PROCEEDINGS

of the

NORTH DAKOTA ACADEMY OF SCIENCE

Founded December, 1908

VOLUME XIII

1959

OFFICERS

President - -	Harold J. Klosterman
President-Elect -	Vera Facey
Secretary-Treasurer	Ben G. Gustafson
Historian - - - -	George A. Abbott

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GRAND FORKS, NORTH DAKOTA
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PROFESSIONAL PAPER SECTION

FIFTY-FIRST ANNUAL MEETING
NORTH DAKOTA ACADEMY OF SCIENCE

FRIDAY, MAY 1, 1959

The fifty-first annual meeting of the North Dakota Academy of Science was held in Pioneer Hall at the Minot State Teachers College. President Arthur W. Koth called the meeting to order at 9:15 a.m.

Greetings were extended to the good crowd and announcements were made concerning the program and necessary committee meetings.

President Arthur W. Koth appointed P. C. Sandal of the N.D.A.C. to act in place of Harry Mason of Jamestown on the Nominating Committee. He requested them to be ready to report by 11 a.m.

The seven morning papers proceeded in order. A coffee break was held at 10:30 a.m.

The business meeting was called to order at 11:30 a.m. and the Nominating Committee reported. The members of the Committee were:

E. D. Coon, Chairman
Warren Whitman
P. C. Sandal

The Slate presented was:

President	Harold Klosterman, NDAC
President-elect	Vera Facey, UND
	Edith Larson, UND
Secretary-Treasurer	Ben G. Gustafson, UND
Historian	George A. Abbott, UND
Executive Committee	Arthur W. Koth, ex-officio, UND
	C. C. Moore, Minot
	Hugh Robinson, Valley City
	Vernon Youngs, Bottineau
	Paul Sandal, NDAC

Warren Whitman moved the acceptance of the report and Rae H. Harris seconded the motion. Carried.

Secretary Ben G. Gustafson then reported on the Joint Resolution passed by the Legislative Houses making the North Dakota Academy of Science the "Official State Academy of Science."

The meeting adjourned at 11:50 a.m. for lunch in the Pioneer Hall Cafeteria. Seventy-six members had registered in during the morning session.

The afternoon meeting was called to order in the Pioneer Hall Lounge by President Arthur W. Koth at 1:15 p.m.

Dr. George A. Abbott presented the invited paper, "Our Growing

Knowledge of the Humic Acids". This was done in the fine style which has always been the mark of work done by this grand champion of science. The presentation was scholarly and was well received, a long question period followed.

The student papers, 9 through 16 were then presented. The judging committee was composed of John Hundley, UND; Vera Facey, UND; Cyril C. Moore, Minot; Paul C. Sandal, NDAC, and D. Stuart Frear, NDAC.

The meeting adjourned for the afternoon at 4:30 p.m.

The Academy assembled at the Bishop Ryan High School Gymnasium at 6:15 p.m. for the Annual Dinner of the Society. About 150 members and guests were present. This was a joint meeting with the Red River Valley Section of the American Chemical Society and the Sigma Xi chapter at the University. President Arthur W. Koth presided.

Greetings were extended by President C. P. Lura of the Minot State Teachers College, special guests were introduced, and the new officers of the Academy of Science were presented along with the Officers of the Chemical Society and the Sigma Xi Chapter.

The North Dakota Foundation for Engineering and Science Scholarships were then announced by E. J. O'Reilly, the Scholarship Committee Test Chairman for the Foundation. Those who were present were introduced by him. The recipients of the scholarships, worth $200.00 each, were announced as:

Science:

Robert F. Dugan, Jamestown High School
Richard R. Sturgeon, Grand Forks High School
Robert Boettcher, Riverdale High School
Bonita Schimdt, Riverdale High School

Engineering:

Alfred H. Clausen, Jamestown High School
John Freeman, Jamestown High School
Ronald Hoff, Williston High School
Clarence Kregness, Wildrose High School
George A. Plaas, Grand Forks High School
Arthur Winter, Bismarck High School
Loren Lindberg, Grafton High School
Jerome S. Knutson, Grand Forks High School

John A. Hundley then introduced the winners of the A. Rodger Denison awards for the Student Papers. The winners were:

1st. Thomas Farley, N.D.A.C.
The Syntheses and Studies of the Isoxazoles.

2nd. Cortes L. Perry, U.N.D.
A Spectrphotometric Study of the Dissociation of Dinitrogen Tetroxide.

3rd. Bruce D. Unger, N.D.A.C.
Electrochemistry of Some Heterogeneous Cells.

Dean Ralph A. Dunbar then introduced the guest speaker, Dr. Charles Koelsche, of the Department of Health, Education and Welfare in Washington, D. C., and the Toledo University faculty. The subject of his lecture was, "The Implications of Recent Research in Upgrading Science Education in Our Secondary Schools." Dr. Koelsche is a pioneer researcher in this field and is currently the Director of a "National Science Survey of Secondary Schools" in which North Dakota is participating. The current work which is being done gives much promise for future progress. Dr. Koelsche was well received and graciously spent a long time answering questions after his lecture. There is a long gap to bridge between what science is needed for different leads of training and how this shall be presented in the class room, based upon minimum standards of teacher preparation and science facilities. There is a great deal of variation in schools and there is much work to be done if any progress is to be made.

SATURDAY, MAY 2, 1959

The Saturday morning meeting was called to order by President A. W. Koth at 8:45 a.m. We were notified that paper number 22 on the program would not be presented at this time. The balance of the program of papers proceeded as scheduled.

The business meeting of the Academy was called at 10:45 a.m. by Pres. A. W. Koth after a pleasant coffee break.

The committee reported the results of the election.

Harold J. Klosterman	President
Vera Facey	President-elect
Ben G. Gustafson	Secretary-treasurer
George A. Abbott	Historian
Arthur W. Koth, ex-officio	Executive Committee
Cyril C. Moore	Executive Committee
Vernon Youngs	Executive Committee

Certified — G. S. Klovstad, Tellers Chairman

Rae H. Harris moved the minutes for the 1958 meeting be approved, as printed. Seconded by E. J. O'Reilly. Carried.

Ben G. Gustafson presented the Financial Report of the Academy, which had been audited and approved by the Audit Committee—Wilson M. Laird and Alan H. Meldrum. Ben Gustafson moved the acceptance of the report. Seconded by E. J. O'Reilly. Carried.

Franz Rathmann gave a report on the A.A.A.S. meeting (125th) which he had attended Dec. 26 to 31, 1958. He reported highlights of the meeting and gave Journal references for the complete report. George A. Abbott moved the report be accepted. Seconded by P. C. Sandal. Carried.

William Downing reported for the Committee on Resolutions (William Downing, Theodore Snook, E. A. Helgeson). William Downing moved the acceptance of the report. Seconded by Theodore Snook. Carried.

Rae H. Harris reported for the Publications Committee. He moved the acceptance of the report. William Downing seconded. Carried.

Warren Whitman reported for the Membership Committee (Warren C. Whitman, Richard E. Frank) and reported on new members approved by the committee. He moved the approval of the report. Seconded by Franz Rathmann. Carried.

The report of the election of officers was given and accepted. The elected officers accepted. Harold J. Klosterman took over as President.

NEW BUSINESS

E. D. Coon moved the Academy appropriate $150.00 to the Secretary's Office to be used for secretarial help. Seconded by Ralph Dunbar. Carried.

Ralph Dunbar moved the selection of the site for the 1960 meeting to be referred to the Executive Committee. Seconded by Rae H. Harris and Warren C. Whitman. Carried.

Ralph Dunbar then presented an invitation for the Academy to hold the 1960 meeting on the campus of the North Dakota Agricultural College.

President Harold J. Klosterman called a meeting of the Executive Committee following lunch.

The Academy then adjourned to the Pioneer Hall Cafeteria for Noon Luncheon. The fifty-first meeting of the North Dakota Academy of Science was officially closed.

Respectively Submitted,

Ben G. Gustafson
Secretary-Treasurer

Arthur W. Koth
President

Financial Statement May 1, 1958 to April 28, 1959

North Dakota Academy of Science

RECEIPTS:		
Balance 5/1/58		915.59
Revenue Deposits 5/1/58 to 4/28/59		
Denison Awards	190.00	
Foundation	321.00	
Dues	358.00	
Cash on Hand 5/1/58	72.52	
Reprints & Cuts	161.58	1103.10
Cash on Hand 4/28/59	96.23	96.23
(Found. 56.00, Reprints 18.25, Postage on hand 21.98)		
TOTAL		2114.92

EXPENDITURES:

Foundation	321.00	321.00
Postage	101.20	101.20
Press Reprints	135.20	
Posters	14.55	
Stationary	9.85	
Proceedings	152.75	
History	172.50	
Programs	35.90	520.75
Bank Charges	1.38	1.38
Science Fair	25.00	25.00
A.A.A.S. Dues	6.00	6.00
A.A. Shapley—Expense	6.00	
	172.00	178.00
NDAC Student Union—Banquet Expense	20.83	20.83
Clerical Help	8.00	8.00
Inscribing Certificates	16.00	16.00
Denison, on Awards	90.00	90.00
Denison, on Publications	100.00	100.00
BANK BALANCE		726.76
		2114.92

Proceedings Costs 1958 Volume XII

NDAC	350.00	
UND	350.00	
Jamestown College	50.00	
Denison	100.00	
Academy	152.75	1002.75
History	172.50	172.50
Postage	35.45	35.45
TOTAL		1210.70

UNPAID DUES 1959:

2 x 8	16.00
8 x 6	48.00
19 x 4	76.00
73 x 2	146.00
	286.00

We hereby certify that we have checked this statement and find it to be correct.

Alan H. Meldrum
Wilson M. Laird
Audit Committee

INFLUENCE OF EARLY SEASON CLIPPING ON THE PRODUCTIVITY OF NATIVE GRASS

Warren C. Whitman

Department of Botany

North Dakota Agricultural College, Fargo, North Dakota

ABSTRACT

It is commonly assumed that continued heavy grazing of native grass vegetation in western North Dakota during the spring and early summer is injurious to the vegetation and results in lowered forage yield. However, there are few quantitative data available to substantiate this assumption. To obtain some data on the actual effects of heavy early-season utilization on the productivity of native grass a study was initiated at the Dickinson Experiment Station, Dickinson, North Dakota, using clipping techniques to simulate grazing on small plots.

Replicated 1-meter-square plots were clipped at successively later dates in the spring and early summer during the period 1954-57. One set of plots was clipped on May 10, a second on May 20, the third on May 30, and so on at successive 10-day intervals through June 30. Vegetation was clipped at a height of 1 inch, which represents very heavy utilization.

By 1957, four years after the initiation of clipping, the plots that were clipped first on May 10 of each year were producing only about half as much forage as those first clipped on June 30 of each year. There was very nearly a direct linear progression in grass yields at each 10-day interval from May 10 to June 30.

Under all dates of clipping there was a reduction in density of the taller grasses and an increase in the cover of the shorter grasses, indicating a tendency for the conversion of the original mixed grass vegetation to a short grass type.

While the influence of heavy grazing will probably not be as injurious as the clipping treatments, it is concluded that heavy early season utilization does reduce the productivity of native grassland in western North Dakota. Over a period of years such treatment tends to convert the mixed grass type of the region to a type dominated largely by short grasses.

EPOXY RESINS FROM LIGNITE COAL TARS

R. E. DUNBAR and JOHN B. LALONDE

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Epoxy resins were first prepared in the early 1940's by Greenlee, Zech and Kell (3). Although they soon proved to be very popular

in Europe, they did not gain in productivity in this country until several years later. (4). The usual preparation of these resins consists of the formation of polyhydric phenol, from phenolic material and a ketone or aldehyde in the presence of a mineral acid (5). Acetone and phenol, for instance, would produce 2,2-bis-(4-hydroxyphenyl) propane, ordinarily called bisphenol A. In the presence of sodium hydroxide as a catalyst, this bisphenol will polymerize with epichlorohydrin to form the final linear epoxy resin. Because of the abundance of lignite coal, and the relatively low cost of lignite coal tar, it was decided to investigate these materials for possible use in their production of additional epoxy type plastics.

MATERIALS AND METHODS

The lignite coal tar used in this investigation was a typical sample of low temperature product which had been produced by the carbonization of lignite coal at a temperature of 620° C. This tar was generously provided by Mr. L. Woodward, Plant Superintendent of the Dakota Briquets and Tar Products, Inc., of Dickinson, North Dakota. The tar had been crudely refined by one distillation at the coking plant, and the distillate presented the fraction boiling up to an approximate temperature of 375° C. At room temperature there was a thick layer of light colored solids floating on the black distillate. Before each analysis of the distillate was performed, the total product was heated to 40° C. and stirred thoroughly to effect solution of the solids. Thus, any analysis performed on this homogeneous material did yield consistent and representative results. Specific results of these analyses of the distillate are recorded in Tables I and II.

TABLE I

Analysis of the Lignite Coal Distillate

D 35/4 of the distillate	0.9635
n 35/D of the distillate	1.5328
Phenol content of the distillate	27.9%
Carboxylic acids in the distillate	0.0%
Tar base content of the distillate	1.7%
Neutral oils in the distillate	69.3%
Water content of the distillate	1.1%
Solids in the distillate, Weight	10.2%
Phenols in solids, volume	0.0%

TABLE II

Fractionation of the Lignite Coal Distillate

Boiling Range of Small Fractions

	Percentage	
	Weight	Volume
Less than 170° C.	2.9	3.6
170-200° C.	1.0	1.2
200-210° C.	1.1	1.3
210-225° C.	1.6	1.6
225-240° C.	2.5	2.4
240-265° C.	6.7	6.4
265-285° C.	10.0	10.0
285-315° C.	23.1	22.4
315-358° C.	30.6	29.8
Residue	18.3	——

All distillations of the lignite tar was conducted in a 350 ml. modified Enger flask. The modified flask differed from the true Engler flask (10), in the following respects. The take-off tube was only 11 cm. from the bottom of the flask rather than 15 cm., and the upper half of the bulb and lower half of the neck were wrapped first with a layer of aluminum foil followed by one thickness of asbestos cord. The vapors from the distillation were cooled and collected by a West-type condenser, and the condensate was collected in previously weighed graduated cylinders. The amount of water present in the distillate was conveniently determined by distilling a sample of the tar to a temperature of 210° C. and noting the amount of water that separated out as a perceptible bottom layer in the receiving flask. The percentage of carboxylic acids, phenols, and tar bases were estimated conveniently and accurately by recording the diminutions in volume of the original tar after extractions with potassium carbonate, sodium hydroxide, and sulfuric acid respectively. A tar-acid separatory funnel (11) was employed in the test. The diminution method, or more commonly designated as the contraction method, is treated comprehensively by both Fisher and Eisner (1), and Weiss (11). These references should be consulted for further details.

Numerous procedures for the isolation of phenols from coal tar have been proposed (9, 7). The present study employed predominately the more common practice of extracting the phenols with sodium hydroxide. The tar distillate (500 ml.), was shaken thoroughly in a large separatory funnel with 450 ml. of a 10 per cent sodium hydroxide solution. After standing for several hours, the mixture had separated into two distinct layers, and the lower phenolic layer was drawn off and a solution of 20 per cent sulfuric acid added to the phenolic until a pH of 4-5 was achieved. On attaining this pH, a thick brown oil separated on the upper surface

of the solution of the sodium salts. Both layers were poured back into the separatory funnel along with 300 ml. of commercial benzene and thoroughly agitated. The upper benzene-phenol layer completely separated in 30 minutes, and was then transferred to an Engler flask where all the benzene was removed from the phenols by distillation. This procedure gave an overall average yield of 30 per cent by weight of phenols from the original coal tar distillate. Further fractionation of the phenols was attempted by distillation at 170-335° C. Still another sample was prepared by distilling the original coal tar distillate at 100-295° C., after which the phenols were isolated from this fraction by the customary method. These were distilled below 285°, and 85 g. of a more highly purified phenol fraction was isolated from 1,100 g. of the original lignite coal distillate.

The bisphenols were prepared from the lignite phenols by standard procedures (6). Acetone and lignite phenols were used in a 1:3 weight ratio. After three weeks the bisphenols were steam distilled, chilled and filtered, yielding at this stage only a dark tary mass. The quality was greatly improved by triturating the resin with 20 percent sodium hydroxide over a prolonged period, washing and drying. The epoxy resins, formed from lignite bisphenols, were now prepared by traditional methods, washed and dried. Epichlorohydrin (9.2 g.) and 17 g. of each lignite bisphenol were introduced into a 500 ml. wide-mouthed titration flask. The flask was equipped with a reflux condenser, thermometer and a sealed stirring device. Heat was applied and 44 g. of a 10 per cent sodium hydroxide solution was added dropwise with stirring. The solution was then refluxed 1 hour at 100-4°, the light yellow alkaline liquor poured out of the flask, and the residual resin was washed with boiling water until free of alkali. The flask was then chilled and the solid resin was then transferred to a small metal panel and heated 4 hours at 120°, and then one additional hour at 150°. The resulting resins were reddish to black in color, and apparently had the same desirable characteristics as similar products made from other commercial starting materials.

DISCUSSION AND SUMMARY

Although lignite phenols have been used previously to produce Bakelite resins (2), no attempt can be found of previous efforts to produce epoxy resins from such materials.

It is obvious from this study that there is only a meager amount (less than 1 per cent) of phenol and the three cresol isomers present in the lignite coal tar distillate. If the preparation of bisphenols were limited to these compounds as starting materials, the production of epoxy resins from lignite coal tar would be commercially unfeasible. But Shokal and Mueller (8), have preapred bisphenols from highly substituted phenols and even naphthol. The high yields

of lignite bisphenols obtained in this study add further support to the genuine reactivities of the higher molecular weight phenolic compounds.

The bisphenols produced from lignite tars were originally inclined to be dark and noncrystalline. However, their quality was greatly improved by treatment with 20 per cent sodium hydroxide solution, and subsequently produced desirable resins.

Epoxy resins were prepared by condensing the numerous phenolics present in lignite coal tar with epichlorohydrin. These resins appear to have many possible and practical uses.

BIBLIOGRAPHY

1. C. H. Fisher and Abner Eisner, "Determination of Tar Acids and Bases by Extraction Methods." Ind. Eng. Chem., Anal. Ed., **9** 215-18 (1937).
2. W. Franta and I. Lavine, "Development of North Dakota Lignite. XI. Influence of Catalysts in Reaction between Lignite Tar Distillate and Formaldehyde," Ind. Eng. Chem., **28,** 119-21 (1936).
3. S. O. Greenlee to Devoe and Reynolds Co., Inc., U. S. Patent, 2,456,408 (1949).
4. G. M. Kline, "The Year 1952 in Review," Modern Plastics, **30,** 111-21 (1953).
5. S. Kohn and E. Schub, U. S. Patent, 1,978,949 (1935).
6. M. E. McGreal, V. Niederl and J. B. Niederl, "Condensations of Ketones with Phenols," J. Am. Chem. Soc., **61,** 345-50 (1939).
7. A. Radasch and W. Bywat, Can. Patent, 363,130 (1937).
8. E. Shokal and A. Mueller, U. S. Patent, 2,548,447 (1951).
9. Z. Stinnes, Brit. Patent, 245,633 (1925).
10. J. M. Weiss, "Methods of Analysis Used in the Coal-tar Industry. II-Distilled Tars and Pitches." Ind. Eng. Chem., **10,** 817-23 (1918).
11. J. M. Weiss, "Methods of Analysis Used in the Coal-tar Industry. III-Heavy and Middle Oils." Ind. Eng. Chem., **10,** 911-16 (1918).

SEQUENTIAL ANALYSIS IN ASSIGNMENT OF GENETIC SEX BY CHROMATIN PATTERN: APPLICATION TO MEASURED DATA NORMALLY DISTRIBUTED (ONE-SIDED ALTERNATIVE)

Edwin G. Olmstead

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ABSTRACT

Several investigators have shown that a metachromatic body (sex chromatin body) is seen in the nuclei of large numbers of somatic cells of genetic females and in lesser numbers in the somatic cells of genetic males. Greenblatt et al showed in 125 human

subjects that the distribution of sex chromatin bodies in oral mucosal scrapings in females was 49.1 ± 14.4 per 100 cells and in males 2.78 ± 1.98 per 100 cells.

In an attempt to assign genetic sex to 50 human subjects by the number of sex chromatin bodies per 100 mucosal cells the hypothesis (Ho) was set up that each subject was male. With classical statistics it would be necessary to count 100 cells on each slide, find the mean and variance, and by the appropriate test determine whether this mean was significantly different from the mean of the male group. This would require counting 5000 cells in the 50 subjects.

Using Walds sequential analysis, the number of observations required depends on the outcome of the observations and is not a predetermined, but a random, variable. In testing H_o a rule is given for making one of the following 3 decisions at any observation (1) to accept H_o, (2) to reject H_o, (3) to continue making additional observations.

With the above distributions, let p = proportion of chromatin positive cells in any 100 cells and $p_o = 0.05$ and $p_1 = 0.20$. H_o is accepted if $p \leqq 0.05$ (subject is male) and H_o is rejected if $p \geqq 0.20$ (subject is female). Let $\alpha = 0.01$ and $\beta = 0.01$ The test procedure is so devised that the probability is $1 - \alpha$ that H_o will be accepted at $p \leqq p_o$ and the probability is β that H_o will be accepted when $p \geqq p_1$.

