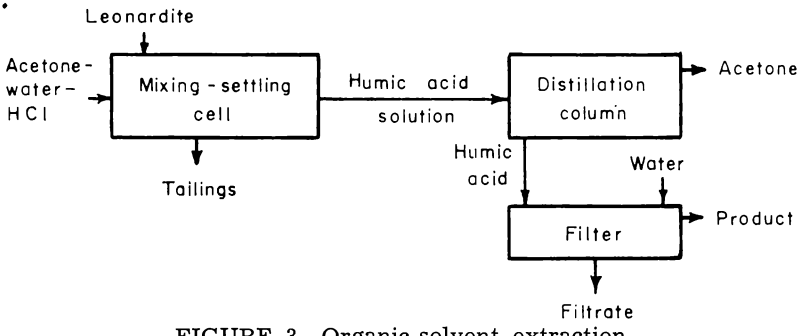

FIGURE 3—Organic-solvent extraction.

of mineral acid used in the pretreatment. The several preliminary experiments conducted revealed that the most efficient extraction was accomplished using one liter of 80-20 acetone-water (percent by volume) and 10 grams of HCl (basis: hydrogen chloride) per 100 grams of leonardite (moisture-free). Ten grams of HCl per 100 grams of leonardite is slightly in excess of the acid that will be

necessary to replace the calcium ion with hydrogen ions in an average leonardite sample. Sulfuric acid was tried in place of HCl as the source for the displacing H-ions, but the resulting $CaSO_4$, mixed with the humic acids, resulted in an unfilterable product with a high ash content. In the first experiments, the mode of extraction was a countercurrent column. An acetone-water-HCl pretreated leonardite slurry was added to the top of the column while a solution of acetone-water was forced slowly up through the slurry. The yields of humic acids were good, but the ash content of the product was high, indicating some carry-over of ash. Later experiments showed that sedimentation of ash and non-humic carbonaceous material in an acetone-water-HCl solution is quite rapid; thus, a simple settling tank replaced the counter-current column in the process. A flow diagram of the process appears in figure 3. The results of the experiments appear in Table V.

TABLE V

ANALYSIS OF THE ACETONE-WATER-HCl EXTRACTION OF HUMIC ACID FROM LEONARDITE, MOISTURE-FREE BASIS, PERCENT

Feed	Product			Tailings	
Ash	Yield	Ash	NaOH-soluble	Yield	Ash
17.8	64.9	1.8	96.8	31.1	38.2
		(C	63.5		
Elemental		(H	3.8		
(Moisture-and		(N	1.0		
ash-free)		(S	0.7		
		(O	31.0		

NOTE—Not included in data is loss of water- and acid-soluble material.

DISCUSSION

A comparison of the three processes investigated reveals the drawbacks of the float-sink and the flotation processes. The float-sink separation requires a non-polar medium, carbon tetrachloride, which is absorbed to some extent on the leonardite. The use of CCl_4, plus the fact that the leonardite must be partially dried before separation, makes this process unattractive commercially. The flotation process did not produce the desired results. Owing to the low hydrophobicity of leonardite, caused by the large number of carboxyl and hydroxyl groups on the micelle's periphery, the yields of humic acids were low and their ash contents high. Attempts to precondition the leonardite with a light neutral fraction of coal tar to increase its hydrophobicity failed. Changing the frothing agents several times also gave poor results. The acetone-water-HCl extraction of humic acids lends itself most favorably to a commercial process. The yield of low-ash product is high. The acetone is easily recovered by distil-

lation at a low temperature, and the loss is very small. Acetone does not react with, nor is it absorbed on, the humic acids. The process requires simple equipment (a sedimentation setup works quite well), and the insolubles settle rapidly. The humic acids are easily filtered once the acetone is removed, and a minimum amount of wash water is needed to obtain a low-ash product.

REFERENCES

1. Abbott, G. A. Proc. N. Dak. Acad. Sci. 13, 25 (1959).
2. Bulletin of the Central Fuel Research Institute, India. (Sept.-Dec. 1959) 124.
3. Charmbury, H. B., Polansky, T. S., Mechanization 24, 24 (Jan, 1960).
4. Fowkes, W. W., Frost, C. M., BuMines Rept. of Inv. 5611, 12 (1960).
5. Frost, C. M., Hoeppner, J. J., Fowkes, W. W., J. Chem. Eng. Data 4, 173 (1959).
6. Higuchi, Kozo, "The Chemistry of Humic Acids and Some New Utilization of Lignite. (Unpublished manuscript).
7. Oden, S., Th. Steinkopff, Dresden and Leipzig (1922) 199.
8. Polansky, T. S., Kinney, C. R., Ind. Eng. Chem. 39, 925 (1947).
9. Sprengel, Archiv fur die sanante Naturlehre 8, 145-220 (1926).

ASCORBIC ACID AS AN ANALYTICAL REAGENT FOR METAVANADATES

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ABSTRACT

Metavanadates (VO_3^-) react with ascorbic acid producing an intense green coloration against a white background. The color does not originate from the green ion, vanadium (III), because ascorbic acid and vanadium (IV) do not react. The solution changes immediately from green to colorless with microgram quantities of vanadium and to greenish-blue with larger quantities. The transient green color is much more intense than the greenish-blue color. With a spot technique the former can reveal the presence of as little as five micrograms of metavanadic vanadium at a dilution of 1 : 10,000 in an unknown. No other cation or anion gives this test. Interfering cations of mercury and silver, which give a black precipitate, and the colored ions of cerium, cobalt, copper and nickel can be elimi-

nated by adding sodium hydroxide until slightly basic and then filtering.

In a steel sample containing one per cent each of chromium and manganese, two-tenths per cent of vanadium was identified by dissolving the sample in 6 N nitric acid, evaporating almost to dryness, extracting with water, and then adding a drop of saturated ascorbic acid solution to a drop of the sample solution. The solution changed, in this case, from orange to transient blue then colorless.

THE SPECIFICITY OF THE α-CHYMOTRYPSIN CATALYZED HYDROLYSIS OF SOME CHLORINATED ACETATES

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ABSTRACT

The enzyme chymotrypsin has a high degree of specificity towards those α-amino acid esters which possess a phenylalanine type of structure, such as N-acetyl-L-tyrosine ethyl ester. The purpose of this investigation is to present evidence to show that electronegative substituents in the α-position of simple non-amino acid esters increases their specificity.

A series of acetate derivatives were studied and their deacylation specificity increased in the following sequence: acetate, chloroacetate, dichloroacetate and trichloroacetate. The Michaelis constants, which are concerned with enzyme-substrate complex formation, were determined. These constants together with those for deacylation are used to compare the specificity of these esters to the specific substrate N-acetyl-L-tyrosine ethyl ester.

Evidence was obtained which insinuates that acetyl and chloroacetylchymotrypsin are definite intermediates. Published work indicates that the hydroxyl group of a serine residue in chymotrypsin is probably acylated. If this is true, and the decomposition of these acyl-enzyme intermediates involves acid-base catalyzed hydrolysis, then the results for deacylation should parallel those for the spontaneous hydrolysis of the corresponding ethyl esters. This is not found to be the case.

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[1]National Institutes of Health Predoctoral Fellow.