Where m is the number of inspected cells (1, 2, 3 . . . . n) the decision to accept Ho may be calculated.

$$a_m = \frac{\log \frac{\beta}{1-\alpha}}{\log \frac{p_1}{p_o} - \log \frac{1-p_1}{1-p_o}} + m \frac{\log \frac{1-p_o}{1-p_1}}{\log \frac{p_1}{p_o} - \log \frac{1-p_1}{1-p_o}}$$

$$= -2.92 + 0.11m$$

And, similarily, the decision to reject H_o

$$r_m = \frac{\log \frac{1-\beta}{\alpha}}{\log \frac{p_1}{p_o} - \log \frac{1-p_1}{1-p_o}} + m \frac{\log \frac{1-p_o}{1-p_1}}{\log \frac{p_1}{p_o} - \log \frac{1-p_1}{1-p_o}}$$

$$= 2.92 + 0.11m$$

Buy using sequential analysis the genetic sex in 25 female subjects was correctly assigned after counting 16 ± 14 cells per slide and in the male after counting 32 ± 8 cells per slide. 390 cells were counted in 25 females and 809 cells in 25 males. This total of 1199

cells counted in the 50 subjects is only about ¼ as many as necessary to arrive at an equally significant decision employing classical statistical methods.

GIBREL AN AID TO EMBRYO CULTURE MEDIA FOR *HORDEUM VULGARE*[1]

A. B. Schooler

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INTRODUCTION

Many barley breeders are very much concerned about the disease spot blotch (organism, **Helminthosporium sativum**) affecting cultivated barley, **Hordeum vulgare.** Only moderate resistence to this disease has been found in the world collection of cultivated barley. However, many of the wild species of **Hordeum** have been found highly resistant, although not immune to attack by **H. sativum.** Species crosses or hybridization are being attempted in hopes of transferring the wild species type of resistance to cultivated barley. Species crosses to cultivated barley were attempted by Konzak **et. al.** (1) in 1951, and by others prior to this time with the aid of embryo culture. It is possible that the wild species may have to be hybridized before crosses can be made directly with **H. vulgare.** This study was conducted to determine a suitable culture media for use in culturing embryos of **Hordeum** species hybrids. Rappaport (3) reported an extensive summary of work on cultural media in 1954.

MATERIALS AND METHODS

Embryos were excised from eight central spikelets located in the central portion of six spikes of equal maturity Traill barley. One embryo from each spike was grown in each of eight nutrient medias containing the following micrograms/ml. of Gibrel: 0, 0.50, 1.00, 1.50, 2.00, 2.50, 3.00, 3.50. Spikes as sources of embryos provided six samples of each treatment. The basic media were similar to that reported by Randolph and Cox (2) with variables being additions of seven concentrations of Gibrel.

All concentrations of nutrient agar were transferred to two ounce stopped bottles and sterilized for fifteen minutes at fifteen pounds pressure. Excised embryos were transferred to the cooled nutrient media (scutellum on the agar) under sterile conditions and grown in a 70° F. chamber with florescence lights. After seven days measurements of shoot and root growth were made in centimeters.

RESULTS

The average growth in centimeters of roots and shoots of excised barley embryos is shown in Table I.

TABLE I

Shoot and Root growth of excised embryos of cultivated barley, in centimeters, after seven days on culture media.

Item	Gibrel microgram/ml.	Av. length* of Shoots	Av. length** of Roots
1.	Control	6.7	3.5
2.	0.50	8.5	4.1
3.	1.00	8.7	3.4
4.	1.50	8.2	2.8
5.	2.00	7.8	2.5
6.	2.50	6.2	2.3
7.	3.00	5.4	1.1
8.	3.50	5.7	1.1
*LSD 1% level 1.17			
5% level 0.87			
**LSD 1% level 1.31			
5% level 0.98			

Highly significant differences were found in shoot growth among treatments. The growth in treatments 2 and 3 was significantly greater, and treatments 7 and 8 significantly less than the control. Significant differences in root growth also existed among treatments with 7 and 8 showing the greatest depressing effect.

Shoot growth was notably less than in the control as the concentration of Gibrel exceeded 2.50 micrograms/ml. in the growth media. Additions of Gibrel above 1.00 micrograms/ml. in the media reduced root growth well below the growth in the control. The optimum concentration of Gibrel in the media for stimulating embryo growth was 1.00 micrograms/ml. for shoots and .50 micrograms/ml. for roots.

DISCUSSION

Relatively low concentrations of Gibrel in the media appeared to be optimum in stimulating growth of excised embryos of **Hordeum vulgare.** Additional unpublished results indicated that it is a definite aid in producing growth of excised embryos of **Hordeum** crosses.

Embryos of species crosses are removed before maturity because of endosperm collapse. This phenomenon has been reported by Konzak **et. al.** (1) and other workers. The embryos of these crosses under certain conditions can be removed before maturity to nutrient agar and growth will continue. If they are left on the parent plant without endosperm formation, they generally die either before maturity or before germination of the shriveled seed. It appears best to leave the young embryo with the parent plant until the caryopsis has started to show signs of endosperm collapse. This period may be eight or ten days or as long as twenty days after pollination, depending on the temperature in which the parent

plants are growing. Generally, the best results are obtained with the longer periods of time before placing embryos on nutrient agar.

SUMMARY

Nutrient agar media containing 0.50 and 1.00 micrograms/ml. of Gibrel stimulated the early growth of exercised embryos of **Hordeum vulgare.** Since growth levels were similar as the embryos aged, this stimulus appeared promising in promoting rapid establishment of excised embryos. Consequently, it is anticipated that excised embryos of **Hordeum** species crosses should be more likely to survive and continue growth on nutrient agar media containing relatively low concentrations of Gibrel.

BIBLIOGRAPHY

1. Konzak, C. F., Randolph, L. F., and Jensen, N. F. Embryo Culture of Barley Species Hybrids. Jour. Hered. **42**:125-134. (1951.)
2. Randolph, L. F., and Cox, Leland G. Factors Influencing the Germination of Iris Seed and the Relation of Inhibiting Substances to Embryo Dormancy. Proceedings of the American Society of Horticultural Science **43**:284-300. (1943.)
3. Rappaport, Jacques, In Vitro Culture of Plant Embryos and Factors Controlling Their Growth. Bot. Rev. **20**:201-225.(1954.)

[1]Published with the approval of the Director of the North Dakota Agricultural Experiment Station.

ESTABLISHMENT OF THE SECONDARY BRONCHI IN THE WHITE PEKIN DUCK *ANAS PLATYRHYRYNCHOS* LINNAEUS

John M. Delphia

Department of Zoology

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The purpose of the present study is to establish the time of origin, place of origin and general destination of the secondary bronchi in the embryo of the White Pekin Duck. The origin of the airsacs in the White Pekin Duck was given by Delphia in 1958.

White Pekin Duck embryos from three and one-half days incubation through eighteen days incubation were prepared for sectioning by routine histological methods. Embryos were sectioned serially in transverse, frontal or sagittal view. Photomicropgraphs, camera-lucida tracings and tracings from direct projections were used to make diagrammatic reconstructions of the secondary bronchi and the mesobronchus for each day of incubation. The terminology for the secondary bronchi is a modification of that of Locy and Larsell in 1916.

The entobronchi arise from the dorsal, mesial, dorsomesial and dorsal lateral surface of the pre-vestibular region of the meso-

bronchus and send branches to the ventromesial, anteromesial and posteromesial surfaces of the lung. The ectobronchi arise along the dorsal and dorsomesial surfaces of the remainder of the mesobronchus and send branches anteriorly, dorsomesially and dorsomesioposteriorly. The lateroventrobronchi arise from the ventral margin of the vestibular and post-vestibular region of the mesobronchus and travel laterally and ventrally toward the peripheral lung margin.

The following table indicates the time of origin of each of the secondary bronchi in the three major groups:

Time of Origin of Major Secondary Bronchi in White Pekin Duck

Ento-bronch	Day of Origin	Lateroventro-bronchi	Day of Origin	Ecto-bronchi	Day of Origin
1	6	1	8	1	7
2	6.5	2	7	2	6.5
3	6.5	3	7	3	7
4	7	4	8	4	8
5	9	5	9	5	8
		6	9	6	8
		7	9.5	7	9
		8	9.5	8	9
		9	9.5	9	9.5
		10	9.5	10	9.5
		11	9.5	11	10
		12	9	12	10
		13	10		
		14	9		

Numerous smaller or lesser secondary bronchi originate from ten through fifteen days incubation. These structures originate on the **Dorsolateral, lateral, ventrolateral** and **ventromesial** surfaces of the vestibular and postvestibular regions of the mesobronchus. There are twelve or more such smaller secondary bronchi in each of the above groups.

The secondary bronchi of the White Pekin Duck were compared with their counterparts in the chicken.

A METHOD OF STUDYING TRAVEL TIME ANOMALES OF HIGH FREQUENCY RADIO WAVES

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INTRODUCTION

In recent years there has been considerable interest in the use of radio waves for propagation of precise time and frequency standards.[1 4 0 7]

Frequency variations have been observed by several authors;[3 4 6] most of the observers have placed emphasis on the standard frequency transmissions. The present authors have constructed apparatus suitable for measurement of time variations in a signal received via the ionosphere from WWV, the National Bureau of Standard's standard time and frequency radio station.

Astronomical observations are carried out by the United States Naval Observatory to keep a standard time. Their measurements are made available through standard time signals transmitted on several frequencies by radio station WWV. Each second a timing signal consisting of five cycles of a coherent 1000 cycle/second waveform is transmitted (Figure #4 waveform 3). The beginning of the first cycle of this waveform is the beginning of the standard second. Hereafter the above described signal will be called 'the timing waveform'.

This paper will describe only the apparatus used for the measurements; the results of the measurements will be published in the near future. First a description of the local clock will be given, then the method used for extraction of the required information from timing wavefore will be described.

The time variations in propagation may be caused by three factors:

Figure #1.

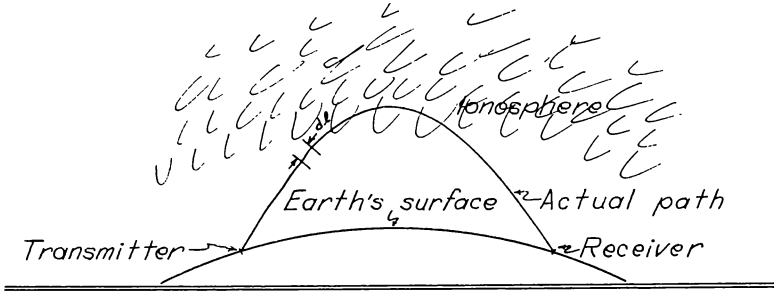
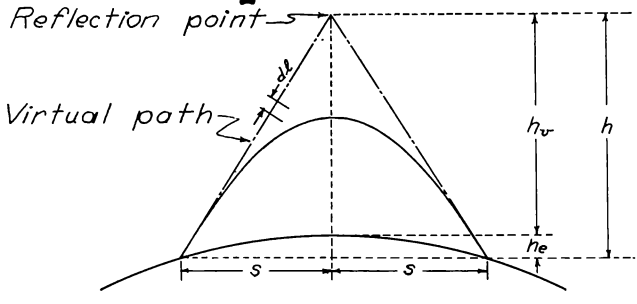


Figure #2.



a. the change in the height of the ionosphere,
b. the change in the distance between the receiving and transmitting station, and
c. the variations of group velocity in the ionosphere.

The actual path shown by the arrows is due to a gradual refractive process because of the dependence of group velocity on electron concentration. In many cases it is convenient to replace

In the general case $$\frac{dt_t}{dt} = \frac{\partial t}{\partial l}\frac{dl}{dt} + \frac{\partial t_t}{\partial u}\frac{du}{dt} \quad (1)$$

where t_t means the travel time of the wave from transmitter to receiver.

Also, $$t_t = \int_0^l \frac{dl}{u} \quad (2)$$

Eq. 1) and 2) are best evaluated in terms of the virtual height in Fig. No. 2.

In this case $$l = 2(h^2 + s^2)^{\frac{1}{2}} \quad (3)$$

and $$dl = \frac{2n\,dh}{(h^2 + s^2)^{\frac{1}{2}}} \quad (4)$$

since $ds = 0$ (the receiving and transmitting stations are stationary) and the assumed symmetry of the path.

Substitution of Eq. No. 4 in Eq. No. 1 and No. 2 gives

$$\frac{dt_t}{dt} = \frac{2\cos\theta}{c}\frac{dh}{dt} \quad (5)$$

Since

$$h = h_v + h_e \quad (6)$$

and

$$dh_e = 0, \qquad dh = dh_v \quad (7)$$

Then

$$\frac{dt_t}{dt} = \frac{2\cos\theta}{c}\frac{dh_v}{dt} \quad (8)$$

Thus, the change in travel time is a direct function of the velocity of the virtual height (h_v) of the ionosphere and the Cosine of the angle of incidence of the transmitted wave on the ionosphere.

With the apparatus to be described $\frac{dt_t}{dt}$ may be approximated, thus a great deal of information regarding the vertical velocity of the ionosphere may be calculated from Eq. No. 8. This information about the velocity will contribute to the knowledge of the errors in time measurements and may add to the information required to predict the errors.

the actual path by a virtual path along which the group velocity (u) is that of the speed of light (c). This virtual path is shown in Fig. 2.

APPARATUS

Local Clock: The local clock utilizes a quartz crystal oscillator operating at a frequency of one megacycle per second. The quartz crystal is temperature controlled and maintains a stability of a few parts in 10^8 per day. The frequency of the oscillator is divided successively by factors of 10 to obtain frequencies of 100 kc., 10 kc., etc., down to 1 pulse per second.

Hereafter the pulse produced once each second will be referred to as the one second clock pulse. Successive one second clock pulses will be spaced 1 second $\pm$ 1 x 10^{-6} seconds.

General: The basic measurement performed by the system is the determination of the time interval between the occurrence of the one second local clock pulse and a specific point on the timing waveform.

The attainable accuracy of timing is a function of the rate of change of amplitude with phase. It is readily seen that at the axis-crossings the waveform is changing at a maximum rate. From the standpoint of timing, any axis-crossing would provide a suitable phase to which to measure the time.

High frequency radio transmissions are subject to sporadic changes in the ionsphere which give rise to rapid fluctuations in the amplitude of received signals. Noise of atmospheric and man-made origins also accompany the desired signals. It was deemed desirable and perhaps even necessary to automatically reject signals of insufficient amplitude and those accompanied by excessive interference. Both amplitude and time discrimination are used to provide a screening of signals. In the present model of the system, the negative-going crossing of the axis by the fourth cycle is the point to which the time is measured.

The Timing Operation: Perhaps the most easily understood description of system operation is the following through of the sequence of steps performed during one measurement cycle.

The local clock oscillator-divider chain is first synchronized to allow the one second clock pulse to occur approximately two milliseconds before the beginning of the timing waveform.

The one second clock pulse opens both electronic gates #1 and #2. (Refer to Figures 3 and 4.) The opening of gate #2 permits transmission of the one megacycle signal to the decimal scaler. The opening of gate #1 permits the passing of the receiver output to the Schmitt triggers.

The Schmitt trigger in the upper branch of the block diagram produces an output pulse at point #4 each time the voltage at its input terminal becomes more **positive** than an adjustable reference level. These output pulses (which occur at one millisecond intervals) operate a circuit which produces a pulse at point #5 coincident with

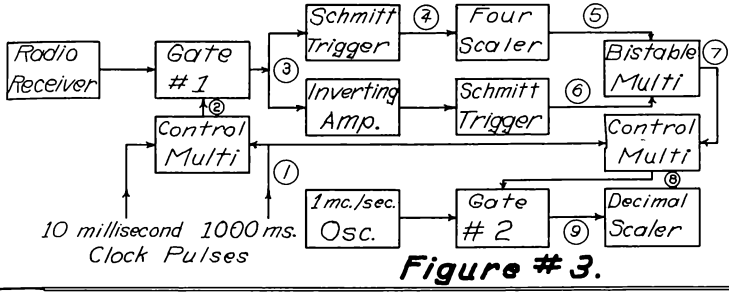


Figure #3.

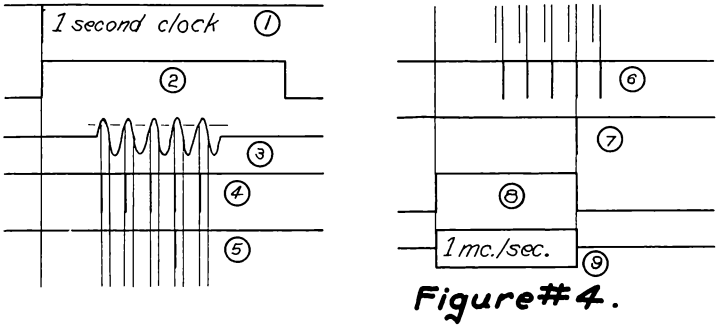


Figure #4.

the fourth input pulse. This changes the state of the bistable allowing a pulse from the lower Schmitt trigger to produce an output at point #7.

The inverting amplifier and Schitt trigger in the lower branch produce a pulse at point #6 for each **negative-going** axis crossing of the signal at point #3. The pulses at point #6 will not change the state of the bistable until after the change of state produced by the pulse at point #5.

Thus, a pulse at point #7 will appear coincident with the first pulse at point #6 which occurs after the pulse at point #5. This pulse at point #5. This pulse at point #7 will close gate #2.

Since gate #2 was opened by the one second clock pulse, it is apparent that the decimal scaler reads directly in microseconds the time interval between the one second clock pulse and the negative-going axis crossing of the fourth cycle of the WWV timing waveform.

Ten milliseconds after the occurrence of the 1 second clock pulse, a reset pulse from the local clock closes gate #1 and resets the count 4 circuit. The apparatus is then ready to make another measurement 990 milliseconds later when the next 1 second clock pulse occurs.

CONCLUSION

The possible applications of the system include its use for refinement of precision timing observations and as a means of studying ionospheric changes. With automatic means of recording and handling the data it might prove to be a fruitful means of investigating the long and short term variations of apparent ionospheric heights.

Studies of the propagation of radio waves at oblique incidence have not received a great deal of attention to date because of lack of data. Correlation of travel time data with signal strength and angle of arrival data might shed new light on some of the unsolved problems of radio wave propagation.[5]

ACKNOWLEDGEMENTS

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BIBLIOGRAPHY

1. Essen, L. "Standard Frequency Transmission", Proc. IEE, **101,** pt. 3, 249-255; (1954).
2. National Bureau of Standards, Boulder Labs., Colo., "Standard Frequencies and Time Signals WWV and WWVH", Proc. IRE, **44,** 1470-1473; (1956).
3. Ogawa, Toru "Frequency Variations in Short-Wave Propagation", Proc. IRE, **46,** 1934-1939; (1958).
4. Pierce, J. A. "Intercontinental Frequency Comparison by Very-low-frequency Radio Transmission)), Proc. IRE, **45,** 794-863; (1957).
5. Smith-Rose, R. L., et al. **Advances in Electronics and Electron Physics, 9,** 1957, Academic Press, Inc., New York; pp 210-235.
6. Steele, J. M. "The Standard Frequency Monitor at the National Physical Laboratory", Proc. IEE, **102,** 2, 155-165; (1955).
7. Tahahashi, Ogawa, Yamano, Hirai, and Takinchi, "Doppler Shift of the Received Frequency from the Standard Station Reflected by the Ionosphere", Proc. IRE, **45,** 1408; (1957).

PHAGOCYTIC ACTIVITY IN THE RAT'S SPLEEN

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ABSTRACT

Phagocytic cells are known to occur in large numbers in the spleen. They are instrumental in the removal from incoming blood of old erythrocytes, cell debris and particulate matter. Just how splenic phagocytes come in contact with such material is not entirely clear and appears to vary with different animals.

Marshall ('56) showed that most of the cells of the body which possess marked phagocytic powers can be blackened by a silver nitrate reduction technique. He called such cells metalophils. In applying Marshall's technique to sections of rat spleen, it was found that in addition to the numerous red pulp metalophil cells, there was a unique dense aggregation of these cells around the margins of the white pulp in relation to the perifollicular space. Blood from white pulp capillaries enters this space, which is lined in part by endothelial-like cells, and then infiltrates the marginal zone to enter the red pulp proper.

The dense ring of metalophils would then represent the first encounter of splenic blood with potential phagocytes. Preliminary injections of Indian ink show that some of these cells ingest ink. However, metalophil cells are more numerous than ink-containing cells.

OUR GROWING KNOWLEDGE OF THE HUMIC ACIDS

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Invited Paper for the 51st Annual Meeting of the North Dakota Academy of Science, at Minot, North Dakota, May 1-2, 1959.

I appreciate the honor and privilege of giving this Invited Paper, although I feel some trepidation when I recall the splendid papers presented by my predecessors. But there is some comfort in the thought that, after all, you did ask for it.

I have chosen to discuss briefly "Our Growing Knowledge of the Humic Acids", because I have been actively interested in these elusive materials; and especially because of the new interest and

importance they have acquired in recent years. They now are of vital concern to the agronomist, the soil scientist, the agricultural chemist, the agricultural economist, the geologist, the fuel chemist, the chemical engineer, the physical chemist, the colloid chemist, the synthetic organic chemist; even to the oil well driller and other industrialists who now use humic acids in carload lots. They should also be of interest to those of us who grow a few flowers and vegetables.

Throughout the years, many famous chemists have devoted their great talents to the study of these humic materials; notably Thomson, Berzelius, Hoppe-Seyler, Bertholet, and later, Oden, Fuchs, Stach, Fischer, Schrader, Arnold, Gillet, Kreulen, and many others including a number of capable Russian soil scientists, who have left their imprint; for today, even in the United States, our soil types bear Russian names.

As early as 1826, Sprengel, in Germany, (1) applied the term "Humic Acid" to the brown amorphous precipitate which he obtained by acidifying the black liquid extracted from decayed organic matter by alkali. He dried the product to a brown, amorphous powder.