DATA ANALYSIS DURING AN ATTEMPT TO USE RADIOACTIVE PHOSPHOROUS AS A TRACER TO DETERMINE AIR CLEANER EFFICIENCY

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ABSTRACT

The original proposal and test procedure have been published (1). Data taking and analysis were incomplete at that time.

The final accumulation of data yielded 71 effi values. These efficiencies were obtained by measuring the r ctivity of aerosol collected on filter papers from equal quantities air above and below the air cleaner.

The efficiencies were calculated from a wide range of total radioactive counts. Since the accuracy of radioactive counting increases with increased total accumulated counts and with decreased background counts, the expected accuracy of each efficiency determination could not be expected to be the same. The wide range of efficiencies for each flow rate could be, at least partly, due to statistical variation and not to a shortcoming of the test procedure.

An analysis of radioactive counting error was made, and a statistical test suitable for this application was derived. Utilizing the standard deviation, taking into account background counts, and finally expressing the accuracy range of efficiency for each determination, allowed a comparative evaluation of each effi cy determination.

When those efficiencies judged to be most accurate v lotted, the earlier mentioned range for each air-flow rate wa creased markedly. This indicated that if a certain statistical acc cy were maintained, the test method would give much more accurate results.

It remained, therefore, to devise a method of specifying minimum conditions which, if met, would result in the required efficiency accuracy. This was done by utilizing the statistical principles already developed.

This method of air cleaner testing has accuracy comparable to other methods reported in current literature as well as pote tial for development. The major short-coming is radiation hazard to the surroundings.

REFERENCE

1. Multhaup, E. L., Proc. N. Dak. Acad. Sci., 16, 62 (1962).

DISTRIBUTION OF MAFIC AND ACCESSORY MINERALS IN THE TUNK LAKE GRANITE PLUTON, SOUTHEASTERN MAINE

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ABSTRACT

The Tunk Lake granite pluton, located 35 miles southeast of Bangor, Maine, has a nearly circular outcrop area of 70 square miles. Initial field and laboratory study has shown marked mineralogical variation from the margin of the pluton to its core. The mafic minerals form a sequence: magnetite-aegerinaugite-hornblende-biotite-chlorite. Magnetite and aegerinaugite are dominant in the marginal chilled zone. Toward the center of the outcrop area, hornblende, biotite, and chlorite appear, each successively, as the most common mafic mineral.

Small amounts of secondary riebeckite and Fe'''-rich biotite are characteristic of rocks transitional between aegerinaugite-magnetite granite and hornblende granite in the Tunk Lake pluton. Sphene and allanite are characteristic of rocks transitional between hornblende granite and biotite granite. The accessary minerals zircon and allanite-epidote are common as euhedral to subhedral crystals in the outer rocks of the pluton, but farther inward are less common, occurring as anhedral to subhedral grains. Magnetite and apatite are common accessories throughout the pluton.

UPPER CRETACEOUS ECHINOIDS FROM NORTH DAKOTA

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ABSTRACT

Although a few specimens of echinoids have been reported from the Pierre Shale in Wyoming and South Dakota, until recently none has been found in North Dakota. Echinoderms are still among the rarest fossil invertebrates in the state. In 1956, seven specimens of *Hemiaster humphreysanus* Meek and Hayden were found in the upper Pierre Shale on the east bluff of Little Beaver Creek, Bowman County, about 5.5 miles southwest of Marmarth, North Dakota. In

June, 1962, one specimen of a new species of *Hardouinia*, resembling *Hardouinia taylori* (Warren) from the Cretaceous of Alberta, was found in the Timber Lake Member of the Fox Hills Formation in a road cut about 9.5 miles west of Linton, Emmons County, North Dakota. This is the first and only echinoid to be reported from the Fox Hills Formation.

The clastic lithology of the upper Cretaceous in North Dakota does not lend itself to occurrence nor preservation of echinoderms. This is especially true of the upper part of the Timber Lake Member of the Fox Hills Formation where the only other evidence of the marine nature of this part of the section at the Emmons County echinoid locality is the occurrence of the supposed fossil crab burrow, *Ophiomorpha* (= *Halymenites*).

It is hoped that reporting and illustrating these rare fossils will aid in further finds and elucidation of upper Cretaceous echinoderms in North Dakota.

GEOLOGY ALONG THE PORTAL PIPELINE, LAKE AGASSIZ PLAIN[1]

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INTRODUCTION

The Portal pipeline was completed between Lignite, North Dakota, and Clearbrook, Minnesota, during the summer and fall of 1962. The entrenching of this pipeline offered a unique opportunity to observe continuous exposures across the Glacial Lake Agassiz Plain. These observations were made by geologists of the North Dakota Geological Survey. The purpose of this paper is to report these observations and to compare some of them with previous reports.

The close of the last major glaciation (Wisconsinan) is marked in this area by the deposits of the Glacial Lake Agassiz. No definite age has been determined for the beginning or final drainage of the lake, but some deposits underlying Lake Agassiz sediments at Moorhead, Minnesota, have been dated at 9,930 ± 280 (13) and 11,238 ± 700 (7) years before the present. The lake was formed as the ice receded from the Red River Valley and the meltwaters were dammed by the ice front lying to the north and east. During this period drainage developed to the south through the Glacial River Warren. The lake was gradually lowered and the successively lower levels are

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marked by the Herman, Norcross, Tintah and Campbell beaches. The most prominent of these is the Campbell beach which is thought to have been formed when the River Warren had cut down to bedrock, thus slowing considerably the rate of lowering of the lake. Elson (1) referred to this period of southward drainage as the Lake Agassiz I stage.

Upham (9) included the McCauleyville beaches in the southward drainage stage of the lake. He thought that the ice then gradually receded and a lower outlet to the north and east was opened. The successively lower levels of this stage are marked by the Blanchard, Hillsboro, Emerado, Ojata and Gladstone beaches.

Elson believed that following the Lake Agassiz I stage the lake was completely drained by the northeastward drainage. Then a readvance of ice, interpreted by him to be the Valders advance, again blocked the northeast drainage and his Lake Agassiz II stage be-

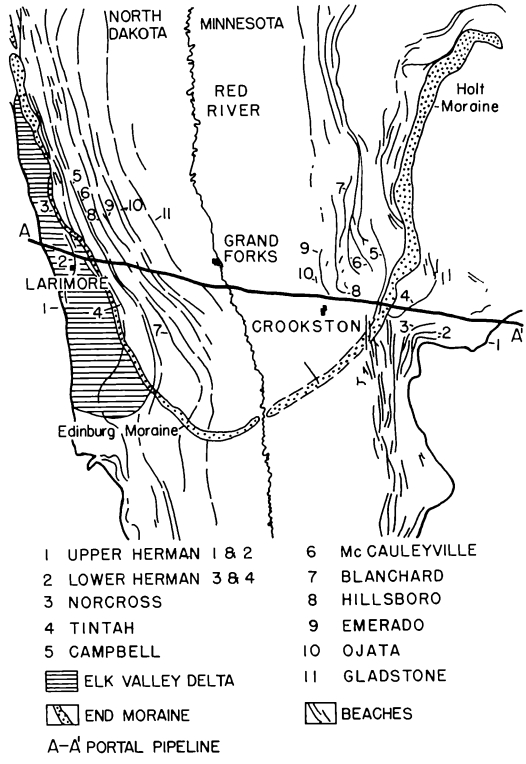

FIGURE 1—Index map showing route of Portal Pipeline across the Glacial Lake Agassiz Plain. North Dakota geology after Lemke and Colton (4). Minnesota geology after Leverett, (6).

gan (1). At this time the basin was again filled, temporarily as high as the Tintah or Norcross stand; but as the overflow cut through alluvial deposits near Browns Valley, the lake level rapidly subsided to the second Campbell strandline. During this interval the drainage was again to the south, but as the ice receded the lower outlets to the north and east were again opened and the lower beaches were formed at this time. Finally drainage was to the north through what is now Lake Winnipeg and the Nelson River.