For more than a century, spirited controversy has characterized investigations in this field. Even today agriculturists and soil scientists have failed to reach a general agreement concerning the nature of the humic acids. They have not even succeeded in formulating a universally acepted definition of them.

In 1936, when Dr. S. A. Waksman[2] published his well known comprehensive book on "Humus, Origin, Composition, and Importance in Nature", the controversy over humic acids continued. Many insisted that humic acids should not be regarded as specific chemical compounds; but only as highly complex, variable mixtures of many ill-defined materials. Dr. Waksman, himself a soil microbiologist rather than a chemist, evidently was disgusted with the prevailing confusion; for he stated: "One therefore may feel justified in abandoning the whole nomenclature of "Humic Acids" . . . preserving "Humus" because of its historical importance . . . to designate the organic matter of the soil as a whole." Thus he did not attempt to clarify the problem; but merely chose to abandon it. Actually the confusion, in large measure was due to the persistant failure to distinguish clearly between the loose term "Humus" and the specific name "Humic Acid" as applied to definite chemical compounds found in that Humus. But even Dr. Waksman himself found it necessary to deal more specifically with his Humus; for at times he uses such expressions as "well ripened humus", "fully synthesized humus," "an acid humus", etc. Because of the author's prestige, his book had the effect of directing the efforts of the scientist more toward the biological rather than the chemical aspects of soil behavior. Accordingly, it is not surprising that much of the basic chemistry of the

humic acids has been learned from fuel investigations rather than from soils studies per se.

Fuel chemists are interested in humic acids primarily because they believe that these substances represent at least one of the intermediate stages in the ultimate conversion of vegetable matter into coal. They hope that further study of these substances may lead to a better understanding of the physical and chemical mechanisms involved in the coalification process.

But long before the fuel chemists had become interested, an enormous literature dealing with humus and humic acids had accumulated. Oden alone gives 386 references. To these earlier contributions, now must be added a large and growing literature dealing with preparation and properties of the synthetic humic acids. Yet, most of the significant advances have been made comparatively recently. This is indicated by the fact that as recently as December 1, 1939, Dr. Ervin Lavine, then Professor of Chemical Engineering at the University, in his discussion of Humic Acids characterized them as "an important group of substances concerning which little is known at present".

It was a forward step when Oden (3) discarded the provisional definition of the humic acids as "the black, gummy products formed by the decay of organic matter in the soil", in favor of a chemical definition, as "Those humus substances that can split off hydrogen ions and give typical salts with strong bases with formation of water." At once this served to bring the black muck into the chemical laboratory, where soon it received attention from the physical chemist and the colloid specialist.

As early as 1912, the author examined a specimen of a black colloidal gel which had been found in a roadside ditch near lignite deposits, and reported it to this Academy under the title: "Lignite Jelly—A Natural Reversible Colloid." He brought it to the attention of Dr. A. G. Leonard, then Professor of Geology at the University, and State Geologist, with the prediction that he would find large deposits of it in the form of "weathered lignite." This proved to be true, and on account of Dr. Leonard's thoro study of these deposits, rich in humic acids, they have received the mineral name of "Leonardite". The author has continued his studies of humic acids over a period of many years, especially their colloidal behavior which was investigated with the able assistance of a graduate student, Cecil Lohn. The results were summarized and published in the Proceedings of the North Dakota Academy for 1949, under the title: "Humic Acids from Weathered Lignite." (4)

The pH of humic acid is found to be about 3.8. The acid itself, and its soluble salts behave as typical reversible colloids. Their micelles carry negative electric charges, and in some respects behave as suspenoids; but in most of their behavior they act predominately as typical emulsoids, forming characteristic hydrophylic sols and gels.

This colloidal behavior largely accounts for the beneficial effects in fertile soils. From molecular weight measurements, both physical and chemical, it appears that in solution the alkali humates may have lower molecular weights than that of the acid itself. Sodium humate, for example, is believed to exist in dilute aqueous solution in the form of a monomer which undergoes ionic dissociation. In this behavior it suggests the properties of certain soaps, found by McBain to exist in dilute solutions as typical electrolytes, while in concentrated solution forming true colloidal sols and gels.

In 1920, Fischer and Schrader (5) demonstrated that mineral coals could be converted by oxidation into a black alkali-soluble material for which they proposed the name of "regenerated humic acids". Five years later, Francis and Wheeler (6) not only clearly and finally confirmed that fact; but also they showed that the percentage composition of the black materials is practically the same regardless of the coal employed.

These observations, as well as the discovery of large deposits of natural materials rich in humic acids, served to provide chemists with better source materials for investigation, and progress became more rapid. Gillet (7) so improved the procedure of coal oxidation that it became an industrial process.

Recent determinations of the molecular weights of humic acids are more concordant, giving results that lie in a fairly narrow range of about 1200 to 1500, according to values proposed by many workers in this field. Lacking suitable methods, early investigators were unable to distinguish between equivalent weight and molecular weight; but Oden (8) in 1919 had found values of the equivalent weights of humic acids from peat, ranging from 320 to 345, and he stated that the acids were tetrabasic. If so, the calculated molecular weights of 1280 and 1380 respectively, are in reasonable agreement with values generally accepted.

Modern physical and chemical methods now make possible the identification of certain active groups or characteristic linkages in molecular structures. Such methods have been applied successfully to humic acids adding materially to our knowledge of their molecular structure. The assumed presence of carboxyl groups has been confirmed by converting the humic acids into their acid chlorides, and then to the corresponding acid amides.; also by converting the acids to their esters. The number of carboxyl groups per molecule, long has been a subject of lively discussion. So long as the molecular weight itself was in doubt, that number remained uncertain. But for the tentatively accepted molecular weight, the acid-chloride reaction, and especially the reaction with di-azo-methane appear to fix that number as four—or one for each chemical equivalent. It is interesting that Kreulen (9) and his associates in their study of the pyrolysis of humic acid under carefully regulated conditions, found that even at 220 degrees C., the quantity of carbon dioxide split off,

approached the theoretical amount corresponding to four carboxyl groups per molecule.

That phenolic hydroxyl groups are present in the humic acid molecule also is well established. It can be demonstrated by etherification of the acid and by the quantitative conversion of these groups to amino groups by the action of ammoniacal ammonium sulphite solution. Oxygen, thus known to exist in carboxyl and hydroxyl groups, is believed to exist also in other conditions in the humic acid molecule; almost certainly in ether linkage, and possibly also in keto and even quinoid linkage. Phenolic Hydoxyl implies the presence of aromatic rings, believed to be simple benzene rings rather than multi-aromatic rings. Further, the behavior of the humic acids suggests that other naturally occuring cyclic systems are almost certainly a part of the structure of the humic acid molecule. Such five-member rings as furan, containing oxygen, thiophene, containing sulphur, or pyrol, containing nitrogen. It is possible that nitrogen also may occur in a six-member ring as pyridine, or its derivatives, or in amino, amide, or imide groups. In 1957, Gillet (7) in a summary of his series of comprehensive investigations, proposed a tentative structural formula intended to account for the known facts and plausible theories concerning the molecular structure of humic acids. But, before considering Gillet's structural formula in further detail, it may be well first to examine the elemental composition of humic acids from different sources, and the empirical formulas proposed for them.

In 1956, Kreulen (10) and his associates, published a detailed discussion and summary of the state of research at that time bearing on the constitution of humic acids, and their role in coal formation. They point out that the belief, common in Oden's time (1919), that variations in the composition of humic acids reported by different investigators could be explained as due to absorbed impurities, is no longer tenable and has been abandoned.

Likewise the prevailing idea that humic acids are formed in nature only from lignin. They insist that the composition of the natural humic acids actually does vary within limits, and that they may be formed from a variety of basic materials, such as cellulose, sugars and other carbohydrates, and even from proteins under the action of various organisms. The March number of Chemical Abstracts mentions an investigation by James Magandon and Paul Simonons, University of Lerwain, Belgium, in which Glucose, labeled with radioactive carbon 14 was mixed with soils and incubated for 60 days. Most of the radioactivity was then found to be associated with the humic acid and closely related materials, indicating the formation of humic acids from the sugar.

Yet despite these variations, it is a striking fact that the fundamental building blocks of the humic acids appear to arrange themselves always to form a definite characteristic pattern or stable

structure whose properties are determined chiefly by certain active groups common to all of them.; notably, phenolic hydroxyl and carboxyl groups. These, together with the relatively high molecular weight account for the colloidal properties. These investigators further state that humic acids and lignin-like materials are so closely related in coal formation that a sharp boundary cannot be drawn. However, the formation of coal from these two materials must be considered as parallel phenomena; for humic acid formation is not a necessary preliminary to coal formation. Humic acids are formed only under conditions of oxidation and these conditions are not necessarily a stage in coal formation.

The formation of coals from humic acids, and the regeneration of humic acids from coals indicates a process that is reversible. While humic acids under certain conditions are converted into coal, this does not always necessarily occur; for large deposits rich in humic acids are found in the Upper Cretaceous, many millions of years older than lignites and even older coals. Such deposits also may occur in the regions where deposits of "weathered lignite" also are found, as pointed out by Professor Kohanowski in his paper on the "Origin of Leonardite" published in the Proceedings of this Academy for 1957.

In his exhaustive studies of the oxidation of coals, Gillet and his associates followed the chemical changes by means of reaction balances and elemental analyses. A selected coal from Beringen was used. Its composition was sufficiently uniform to be expressed by the empirical formula $C_{20} H_{22} O_2$. The coal, coarsely ground to 2 mm particle size was heated in air or oxygen to about 220 degrees C. For a coal of that formula, the regenerated humic acids, for which Gillet proposed the name, "authraxylic acids", have the formula c_{20} H_8 O_8. He claims that this formula and formula weight of 376 account for all experimental results obtained by himself and earlier authors. Neglecting minor constitutents and expressing the carbon, hydrogen and oxygen as 100%, the percentages for the formula C_{20} H_8 O_8, are as follows:

Calculated:	63.85	2.12	34.03
Found:	64.00	2.14	34.00

Balance: Total yield, calculated from the ratio of formula weights:

$$\text{Humic Acid / Coal} = \frac{C_{20}H_8\ O_8}{C_{20}\ H_{22}\ O_2}$$

Calculated: 93.5% Found: 95%

The humic acids from oxidized coal exist in the form of anhyride or lactone, as might be expected since they are formed at high temperature. In dilute alkaline solution they undergo re-hydration, apparently a little beyond the theoretical restoration of carboxyl groups. Gillet also exposed humic acids to the prolonged action of 1.5% sodium amalgam or to cathodic reduction in alkaline solution

and found that a profound reaction of hydrolysis and hydrogenation occured. The acid-insoluble precipitate then corresponds to the formula $C_{11}H_{10.7}O_{1.5}$.

Further elaborate experiments were made by Gillet in reduction and hydrogenation of the humic acids, employing two different methods. Reduction and hydrolysis with 1.5% sodium amalgam, and by means of electrolysis. He then compares his results with those of F. Zetsche and A. Reinhart who reduced humic acids from different sources with solid sodium amalgam, 3%. Na. They reduced "a natural humic acid", an extract of lignite, and an artificial humic acid" obtained by a mild polymerizing oxidation of pyrocatechol. These authors published results of elemental analyses on their principal products of reduction after exhaustive esterification and etherification, giving the formula for their principle product as

$$R(OCH_3)n\ (OCOCH_3)m$$

From which Gillet calculates the composition of the material before esterification to be R(OH)n(OH)m

Applying his method of elemental analyses, calculated and found, he arrives at the empirical formula of $C_{14}H_{10.8}O_{5.21}$ as compared with his own formula of $C_{14}H_{10.7}O_{4.5}$ Considering the wide differences in source materials and the procedures employed, these formulas are practically identical. Commenting on this comparison, Gillet says: "At the outset of our research we thought, along with many other authors, that three materials of as different origins as these also might have very different compositions. The contrary seemed to us problematical, in any case, insufficiently proved. However the above comparisons forced the conclusion that the compositions of the three materials are identical, or in any case closely related."

In the present work, Gillet neglected the nitrogen and other minor elements in as much as many materials that satisfy the definition of humic acid contain no nitrogen. But for comparison he took from the literature a number of elemental analyses of what he called the "most-classical humic acids, converting them to the basis of C plus H plus O equals 100%.

The close agreement in composition of humic acids from widely different sources is shown in Table 1. The first was extracted from a humic shale from Texas, the second from "weathered lignite" in North Dakota, the next two samples were prepared by Dr. Howard, of Carnegie Tech. from Pennsylvania bitumenous coals by oxidation with nitric acid. The remaining samples reported by M. M. Kononova, include Merke's commercial humic acid, and typical samples from Russian soils. A more reliable comparison is shown in Table 2, where ratios of Carbon to Oxygen for the various samples are shown. The Podsolic soil and the Merke sample are purposely omitted as they may not represent fully synthesized humic acids, or at any

TABLE 1

Elemental Composition of Humic Acids from Different Sources

Analyst.	Fowkes.	Abbott.	Howard.	Howard.
		North Dakota	Penn.	Penn.
Source.	Texas Shale	Leonardite.	Bit. Coal	Bit. Coal
Carbon	63.98	61.95	60.75	62.17
Hydrogen	3.39	2.82	3.12	3.31
Nitrogen	1.77	1.59	2.72	4.05
Oxygen (Difference)	29.94	29.58	28.90	31.90

Analyses reported by M. M. Kononova, Pochvovedenie (Soil Science), Nov. 7, 1943.

Source.	Humic Acid.	Soil.	Soil.	Earth.	Earth.
	Mercke's	Podsolic	Podsolic	Black	Black
Carbon	58.65	56.67	61.56	62.55	61.84
Hydrogen	4.42	4.79	4.00	2.78	4.21
Nitrogen	3.63	5.14	5.58	3.32	3.28
Oxygen (Diff.)	33.30	33.40	30.96	31.35	30.67

TABLE 2

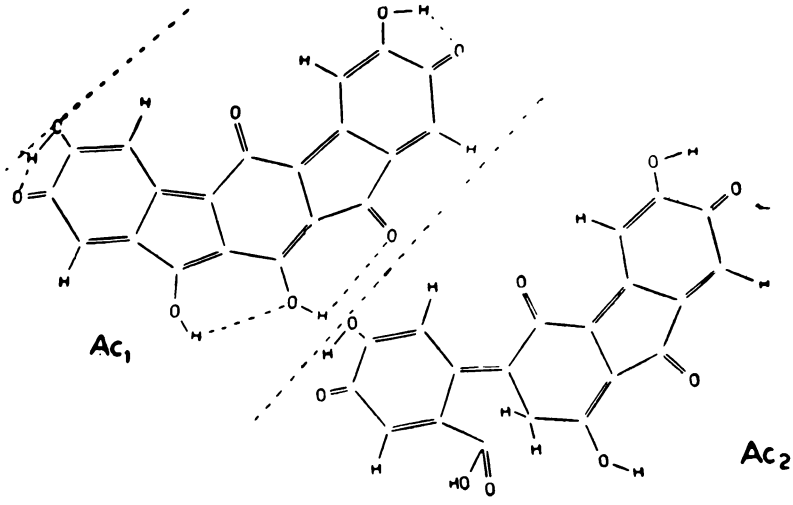
Comparison of Carbon/Oxygen Ratios in Humic Acids from widely different Sources.

Source	C/O Ratio
Leonardite (North Dakota)	2.09
Bitumenous Coal (Penn.)	2.10
Bitumenous Coal (Penn.)	1.95
Humic Shale (Texas)	2.10
Dark Chestnut Soil (Russia)	1.99
Ordinary Black Earth (Russia)	1.99
Ordinary Black (Russia)	2.10
Mean,	2.045

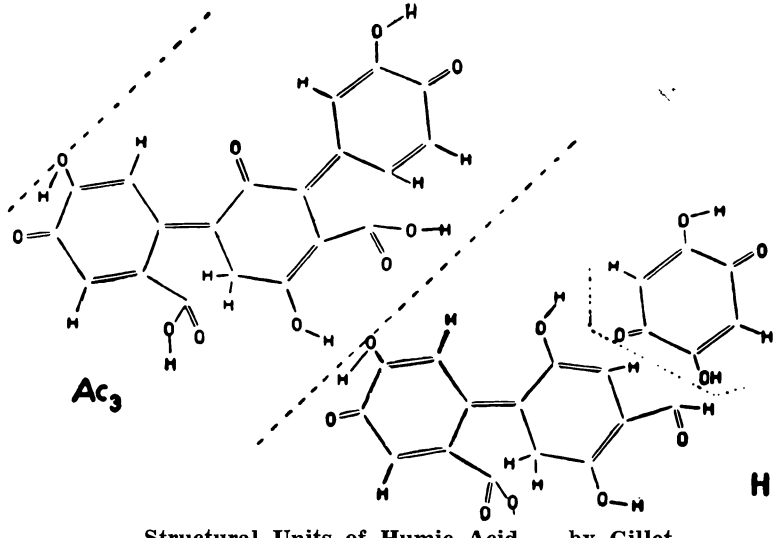
rate may contain alkali-soluble lignin-like substances with considerable methoxy content. Wide variations in the Nitrogen contents are not surprising.

Returning to the consideration of the plausible molecular structure of humic acid, we know that in recent years great advances have been made in determining the structures of high polymers or "giant molecules", particularly in the fields of plastics, synthetic fibers, and elastomers or synthetic rubbers. But it is quite apparent that the humic acid molecule cannot possess a structure similar to any of these; for humic acids are neither filamentous, thermo-plastic, nor elastic. As previously stated, in 1957 Gillet proposed a structural formula intended to account for the known facts and plausible theories concerning the molecular structure of humic acids. (Table) This table represents his tentative formula for the monomer or basic structural unit. This is seen to consist of three benzene rings separated

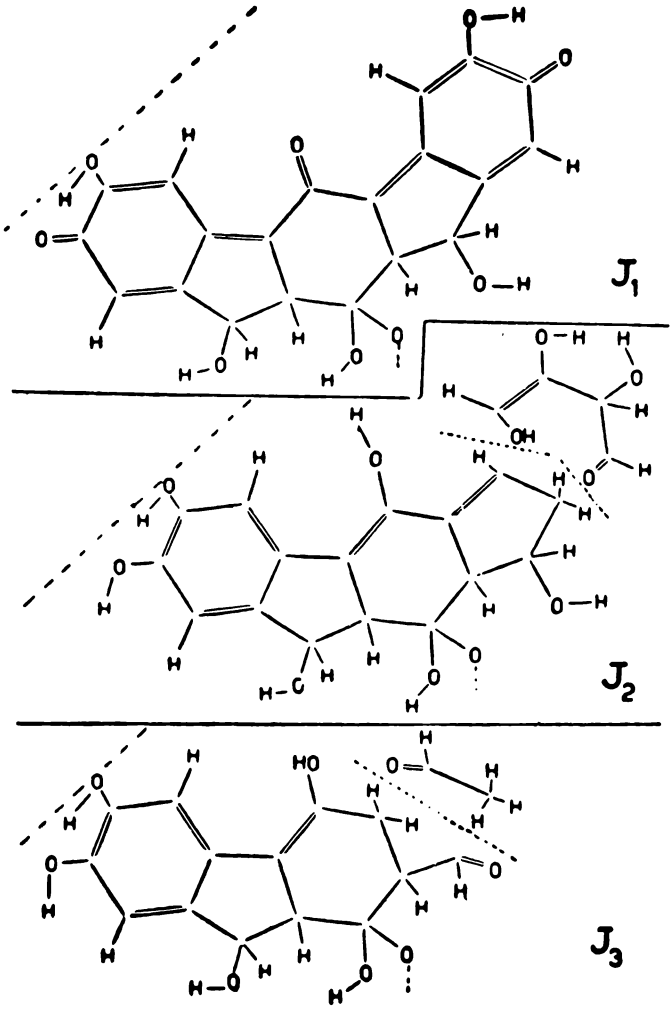
by five-member furan rings, corresponding to the formula, $C_9 H_8 O_4$ with a formula weight of 376. The polymer is visualized as formed from the monomers by oxygen ether linkages and by hydrogen bridges. Side chains are believed to be possible through the opening of five-member rings, and conversely such rings may be formed by closing of carbon side chains.



Structural Units of Humic Acid — by Gillet



Structural Units of Humic Acid — by Gillet



Structural Formula of Humic Acid — by Gillet

While admittedly only tentative and somewhat hypothetical, Gillet's formula does suggest possible explanations for certain observed variations. For example, certain humic acids, particularly those prepared from sulphur-containing coals, retain sulphur in organic combination which is not easily lost. This would be expected if instead of a furan ring containing oxygen, the molecule contained a thiophene ring containing a sulphur atom. Kreulen cites the

example of a sulphur-coal containing more than ten percent of organically-combined sulphur. When oxidized to yield humic acids they contain as much as 8 per cent of sulphur. He found that sulphur partly replaces oxygen and an essential part of the sulphur is in ring structure. 8 per cent seems like a large amount of sulphur; but when reduced to equivalents it does not even correspond to 4 atoms per molecular, or on the average not more than a single atom of sulphur can be present in the unit structure. Similarly, other variations are readily explained as due to hydration or dehydration, or possible substitutions in side chains. It is not surprising that the formula can provide for such structural flexibilities. Rather it is more remarkable that materials derived from so many widely different sources should be found to conform so closely to such a definite structural pattern.

Sooner or later, it was inevitable that humic acids would be subjected to spectroscopic investigation. In 1950 (12) Scheffer and Welte made a systematic study of the absorption spectra in the visible and ultra-violet range. They hoped that the spectra would serve to identify a specific humic acid or type. But in that they were disappointed; for in that region such spectra are not characteristic even for an individual humic acid, for the reason that many excitation states for the electrons are possible, so that with normal resolving powers, no reproducible maxima or minima can be found. For humic acids, therefore, ultra-violet spectra are not characteristic. Fluorescence, observed in many humic acids is another serious disturbing factor. It is usually ascribed to resonance, which is provided for in Gillet's oxygen and hydrogen bridges.

Infra-red spectra give greater promise, and many investigations of the Infra-Red absorption spectra of humic acids have been published, and others are in progress. The field is comparatively new, and there appears to be lack of agreement not only as to the Maxima and Minima observed; but even less agreement in the interpretation of the significance of the spectra observed. One of the most comprehensive and thoro investigations was that of W. Ziechmann (13) appearing in the German Journal Brennstoff-Chemie, in 1958. Time does not permit even a cursory review of this interesting study; but brief mention may be made of the methods used and some of the tentative conclusions. A unique feature was the preparation of hundreds of samples of synthetic humic acids—mostly from polyhydroxy benzenes, by gradual polymerizing oxidation, and systematic examination of the infra-red spectra along the path to final conversion to humic acids. In that way he idetnified many active groups many of which disappeared step by step; but certain linkages appeared to persist in the final products and he was able to make plausible assumptions. He introduced nitrogen from ammonia in some cases and states that: "On account of the mild reaction conditions it is to be expected the nitrogen passes from the original

material to the humic acid in little-altered form; thereby certain structural evidence can be obtained." He further states that nitrogen has the ability to substitute for oxygen in bridge formation, and that itself effects the union of ring systems. This ring-joining certainly can be accomplished by nitrogen as well as by other substituents, and this suggests a valid reason for the apparent disordered variety in humic acids. Another interesting observation was that the positions of even the best defined infra-red bands is often shifted by the close proximity of other active groups, and therefore they are influenced by structural isomerism. This effect due to isomerism was clearly observed by Kaatz and O'Reilly in their study of the "Infra-Red Spectra of Substituted Anilines." This indicates the difficulties involved and the care that must be taken in transfering data observed in simple compounds to the complex structures of these humic acids. Another unique feature of Ziechmann's work was his use of the "overtones" of infra-red bands to confirm uncertain features in the fundamental wave bands. His work seems to establish the presence of ether linkages and hydrogen bridges in the humic acids.

In conclusion, the picture we form of the humic acid molecule is that of a basic curriculum with limited electives—a fundamental pattern that may permit limited variations.

Although our present knowledge of the constitution of the humic acid molecule still is limited, neverthless it is sufficient to explain its most important properties and behavior. Thus the slight solubility of the free acid naturally results from its hydrocarbon derivation and its relatively high molecular weight. It's ion-exchange and salt-forming capacity, obviously are contributed by its carboxyl groups, which make possible the formation of a double-layer in polar media, resulting in colloidal dispersion. The hydrophylic character of the colloid is further strengthened by the polar phenolic hydroxyl groups. Finally the monomeric state of the soluble alkali humates is to be expected in a polar solvent if the monomers in the polymer are held together by hydrogen brigdes. Now that humic acids are being investigated with the powerful modern methods available, we may expect soon to see a clarification of many of the most baffling problems.

BIBLIOGRAPHY

1. Sprengel. Archiv fur die sanante Naturlehre. Vol. 8, 145-220, (1926).
2. Waksman. Humus, Origin, Chemical Composition, and Importance in Nature. Macmillan, (1936).
3. Oden, Die Huminsaure. T. Steinkokoff. Dresden und Leipsic (1922).
4. Abbott. "Humic Acids" from Weathered Lignite. Preceedings of the North Dakota Acad. of Sci. Vol. III, 21-24, (1949).
5. Fischer and Schrader. Brennstoff-Chemie, **2,** 37-45, (1922).

6. Francis and Wheeler. J. Chem. Soc. **129,** 2958, (1957).
7. Gillet. VII. The Humic Acids. Brennstoff-Chemie **38,** (9/10), 151-6, (1957).
8. Gillet, loc. cit.
9. Kreulen. Brennstoff-Chemie, **37,** (-/2), 14-19, (1956).
10. Kreulen. loc cit.
11. Kaatz and O'Reilly. Infra-Red Spectra of Substituted Aniliness. Proceedings of the North Dakota Acad. of Sci. Vol. XII, 33-34, (1958).
12. Kononova. Pochvovedenie, No. 7, (1943).
13. Ziechmann. Brennstoff-Chemie, **39,** 353-9, (1958).
14. Zetsch und Reinhart. Brennstoff-Chemie, **20,** 84, (1939).

TITRIMETRIC pH STUDIES ON THE KETO-ENOL TAUTOMERISM AND THE ENOL ACID-DISSOCIATION OF ACETOACETALDEHYDE (BUTANONE-3-AL-1)

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INTRODUCTION

Previous studies on acetoacetaldehyde have indicated that it exists as a keto-enol tautomer (1); i.e. a compound which has the hydrogen of the methylene group activated by a carbonyl group and can exist in the three forms:

$CH_3\text{-}C(OH)=CH\text{-}CHO \leftrightarrows CH_3\text{-}CO\text{-}CH_2\text{-}CHO \leftrightarrows CH_3\text{-}CO\text{-}CH=CHOH$

in mutual equilibrium.

The interconversion of the above isomers is the phenomenon of tautomerism. An activated hydrogen migrates from carbon to oxygen to give the enol form, and since in this substance the hydrogen also occupies an activated position, it can migrate back again. The tautomeric migration of hydrogen in either direction is called an alpha, gamma shift (2); in each case hydrogen attached to an alpha carbon atom adjacent to a beta, gamma double-bond migrates to the gamma position:

$$\overset{b\ g\ \ a}{-CO\text{-}CH_2\text{-}} \leftrightarrows \overset{b\ \ a\ \ \ g}{-C(OH)=CH\text{-}}$$

(a = alpha; b = beta; g = gamma)

Acetoacetic ester has been studied widely for its tautomeric properties. However, the methods used for this compound would be unsuitable for studies on acetoacetaldehyde.

In the enol form acetoacetaldehyde ionizes:

$$CH_3\text{-}CO\text{-}CH=CHOH \leftrightarrows CH_3\text{-}CO\text{-}CH=CHO^- + H^+$$

This ionization can presumably be assumed instantaneous with the formation of the enol form.

EXPERIMENTAL PART

To study the keto-enol tautomeric equilibrim of acetoacetaldehyde, pH-titrations of its sodium salt were used. Accurately standardized exactly 0.1000N HCl was used. These were run at constant temperature; either at 0° C. or at 25° C. A definite volume of HCl was rapidly added to 100 ml. of the 0.0450N solution of the sodium salt, and the subsequent changing pH was plotted as a function of time. The volumes of HCl added were varied from one determination to the next, from 4 to 20 ml.

The initial pH of the sodium salt solution was 10.4 in each case, and the time taken to add the HCl was always 30 seconds. See Addenda for Table I. pH vs. time curves were constructed for each determination, and the pH_o was obtained by extrapolation back to zero time. pH_t was also determined, where t = 1 hour. See Addenda for Table II.

From the pH_o and pH_t values, the pK_o and pK_t values were calculated by means of the following equations: (3)

$$pK = pH - \log \frac{C(\text{Na acetoacetaldehyde})}{C\ (HCl)}$$

The C (Na acetoacetaldehyde) is equal to the initial concentration of the sodium salt times the dilution factor. The C(HCl) is equal to the volume of HCl added expressed in milli-equivalents, and the pH is equal to the pH of the solution at any time t.

The initial minimum values of pH for each run are used to determine the acid strength, i.e. K_o and pK_o, of the enol form as an acid, and the pH_t values yield the over-all acid strength, K_t and pK_t, of the Keto-enol tautomer system as an acid.

The pK_o and pK_t values were calculated from Table II. See Addenda for Table III.

The K_o and K_t's and the ratio K_t/K_o, which represents the equilibrium in the keto-enol tautomer system, were then calculated. (See Addenda for Table IV.)

DISCUSSION

The calculated pK_o values at 0° C. are rather constant and indicate an initial pK in the range of 6.00. The over-all acid strength in terms of pK_t is also constant at 0° C., having an average value of about 7.60.

At 25° C. this is not the case. The pK values initially and finally are rather erratic and there is a great deviation. An earlier publication (1) stated that acetoacetaldehyde is very unstable at room temperature.

In 1952, R. G. Pearson and co-workers (4) obtained a value for the K_a of acetoacetaldhyde at 25° C. in aqueous solution. This value was .0000012 and compares very well with the one obtained here, .0000016. The method these workers used was not indicated.

When a portion of HCl is added to the Na salt solution the pH first falls sharply as the pseudo-acid enol form of acetoacetaldehyde is liberated. The pH immediately rises, first rapidly, and then very slowly, as the enol form is converted to the non-acid keto-aldehyde tautomer. Due to insufficient data the rate constant of this conversion has not yet been evaluated.

In an earlier publication (1) the keto-enol tautomeric system was reported to have a composition of about ¾ keto and ¼ enol. Our data obtained here indicate that the composition is 99+% for the keto form and < 1% for the enol form. Our present data were obtained for an aqueous solution however, while our earlier data were obtained on the pure compound using refractive index measurements. Work is still being pursued in this area.

SUMMARY

1. The equilibrium of the keto-enol forms of acetoacetaldehyde has been studied by pH titration measurements. The results indicate that in aqueous solution more than 99% of the material is in the keto form.
2. The pH titration data indicate a pseudo-acid K_a value of .0000016 at 0° C.
3. The titrations at 25° C. did not yield a constant value. This is believed due to the instability of the free aldehyde in aqueous solution at this temperature.

BIBIOGRAPHY

1. Dahm, Donald, Johnson, R., and Rathmann, F. H., Proc. North Dakota Academy of Science, Vol. XII, (1958), pp. 19-23.
2. Fieser, L. F., and Fieser, Mary, **Organic Chemistry,** D. C. Heath and Company, Boston (1956), pp. 217-18.
3. Glasston, S., **Elements of Physical Chemistry,** D. Van Nostrand and Co., New York (1946), pp. 505, 522, 528, 542-43.
4. Pearson, R. G., and Dillon, R. L., **J. Am. Chem. Soc., 75,** 2439 (1953); also private correspondence.

ADDENDA

TABLE I

pH vs. Time Data
Sample data for 5 ml., 10 ml., and 15 ml. volumes of HCl added

	5 ml.		10 ml.		10 ml.	
Time (Min.)	0° C.	25° C.	0° C.	25° C.	0° C.	25° C.
0	7.10	7.40	6.60	6.60	6.35	6.50
0.25	7.20	7.65	6.65	7.10	6.40	6.95
0.50	7.40	7.90	6.80	7.30	6.50	7.00
0.75	7.55	7.92	6.90	7.40	6.65	7.10
1.00	7.70	7.97	7.00	7.45	6.80	7.20
1.25	7.80	8.00	7.10	7.50	6.90	7.30

1.50	7.85	8.02	7.20	7.52	6.95	7.35
1.75	7.95	——	7.30	7.55	7.00	7.40
2.00	8.00	8.05	7.35	7.57	7.10	7.42
3.00	8.10	8.10	7.50	7.60	7.20	7.45
4.00	8.12	8.15	7.55	7.65	7.30	7.48
5.00	8.12	8.20	7.60	7.70	7.31	7.50
6.00	8.17	8.25	7.61	7.75	7.32	7.53
7.00	8.19	8.30	7.62	7.80	7.34	7.55
8.00	——	8.32	7.64	7.85	7.35	7.57
9.00	——	8.35	7.65	7.90	7.37	7.60
10.00	8.20	8.38	7.66	7.95	7.38	7.62
11.00	——	8.40	——	7.98	——	7.65
12.00	——	8.42	——	8.00	——	7.68
13.00	——	8.45	——	8.02	——	7.70
14.00	——	8.48	——	8.04	——	——
15.00	8.24	8.49	——	8.05	——	——
16.00	——	8.50	——	——	——	——
17.00	——	8.51	——	——	——	——
18.00	——	8.52	——	——	——	——
19.00	——	8.53	——	——	——	——
20.00	8.30	8.55	——	8.10	——	——

TABLE II

pH_o and pH_t values obtained at 0° C. and 25° C. (t = 1 hour)

HCl added (ml.)	0° C.		25° C.	
	pH_o	pH_t	pH_o	pH_t
0	10.4	10.4	10.4	10.4
4	7.15	9.15	7.75	9.40
5	6.75	8.75	6.85	8.50
8	6.45	8.35	8.10	7.75
10	6.30	8.20	5.75	7.40
15	6.05	7.90	5.25	6.90
16	5.95	7.65	5.20	6.85
20	5.85	7.55	5.10	6.75

TABLE III

pK_o and pK_t values calculated from Table II

HCl added (ml.)	0° C.		25° C.	
	pK_o	pK_t	pK_o	pK_t
4	6.16	8.16	6.76	8.41
5	5.87	7.87	5.97	7.62
8	5.81	7.71	5.46	7.11
10	5.78	7.68	5.23	6.88
15	5.78	7.63	4.98	6.63
16	5.72	7.42	4.97	6.62
20	5.79	7.49	5.04	6.69

TABLE IV

Values K_t/K_o and K_t calculated (t = 1 hour)

	0° C.			25° C.		
HCl added (ml.)	$K_o \times 10^6$	$K_t \times 10^6$	K_t/K_o	$K_o \times 10^6$	$K_t \times 10^6$	K_t/K_o
4	0.6	0.6	100	0.2	0.4	200
5	1.4	1.4	100	1.1	2.4	218
8	1.6	2.0	126	3.5	7.8	224
10	1.7	2.1	126	5.9	13.2	224
15	1.7	2.4	141	10.0	23.4	234
16	1.9	3.8	200	11.0	24.0	218
20	1.6	3.2	200	9.1	20.4	224

POSITION OF *OREOPITHECUS BAMBOLII* IN MODERN MAN'S EVOLUTIONARY RECORD

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Man's intense curiosity about himself has led him to search into the past in an attempt to uncover his ancesters. The resulting science of human paleontology has led to the discovery of various remnants of human forms existing in bygone ages. These human remnants constitute what is known as the "fossil record." Man's fossil record can be divided into two evolutionary groups: Hominids and Hominoids. A Hominoid is any member of the taxonomic group including pongids (anthropoid apes) and Hominids (man and his immediate forerunners).

We are concerned today with the Hominoid group and with one facet of the entire group, consisting of three definite types: **Proconsul africanus, Oreopithecus bambolii,** and **Australopithecus africanus.** These three types precede the earliest known human, **Pithecanthropus erectus.**

We are concerned, principally, with the **Oreopithecus** type. Recent discoveries of **Oreopithecus** remains indicate man may well be 10 million years older than scientists suppose. In other words, distinct human traits appeared in man's evolutionary record 10 million years earlier than had been previously suspected. **Oreopithecus** may be the vital transition stage between early ape-men and earliest man. He may constitute a major factor in man's evolutionary record.

To see why this is true, we should first consider and compare the types belonging to the Hominoid group. (Chart of "Comparisons" here.)

There are five traits distinguishing man from other animals: his chin, posture, teeth, brain size, and limbs. Man is the only animal to possess a chin, a trait distinctly human. Man walks erect; the structure of his bones is adapted to such erect posture. Man's teeth

have several distinct features, lacking the simian gap found in all ape forms. The upper and lower canines do not interlock to form gaps in the upper tooth arch for reception of the lower canines, or in the lower tooth arch for reception of the upper canines. Man's average cranial capacity is 1500 cc. Finally, man's limbs are adapted to erect posture, his arms being shorter than his legs.

Let's begin with the most primitive and ancient of the types—**Proconsul africanus.** This animal lived some 25 million years ago, and is considered to be the common ancestor of apes and man. Fossils include bones of some young animals and one fully adult male. (Chart shown.) Not his position on the chart, and that his chin is lacking. He possessed: apelike teeth, cranial capacity equaling large anthropoid apes, apelike limps, and arms longer than legs.

Next we come to **Australopithecus** who existed 750,000 years ago. He was the first near-human type and displayed various human traits: rudimentary chin, semi-erect posture, teeth similar in arrangement and pattern to modern man, relatively large brain in comparison to body weight, and limbs more humanly proportioned.

Succeeding **Australopithecus** is the earliest known human, **Pithecanthropus erectus,** displaying: well-developed chin, erect posture, teeth of a human type, cranial capacity approaching modern man—900 cc., and limbs proportionate to modern man.

Note the gradual trend throughout from a less complex, apelike stage to a more human form.

Oreopithecus fills the evolutionary gap between **Proconsul** and **Australopithecus,** illustrating human characteristics were in evidence long before scientists had suspected. **Oreopithecus** shows: traces of a chin, may have walked erect, teeth of a somewhat human type, and limbs more proportionate to man.

What about these recent **Oreopithecus** discoveries? Fossil remains of **Oreopithecus** have existed since 1872 but no complete skeletons have been available. Lacking were pelvic girdles, arm and leg bones essential to determining the evolutionary nature of **Oreopithecus.** No definite conclusions could be made regarding this type. The bones were classified as belonging to an extinct monkey that scientists named **Oreopithecus.**

Relegated to this position, **Oreopithecus** almost became a forgotten entity. Then, in 1949, the Swiss paleontologist, Johannes Hurzeler, after carefully analyzing the **Oreopithecus** remains, became convinced **Oreopithecus** was not a monkey but a higher type. In 1954, Hurzeler declared his theory concerning **Oreopithecus:** that **Oreopithecus** was not only a Hominoid but that he was a primitive Hominid, therefore a representative of the evolutionary line leading directly to modern man. After presenting his theory in New York City (1956) Hurzeler received support from the Wenner-Gren Foundation for Anthropological Research to aid his search for an

"entire" **Oreopithecus** skeleton. In an ancient coal mine in Bacinello, Italy he found a complete **Oreopithecus** skeleton. This discovery has served to tentatively confirm his theory that **Oreopithecus** is more man than ape. Among Hurzeler's findings were such fossil specimens as: a nearly complete skull, portions of a lumbar and sacral sections of the spine, major articulated portion of a hand, two mandibles, one with eight teeth attached, one toothless, but showing rounded mandibular symphisis and high position of the mental foramen, upper jaw with six teeth and palate, fragmentary upper jaw with a molar attached, foot bones, and finger bones.

After 20 years of studying all the available **Oreopithecus** remains, Hurzeler is convinced **Oreopithecus** is more man than ape and belongs in the evolutionary record of man.

In studying these specimens other anthropologists confirm his conclusions: that the dentition is Hominid in pattern, the skull Hominid in nature, and the bodily extremities suggestive of what might be expected in an early Hominid; that the form and development of the spine indicate an upright posture. Therefore anthropologists believed, in general: **Oreopithecus** was more manlike than apelike.

More intensive research is now needed to prove conclusively that **Oreopithecus** is the essential transition element searched for by human paleontologists to link the Hominoids and the Hominids. **Oreopithecus** may prove to be a vital factor in man's incessant search for his ancestors and may extend man's existence on earth 10 million years farther into the past.

BIBLIOGRAPHY

"Chunk of Coal Yields a Major Missing Link; **Oreopithecus** Bones in Italian Mine," **Life,** 45:62-4, (August 18, 1958).

"Clue to Earliest Man? **Oreopithecus," Newsweek,** 48:68, (July 23, 1956).

"Coal Man; **Oreopithecus," Time,** 72:58, (August 18, 1958).

Dodson, Edward O. **A Textbook of Evolution.** Philadelphia, W. B. Saunders, 1952.

Eisely, L. C. **"Oreopithecus:** Homunculus or Monkey?" **Scientific American,** 194:91-2, (June, 1956).

"Fossil Skeleton May Tell Man's Place in Evolution; **Oreopithecus," Science News Letter,** 74:104, (August 16, 1958).

Hooton, Earnest Albert. **Up From the Ape.** New York, the Macmillan Company, 1946.

Jacobs, Melville and Stern B. **General Anthropology.** New York, Barnes and Noble, 1952.

Montagu, A. "Man: His First Million Years," **Saturday Review,** 40:29, (November 2, 1957).

Moody, Paul A. **Introduction to Evolution.** New York, Harper and Brothers, 1953.

Shull, Franklin A. **Evolution.** New York, McGraw-Hill, 1951.
Straus, W. L. Jr. **"Oreopithecus bambolii," Science,** 126:345, (August 23, 1957).
"10-Million-Year-Old Jaw, **Oreopithecus," Scientific American,** 194:61, (April, 1956).
Terra, H. de. "New Approach to the Problem of Man's Origin; **Oreopithecus," Science,** 124:1282-5, (December 28, 1956).

A SPECTROPHOTOMETRIC STUDY OF THE DISSOCIATION OF DINITROGEN TETROXIDE

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INTRODUCTION

The dissociation of dinitrogen tetroxide, $N_2O_4 = 2NO_2 = 2NO+O_2$, has been studied by vapor density methods (1, 7, 11) and more recently by optical methods in conjunction with the kinetics of the reactions of NO_2(6,8,10) and by magnetic susceptibility methods (12). The work done in the more recent investgations over short temperature ranges below 40°C and above 200°C confirms the vapor density investigations. This indicates that the first reaction, $N_2O_4 = 2NO_2$, proceeds to completion at 150°C. Then the reaction, $2NO_2 = 2NO + O_2$, proceeds above 150°C going essentially to completion around 650°C. The region from 85°C to 200°C has not been investigated for the purpose of characterizing the equilibrium mixture throughout the entire temperature range of the two equilibria.

With this idea in mind, Coon and Mac Rhoades (2), proposed to follow the equilibrium by a photometric method using the visible light of a 6 volt tungsten lamp with a photocell as a quantitative detector of the light absorbed by NO_2. The other equilibrium species being uncolored were assumed to be transparent to visible light. Instead of finding a maximum absorption at 150°C, the point of maximum concentration of NO_2 according to vapor density investigations, Rhoades and Coon had not found a maximum absorption at 180°C, the upper temperature limit of their experiments.