The area of investigation lies almost wholly within the Lake Agassiz Plain district, Western Lake section of the Central Lowland province (2). A subdivision of this, the Elk Valley Delta subdistrict, was crossed by the pipeline trench in western Grand Forks County. The lowest elevation of the trench was where it crossed the Red River at an elevation of about 790 feet and the highest elevations were at about 1220 feet on the North Dakota side and about 1180 feet on the Minnesota side of the River.

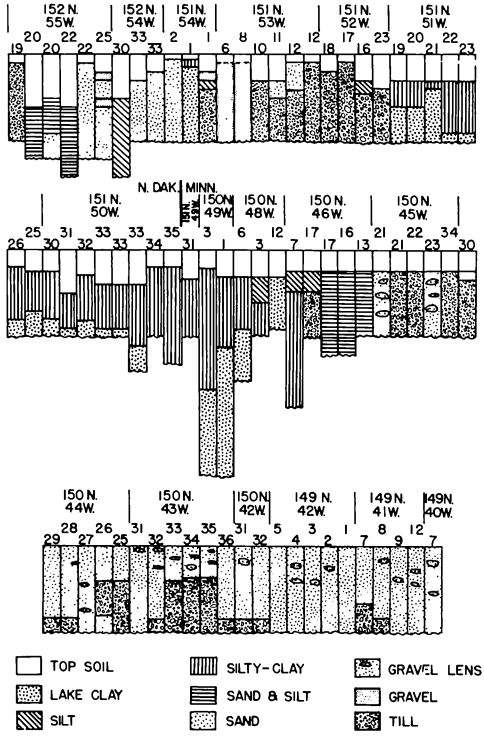

FIGURE 2—Columnar sections at selected points along Portal Pipeline trench.

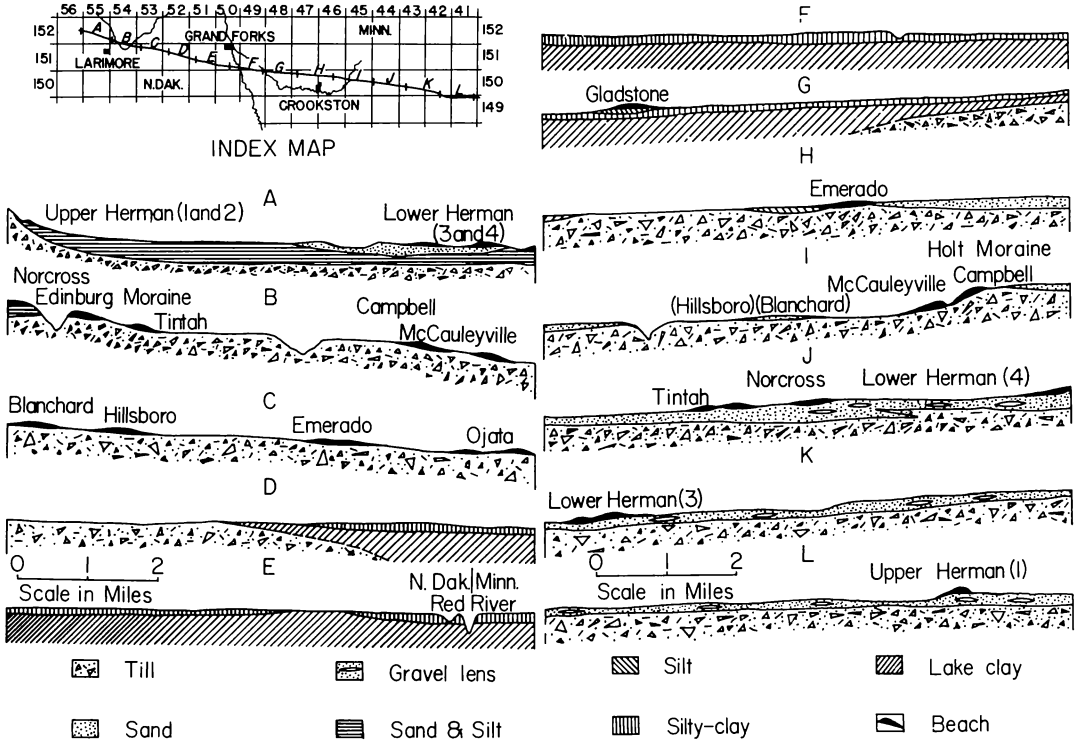

FIGURE 3—Schematic cross section of Lake Agassiz Basin as observed along the Portal Pipeline trench.

The trench was generally excavated to a depth of five feet except where it passed under drainageways. In these areas the trench was generally excavated to about eight feet and in some cases as much as 15 feet. Where it crossed major drainages, such as the Red River, the trench was excavated to depths about 35 feet blow the general surface. However, many of the deeper excavations were obscured by water in the trench. The detailed lithology at selected points along the trench is shown in the columnar sections (fig. 2).

TABLE I

LOCATION AND ELEVATION OF GLACIAL LAKE AGGASSIZ BEACHES

	NORTH DAKOTA		MINNESOTA	
Beach	Location	Elevation (feet)	Location	Elevation (feet)
Gladstone[1]	———	———	SESESec Sec. 4	840
Ojata, lower[2]	NE Sec. 22 T151N, R52W	870	———	———
Ojata, upper[2]	SW Sec. 16 T151N, R52W	880	———	———
Emerado	NENE Sec. 18 T151N, R52W	900	SWNE Sec. 17 T150N, R46W	900
Hillsboro[2]	SWNE Sec. 10 T151N, R53W	930	———	———
Blanchard[2]	NENW Sec. 9 T151N, R53W	948	———	———
McCauleyville	SESE Sec. 6 T151N, R53W	980-990	SWNW Sec. 23 T150N, R45W	990-995
Campbell, lower[1]	SWSE Sec. 6 T151N, R53W	1000-1010	SENW Sec. 23 T150N, R45W	1000
Campbell, upper	———	———	SWNE Sec. 23 T150N, R45W	1012-1015
Tintah	SENE Sec. 33 T152N, R54W	1060	SWNE Sec. 28 T150N, R44W	1055
Norcross, lower	NENE Sec. 32 T152N, R54W	1080-1090	NESW Sec. 27 T150N, R44W	1090
Norcross, upper	NENW Sec. 32 T152N, R54W	1100-1110	NWSE Sec. 27 T150N, R44W	1100
Lower Herman 4	SESW Sec. 30 T152N, R54W	1120	SWNE Sec. 31 T150N, R43W	1135
Lower Herman 3	SESW Sec. 25 T152N, R55W	1130	NESE Sec. 32 T150N, R43W	1145
Upper Herman 2[2]	SENE Sec. 19 T152N, R55W	1150	———	———
Upper Herman 1	SE NW Sec. 19 T152N, R55W	1160	SENW Sec. 9 T149N, R41W	1170

1. These beaches not seen in North Dakota.
2. These beaches not seen in Minnesota.

The field procedure was to drive or walk along the trench. Lithologic changes were noted, samples were collected, and an effort was made to locate plant or animal remains which might be used to date the sediments. A relatively abundant molluscan fauna was found at one locality, but the rest of the samples were barren.