Coon and Strieb (5) continued the investigation using a Beckman DU spectrophotometer modified with an oven to extend the temperature range of the work. Using monochromatic light of wavelength 6630 A, they found the maximum absorption to occur around 320°C. They also investigated the effect of excess NO or O_2 on the equilibrium, finding that it was affected only slightly by either gas. An attempt to find a suitable working wavelength in the ultraviolet region to follow the appearance of NO was unsuccessful due to the extremely high, non-specific absorption of N_2O_4 throughout the ultraviolet spectrum.

Coon and Siefker (3) continued the investigation in the visible region and extended it into the ultraviolet region to characterize the disappearance of N_2O_4. They found that the temperature of maximum absorption of light by NO_2 varied with the wavelength of light being used, the maximum absorption occurring between 240° and 320°C. At 2500A, N_2O_4 appeared to be completely dissociated above 150°C. Their work cast doubt on the validity of the vapor density assumptions.

The present investigation includes determinations in both the ultraviolet and visible regions. Curve 1, Figure 1, shows a typical run at 4000A, a wavelength favored by the reaction-kinetics investigators (8-10). The absorption of light increases to a maximum around 160°C, indicating the appearance of NO_2, then drops off slowly with the disappearnce of NO_2 at higher temperatures. Curve 2, Figure 1, shows a typical run at 2500A, which indicates the almost linear disappearance of N_2O_4 up to 90° and then the non-linear disappearance of N_2O_4 between 90° and about 200°C.

Curve 3, figure 1, is a determination made at 2261A, a wavelength

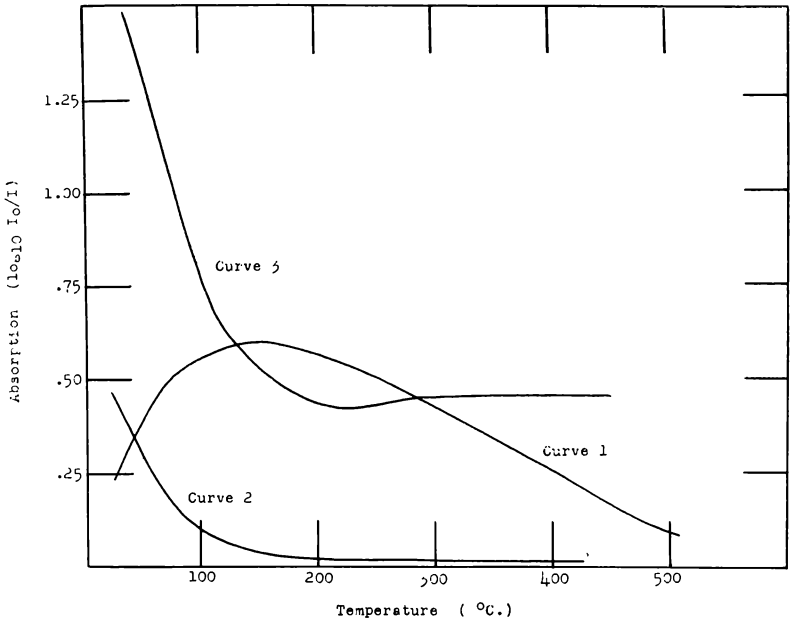

FIGURE 1

of a very strong but narrow absorption band for NO gas and the non-specific absorption of N_2O_4. The absorption drops off rapidly up to 200°C but does not increase as the concentration of NO increases with increasing temperature. Therefore it does not allow

determination of the concentration of NO gas. This wavelength however allowed the determination of the temperature at which NO gas first appears in the equilibrium mixture. A more detailed account of the findings and results of this study will be published at a later date.

MATERIALS AND METHODS

The instrument used in this investigation was a Beckman "Model DU" Quartz Spectrophotometer. The usual cell compartment was removed and replaced with a specially built oven to allow temperatures up to 600°C. The construction of the oven and thermocouple used to measure temperature is described in detail by Siefker and Coon (4) (in a paper which was delivered before the North Dakota Academy of Science in 1957). A Beckman Spectral Energy Recording Adapter was used to obtain complete spectra of the equilibrium at various temperatures and wavelengths. The SERA, as it is commonly called, allows the Beckman DU Spectrophotometer to be used as a single-beam automatic recording spectrophotometer as well as a manually operated, double-beam ratio-indicating instrument. The absorption cells used were made of fused quartz. The sample cell was filled by allowing N_2O_4-NO_2 gas in equilibrium with liquid

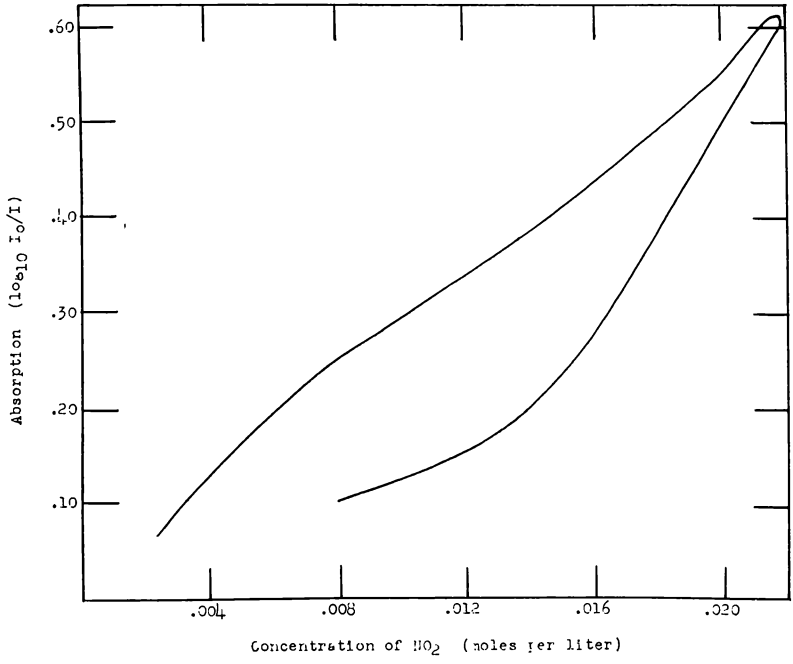

FIGURE 2

N_2O_4-NO_2 at O°C to distill into the evacuated cell which was thermostatted at 25°C.

Data were obtained by measuring the change of absorption with temperature at several fixed wavelengths which correspond to peaks (maxima) in the absorption spectrum. The temperature was varied 20° to 40°C and 10 minutes or more elapsed after each increment of temperature to allow equilibrium to be established. At each temperature the absorption was measured 3 to 5 times at 2 minute intervals to obtain reliable average temperatures and absorption readings. In addition, the spectrum was scanned on both sides of the selected wavelengths to determine any changes in the absorption spectrum, such as the first appearance of a characteristic absorption peak or the gross shifting of the peak from the wavelength which was initially determined at room temperature.

DISCUSSION

By scanning the spectrum in the region of the absorption peak of NO gas at 2261A it was determined NO gas first appeared in the equilibrium mixture at a temperature of about 70°C, well below the temperature predicted for its appearance by vapor density measurements. Thus doubt is cast on the validity of vapor density measurements of the proper concentration of NO_2. The equations developed from vapor density measurements indicate that the maximum concentration of NO_2 appears at 150°C. Below 150°C, NO gas is not believed to appear and above 150°C, the equations do not consider N_2O_4 to be present.

When a Beer's Law graph of absorption vs concentration is plotted, a graph such as figure 2 is obtained. This graph is obtained by plotting observed absorptions values vs the concentration of NO_2 as predicted by vapor density measurements. The curve is a straight line between 30° and 90°C. The slope then undergoes an increase between 90° and 200°C and again becomes a straight line between 200° and 400°C. In a Beer's Law graph a straight line through the origin indicates that absorption is directly proportional to the concentration, and the slope of the line is the absorption coefficient. If NO_2 follows Beer's Law, that is, if the absorption is directly proportional to concentration, the change in the slope should not take place and the two "legs" of the graph should superimpose.

If the concentration is correct as predicted by vapor density measurements, it is readily seen from the graph that NO_2 does not follow Beer's Law. Dixon (6), using a spectrophotometer with a 40A spectral slit width, found NO_2 does obey Beer's Law between 4000A and 7000A up to 85°C. Rosser and Wise (9) using a filter photometer with a broad band of light centered around 4400A found the absorption coefficient of NO_2 constant between 257° and 747°C. Steese and Whittaker (10) in their spectrophotometric study of the liquid-phase equilibrium, $N_2O_4 = NO_2$ in pure N_2O_4 assumed the absorption coefficient of NO_2 to be the same in the liquid and the gas phases up to

20°C. Magnetic susceptibility measurements by Whittaker (12) indicated that no error was introduced by this assumption.

CONCLUSIONS

This study qualitatively confirms the vapor density prediction that the maximum concentration of NO_2 appears at about 150° C but that the maximum concentration is not necessarily twice the original concentration of N_2O_4. The lack of correlation between the two methods of following the equilibrium may be due to any one or all of several effects:

1. The equilibrium is undoubtedly more complex than the simple dissociation assumed by the vapor density workers. The early appearance of NO found in this study is the first definite experimental evidence to this effect.

2. The absorption coefficient of NO_2 probably is not independent of temperature. The Beer's Law graph obtained in this study seems to bear this out. Due to the equilibrium situation, the temperature dependence of the absorption coefficient of NO_2 cannot be established by direct means.

3. NO_2 is probably not the only absorbing species in the visible region. It seems to be the only absorbing species at 4000 A since the maximum absorption occurs near 150°C. However the maximum absorption at 320° C obtained at 5000 A by Coon and Siefker indicates the presence of another colored combination of nitrogen and oxygen.

4. The spectrum of the equilibrium mixture is characterized by a profusion of narrow, closely spaced bands. The resolving power of the Beckman DU spectrophotometer allows the use of only the broadest of these bands. Even these broad bands are averaged out considerably as evidenced by the inability to quantitatively determine the concentration of NO at its absorption band at 2261 A. An instrument with greater resolution is needed to better follow the equilibrium.

SUMMARY

1. Experimental details of a spectrophotometric method for following the dissociation of N_2O_4 to temperatures up to 600°C is presented.

2. The assumption that the equilibria are clear-cut and separate, the first proceeding to completion at 150°C before the second is initiated, is shown to be in error.

3. The lack of correlation between the spectrophotometric data and the data obtained by vapor density calculations of the concentration of gases in the equilibrium explained.

ACKNOWLEDGEMENT

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LITERATURE CITED

1. M. Bodenstein and F. Boes, Messungen des Gleichgewichts N_2O_4 = $2NO_2$, Z. Physik. Chem., **100,** 75 (1922).
2. E. Coon and M. Rhoades, unpublished Master's Thesis, University of North Dakota, 1951.
3. E. Coon and J. Siefker, unpublished Master's Thesis, University of North Dakota, 1957.
4. E. Coon and J. Siefker, A Spectrophotometric Study of the Dissociation of Dinitrogen Tetroxide, Proc. N. Dak. Acad. Sci., **XI,** 10 (1957).
5. E. Coon and W. Strieb, Unpublished Master's Thesis, University of North Dakota, 1955.
6. J. Dixon, The Absorption Coefficient of Nitrogen Dioxide in the Visible Spectrum, J. Chem. Phys., **8,** 157 (1940).
7. W. Giaque and J. Kemp, Thermodynamic Properties of N_2O_4 and NO_2, J. Chem. Phys., **6,** 40 (1938).
8. T. Hall and F. Blacet, Separation of the Absorption Spectra of NO_2 and N_2O_4 in the Range of 2400-5000A, J. Chem .Phys., **20,** 1745 (1952).
9. W. Rosser and H. Wise, Kinetics of Reaction Between Hydrogen and Nitrogen Dioxide, J. Chem. Phys., **26,** 571 (1957).
10. C. Steese and A. Whittaker, Spectrophotometric Study of the Liquid-Phase Equilibrium N_2O_4 = $2NO_2$ in Pure Nitrogen Tetroxide, J. Chem. Phys., **24,** 776 (1956).
11. F. Verhoek and F. Daniels, The Dissociation Constants of Nitrogen Tetroxide and of Nitrogen Trioxide, J. Am. Chem. Soc., **53,** 1250 (1931).
12. A. Whittaker, Magnetic Susceptibility Study of the Liquid-Phase Equilibrium N_2O_4 = $2NO_2$ in Pure Nitrogen Tetroxide, J. Chem. Phys., **24,** 780 (1956).

PREPARATION OF PYRAZOLE DERIVATIVES OF ACTOACETALDEHYDE. The 1-α-NAPHTHYL AND THE 1-(2',5'-DICHLOROPHEYL)-3-METHYL PYRAZOLES

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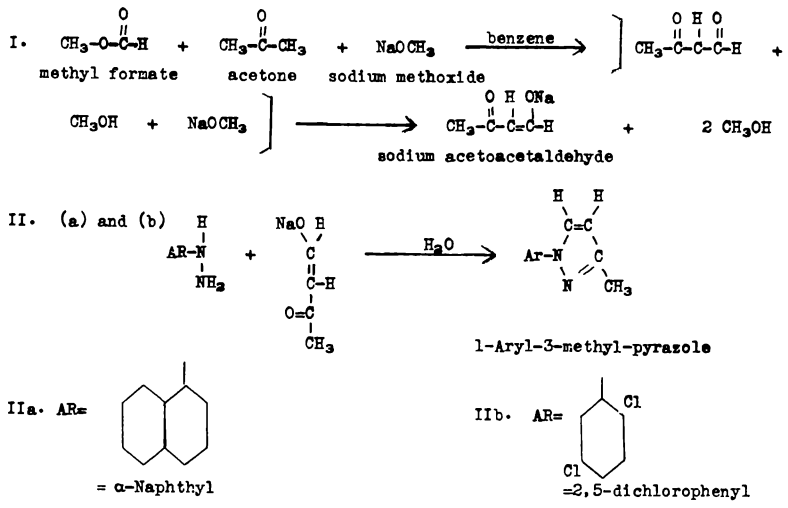
INTRODUCTION

In connection with the characterization of acetoacetaldehyde[1,2] it was desirable to prepare some more crystalline pyrazole derivatives of acetoacetaldehyde from its sodium salt.[3]

Equations for the Reactions



EXPERIMENTAL

I. The **sodium salt of acetoacetaldehyde** was prepared by a new method a modification and extension of a method reported by Maury and Ringwald.[1]

The new method has several advantages over the old method of preparation previously used and reported[2,3], in that it does away with the use of absolute ether as the reaction medium (benzene is now used), and the need for a vacuum distillation, and that it cuts the reaction time by two-thirds.

To 1.5 liters of absolute methanol 170.3 grams of metallic sodium was added, in small portions, to form the sodium methoxide. To get rid of the excess methanol the principle of azeotropic solutions was used, rather than a vacuum distillation. From linear graphic plots[4] of logarithm of pressur vs, $\frac{1}{T\,°C + 230}$ and logarithm of mole percent methanol vs. boiling point for the benzene-methanol azeotrope, the amount of benzene needed to take care of the residual methanol was calculated. To take care of the 1.25 liters of methanol left over the calculated amount of benzene was 1.4 liters. The benzene was added in 500 ml. portions and distilled on a steam bath until the boiling point of the distillate reached and leveled off at 79.° C. The actual amount of benzene used was 2 liters to insure that all the methanol was removed. Dry benzene was added, up to a total of 4.8 liters, to the methanol-free sodium methoxide. To the mixture (containing 400 g. of sodium methoxide) a solution containing 540 ml. (7.4 moles) of acetone and 460 ml. (7.4 moles) of methyl formate was added dropwise, with strong stirring, keeping the temperature

of the mixture below 60° C. The mixture was stirred for 4 hours. The resulting mushy white precipitate was collected in a suction filter, and dried **in vacuo** overnight. Slight heating facilitates drying.

Yield of sodium acetoacetaldehyde = 723 gr. = 90% of theoretical.

ANALYSIS

Percentage of sodium in sodium acetoacetaldehyde as found by conversion to sodium sulphate (Na_2SO_4) with conc. H_2SO_4, and fusion at red heat:

Percentage Na Calculated for $C_4H_5O_2Na$ = 21.3%
Found = 20.6%

IIa. **1-Naphthyl-3-Methyl-Pyrazole** ($C_{11}H_{12}N_2$) was prepared by stirring together 1.95 g. (0.010 moles) of 1-α-naphthyl-hydrazine hydrochloride and 1.08 g. (0.010 moles) of sodium acetoacetaldehyde in 400 ml. of water for 5 hours. The red-brown oil that separated out was extracted with ether.

The ethereal extract was dried with anhydrous sodium sulphate, the ether distilled off and the residual oil distilled **in vacuo** using a water aspirator. An extremely viscous red-brown oil was obtained, b_{14}mm, 120-135° C. This oil crystallized after several hours, m.p. 80-87° C.

The crystals are very soluble in ether, benzene and methanol; fairly soluble in petroleum ether and heptane; and slightly soluble in large amounts of hot water.

IIb. **1-(2, 5-Dichlorophenyl)-3-Methyl-Pyrazole** ($C_{10}H_8Cl_2N_2$) was prepared by dissolving 1.77 g. (0.010 mole) of 2, 5-dichlorophenyl-hydrazine in 100 ml. of benzene and adding this solution to a 100 ml. water solution containing 1.08 g. (0.010 moles) of sodium acetoacetaldehyde, 6 ml. of 2N acetic acid (0.012 moles) and 4 g. of (0.05 moles) sodium acetate. This mixture was stirred until the benzene had evaporated (about 6 hours) leaving a brown, water-insoluble oil. This oil was extracted with ether, the ethereal extract dried with anhydrous sodium sulphate, and the ether distilled off.

The residual oil was distilled **in vacuo** using a water aspirator. Two fractions were collected. (1) An orange oil that crystallized after several hours, $b_7$mm, 135-145° C.; (2) a dark brown oil, $b_9$mm, 110-125° C., that also crystallized after several hours.

The orange crystals are very soluble in benzene, methanol, ether and acetone; fairly soluble in petroleum ether, and sparingly soluble in hot water.

The crystals are fairly soluble in very dilute HCl solution (0.01 N) and recrystallization occurs upon exact neutralization with ammonium hydroxide. They are also soluble in dilute NH_4OH solution (0.005N), and reprecipitate on neutralization.

1. 1-(α-Naphthyl)-3-methyl-pyrazole

The crude product was dissolved in benzene, partially decolorized by Norit and the benzene allowed to evaporate. Some very slightly

decolorized crystals formed on the side of the beaker. These crystals gave a melting point range of 83-88° C. This was the best obtained in our work. With more time and work, a better melting point could be obtained.

2. 1-(2, 5-dichlorophenyl)-3-methyl pyrazole

The best melting point range obtained was 80-87° C. Attempts at recrystallization were generally unsuccessful. In most cases an extremely viscous oil was obtained rather than crystals.

BIBLIOGRAPHY

1. L. Claisen and N. Stylos, Ber., 31, 114 (1888).
2. D. Dahm and F. H. Rathmann, Proc. North Dakota Academy of Science, Vol. XII (1958).
3. S. Ebel, M. D. Enger, R. Johnson, F. H. Rathmann, J. Swenson, Proc. North Dakota Academy of Science, Vol. XII (1958).
4. Thomas C. Jacobs, Pyrazoles and Related Compounds in **Heterocyclic Compounds,** R. C. Elderfield, Vol. 5, 45-161. Copyright 1957, John Wiley and Sons, Inc., New York.
5. D. T. Maury, E. L. Ringwald; Trivinylbenzene from Triacetylbenzene, **J. Amer. Chem. Soc.,** Vol. 72, pp. 2037-2038 (1950).
6. H. Skolnik, Effect of Pressure in Azeotropy, **Indus. Eng. Chem.,** Vol. 43, pp. 172-176 (1951).

ELECTROCHEMISTRY OF SOME HETEROGENEOUS CELLS

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INTRODUCTION

Many studies of the behavior of concentration cells consisting of a two-phase liquid system have been reported. Few of these were concerned with the transport of metal ion[2]. No studies of these cells have been found in which an organometal chelate is in any one phase. Beutner[1], in 1913, reported an empirical study of many cells having several liquid phases. Beutner attempted to explain the potentials of his cells on the grounds that they were concentration cells without a liquid junction. This was thought to be true since the inorganic salt compartments were considered to be metal electrodes. Beutner's work was successful when he measured the potential of the two cells separately, and then joined the two cells together and measured this potential. Beutner's assumption, however, was that the potential measured was a function only of the concentration difference of a common ion. Beutner, himself, could not explain the potentials he obtained later when no common ion was present. Thus a theoretical explanation is still not available for the potential

of most of his cells.

This paper reports an attempt to measure cell potentials in a two-phase concentration cell for which a theoretical interpretation of the data is possible.

THEORY

Cells of the following type were used in this study.

Hg, Hg_2Cl_2, 0.1N KCl	‖	0.1N KCl $Ni(NO_3)_2$ C_1 in H_2O	|	Ni $(C_4H_7N_2O_2)_2$ saturated solution in 1,2-$C_2H_4Cl_2$	0.1N KCl, $Ni(NO_3)_2$ C_2 in H_2O	‖	O.1N KCl, Hg_2Cl_2, Hg
		A			B		

The potential difference expected with this type of cell would be mainly a function of the concentrations of the metal salts in the inorganic compartments. The potential expected is expressed by the Nernst equation:

$$E = (RT/nF) \ln C_1/C_2 \quad (1)$$

$$E = 0.0000994\ T \log C_1/C_2 \quad (2)$$

where E = potential difference,
R = gas constant,
T = temperature, degrees Kelvin,
n = number of faradays per mole of reaction,
C_1 and C_2 = concentrations of metal ion in the inorganic compartments,
and F = Faraday's constant.