The elevation of the beaches (Table I) were determined by plotting the beaches on topographic sheets. Elevations in North Dakota are from the United States Geological Survey 15 minute topographic

maps for Emerado and Larimore Quadrangles. For the Minnesota area elevations are from the Army Map Service 1/250,000 series, Grand Forks, North Dakota; Minnesota Sheet (NL-14-3). These elevations are generally in close agreement with those of previous surveys, but a few of them are slightly different.

Thickness of top soil was measured along the pipeline in North Dakota to the nearest one quarter foot. The thickness of top soil in the clay and delta deposits was fairly consistent but in the till it was variable. Top soil in the silty-clay of the lake basin averaged about 1.5 feet, while the top soil of the delta averaged 2.8 feet. Till which lies at an elevation between the clay and delta has an average thickness of 0.7 feet. The variation in thickness is probably accounted for, mainly, by the different lithologies; although the time of exposure to weathering may be a minor factor.

GENERAL LITHOLOGY

The predominant lithology seen in a cross-section (fig. 3) of the lake basin is the till which underlies the lake sediments throughout the area of investigation. The till is generally a clayey till on the North Dakota side, but is generally somewhat silty to sandy on the Minnesota side of the River.

Lake clays and silts are confined to the central part of the basin and form a relatively thin veneer overlying the till. The clays and silts are yellowish-brown, contain common iron-staining and are generally calcareous. At two localities, where the trench crossed drainageways, the lowermost clays contained some white, calcareous nodules and thin, white, very calcareous seams.

The beach deposits generally consist of sand or sand and gravel. The individual sand and gravel units are generally lenticular in shape, and the coarsest material is concentrated near the crest of the ridges.

An area of silt and sand overlies the till in the area west of the Edinburg-Holt moraine in North Dakota. These deposits have been referred to as the Elk Valley delta. An area of silt and sand overlies the till in the area east of the Edinburg-Holt moraine in Minnesota, also. This unit is relatively thin, often only 2 to 3 feet thick along the line of the trench, and may be an area of outwash. The outwash may be associated with the Edinburg-Holt moraine, or it may be associated with the Erskine moraine which lies just to the south of that area.

BEACHES

The youngest beach observed along the trench was the Gladstone beach which was noted as a slight rise in the Minnesota segment of the trench. No beach deposits were present, so this is probably what Upham referred to as a wave cut beach (11). There was no indication of this beach in the North Dakota segment.

The Ojata beach was not observed in the Minnesota segment, but it was observed as two distinct wave cut beaches with no sand deposits in the North Dakota segment.

The Emerado beach is a rather inconspicuous ridge composed of silt and sand on the Minnesota side of the basin. In North Dakota this beach is a very prominent ridge about 500 feet wide, rising about 10 feet above the surrounding area; and it is composed of sand and gravel. About 250 feet in front of the main ridge the beach deposits feathered out above the underlying till.

The Hillsboro beach was not present in the Minnesota segment but is represented by a distinct ridge composed of sand and gravel in the North Dakota segment of the trench. Likewise, the Blanchard beach was not present as a distinct topographic feature in the Minnesota segment. However, an area of sand overlying the till a few miles west of the McCauleyville beach may marke this lake level. In North Dakota, the Blanchard beach is a prominent ridge composed of sand and gravel.

In Minnesota, the McCauleyville beach is a conspicuous ridge composed of sand and gravel which lies about a quarter of a mile west of the upper Campbell beach. Both the lower and upper Campbell beaches are prominent ridges composed of sand and gravel. The lower areas between the beach ridges are composed of sand and are now swampy areas. Similarly, in North Dakota, the McCauleyville and Campbell beaches are within a quarter of a mile of each other and are marked by distinct ridges composed of sand and gravel; but only one Campbell beach was noted along the trench.

The Tintah beach is a prominent ridge composed of sand and gravel in the Minnesota segment. Two smaller ridges, composed of sand and gravel (perhaps offshore bars?), lie to the west of the main beach ridge. The lower areas between the ridges are composed of sand and are swampy areas. In North Dakota, the Tintah beach is composed of sand; and the beach deposits overlie the till.

The Norcross beach is about a mile east of the Tintah beach in Minnesota. The lower beach is marked by a slight rise composed of sand and the upper beach is a prominent ridge composed of gravel and sand. In North Dakota, the Norcross beaches were crossed where they border the Turtle River. Both beaches are composed of sand; and, as in Minnesota, the upper beach is the most prominent. The upper beach lies on Elk Valley delta deposits and the lower beach lies on the margin of the delta deposits.

The Herman beaches are low, gentle rises composed mainly of sand but with minor gravel deposits overlying sand in the Minnesota segment. Similarly, in North Dakota the lower Herman beaches are composed of sand with some gravel overlying silt and sand.

The upper Herman beaches are composed of sand and gravel overlying sand in Minnesota, whereas in North Dakota the upper

Herman beaches are noted as distinct topographic rises; but there are no beach deposits of sand and gravel.

EDINBURG — HOLT MORAINE

A moraine, first recognized by Upham (12), extending from Edinburg, North Dakota, to near Hillsboro, North Dakota, has been named the Edinburg moraine by Lemke and Colton (4). Similarily, a moraine which is clearly traceable from Lake of the Woods County to southern Polk County in Minnesota has been named the Holt moraine by Leverett (5). It is now thought that these moraine were formed by the same glacial advance and are called the Edinburg-Holt moraine (4). The Edinburg-Holt moraine is a well defined moraine on its northern end and decreases in prominence to the south. Leverett (5) thought parts of it were deposited in ponded waters especially near its southern end which could account in part for the decrease in prominence.

The Edinburg-Holt moraine is difficult to recognize where crossed by the pipeline in North Dakota and Minnesota. In North Dakota the pipeline crosses the moraine in the area of the Norcross and Tintah beaches. The moraine is indicated by a rise in slope, an abundance of boulders, and some local relief; this relief is generally less than five feet. In Minnesota, the pipeline crosses the moraine in the area of the Campbell beach. Here the features of the moraine are similar to those in North Dakota, except that it appears as a continuous linear element when seen from a few miles west.

DELTA AND OUTWASH DEPOSITS

Upham (10) applied the term "Elk Valley delta" to the silt and sand deposits which lie between the Edinburg-Holt moraine and the escarpment which forms the western shoreline of the lake. Since that time there has been some discussion as to whether these deposits are actually lake deposits or proglacial deposits which have been reworked by the lake during the Herman to Norcross interval of Lake Agassiz.

The silt and sand are generally well sorted deposits. A few gravel lenses were noted. The thickness of these deposits is not known, but they have been estimated to be about 30 feet thick in this area (3). The trench did not penetrate the complete thickness of these deposits at any locality.

Deposits of silt and sand extend from the Edinburg-Holt moraine to the Upper Herman beaches in Minnesota, also. These deposits are generally well sorted, but they are coarser, contain more gravel lenses, and are generally thinner than the deposits of the Elk Valley delta. Again, a question arises as to whether these are lake deposits or proglacial deposits which have been reworked by the lake. A molluscan fauna, which indicates permanent water, has been collected from these silt and sand deposits from the area about a mile

east of the Norcross beaches. A study of this fauna was made by Tuthill (8).

SUMMARY

The lithologic observations along the trench generally confirm those made by previous investigators. However, the silt and sand deposits of Minnesota and of the Elk Valley delta suggest the following sequence of events. The silt and sand deposits of the Elk Valley delta, whether they be deltaic deposits or proglacial deposits, are clearly associated genetically to the deposition of the Edinburg-Holt moraine. Similarly, the distribution of the silt and sand deposits overlying the till in Minnesota suggests that these deposits are associated genetically with the Edinburg-Holt moraine although they might also be associated with the Erskine moraine which borders the lake basin on the east and south. If these deposits were laid down in the lake, then they must represent early Lake Agassiz I deposits; because the Herman to Norcross beaches in North Dakota and the Herman to Campbell beaches in Minnesota lie on these silt and sand deposits. The Campbell beach crosses the Edinburg-Holt moraine near where the trench crosses the moraine in Minnesota. This beach, as well as the Tintah, Blanchard, and Hillsboro beaches, crosses the moraine in the area south of the pipeline trench on the North Dakota side of the basin; this further dates the moraine deposits as either pre-Lake Agassiz I or contemporaneous with the pre-Tintah lake level. Precise dating must await radiocarbon dates from the lake and moraine deposits.

REFERENCES

1. Elson, J. A., 1957, Lake Agassiz and the Mankato-Valders problem; Science, v. 126, no. 3281, p. 999-1002.
2. Fenneman, N. M., 1946, Physiographic divisions of the United States: U. S. Geol. Survey (map).
3. Laird, W. M., 1944, The geology and ground water resources of the Emerado quadrangle, North Dakota Geol. Survey Bull. 17, p. 24.
4. Lemke, R. W. and Colton, R. B., 1958, Summary of the Pleistocene geology of North Dakota in Mid-Western Friends of the Pleistocene Guidebook 9th Ann. Field Conf.: North Dakota Geol. Survey Misc. Ser. 10, p. 41-57.
5. Leverett, Frank, 1932, Quaternary geology of Minnesota and parts of adjacent states, U. S. Geol. Survey Prof. Paper 161, p. 117.
6. ————————, 1914, Surface formations and agricultural conditions of northwestern Minnesota, Minn. Geol. Survey Bull. 12, Sheet 1.
7. Rosendahl, C. O., 1948; Ecology 29, p. 289.
8. Tuthill, S. J., 1963, Molluscan Fossils from upper Glacial Lake Agassiz sediments in Red Lake County, Minnesota, N. Dak. Acad. Sci., Proc., v. 17.

9. Upham, W., 1896, The Glacial Lake Agassiz, U. S. Geol. Survey Mono. 25, p. 226-227.
10. Ibid., p. 333-336.
11. Ibid., p. 463.
12. Ibid., PL. XVII.
13. Wright, H. E., and Rubin, M., 1956, Radiocarbon dates of Mankato drift in Minnesota: Science, v 124, no. 3223, p. 625-626.

STUDY OF THE MARTIN RIVER GLACIER IN SOUTH-CENTRAL ALASKA[1]

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ABSTRACT

An investigation of the Martin River Glacier in south-central Alaska was undertaken by a party from the Geology Department of the University of North Dakota during the summer of 1962. The purpose of the investigation was to study the deposits associated with the glacier and to determine the relationships of molluscs and sediments in lakes on and adjacent to this glacier.

The ultimate purpose is to compare the mechanism of deposition of a modern glacier with the mechanisms postulated for the late Wisconsinan ice sheet in south-central North Dakota. This may result in a better understanding of the Wisconsinan deposits and the climatic environment during late Pleistocene time in North Dakota.

Dendrochronological studies of selected trees were made adjacent to the Martin River Glacier to determine the dates of glacier moraines. The most massive recent moraine was discovered to have formed between 1720 and 1820. This date corresponds closely to the "Little Ice Age" when glaciers all over the world advanced. The thicknesses of the rings also disclose the growth conditions at the time they were formed and thus give some idea as to the climatic environment.

Studies of several ice sinkhole lakes on the glacier revealed how rapidly they can drain, thereby increasing their depth and resulting in a "karst" type topography. Ice-cored moraines were also found which illustrate how at least part of the "dead ice" moraine in North Dakota may have formed.

From the interpretation of the deposits of the Martin River Glacier and from the study of the biological and physical limnology of the lakes associated with this glacier, it is concluded that the climate of the late Pleistocene in North Dakota may have been considerable milder than is commonly believed.

[1] This study was supported by National Science Foundation Grant G22016.

MOLLUSCAN FOSSILS FROM UPPER GLACIAL LAKE AGASSIZ SEDIMENTS IN RED LAKE COUNTY, MINNESOTA[1]

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INTRODUCTION

During the summer of 1963 Mr. C. G. Carlson, Mr. W. P. Eastwood, and Mr. T. F. Freers, geologists of the North Dakota Geological Survey, were assigned by Dr. Wilson M. Laird, State Geologist, to study the lithology of the sediments exposed in a 5 foot deep trench which was dug for the Portal Pipeline. The pipeline extends from Lignite, Burke County, North Dakota, to Clearbrook, Clearwater County, Minnesota, and crosses the Glacial Lake Agassiz Plain in the latitude of Grand Forks, North Dakota. Carlson and Freers discuss the results of their research elsewhere in this volume of the Proceedings.

In examining sediment samples taken during the course of the field investigation, Carlson discovered one sample which contained an abundant molluscan fauna. This report deals with the fossil content of that single sample. The molluscan fauna is listed and figured; and a paleoecologic reconstruction, based on the modern ecology of the various species, is hypothesized.

ACKNOWLEDGMENTS

I wish to express my appreciation to Mr. Carlson for giving me the collection. Dr. Laird encouraged this study and provided financial support for the preparation of the plate. I am grateful to Mr. Merlyn Heimbecker for photographing the specimens.

GLACIAL LAKE AGASSIZ

Glacial Lake Agassiz was a large body of water which flooded parts of Manitoba, Minnesota, and North Dakota at least twice during the Wisconsinan Stage (50,000-70,000 to 5,000 C^{14} years B.P.) of the Pleistocene Epoch (1,000,000 years to present). The ponding of the waters which flowed northeastward before the incursion of continental glaciers in the upper Midwest, was occasioned by a widespread blockage caused by the glaciers as they expanded from a center of accumulation in the area of Hudson Bay and Labrador. As the glaciers expanded into the area of Manitoba, northern Minnesota, and eastern North Dakota, water accumulated; and an outflow of Glacial Lake Agassiz was established in the valley of the present

[1]Published by permission of the State Geologist, North Dakota Geological Survey

Minnesota River. During Woodfordian time (22,000 to 12,500 C'' years B.P.) the glaciers overrode the eastern two-thirds of North Dakota and almost all of Minnesota. Thus the Glacial Lake Agassiz basin must have been covered by glacier ice during this period of maximum glaciation.