Equation (2) predicts that a plot of the potential versus log C_1/C_2 should give a straight line with a slope of 0.0295 at 25°C. The assumption inherent in this equation is that only the nickel ion is transported across the ethylene chloride phase. The liquid junction potential at junctions A and B should be very small compared to the cell E.M.F. if the measured cell potential is to be set equal to E in the Nernst equation. This is a reasonable approximation if the experiments are designed with this object in view, namely, the addition of equal amounts of KCl to each side of the liquid junction in concentrations larger than the metal ion concentration.

EXPERIMENTAL

Nickel dimethylglyoxime and copper acetylacetonate were prepared by standard procedures.[4,5] The respective metal chelate was dissolved in ethylene chloride and placed in the center compartment of the cell (Fig. 1) by means of a funnel. The side compartments of the cell were filled with different concentrations of the respective salt solutions using a pair of pipets. Intermixing of the two inorganic solutions was prevented by using the two pipets. After it had been ascertained that a potential could be measured by means of a Beckman Model GS pH electrometer, potential measurements were made keeping the concentration of the solution in one of the inorganic compartments constant (0.1M) throughout a set of experiments while

the other was varied from 0.01M to 0.0000001M. The salt solutions used with the respective chelates were $CuSO_4$, $Cu(NO_3)_2$ and $Ni(NO_3)_2$. The copper solutions were filtered to remove visible impurities in the solutions. (These were prepared from A.C.S. Reagent Materials.)

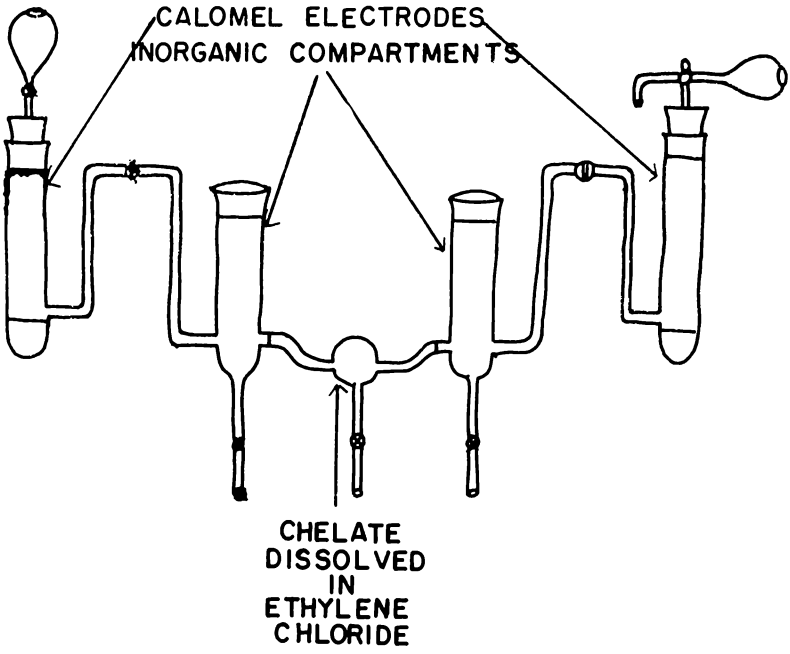

FIG. 1 Schematic Drawing of the Cell.

The cell was kept at a constant temperature in an oil bath. Measurements were made at 25°C and 40°C. A set of measurements was also made with cells containing a mixture of $Cu(NO_3)_2$ and $Ni(NO_3)_2$ at various concentrations in the side compartments and nickel dimethylglyoxime dissolved in ethylene chloride in the center compartment. Readings were taken after ten, thirty, and sixty minutes.

The cell was coated with "Desicote" (A. O. Beckman Co.) to help prevent electrical leaks. The system was grounded to a water pipe, surrounded with screen which was grounded, and set upon a copper plate which was grounded to the same water pipe as above.

RESULTS

Plots of the potential versus the logarithm of C_1/C_2 were made for copper nitrate — copper acetylacetonate and nickel nitrate— nickel dimethylglyoxime for the experiments made at 25°C. These graphs are shown in Fig. 2 and the corresponding data are in Tables

I and II. All of the impurities might not have been removed from the copper solution by filtration.

The slopes of the lines calculated from the plots are both 0.009 volts. This is smaller than would be expected from Equation (2). Evidently the transference numbers of nickel ion and copper ion in the ethylene chloride phase are less than 1. The cation transference number calculated from Equation (3) is 0.30.

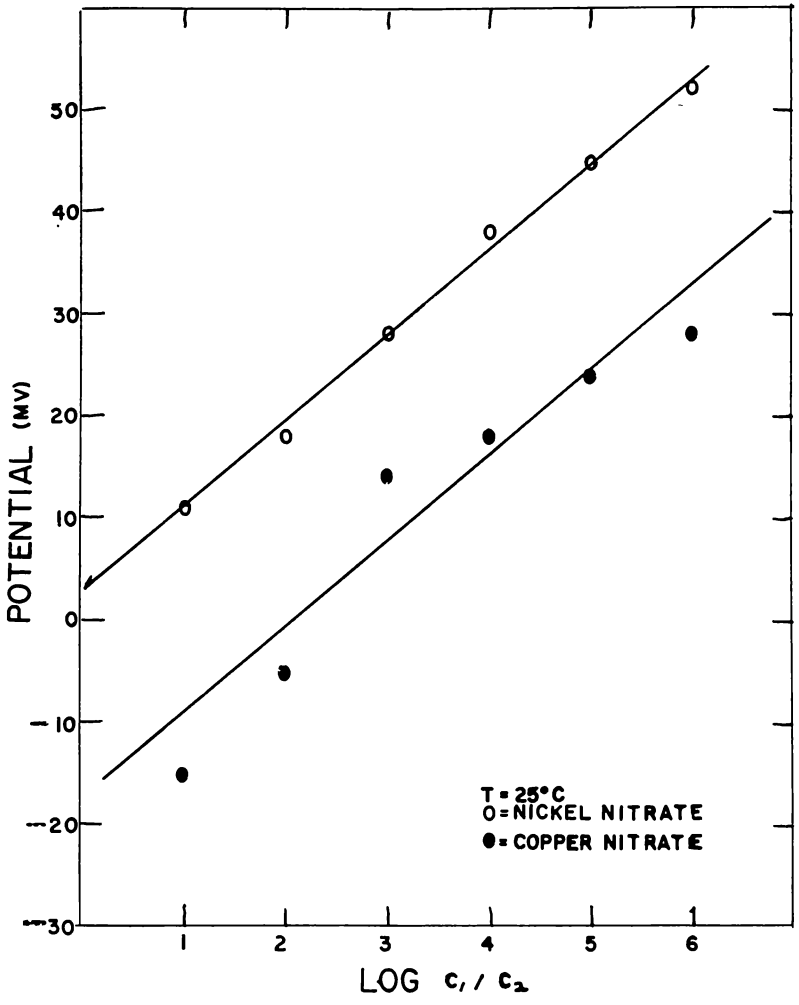

FIG. 2 Graph of the potential versus the log of the ratio of the metal ion concentrations. 25°C.

TABLE I

Potentials Measured Using Copper Ion at Concentrations C_1 and C_2 and Copper Acetylacetonate at 25°C

C_1 (M)	C_2 (M)	log C_1/C_2	Average Potential (mv.)
0.100	0.0100	1.0	+15
0.100	0.00100	2.0	+ 5
0.100	0.000100	3.0	—14
0.100	0.0000100	4.0	—19
0.100	0.00000100	5.0	—24
0.100	0.000000100	6.0	—28

TABLE II

Potentials Measured Using Nickel Ion at Concentrations C_1 and C_2 and Nickel Dimethylglyoxime at 25°C

C_1 (M)	C_2 (M)	log C_1/C_2	Average Potential (mv.)
0.100	0.0100	1.0	—11
0.100	0.00100	2.0	—18
0.100	0.000100	3.0	—28
0.100	0.0000100	4.0	—38
0.100	0.00000100	5.0	—45
0.100	0.00000010	6.0	—52

$$E = (t_+ RT/nF) \ln C_1/C_2 \qquad (3)$$

The potentials of the cell measured at 40°C were erratic, and are given in Table III. The plot, Fig. 3, resembles a parabola. The erratic behavior could be due to the fact that the oil at this higher temperature tended to remove the stopcock grease from the stopcocks and the ball and socket joints connecting the calomel electrodes to the side compartments of the cell. This was overcome to a great extent by coating these connections with a stopcock grease made from equal parts of glycerol and bentonite clay.[3]

The results of the cell measurements made when mixtures were placed in the side compartments were even more erratic than those at high temperatures. Duplicate runs would not give reproducible E.M.F. readings. Further work should be done on this part of the experiment.

Duplicate measurements were made for each set of concentrations, and the potentials were reproducible to ± 2.00 mv. on different stock solutions and 0.5 mv. using the same solutions.

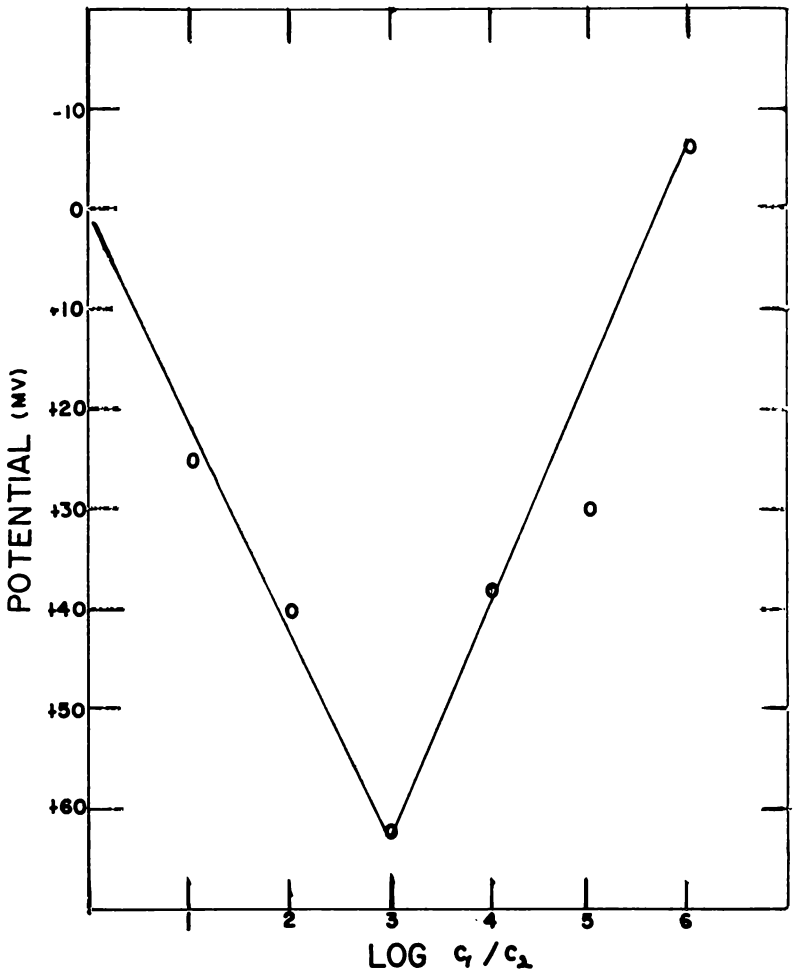

FIG. 3 Graph of the potential versus the log of the ratio of the metal ion concentrations. 40°C.

TABLE III

Potentials Measured Using Nickel Ion at Concentrations C_1 and C_2 and Nickel Dimethylglyoxime at 40°C

C_1 (M)	C_2 (M)	log C_1/C_2	Average Potential (mv.)
0.100	0.0100	1.0	+25
0.100	0.00100	2.0	+40
0.100	0.000100	3.0	+62
0.100	0.0000100	4.0	+41
0.100	0.00000100	5.0	+30
0.100	0.00000010	6.0	— 5

ACKNOWLEDGEMENTS

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BIBLIOGRAPHY

1. Beutner, R., "On a New Kind of Electromotive Force and Some Possible Applications to Physico-Chemical Problems." J. Am. Chem. Soc. **35,** 344 (1913); "Studies on a New Kind of E.M.F. II. Cell Arrangement of Aqueous and Nitrobenzene Solutions Containing One Common Ion in Both Phases." **36,** 2040, 2045 (1914).
2. Dole, Malcolm, **Principles of Experimental and Theoretical Electrochemistry,** McGraw-Hill Book Company, New York, 1935, pp. 372-389, 427-442.
3. Hodgman, Charles D., **Handbook of Chemistry and Physics** 34th edition, Chemical Rubber Publishing Co., Cleveland, 1952, p. 2788.
4. Morgan, Gilbert T., and Moss, Henry Webster, "Researches on Residual Affinity and Co-ordination. Part I. Metallic Acetylacetones and their Absorption Spectra." J. Chem. Soc. **105,** 189 (1914).
5. Patterson, Jr., Andrew, **Quantitative Analysis,** Henry Holt and Company, New York, 1952, p. 383.

CHEMICAL STUDIES ON THE BLOOD PLASMA OF THE CHINCHILLA

(Chinchilla lanigera)

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INTRODUCTION

At present, the chinchilla holds a prominent position in the fur industry of the United States. It was believed that blood analysis

of this animal might be of importance in the comparison of apparently normal chinchillas to diseased ones or to other fur bearing laboratory animals. Electrophoretic patterns of the serum protein of six apparently normal chinchillas were reported in 1953[1], but no reference to flame photometric analysis of chinchilla serum was found in the literature. The purpose of this paper is to present data concerning the electrophoretic and flame photometric analyses of the plasma of the chinchilla.

Materials and Methods

Two samples of blood, taken at approximately a twenty-one day interval, were drawn from sixteen apparently normal chinchillas. The animals were anethetized with an intraperitoneal injection of sodium pentobarbital and approximately 2 ml. of blood was taken by cardiac pncture. Heparin was used as an anticoagulant.

The Spinco Model R paper electrophoresis system was used to migrate and isolate the alpha, beta and gamma globulin and the albumin components. These components were calculated by the use of a Spinco Analytrol and recorded in percent of total area.

Sodium, potassium and calcium levels of the blood plasma of the sixteen chinchillas were determined with the Coleman Model 21 Flame Photometer. The two sets of data were averaged to obtain an experimental standard for each animal and the results recorded in milliequivalents per liter.

RESULTS

TABLE I

Electrophoretic Data of Serum Proteins

(in percent of total area)*

Animal No.	Albumin	Alpha globulin	Beta globulin	Gamma globulin
1	41.4	5.1	25.6	27.9
2	44.2	4.3	25.6	26.8
3	46.5	4.6	23.4	25.5
4	49.4	5.3	22.2	33.1
5	45.5	4.5	27.4	22.6
6	47.0	5.1	24.2	23.7
7	47.6	5.7	21.4	22.9
8	45.5	4.5	26.0	24.0
9	45.6	4.9	23.7	26.8
10	55.3	4.4	20.0	20.3
11	51.2	4.1	21.2	23.5
12	42.4	4.8	25.5	27.3
13	40.0	5.7	28.5	26.8
14	51.9	4.7	24.0	20.4
15	45.4	4.5	27.3	22.8
16	50.8	4.9	23.2	21.1

Arithmetic Mean	46.9	4.8	25.6	24.1
Standard Deviation	4.0	0.6	1.4	4.5

*The electrophoresis graphs were computed in cm. x 10^{-1}. The percent of total area refers to the ratio between the individual components and the total area of the graph derived from the Analytrol.

TABLE II

Flame Spectrophotometric Data of Serum Electrolytes (in milliequivalents per liter)

Animal No.	Sodium	Potassium	Calcium
1	141	3.6	6.1
2	128	4.1	6.2
3	128	3.2	6.6
4	145	3.7	7.5
5	136	3.9	6.1
6	145	4.0	6.6
7	136	3.4	6.0
8	132	3.7	7.4
9	140	4.5	6.7
10	140	3.5	6.2
11	134	3.4	6.3
12	131	3.5	6.6
13	135	4.0	6.3
14	144	3.1	6.1
15	142	3.0	6.8
16	131	3.0	7.0
Arithmetic Mean	137	3.6	6.5
Standard Deviation	5.0	0.34	0.37

DISCUSSION

The electrophoretic data obtained in this project differed from the work done by Stauber, **et al**[1]. Their data were obtained with a Klett electrophoresis apparatus using blood serum. These data were obtained with a Spinco electrophoresis system using blood plasma. No previous reference to flame photometric analysis on the chinchilla could be found in the literature.

SUMMARY

Data concerning the electrophoretic and flame photometric analyses of the plasma of sixteen apparently normal chinchillas were obtained and recorded. These blood analyses may be used to compare apparently normal chinchillas to diseased ones or to other fur bearing laboratory animals.

ACKNOWLEDGEMENTS

The authors wish to express their appreciation to the Veterinary Science Department for the use of its apparatus and materials. We wish to thank E. J. Bergman of Valley City, North Dakota who donated the chinchillas used in this experiment.

BIBLIOGRAPHY

1. Stauber, Ochs, and Coy. Electrophoretic Patterns of the Serum Protein of Chinchillas and Hamsters Infected with **Leishmania donovani.** Experimental Parasitology, **3** (4): 325-335. (1953).

SYNTHESES AND STUDIES IN THE ISOXAZOLE SERIES. THE 5-(PARA-CHLOROPHENYL)-ISOXAZOLES

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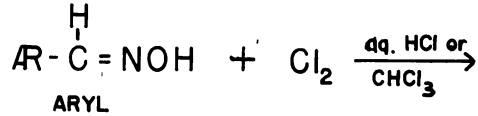
INTRODUCTION

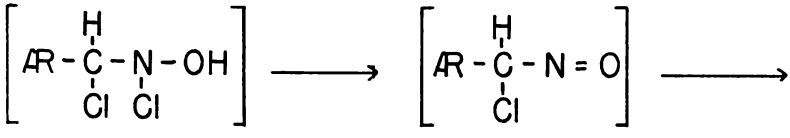
The purpose of the work reported here was to prepare and study new compounds in the isoxazole series. The isoxazole ring compound was prepared in the same manner as reported by Adolfo Quilico and

EQUATIONS OF REACTIONS

aryl group = para-chlorophenyl

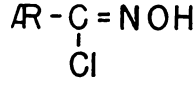


ARYL CARBOXALDOXIME



INTERMEDIATE

NITROSO INTERMEDIATE (BLUISH-GREEN)

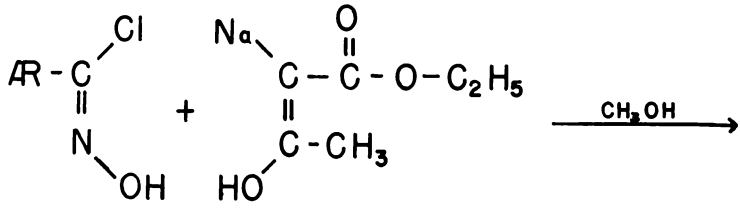


I′ CHLOROARYLCARBOXALDOXIME

FIG. 1

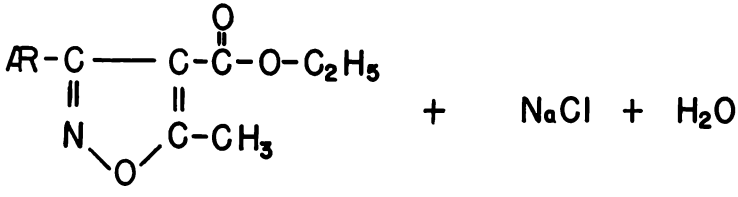
Raffaello Fusco (2). Further studies have been carried out by Quilico, Panizzi, Cavazzati, and Rathmann (1, 3, 4, 5) and by Rathmann and Wollan (6).

The final compound aimed at in the series of reactions reported here will be the isoxazole aldehyde. The preparation proceeds as indicated by the following equations:



1'CHLORO ARYL-CARBOXALDOXIME

SODIUM ACETO-ACETIC ESTER



3-METHYL-5-ARYL ISOXAZOLE-4-CARBOXYLIC ACID ETHYL ESTER

FIG. 2

$3\text{-}CH_3\text{-}5\text{-aryl-}C_3ON\text{-}4\text{-}COOC_2H_5 + NaOH \longrightarrow$
3-methyl-5-aryl-isoxazole-4-carboxylic acid ethyl ester

$3\text{-}CH_3\text{-}5\text{-aryl-}C_3ON\text{-}4\text{-}COOH$
3-methyl-5-aryl-isoxazole-4-carboxylic acid

$3, 5\text{-Isox-}4\text{-}COOH + SOCl_2 \longrightarrow 3, 5\text{-Isox-}4\text{-}COCl$
3-methyl-5-Aryl-isoxazole-4-carboxylic acid chloride

$3, 5\text{-Isox-}4\text{-}COCl + C_6H_5NH_2 \longrightarrow 3, 5\text{-Isox-}4\text{-}CONHC_6H_5$

$3, 5\text{-Isox-}4\text{-}CONHC_6H_5 + SnCl_2 + HCl \longrightarrow$
$3, 5\text{-Isox-}4\text{-}CHO + C_6H_5NH_2 \cdot SnCl_4 \cdot HCl$
3-methyl-5-aryl-isoxazole-4-carboxaldehyde

EXPERIMENTAL

ARYL CARBOXALDOXIME

Para-chlorobenzaldoxime

To 7.0 grams (0.10 mole) of $NH_2OH \cdot HCl$ dissolved in water and cooled in an ice bath were added 14.0 grams (0.10 mole) of **p**-chlorobenzaldehyde and 25 grams of a 40% NaOH solution. The reacted solution was exactly neutralized with concentrated HCl, and the crystals collected and dried. Yield of crude product was 87%. Recrystallization from benzene yielded white needle-shaped crystals melting at 110°C. (Ciamician and Silber reported 110°C.)