During the Twocreekan Substage (12,500 to 11,000C'' years B.P.) the continental glaciers of North America waned and presumably a later Glacial Lake Agassiz reformed. During the Valderan Substage (11,000 to 5,000 C'' years B.P.), ice may have reinvaded the area of northwestern Minnesota and northeastern North Dakota; but the evidence for this period of active glaciation in this portion of the upper Midwest is not conclusive as now known.

The sediments from which the fossils were taken belong to the uppermost sequence formed in Glacial Lake Agassiz. Whether they were of Twocreekan age or of Recent age (5,000 to present) cannot be determined at present. A re-collection of the site could perhaps, provide material for radiocarbon dating.

The vast expanse of the ice front, especially during the recessional stage of Glacial Lake Agassiz, must have contributed huge amounts of cold, turbid meltwater. Because of a lack of vegetative cover, the recently deglaciated areas surrounding the lake must also have contributed large amounts of detritus during the early stages of the recessional lake. Weak thermal stratification can develop in turbid meltwater lakes, due to the effects of solar radiation during the warmer seasons; and this probably occurred in Glacial Lake Agassiz. Thus, it is suggested that the recessional stage of Glacial Lake Agassiz was, according to Hutchinson's classfication (3), a first or second class, atrophic or at most oligotrophic lake. Local areas along the margins may have contained clear water due to inflow from streams which flowed over vegetated terrain, but this would not be expected until the last stages of the lake.

LOCATION AND POSITION OF THE FOSSIL MOLLUSKS

The molluscan fauna was removed, by wet sieving, from a 400 ml. sample of sediments. Carlson collected this sample on August 31, 1962, from a fine sandy to silty lithology 2 feet below the surface in the SW/4 NW/4 Sec. 26, T. 150 N., R. 44 W., Red Lake County, Minnesota. The lithologic unit was traced over a considerable distance and is about 1 mile east of the Upper Norcross beach ridge. The idea that these sediments are the result of deposition in a Recent slough or other similar environment is untenable; because both the species composition of the molluscan fauna and the lateral extent of the lithologic unit in which the fauna occurs precludes this idea.

MOLLUSCAN FAUNA

The following species were identifed from the sediments:

Phylum MOLLUSCA
Class GASTROPODA
Subclass STREPTONEURA
Order MESOGASTROPODA
Superfamily VALVATACEA
Family VALVATIDAE
Genus VALVATA

Valvata lewisi Currier 1868.

Subclass EUTHYNEURA
Order BASSOMMATOPHORA
Family LYMNAEIDAE
Genus LYMNAEA

Lymnaea humilis (Say) 1822.

Superfamily ANCYLACEA
Family PLANORBIDAE
Genus GYRAULUS

Gyraulus parvus (Say) 1817.

Genus ARMIGER

Armiger crista (Linne) 1758.

Family PHYSIDAE
Genus PHYSA

Physa cf. *P. ancillaria* Say 1825.

Order STYLOMMATOPHORA
Suborder HETERURETHRA
Superfamily SUCCINEACEA
Family SUCCINEIDAE
Genus SUCCINEA

Succinea sp.

Suborder SIGMURETHRA
Infraorder AULACOODA
Superfamily ZONITACEA
Family ZONITIDAE
Genus ZONITOIDES

Zonitoides arborea (Say) 1816.

Class PELECYPODA
Order PRIONODESMACEA
Superfamily NAIADEA

fragments of the prismatic layer of naiad shell.

Order TELEODESMACEA
Family SPHAERIDAE
Genus PISIDIUM

Pisidium sp.

The number of specimens representing each species is given below. The number prefixed by the letters UND is the museum number

under which the specimens are curated in the Department of Geology collection at the University of North Dakota.

UND 7043	*Valvata lewisi*	43 specimens
UND 7041	*Lymnaea humilis*	104
UND 7042	*Gyraulus parvus*	96
UND 7047	*Armiger crista*	1
UND 7045	*Physa* cf. *P. ancillaria*	2
UND 7048	*Succinea* sp.	1
UND 7046	*Zonitoides arborea*	2
UND 7044	*Pisidium* sp.	53 valves presumed to represent 27 individuals
UND 7049	Naiads	fragments

PALEOECOLOGY

Valvata lewisi is an operculate, branchiate snail which according to Baker (1) is typical of lakes and shallow water. It is associated with aquatic vegetation and requires clear, seasonally temperate water which does not dry up during periods of low rainfall. It has been found in the northern part of the United States and into Canada to the upper Mackenzie River according to Baker (1).

Lymnaea humilis, Gyraulus parvus, Armiger crista, and *Physa ancillaria* are pulmonate snails and can withstand water conditions which are less stable than can species of *Valvata.* This ability to succeed in adverse conditions of high turbidity, high dissolved solids, and seasonal drying does not preclude their success in water suitable to the species of *Valvata.* All of these pulmonate species have a wide geographic range of occurrence. They are associated with aquatic vegetation and are usually found in shallow water.

The presence of land snails in the fauna, though few in number, is conclusive proof that marginal terrestrial habitats, surfaced with vegetation, existed. *Succinea* and *Zonitoides arborea* are both represented by fragmented shells which lack one diagnostic portion. There is no question that the fragment assigned to *Succinea* is either an immature specimen or the nuclear whorl of a mature specimen of that genus. It is impossible to distinguish specimens of the species *Zonitoides arborea* from members of the species *Nesovitrea binneyana* (Morse) when the last whorl is broken away. This is the condition of both the specimens assigned to *Zonitoides arborea.* The slow expansion of the whorls previous to the last whorl in these broken specimens inclines me to make the tentative assignment in favor of *Z. arborea.*

Pisidium is a genus which is extremely difficult to identify to species. Herrington (2) lists 113 recognized names of species of *Pisidium* for North America alone. He has regrouped these supposed species into 25 species, but has not yet published the characters or life histories of them. For this reason, I have not attempted to assign the *Pisidium* valves found in this fauna to any taxon smaller

than the genus. The reliance upon the literature for the ecologic preferences of the various species is not justified because of the low confidence in the specific assignments of even the most competent workers of the past.

Naiad fragments, mostly prisms from the prismatic layer of the shells of mussels, were found. They are most likely from clams which lived locally at the same time as the gastropods lived. The Cretaceous sediments which once covered western Minnesota were incorporated into the glacial drift. These Cretaceous sediments contained pelecypod fossils which had prisms quite like the more modern freshwater clams, the naiads. Thus it is possible that the prisms, assigned to the superfamily Naiadea here, are actually reworked material from older rocks. The presence of naiads in sediments containing the obviously Pleistocene gastropods is not anomalous. The former frequently form a significant part of the molluscan fauna in modern environments containing the same species of gastropods. Be-

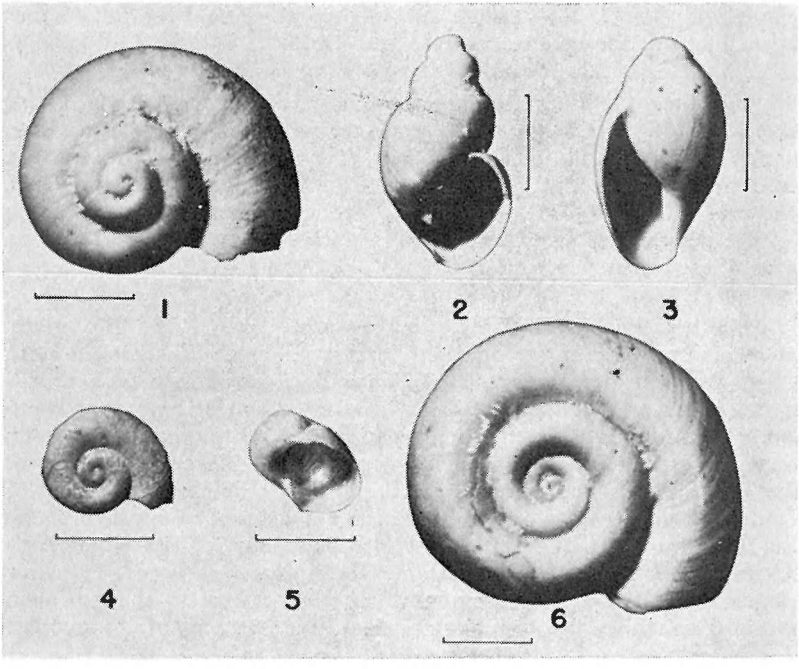

PLATE 1—MOLLUSCAN FOSSILS FROM UPPER GLACIAL LAKE AGASSIZ SEDIMENTS IN RED LAKE COUNTY, MINNESOTA. The line next to the figure equals 1 mm. Fig. 1, *Valvata lewisi* Currier; fig. 2, *Lymnaea humilis* (Say); fig. 3, *Physa* cf. *P. ancillaria* (Say); fig. 4, *Armiger crista* Linne); fig. 5, *Succinea* sp; fig. 6, *Gyraulus parvus* (Say).

cause of the question of their age, naiads have not entered into the paleoecological reconstruction erected here.

The fossils are not representative of a biocoenose. The sediments and the condition of the shells suggests they were transported only a short distance, however. As this sample was taken from sand to silt sized sediments, it is reasonable to assume that the mollusks lived nearby and were transported, after death, only a short distance, either by wave action or by streams which flowed into Glacial Lake Agassiz.

Some of the shells are etched, indicating that they lay in an acid environment after the death of the animal. The unetched surfaces of the vast majority of the shells indicates that the waters in which most of the fauna lived were neutral or basic. Thus it may be assumed that the portion of Glacial Lake Agassiz near where the fossils were deposited had at least two distinct habitats. This is the usual case in lakes today and not at all surprising. The presence of *Valvata lewisi* does indicate a rather surprising condition for Glacial Lake Agassiz, however. At least a portion of the glacially dammed lake was, at one time, clear water. The fossils occur in the uppermost beds of sediments deposited in Glacial Lake Agassiz and indicate that the glaciated margins had become vegetated by this time, thus reducing detritus which *Valvata lewisi* could not have tolerated.

The large number of fossils in so small a sample suggests the presence of a highly successful molluscan fauna, which would not have existed in unvegetated areas.

REFERENCES

1. Baker, F. C., 1928, The freshwater Mollusca of Wisconsin; Pt. 1, Gastropoda: Wisconsin Geol. and Nat. Hist. Survey Bull. 70, p. 23.
2. Herrington, H. B., 1954, *Pisidium* species and synonyms, North America, north of Mexico: *The Nautilus,* v. 67, p. 131-138.
3. Hutchinson, G. E., 1957, A treatise on limnology: John Wiley and Sons, New York, 1, p. 439-440.

A RAPID METHOD FOR CLEANING SMALL MAMMAL SKULLS

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The preservation of mammalian skulls is an essential factor in the maintenance of a museum collection for research and teaching purposes. Normally, the preparation of skulls involves the use of beetles (Dermestidae), or boiling and hand picking. Dermestid

colonies require considerable care, and their use may not be feasible unless large numbers of skulls are to be cleaned. Adequate facilities must be available for maintenance and containment of the colony; because these insects can cause serious damage to study skins and other organic materials. Boiling and hand picking is time consuming and frequently causes damage to fragile structures. A rapid technique has been developed which involves softening of tissues and their removal with a pressure washing system which utilizes a jet of air combined under pressure with hot water.

The tissues may be softened by placing skulls in a dilute ammonium hydroxide solution for two or three hours. The skulls are then boiled briefly. Mouse-sized skulls are boiled from 1 minute to 1½ minutes in a 5% solution of potassium carbonate. The duration of boiling is critical. If the skulls are boiled for too short a time, the tissues will not be sufficiently softened. If they are boiled for too long a time, the teeth and sutures of the skull may be loosened; and the skull will be useless as a specimen. The potassium carbonate solution should first be brought to a boil and the skulls then lowered into the boiling solution in a wire basket for the proper period of time. If the skulls have been properly treated, the tissue will be soft and easily removed.

An air-water jet for the removal of the softened tissues is easily constructed. The necessary materials are a glass T-tube, two eyedropper tubes and rubber tubing. The materials are assembled as illustrated in figure 1.

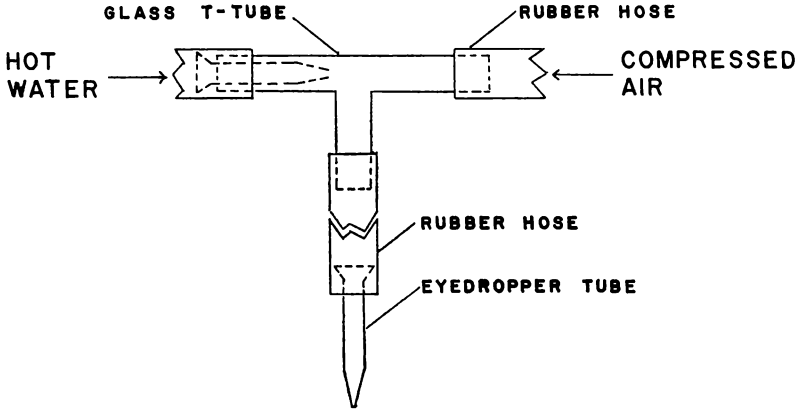

FIGURE 1 — Diagram of pressure washing system.

Because of the pressures involved, all joints should be reinforced with wire and the glass components should be wrapped with cloth. The system is connected to a source of compressed air at a pressure

of about 20 pounds per square inch and to a hot water line; the nozzle should be anchored pointing down into a sink and the skull manipulated in front of it. With the use of the air-water jet, fragile structures are seldom damaged, and mouse-sized skulls may be routinely cleaned in three to five minutes.

THE EFFECT OF VASODILATOR THERAPY ON TOTAL PERIPHERAL RESISTANCE IN SHOCK

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ABSTRACT

Previous studies have described changes in total peripheral resistance during irreversible hypotensive shock. Results differ somewhat and the question of resistance changes in early and late shock is not entirely resolved. This study is concerned with a definition of the resistance changes observed in acute hemorrhagic shock and with an evaluation of the effect of a vasodilator agent (Dibenzyline) on this parameter. Eight adult mongrel dogs were anesthetized with Na Pentobarbital (30 mg/kg) and maintained at approximately 50 mm Hg using a modified Lamson-Fine technique. Arterial and venous pressures were continuously monitored using a Statham strain gauge and a Sanborn polyviso recorder. Resistance was calculated by the formula Pa-Pv/F, in which flow (F) was measured by collecting venous return from both cavae in a calibrated graduate cylinder. Blood was returned to the right atrium via a Sigma-motor pump.