α-Naphthaldoxime and ortho-Chlorobenzaldoxime

These compounds were also prepared and are reported here, although their reactions in the isoxazole series have not been studied, but will be at a future date.

The preparation of α-naphthaldoxime proceeds as does the preparation of **p**-chlorobenzaldoxime, using 31.2 grams (0.20 mole) of the α-naphthaldehyde and 50 ml. of 5M $NH_2OH \cdot HCl$, neutralizing with an equivalent amount of 6M NaOH solution. Recrystallization from ethanol yielded white crystals melting at 98-99°C. (Brandis reports 98°C).

The preparation of **o**-chlorobenzaldoxime is carried out the same way as for p-chlorobenzaldoxime. The amount of material used was the same. The product was vacuum distilled at a pressure of 12 mm of Hg. The boiling point at this pressure was 137°C. A light yellow liquid was obtained which crystallized to form white, needle-shaped crystals melting at 75-76°C. (Erdmann and Schwechten repored 75°C.)

1'-CHLORO-ARYL-CARBOXALDOXIME

1'-chloro-para-chlorobenzaldoxime

The chlorination of the **p**-chlorobenzaldoxime was carried out in both chloroform and a 1.13 specific gravity HCl solution. The solubility of **p**-chlorobenzaldoxime in chloroform is 1:35 by weight and in HCl about 1:110 by weight.

In a flask cooled in an ice bath 15.3 grams of **p**-chlorobenzaldoxime were dissolved in 400 ml. of $CHCl_3$. Chlorine, which was produced by the reaction of 7.3 grams of concentrated HCl and 6.3 grams of $KMnO_4$, was bubbled into the solution at a slow rate. A greenish-blue color due to the nitroso intermediate was observed. When the reaction was completed the chloroform was removed under vacuum. A yield of about 85% was obtained. The white needle-shaped crystals were recrystallized from petroleum ether, melted at 76-77°C.

A Carius determination for chlorine gave:

Calculated for $C_7H_5ONCl_2$	37.32%
Found	37.0 %

1'-chloro-α-naphthaldoxime

The procedure for preparation of 1'-chloro-p-chlorobenzaldoxime

was followed using 4.3 grams of α-naphthaldoxime and 100 ml. of chloroform. The usual brilliant greenish-blue color appeared upon introduction of chlorine.

Upon removal of the chloroform by vacuum distillation, a straw-yellow liquid was obtained. This decomposed very readily upon standing to a dark red, thick paste. No crystals were obtained. It appears the naphthyl group causes complication in the preparation of this compound.

3-Methyl-5-(para-chlorophenyl)-isoxazole-4-carboxylic acid ethyl ester

To a flask cooled in ice 10.0 grams (0.052 mole) of 1'-chloro-p-chlorobenzaldoxime and 58 ml. of sodium aceto-acetic ester were added with shaking. (Sodium aceto-acetic ester is prepared by reacting 2.3 grams of sodium metal with 100 ml. of absolute methanol and refluxing this with 12.5 grams of aceto-acetic ester for one-half hour.) The mixture was allowed to stand for 4-5 hours and the methanol was evaporated off. To the remaining reaction mixture were added 50 ml. of water and 50 ml. of ether. The layers were separated, and the water layer was extracted with ether two more times. The combined ether layers were then washed with a 4% NaOH solution, which also was washed twice with ether. The ether extracts were combined and the solution was vacuum distilled.

The 3-methyl-5-(*para*-chlorophenyl)-isoxazole-4-carboxylic acid ethyl ester boils at 97°C at 9.5 mm of Hg pressure. A yellow liquid with a refractive index of 1.5272 at 11.5°C was obtained. The product crystallized to form white, needle-shaped crystals melting at 81-82°C.

3-Methyl-5-(para-clorophenyl-isoxazole-4-carboxylic acid

One gram of the ester was dissolved in methanol and 2 ml. of a saturated solution of NaOH in methanol was added. The solution was refluxed for one hour. The methanol was evaporated off and water added. A 5% solution of HCl was added until the mixture became acidic to hydrion paper. The white precipitate was collected and recrystallized by dissolving it in a 10% $NaHCO_3$ solution and then acidifying with 5% HCl. The melting point was 177°C.

A Carius determination for chlorine gave:

Calculated for $C_{11}H_6O_3NCl$	14.92%
Found	15.3 %

Conclusion

New compounds which have been prepared are the 1'-chloro-p-chlorobenzaldoxime, the 3-methyl-5-(para-chlorophenyl)-isoxazole-4-carboxylic acid ethyl ester, and the 3-methyl-5-(para-chlorophenyl)-isoxazole-4-carboxylic acid.

BIBLIOGRAPHY

1. Panizzi, L., Gazzetta Chimica Italiana, 72-99 (1942); 73, 99 (1943).
2. Quilico, Adolfo, and Raffaello Fusco, "New Researches in the

Isoxazole Group", Gazzetta Chimica Italiana, 67, 589-603 (1937) Chemical Abstracts 32: 21174.
3. Quilico, A., Luigi Panizzi, and U. Cavazzuti, Gazzetta Chimica Italiana, 68,625 (1938).
4. Quilico, A., and L. Panizzi, Gazzetta Chimica Italiana, 68,411 (1938).
5. Rathmann, Franz H., and Adolfo Quilico, "Studies in the Isoxazole Series", unpublished.
6. Rathmann, F. H., and Jacqueline Kay Wollan, Proc. N. Dak. Acad. Sci., Vol. XII, 26-29 (1958).

INHERITANCE OF RESISTANCE TO THREE STALK ROTS IN CORN

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ABSTRACT

Stalk and root rot diseases of corn are generally prevalent in corn growing regions and are responsible for appreciable annual yield losses. Establishment of these diseases before full maturity results in lodged stands and chaffy grain. Broken and down stalks also interfere during harvest resulting in lost ears and increased fungal deterioration of ears in contact with moist soil. Little information, however, is available on the inheritance of resistance of corn lines to rot organisms of known pathogenecity. This is of basic importance to the development of resistant varieties of corn by breeders.

This study was conducted in 1958 to investigate the disease reaction of five inbred lines, three F_1 crosses and three F_2 progenies which were stem-inoculated with the rot organisms **Diplodea Zeae** (Schw.) Lev., **Gibberella zeae** (Schw.) Petch and **Fusarium moniliforme** (Sheld.) Snyder and Hansen. Individual stalks were inoculated by inserting sterile popcorn kernels uniformly covered with each particular fungus mycelia into a longitudinal incision in the middle of the internode directly below the ear. Over 1400 individual plants were stem-inoculated after pollination was completed. Treated stalks were severed longitudinally and read for disease spread about thirty days after inoculation.

The nature of the inheritance of resistance to the stalk-rot organisms was found to be quantitative with no dominance. Additive gene action was also noted since the F_1 and F_2 means were almost identical to the midparent means. Assuming additive gene action was involved, estimates of heritability for resistance in the broad

sense were calculated. Two models were used in calculating heritability estimates namely:
A:H = $(VF_2 - VF_1)/VF_2$ x 100 and B:H = $(VF_2 - Vp)/VF$ x 100 where H = heritability, V = variance, Vp = mean variance of parents, and Vf_1 and VF_2 = variance of F_1 and F_2 generations, respectively. Positive heritabilities ranged from 19 to 47 (model A) and 44 to 63 (model B) for resistance to **Diplodia** stalk rot. For resistance to **Gibberella** stalk rot, positive heritabilities of 78 (model A) and a range from 10 to 92 (model B) were found. Positive heritabilities for resistance to **Fusarium** stalk rot ranged from 21 to 71 (model B) and 33 (model A). In the series of heritability estimates, three negative heritabilities were realized due to relatively high variability of disease spread within certain non-segregating generations. The overall study resulted in heritabilities for resistance to stalk rot positive and relatively high in eleven out of fourteen estimations.

In general, this genetic analysis of resistance to stalk rots in corn indicated that reasonably effective selection for resistance could be realized on the individual plants basis in segregating generations. Knowledge of this nature becomes a practical tool for the plant breeder in developing a corn breeding program for stalk rot resistance.

TRANQUILIZER EFFECT ON BARBITURATE SLEEPING TIME

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ABSTRACT

Preliminary studies with rabbits have shown that the duration of action of barbiturates may be prolonged by the addition of certain tranquilizers. This report will summarize the effects of chlorpromazine and reserpine, two unrelated tranquilizing agents, upon the sleeping time of pentobarbital and thiopental. The sleeping time of rabbits was determined for each barbiturate given intravenously 25 mg/kg. Following this, chlorpromazine or reserpine was administered parenterally for several days and the sleeping time after 25 mg./kg of the barbiturate was again determined. Our investigations so far indicate that with the dosage used, chlorpromazine increased the sleeping time of both barbiturates while reserpine had less effect.

Rats were used to determine whether the effect of the tranquilizing agents could be related to renal function. Data will be presented on the effects of chlorpromazine and reserpine upon the rate of urine production.

AN ANAYLSIS OF ATTITUDES TOWARD RACES AND NATIONALITIES

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In this study an attempt was made to apply numerical values in the measurement of attitudes toward races and nationalities and to determine the relationship between preferences and knowledge. Concededly, prejudice may sometimes affect choices, if by prejudice is meant the forming of judgments and choices in the absence of, or in spite of, knowledge. The main purpose of this study, however, was to determine whether preferences, aside from prejudices, may have some foundation in actual knowledge.

In designing such a comparative analysis, and mainly to eliminate or reduce possible prejudicial reactions, a preliminary study[2] was made in which a social distance scale[1] was used, consisting of units of measurements, as follows in Table I: kinship by marriage, 5 points; club associate, 4; street neighbor, 3; same job, 2; admission to U. S. citizenship, one point; only as visitor to the U. S. or exclusion, zero and minus-1; or a possible total of 15 points for complete social acceptance.

TABLE I

Racial Preferences As Measured by Social Distance

Social Distance Scale		Average Ratings by 133 Ss		No. Admitted at Each Level	
Possible No. Points	15	Italian	13.3	Possible	10.
Kinship by marriage	5	Hawaiian	12.2	Kinship by marriage	3.4
Club associate	4	Russian	11.6	Club associate	7.0
Street neighbor	3	American Indian	11.2	Street neighbor	7.5
Same job	2	Hebrew	10.2	Same job	8.7
U. S. citizenship	1	Japanese	7.7	U. S. citizenship	9.0
As visitor to U. S. or exclusion	0 -1	Arab	7.2	Less than cit'ship	1.0
		Negro	7.0		
		Hindu	6.8		
		Mexican	6.5		

Ratings were made by 133 **Ss**, upper classmen in college, largely natives of the Dakotas and Minnesota. As shown in Table I, the following ratings were obtained: Italian ,13.3 points; Hawaiian, 12.2; Russian, 11.6; American Indian, 11.2; Hebrew, 10.2; Japanese, 7.7; Arab, 7.2; Negro, 7.0; Hindu, 6.8; and Mexican, 6.5. Incidentally, it was revealed, as indicated in Table I, that of the ten races, statistically, only 3.4 were acceptable for kinship by marriage; 7.0 for club associate; 7.5, street neighbor; 8.7, same job; 9.0, U. S. citizenship; balance, as visitors only or exclusion.

Based on these preliminary findings, an attempt was made to reduce possible prejudices, some of which seemed rather obvious, by selecting another group of ten choices. (Incidentally, no Scandinavians were included because of ancestral influence in many of the **Ss**, perhaps also because the instructor's name has an **sen** suffix;

French was substituted for Italian; Japanese and Chinese were selected to represent Orientals; Turks and Greeks replaced Hebrews and Arabs; German represented the Nordic and offset French; Canadian and Mexican, neighboring people, were included; in listing English it was deemed advisable to omit the Irish, (substituted by Scotch; in all, these were an agreed-upon listing for purposes of the study.)

Thus designed, the purpose of the study was to determine the relationship between preference and knowledge. Ranking as to knowledge was based on the question: "What I know as to their history, culture, way of life, etc.?" Ordinarily, in the absence of numerical scores or other mathematical symbols of value, it is difficult to rank values. When differences are not readily observable, one of the more accurate methods of ranking is by the paired comparison method[3] in which each item is paired against each other item in a series (always by pairs). The sum of the firsts for each item is then used to determine the rank order; in this case, from 1 to 10. Table II presents the rankings by 133 Ss in 1954[2] and a followup five years later by another group of 132 Ss in 1959.

TABLE II

Relationship Between Preference and Knowledge Ranked by Paired Comparison

(a) Paired Comparison in 1954 (133Ss)

Nationality	Preference		Knowledge	
	Sum[a]	Rank	Sum[a]	Rank
Canadian	1121	1	1004	2
Chinese	356	7	450	7
English	944	2	1071	1
French	816	4	798	3
German	717	5	796	4
Greek	483	6	310	9
Japanese	192	10	383	8
Mexican	240	9	619	5
Scotch	851	3	474	6
Turk	265	8	80	10
Totals	5985[b]		5985[b]	

Correlation coefficient: .72

(b) Paired Comparison in 1959 (132Ss)

Nationality	Preference		Knowledge	
	Sum[a]	Rank	Sum[a]	Rank
Canadian	1077	1	1013	1
Chinese	195	10	395	8
English	917	2	996	2
French	814	4	764	4
German	824	3	799	3
Greek	532	6	369	9

Japanese	313	7	487	6
Mexican	206	9	585	5
Scotch	753	5	439	7
Turk	309	8	93	10
Totals	5940[a]		5940[a]	

Correlation coefficient: .77

a. Sum of firsts
b-c. Formula[3] for verification: n(n—1)/2; or 10 x 9/2, or 45 per **S.**
b. Total: 45 x 133 **Ss** = 5985.
c. Total: 45 x 132 **Ss** = 5940.

Table II-a (133 **Ss** in 1954) shows a correlation coefficient of .72 which, according to the Table of Values;[4] is significant at the 5% level of significance .648. Table II-b (132 **Ss** in 1959) shows a correlation coefficient of .77, well above the 5% level of significance at .648, slightly under the 1% level of .794. Especially worthy of note is the change in preference ranking of Chinese from 7th to 10th in the 1959 ranking and the rise in rank of the Japanese from 10th to 7th place. The fact that the Mexicans ranked 9th in preference and 5th in knowledge in both the 1954 and 1959 studies operated to reduce the correlation coefficient in both comparisons, suggesting possible bias, perhaps derived from adverse impressions of migrant Mexican families in the sugar industry in the Red River Valley. (Parenthetically, it may be of interest to note the findings in a subsequent study in which 21 graduate students, mostly teachers, participated; the correlation coefficient of .76 showed striking agreement with the present study.)

The data obtained in the 1954 and 1959 studies afforded a supplementary computation as to consistency of preferences from 1954 to 1959; likewise, as to knowledge. Table III shows a correlation coefficient of .84 as to preferences; Table IV, a coefficient of .94 as to knowledge, both significant at the 1% level.

TABLE III
Rank Order of Preference

	1954	1959
Canadian	1	1
Chinese	7	10
English	2	2
French	4	4
German	5	3
Greek	6	6
Japanese	10	7
Mexican	9	9
Scotch	3	5
Turk	8	8

Correlation coeff. : . 84

TABLE IV
Rank Order of Knowledge

	1954	1959
Canadian	2	1
Chinese	7	8
English	1	2
French	3	4
German	4	3
Greek	9	9
Japanese	8	6
Mexican	5	5
Scotch	6	7
Turk	10	10

Correlation coeff. : . 94

In summary, it appears that there is a highly significant relationship between preference and knowledge as to nationalities, especially when and if the factor of prejudice is reduced or eliminated; that, in the present study, the factor of knowledge remained highly constant during the five-year interval; and that changes in preference as to Chinese and Japanese reduced the correlation to some extent.

To hypothesize that there is only a chance or zero relationship between one's preference and one's knowledge is untenable in so far as the nationalities and 265 Ss were concerned in this study. One is tempted to conclude that people tend to prefer that which they know about, and to defer acceptance when knowledge is meager or lacking; moreover, that promotion of knowledge about other peoples of the world would tend to reduce barriers against acceptance.

BIBLIOGRAPHY

1. Boring, E. C., et. al, Foundations of Psychology, John Wiley & Sons, Inc., New York, 1948, pp. 606-607.
2. Estensen, Ernest V., Laboratory Activites in Psychology, Author, Fargo: 1955, pp. 46, 55-57, 127-128.
3. Underwood, Benton J., Experimental Psychology, Appleton-Century-Crofts, Inc., New York, 1949, pp. 95-103.
4. Underwood, Benton J., et al, Elementary Statistics, Appleton-Century-Crofts, Inc., New York, 1954, p. 232.

AN ADAPTATION OF QUANTITATIVE TYROSINE DETERMINATION TO PERFUSATE STUDIES

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ABSTRACT

We have been studying the intestinal absorption of amino acids in the rat by an *in situ* perfusion technique (Jacobs and Hillman, J. Biol. Chem., **232**:445, 1958). Preliminary studies made in the measurement of L-tyrosine absorption posed, an anlytical problem, since the chemical colorimetric method of analysis (Lowry, *et al.*, J. Biol. Chem., **193**:265, 1951) not only measured residual tyrosine in the perfusate but also developed color with some substance or substances released into the intestinal lumen during perfusion. It was also found that color development with the perfusate samples required a prolonged development time (1 to 1.5 hrs.) before stabilization. It has been found that this "extra-tyrosine" component could be removed by the addition of trichloracetic acid (TCA). Treatment with TCA required neutralization before color development and the intensity of the absorbance was less, but concentration-absorbance relationships held true. The development time could be shortened to 15 minutes or less by heating the sample with color reagents for a period of 1 minute in a boiling water bath. (Supported by N.I.H. Grant No. A-2023).

THE DISTRIBUTION OF FATTY ACIDS IN LINSEED OIL FROM THE WORLD COLLECTION OF FLAX VARIETIES

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INTRODUCTION

Linseed oil has long been used in paint and varnish formulations because of its comparatively short drying time and generally good film properties. The major disadvantage in its use is that it produces yellowing with age, which makes it unsuitable for use in white paints and other light-colored interior finishes. With the increased availability of other vegetable oils which do not have this after-yellowing problem and the advent of latex and acrylic paints, there has been a steady decline in the linseed oil market to the extent that linseed oil now comprises only 40% of the drying oils used in the paint industry as compared to 80% in 1943 (1). This lowered depmand, coupled with an increase in flax production, has made flax a surplus commodity in the United States. With these facts in mind it was decided that something must be done if flax is to maintain its importance as an agricultural product. Two possible solutions are either to find a new variety of flax which would produce an oil more desirable to the paint industry or to find new uses for linseed oil. The outstanding feature of linseed oil that differentiates it from other drying oils is its high content of linolenic acid. It is apparent that any improvement in flax or new uses for linseed oil should improve or utilize this linolenic acid content.

The first step in breeding for an improved linseed oil involved a survey of the quality of the oil from all the known varieties of flax. The United States Department of Agriculture maintains a collection of over a thousand flax varieties obtained from all over the world which was used as a source for the analytical work.

The relative proportions of the constitutuent fatty acids in the oil was used as a preliminary measure of oil quality.

MATERIALS AND METHODS

The flax seed supplied by the United States Department of Agriculture was grown at the following locations: Aberdeen, Idaho; Brawley, California; Brookings, South Dakota; Columbia, Missouri; and Indianhead, Saskatchewan, Canada. Clean, mature seed representative of each individual variety was used for analysis. A total of 1175 varieties including the standard varieties, Bison, B-5128, Redwood and Marine, were analyzed for oil composition as the primary purpose of this work.

The oil for analysis was obtained by crushing the seed in a roller mill and then expressing the oil from the crushed seed by means of a hydraulic press at 70°C. The oil was placed in stoppered tubes and stored at 4°C. The following determinations were conducted:

1. Oil content. The crushed seed was placed in a porous alundum extraction thimble and extracted in a Soxhlet extractor for 24 hours, using Skellysolve "F" as a solvent. The solvent was evaporated and the residual oil dried and weighed.

2. Iodine value. The Wijs method as used by the Americal Oil Chemists' Society (3) was employed.

3. Polyunsaturated acids. The American Oil Chemists' Society method Cd 7-48 was followed in detail (3). The isomerization was conducted at 180°C. for 25 min. in ethylene glycol containing 6.6% potassium hydroxide. Readings were made at 233, 268 and 315 milli mu. The values for each acid are expressed in percent of the acid in the oil.

4. Acid value. A procedure was developed utilizing a non-aqueous system which was very similar to the AOCS method Ka 2-58 (3). By use of dilute reagents and a microburette, acid values as low as 1.0 were readily determined on 0.2 grams of oil.

5. Color. The expressed oils were centrifuged and the clear oil compared with the standards in the 1953 Gardner Standard Colors.

6. Saponification value. The micro method of Marcali and Rieman (2) gave reproducible results on 0.2 to 0.3 grams of oil.