Within 15-20 minutes shock animals showed sharp increases in resistance associated with reduction in flow. Following the administration of Dibenzyline (1.0 mg/kg) all dogs exhibited a marked, sustained decrease in total peripheral resistance from a control of .082 to .047 at 35 min. Flow increased from 784 to 918 cc/min. during the same period of time. The animals appeared to tolerate the prolonged hypotensive episode with no apparent difficulties. The rationale underlying this form of therapy in shock was discussed.

THE EFFECT OF ELECTROLYTES AND ANTIBIOTICS ON THE GROWTH OF PROTEUS VULGARIS

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ABSTRACT

In cystitis and other urinary tract infections, there exists the ability to vary the salt concentration of the external environment of an infectious organism.

With this in mind, growth curves were determined for *Proteus vulgaris*, a urinary tract pathogen, in two percent peptone of varying osmolarities adjusted by the addition of NaCl or lactose, or a mixture of NaCl and lactose. The minimum inhibitory concentrations of penicillin, dihydrostreptomycin, and tetracyclne at various NaCl osmolarities were determined and growth curves at near these minimum inhibitory concentrations were obtained.

Results indicate that osmolarity, within the limits of this study, affects growth rate, providing certain essential constituents are present. Under these conditions Na^+ of Cl^- or both are necessary for growth. NaCl appears to inhibit the activity of penicillin, dihydrostreptomycin, and tetracycline. The extent of this inhibition varies with the choice of antibotic and its concentration.

[1]This study was supported in part by a Tobacco Industry Research Fellowship to the senior author.

INDUSTRIAL WASTES — PROBLEMS IN STABILIZATION

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ABSTRACT

The growth of the potato processing industries in North Dakota from a single plant in 1958 to five or more plants in 1963 presents a unique problem in waste disposal.

One approach to the stabilization of potato waste mixtures has been lagooning with domestic sewage. In North Dakota most lagoons are not sufficiently large to take both the potato waste and domestic sewage.

Another approach to the stabilization of these wastes has been one of aerating the waste with domestic sewage in a small lagoon prior to its discharge into a primary lagoon. At Park River it was found that the limiting factor in stabilization was the high pH of the potato waste. A recirculation approach may be used here to circumvent the high pH problem. At Grafton, an aerator has been placed in the primary lagoon in an attempt to increase the efficiency of the primary lagoon. This project is still underway.

It is suspected that the potato processing plants will increase in number in North Dakota. It is also surmised that lagooning of sewage and industrial wastes is here to stay with the present problem being one of combining the lagooning of domestic sewage and potato wastes. While some steps have been made toward solution of the problem, the final goal has not been attained.

SOME OBSERVATIONS ON THE RATE OF PASSAGE OF CHROMIC ACID, ABSORPTION, AND SECRETION OF SOME NUTRIENTS ALONG THE ALIMENTARY TRACT OF SHEEP

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ABSTRACT

Several experiments have been conducted using sheep fed different rations containing chromic oxide to determine whether chromic oxide could be used as an internal indicator. These sheep were slaughtered and the contents removed from the different sections of the alimentary tract. The contents were analyzed for dry matter, protein, water soluble protein, ash, chromic oxide, lignin, crude fiber, phosphorus and water soluble phosphorus. The results of these experiments indicate that chromic oxide is not a reliable indicator for the measurement of digestion of dry matter and the absorption of nutrients in the rumen. Chromic oxide leaves the rumen more rapidly than the fibrous material. Therefore, a low value for chromic oxide is obtained. Lignin values were indicated to be a truer index for digestion of dry matter than chromic oxide.

A FIELD INSTALLATION FOR THE STUDY OF GRASSLAND MICROCLIMATE[1]

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ABSTRACT

A meteorological station for the observation of gradients in microclimatic factors was set up in mixed grass prairie vegetation at the Dickinson Experiment Station in the spring of 1962. Instruments were installed on a 15° south-facing slope, a 15° north-facing slope and in undisturbed native grass on the small ridge between the two sloping sites.

Air temperatures, soil temperatures, and relative humidity readings are taken hourly, day and night throughout the growing season, and are recorded in a centrally located instrument shelter by means of recording potentiometers. Miles of wind are counted and recorded in the instrument shelter by means of industrial counters. Evaporaiton at each site is measured daily using black and white Livingston atmometer bulbs. Soil moisture is determined at weekly intervals by means of Coleman fiberglass-sandwich units and by gravimetric methods. Precipitation is determined with standard Weather Bureau rain gauges.

Location of sensing units on each site is as follows: thermocouples for soil temperatures at ½", 1", 3", 6", 12", 18", 24", 36" and 48" in the soil; thermocouples for air temperatures at 1", 3", 6", 12", 18", 24", 36", 48", and 60" above the soil; soil moisture units at 1", 2", 3", 6", 12", 18", 24", 36", and 48° depths; anemometers are located at 6", 12", 36", and 60" heights; paired white spherical Livingston atmometer bulbs with one black bulb are located at 6", 12", 18", 24", 36", 48", and 60" heights; relative humidity units (lithium chloride cells) are situated at 6" and 5 feet; a standard rain gauge is located at each site.

Instrumentation for the automatic recording of net radiation data on each site will be installed in the 1963 season.

Details of installation assemblies, recording operations, and calibration and maintenance procedures were described.

Detailed phenological studies of native grass and developing stands of seeded native grass are being made on each of the slope sites. Microclimatological data are being entered on punch cards and readied for machine analysis and correlation with plant growth information.

[1]Study jointly supported by the national Science Foundation and North Dakota Agricultural Experiment Station.

EARLY FLOWERING OF DANDELION AND SILVER MAPLE

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At the 1956 meeting of the Academy I gave some notes on dates of first flowering of some species of plants in this locality, noting that variation from year to year corresponds closely with temperature. I now find that I have been neglecting the most common species, the dandelion.

Each year I remark to a friend, "The dandelions began blooming today," and he replies, "Oh, I have been seeing them for a couple of weeks." Both statements are correct. The first to flower are plants close to the manholes of the campus heating lines. About two weeks later they form a yellow stripe over the line (in recent years this seems changed due to increased heat killing plants), and a few will be open close to the south side of a building. The first week of May they may be seen extending out from the south side of an isolated group of trees and soon are in flower everywhere.

The dandelion, of course, has all its leaves at the ground level. It therefore is especially priviliged in securing maximum effects of spring warmth. By contrast, the silver maple is a large tree with its roots deep in the ground and branches many feet above the ground, completely exposed to vagaries of the weather. One would scarcely expect these two plants to behave in a similar manner.

With very few lapses, this is the 54th year that I have kept records of the dates of first flowers, including the dandelions near the manholes of the heating lines. These were always something of a joke, but when I came to examine the dates I found there was a close correlation (.7829 calculated by a departmental associate, Gale Wolters) between these and those of silver maple, and they happen to come about the same date. Those growing in the open showed little correlation (.1073) with the others.

In the present year the silver maple and the dandelion flowered early, the first dandelion March 28. The weather remained unseasonably warm and the maples were in full bloom March 31. They certainly flowered the day before and probably some still a day or so earlier. This is the fourth year in 50 that the dandelion has opened in March (1910, 1938, 1958). In 1923 it was May 1, but the average is April 13, and that of the maple April 9. The initial date of flowering of the dandelions in the open varied only about half as much (15 days) as for those adjacent the manholes of the heating lines or in protected areas.