7. Gas chromatography. The oil from about 80 varieties was analyzed by this method using an Aerograph chromatograph and a 1 mv. recorder. An eight foot column was used with various polyester resins and solid supports: LAC-446 from Cambridge Industries, on 80-100 mesh Celite, 30% by weight; Craig Polyester-succinate from Wilkins Instrument Co., on 35-80 mesh Chromosorb, 25% by weight, and diethylene glycol succinate polyester prepared in this laboratory, on 60-80 mesh Celite, 20% by weight. Of the three columns, the last gave the best separation of the stearic and oleic acids. Helium was used as a carrier gas. The procedure was as follows: about 0.5 grams of flax seed was placed in a mortar and ground with an equal amount of sand. The mixture was extracted twice with 4 ml. of petroleum ether, the solvent evaporated and the residual oil transesterfied with 3 ml. 0.5 N $NaOCH_3$ in methanol for seven minutes. To the cooled solution was added 2 ml. of a saturated solution of $NaHSO_4$, the mixture shaken and finally 0.25 ml. of petroleum ether added. A 3 mu liter sample of the ether solution was injected into the chromatograph. Average time for separation of the fatty acid methyl esters was eighteen minutes with a column temperature of 197°C. and helium flow rate of 100 ml./min. The areas under each peak on the graph were measured and the composition expressed as per cent fatty acid in the oil.

RESULTS AND DISCUSSION

A. Comparisons between the various varieties are listed below.

1. Oil content. The oil content ranged from 32.4% to 45.8% oil. The standard varieties were near the upper extreme with 41-43% oil. From this data it appears likely that no significant improvement can be made in increasing the amount of oil in flax.

2. Iodine value. The iodine value is a measure of the drying qualities of an oil, i.e., the higher the iodine value, the faster drying the oil. The iodine value of oils analyzed varied from 166, approaching a semi-drying oil, to 198, a fast drying oil. The standard varieties ranged from 185 to 193 iodine value. An oil with higher iodine value will have a faster drying rate but will also show more yellowing. Both of these properties are determined by the linolenic acid content of the oil.

3. Polyunsaturated acids. In all the varieties linolenic acid was the major constituent, varying from 45 to 65% of the oil. The linoleic acid ranged from 7 to 19% and the oleic from 10 to 28%. An interesting relationship was revealed during this analysis, in that the total of the linolenic and oleic acid contents was consistently from 70 to 75%. In other words, an increase in per cent linolenic acid is accompanied by a decrease in the per cent oleic acid and *vice versa.* It has been observed (4) that the iodine value of linseed oil is an indication of the amount of linolenic acid present. This relationship has been substantiated in our studies which showed that the higher the iodine value, the greater the per cent linolenic acid. There was no correlation between the linoleic acid content and the iodine value, oleic, linolenic or saturated acids.

4. Acid value. Most of the oils analyzed had acid values below 2. However, one group of samples from Brawley had values ranging from 10 to 40. This means there were 5 to 20% free fatty acids in the oils in this group. The color of the oils from these samples was noticeably green. These two factors indicate that the flax samples had not yet matured at the time of harvest.

5. Color. The colors of most of the oils were 9 and 10 (Gardner) with a few extremes of 8 and 11.

6. Saponification value. This quantity is a measure of the average molecular weight of the fatty acids. Since the ratio of C_{16} to C_{18} acids in linseed oil is almost constant, the saponification value varied only slightly, 188 to 192.

7. Gas chromatography. The use of a gas chromatograph was found to be the most rapid and convenient means for determining the fatty acid composition in linseed oil. With its use one can determine the amount of each acid present, independent of the amount or type of the other acids present. From this reliably accurate data the iodine value and saponification value can be calculated, eliminating these two time consuming analyses. In addition to linolenic, linoleic and

oleic acids, palmitic and stearic acid were present in the oils, their total varying from 8 to 12% of the oil. Only trace amounts of myristic and palmitoleic were observed. Calculation of the iodine value from the per cent composition obtained by the gas chromatograph agreed very closely, within 2%, with the iodine value determined by the Wijs method.

Comparison of the gas chromatograph data with data obtained by the alkali isomerization method revealed that the linolenic values obtained by the former method were a little lower. However, due to the agreement of the iodine value relationship and the inherent complexity of the alkali isomerization method, it is felt that the gas chromatographic data are more valid.

With the extreme sensitivity of the gas chromatograph and refined procedures, it is now possible to analyze the oil obtained from a single boll of flax.

B. Effect of Location on Composition.

From various varieties of flax grown at Brookings, South Dakota and Aberdeen, Idaho, it was found that those grown at the former location showed lower amounts of linolenic acid than the same variety grown at Aberdeen. However, the four disease resistant standard varieties showed little difference between the two locations. Just what the effect of disease may have been at these two locations is not known.

Two varieties with fairly high linolenic contents were grown at Columbia, Missouri; Aberdeen Idaho; and Saskatoon, Saskatchewan, Canada. Significantly lower iodine values were observed in the samples grown at Columbia, substantiating the common observation that flax grown in northern climates produces oils with higher iodine values than when grown in warmer, humid climates.

C. Variation of Fatty Acid Composition within a Given Variety.

An investigation of the oil composition of individual plants from a given variety was undertaken to determine to what extent the oil composition varies from plant to plant. The seed from fifteen individual plants of each of five varieties has been analyzed for oil composition using the gas chromatograph. It was found that the linolenic and oleic acid contents vary widely from one plant to the next. In one case one plant yielded an oil having 38.2% linolenic acid and a second plant of the same variety grown in the same row yielded an oil having 55.7% linolenic acid. Variations of 6 to 10% in linolenic acid were common. This wide range in variation indicates the heterogeneity which exists in the World Collection varieties. Because of this, the plant breeder must be very cautious in selecting parents for a study of the inheritance of oil unsaturation.

SUMMARY

Linolenic acid was found to be the major constituent in linseed oil from all the varieties of flax, both wild and domestic, with lino-

leic, oleic, stearic and palmitic acids present in lesser amounts. A close correlation was found between the linolenic and oleic acid content in that the total of these two acids consistently ranged from 70 to 75% of the oil. It was also demonstrated that the higher the iodine value, the higher the percentage of linolenic acid content. The use of a gas chromatograph in the linseed oil analysis produced results which were speedily obtained, reliably accurate and allowed the use of very small amounts of seed in performing the analysis.

A significant variation in linolenic acid content was found in oil taken from seeds of different plants within a given variety, grown at the same location.

ACKNOWLEDGEMENT

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BIBLIOGRAPHY

1. "The Fats and Oils Situation", Agricultural Marketing Service, U. S. Dept. of Agriculture, March 1959.
2. Marcali, K., and Rieman, W., "Microdetermination of the Saponification Number of Fats and Oils." Ind. and Eng. Chem., Analytical Edition, **18,** 144 (1946).
3. "Official and Tentative Methods of the American Oil Chemists' Society", 1958 Rev., 35 East Wacker Drive, Chicago 1, Ill.
4. Painter, E. P., "Some Relationships between Fat Acid Composition and the Iodine Number of Linseed Oil", Oil and Soap, **21,** 343-346 (1944).

"DETERMINATION OF ACETONE EXTRACTABLE WATER FROM A PROTEIN-CONTAINING SUBSTANCE BY MEANS OF ELECTRO-CONDUCTANCE"

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Acetone has been used in histological laboratories for a long time as a dehydrating agent for animal tissue. The possibility of using this dehydrating force as a standard for comparison of the water binding capacity of various animal proteins subjected to experimental conditions was considered and investigated.

It was found that water-free acteone with an excess of sodium chloride had a constantly low specific electro-conductance. Water was the only substance which when added in small amount appreciably changed the conductance of the system. Therefore, graded amounts of water (.1 to 1.5 cc) were added to tubes containing 10 cc of water-free acetone and an excess of NaCl (2 grams) and the

amount of water in each tube was plotted against the specific conductance. The curve was linear between 0.9 and 1.3 cc. The following equation for the curve between these two points as determined by the method of least squares. $x = \frac{y + 11.33}{21.41}$ where x = ml of water and y = specific conductance x 10^{1}.

Next, a solution of desiccated gelatin in distilled water was prepared in such a way the weight of water and gelatin in each cc of solution was known. Then samples of different dilutions with distilled water of this stock solution were made and a constant volume of each dilution was added to the acetone salt system. The difference between the amount of water added to the system and the amount of water obtained by the acetone method was called the retained water. A ratio was obtained by dividing the amount of retained water by the amount of protein in the system. For the gelatin and distilled water mixture, the ratio was about 1.2.

ION EXCHANGE RESINS FROM LIGNITE COAL

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The relatively low cost of coal, and lignite in particular, as an organic base for the production of ion-exchange resins, plus the fact that these carbonaceous materials possess some natural ion-exchange properties, makes them of interest as raw materials for possible development as ion-exchangers.

A major factor in using coal and lignite as a raw material is a consideration of its chemical structure and composition (14, 13). Numerous investigators have explored the field of coal structure. The research contributions of Fuchs (6), Wheeler (10), and Howard (11), have greatly extended the knowledge and understanding of the chemical structure of coals. These investigators have shown that brown coal may contain as much as 10% hydroxyl oxygen which is to a considerable extent phenolic in nature. This may be a partial explanation as to why some coals naturally possess some ion-exchange properties. Other groups of equal importance found were the carbonyl, the methoxyl, and the carboxyl (12). In Britain, India, United Soviet Republic, the United States, and other countries, anthracite, bituminous, and lignite coals have been explored (5, 8, 9). The methods of treatment were varied, and included heating, phosphonation, chlorosulfonation, and sulfonation. The general opinion

seems to prevail that treatment with sulfuric acid yields the best ion-exchange product. Furness and Crosfield (7), subjected coal to the action of fuming sulfuric acid, and apparently obtained a superior product. It has subsequently been found that other similar carbonaceous materials when sulfonated, exhibit ion-exchange properties, which indicates that the exchange properties, while initially present, were enhanced by the sulfonation treatment (3, 1). Again in 1942, Furness and his associates (4), published information in

TABLE I

UNITED STATES DEPARTMENT OF THE INTERIOR
BUREAU OF MINES
Charles R. Robertson Lignite Research Laboratory
Grand Forks, North Dakota
Coal Analysis Report

Lab. No. *GF-1816*
Sample of Lignite Can No._____
Description of sample *Baukol-Noonan Lignite, N.D.A.C. School of Chem. Technology*
Sample Received *6/5/57* Analyses Completed *6/26/57*
Analysis Requested by *Chemistry-Physics Section - 220*

	25.81 Air-Dry Loss	Coal (Air Dried)	Coal (As Received)	Coal (Moisture Free)	Coal Moisture + Ash Free
Proximate Analysis	Moisture	11.20	34.12		
	Volatile Matter	36.09	26.78	40.64	45.20
	Fixed Carbon	43.76	32.46	49.28	54.80
	Ash	8.95	6.64	10.08	
		100.00	100.00	100.00	100.00
Ultimate Analysis	Hydrogen	5.31	6.81	4.58	5.10
	Carbon	58.81	43.63	66.23	73.65
	Nitrogen	1.00	0.74	1.13	1.25
	Oxygen	25.30	41.71	17.27	19.21
	Sulphur	0.63	0.47	0.71	0.79
	Ash	8.95	6.64	10.08	
		100.00	100.00	100.00	100.00

British thermal units _____

Fusibility of Ash, °F.
Initial deformation temp
Softening temperature
Fluid temperature

Moisture as determined by xylene method was 35.0%

(Signed)_____
Edward F. Bitzan Chemist

which they described the effects of air oxidation at temperatures below the decomposition temperature of coal.

Hard coals, such as anthracite, sulfonate readily yielding a product that is granular. The resulting coal-based resins undergo exhaustion and regeneration without noticeable particle disintegration. Lignites and other similar soft coals, on the other hand, exhibit the tendency to disintegrate into small particle sizes upon treatment. This feature is one major objection to the use of the lignites as a base for ion-exchange resins.

MATERIALS AND METHODS

The lignite coal used in this investigation was obtained from the Baukol-Noonan Mine at Noonan, North Dakota. It may be considered to be relatively uniform "mine run" although this term obviously carries numerous connotations. The coal was shipped and stored in air tight, 5 gallon pails until actually used. A very comprehensive proximate analysis and ultimate analysis was generously provided by Walter W. Fowkes and Edward F. Bitzan of the Charles R. Robertson Lignite Research Laboratory, United States Department of the Interior, Bureau of Mines, at Grand Forks, North Dakota, and the results are itemized in Table I. This analysis is an extremely important consideration in any study of this type dealing with a variable natural product. The lignite was subjected to no less than seventeen different treatments that might be expected to test or enhance its exchange properties. These included testing the coal as received in 12 to 25, 40 to 60, and 60 to 80 mesh size respectively. Likewise the 12 to 25 mesh size was again similarily tested after heating at 100° to 110° for 1 hour; and the 25 to 40 mesh size after like heat treatment for 1 hour, 4 hours, 8 hours, and 25 hours, respectively. The coal, as received, was sulfonated for 1 hour and tested; then exhausted with hard water, regenerated with brine, and rechecked. A sample was similarly sulfonated for 8 hours and tested. The lignite was next dried for 1 hour at 100° to 110° and different portions were sulfonated for 1 hour, 4 hours, and 8 hours respectively. Finally a portion of the lignite was heat treated for 20 hours and then sulfonated for 8 hours. Samples of the original coal were also phosphonated for 1 hour and 8 hours and comparisons made with similarly sulfonated coals.

The method of acid treatment consisted in placing a known amount of lignite into a flask, equipped with stirrer, reflux condenser, and thermometer and adding enough 20 per cent fuming sulfuric acid to cover the sample. Heat was applied, when needed, to maintain the reaction temperature between 90° and 100°. After the reaction had been continued for the desired length of time, distilled water was added cautiously, the lignite was then washed with distilled water until the effluent gave a pH between 4 and 6. The same general method was used for the phosphonation treatment of the coal, except that 85 per cent phosphoric acid was used.

The samples of raw, dried, and treated lignite were exhausted with standard hard water by an equilibrium method. In this procedure the exchanger was weighed out in duplicate samples of 5, 10, 15, and 20 g. These were placed in 500 ml. Erlenmeyer flasks and a 100 ml. portion of standard hard water was added to each of the flasks. This particular hard water had 5,486 p.p.m. equivalent of calcium acetate or 1.251 g. calcium ion per liter. The stoppered flasks were placed on a mechanical shaker and gently agitated for several hours. They were then allowed to stand several hours until the small particles in the solution settled. A 10 ml. aliquot of the solution was then pipetted from each flask, and titrated by the versene method. The equilibrium reaction was maintained at room temperature, and varied from 23° to 26°.

The versene (sometimes called versonate) method for the determination of water hardness involves the titration of an unknown water sample with standard versene solution (2). The 10 ml. aliquot was diluted with 100 ml. of distilled water, and 0.3 to 0.4 g. of the indicator and 8 to 10 ml. of approximately 8N potassium hydroxide were added to the solution. A magnetic stirrer was used to slowly agitate the mixture during the titration with the standard versene solution.

The regeneration procedure was similar to traditional treatment. The "as received" lignite, which had been sulfonated for 1 hour, was

TABLE II

CAPACITIES TAKEN FROM EQUILIBRIA STUDIES

	Capacities in mg. per g.			
Exchanger	**20 g.**	**15 g.**	**10 g.**	**5 g.**
As received, 12 to 25 mesh	3.90	4.53	5.20	6.20
As received, 40 to 60 mesh	3.95	4.60	5.50	6.80
As received, 60 to 80 mesh	3.80	4.53	5.40	6.40
Heat-treated 1 hr., 12 to 25 mesh	4.05	4.67	5.50	6.80
Heat-treated 1 hr., 25 to 40 mesh	4.15	5.13	5.60	7.60
Heat-treated 4 hours	4.30	5.07	6.10	7.60
Heat-treated 8 hours	4.40	5.20	6.40	8.40
Heat-treated 25 hours	4.10	5.07	6.40	8.40
As received, sulfonated 1 hour	6.10	8.07	11.90	23.40
As received, sulfonated 1 hour regenerated	6.15	8.20	12.30	23.80
As received, sulfonated 8 hours	6.05	8.07	12.00	23.20
Heat-treated, 1 hour, sulfonated. 1 hr.	6.00	7.87	10.80	18.60
Heat-treated 1 hr., sulfonated 4 hrs.	5.50	7.27	10.80	19.20
Heat-treated 1 hr., sulfonated 8 hrs.	8.70	12.00	18.70	36.00
Heat-treated 20 hrs., sulfonated 8 hrs.	6.10	8.13	12.20	24.20
As received, phosphonated 1 hour	5.15	6.13	7.50	10.20
As received, phosphonated 8 hours	5.20	6.33	7.90	10.40
Cullex	6.10	8.13	12.10	24.00
Cullite	5.95	7.87	11.60	19.40

regenerated with a saturated sodium chloride solution for 0.5 hour. The lignite was then washed with distilled water until it tested free of chloride ions with a silver nitrate solution. A 100 g. portion of the regenerated lignite, dried overnight at 55° to 60°, was exhausted with standard hard water.

RESULTS AND DISCUSSION

The ml. of versene required to titrate a 10 ml. aliquot of standard hard water, less the ml. of versene needed to titrate a 10 ml. aliquot of effluent, yields the ml. of versene which represents the decrease in water hardness or calcium retention. This value divided by the ml. of versene needed to titrate 10 ml. of standard hard water gives the per cent of calcium ion retained by the lignite. The total grams of calcium ion present in 100 ml. of hard water was 0.1251 g. The per cent of calcium ion retained times the total grams present in the hard water yields the grams of calcium retained by the lignite, or the ion-exchange capacity. The total results are summarized in Table II.

The original "mine run" lignite coal displayed some ion-exchange or water softening capacity. There appeared to be no significant difference with particle size. Heat treatment of the lignite generally increased the ion-exchange capacity with a maximum improvement at the end of approximately 8 hours. This increase may be associated with oxidation as well as dehydration. The lignite, when sulfonated for 1 or 8 hours, increased in exchange capacity noticeably over the "as received" lignite. Regeneration increased the capacity again slightly as compared to the original 1 hour sulfonated coal. Sulfonation for 8 hours, however, did not produce better results than the corresponding 1 hour treatment on "mine run" coal. Combining the heat treatment with sulfonation might be expected to greatly increase the ion-exchange capacity since each procedure, alone, produced noticeable improvement. However, the lignite which was heat treated for 1 hour and was sulfonated for 1 hour actually had lower exchange capacities for all sample weights than the corresponding "mine run" which was likewise sulfonated for 1 hour. The same was true of the lignite heat treated for 1 hour and sulfonated for 4 hours. Actually the maximum exchange capacity was achieved when lignite was dried for 1 hour and then sulfonated for 8 hours. Subsequently a sample of lignite was heated for 20 hours at 185°, and then sulfonated for an additional 8 hours to see if more drastic heat treatment would increase the exchange capacity of the lignite. Actually a significant decrease occurred.

When "mine run" lignite was phosphonated for 1 hour with 85 per cent phosphoric acid, an inferior product was obtained as compared to similar treatment with sulfuric acid. Similar treatment for 8 hours with phosphoric acid did little to increase the ion-exchange capacity over similar treatment for 1 hour. Both phosphonations did, however, produce exchangers with higher capacities

than those in which heat treatment alone was used. The lignites treated with phosphoric acid, however, appeared to have a better physical structure than those coals receiving similar treatment with sulfuric acid.

It should be emphasized that there is no inconsistency in the exchange capacities as reported in Table II for the 5, 10, 15, and 20 g. samples. These findings are based on an equilibrium study involving the distribution of calcium ions between a fixed but excessive volume of hard water and a variable amount of exchange lignite resin. The capacities in mg. per g. naturally respond consistently with the changing ratio of volume to weight.

Two commercial synthetic water softeners were exhausted in the same manner for purposes of comparison.

SUMMARY

The lignite, as received from the mine, possesses some ion-exchange capacity.

Heat treatment of the raw lignite generally tended to increase the exchange capacity.

Sulfonation of the, "mine run" lignite for 1 hour increased the capacity. Longer treatment increased the capacity little, if any.

Heat treatment of the lignite for 1 hour at 100° to 110°, followed by sulfonation for 8 hours produced the best ion-exchanger.

Phosphonation of the raw lignite increased the capacity more than heating alone, but less than the sulfonation of comparable coal.

BIBLIOGRAPHY

1. A. S. Behrman and H. B. Gustafson to Infilco Inc., U. S. Patent, 2,376,897 (1945).
2. Bersworth Chemical Co., Framingham, Mass., "The Versenes for Exacting Control of Cations in Solution, Technical Bulletin No. 2," Sec. 3, p. 5 (1952).
3. S. J. Broderick and D. Bogard, "Carbonaceous Zeolites from Bituminous Coal," Ind. Eng. Chem., **33,** 1291-1296 (1941).
4. J. Crosfield and Sons, Ltd., R. Furness, and R. Wellington, Brit. Patent, 547,580 (1942).
5. J. G. Dean, R. Heiligman, and R. Riley to Permutit Co., Can. Patent, 420,270 (1944).
6. W. Fuchs and A. G. Sandhoff, "Theory of Coal Pyrolysis," Ind. Eng. Chem., **34,** 567-571 (1942).
7. R. Furness and Joseph Crosfield and Sons, Ltd., Brit. Patent, 486,471 (1938).
8. I. L. Gordon, "Chemical Desalinization of Water," Teplo-Silovoe, No. 2, 29-32 (1941); C. A. **38,** 1592[9] (1944).
9. O. N. Grigorov and I. V. Volf, "Teor. i. Prakt. Primen, Ionoobmen Materialov," pp. 82-89 (1955).

10. F. Heathcoat and R. V. Wheeler, "Studies in the Composition of Coal. The Constitution of the Ulmins," J. Chem. Soc., **1932,** 2839-2847.
11. H. C. Howard, "Evidence for the Cyclic Structure of Bituminous Coals," Ind. Eng. Chem., **44,** 1083-1088 (1952).
12. J. Schuyer and D. W. van Krevelen, "Chemical Structure and Properties of Coal. III. Molar Refraction," Fuel, **33,** 176-183 (1954).
13. J. Schuyer and D. W. van Krevelen, "Coal Science," Elsevier Publishing Co., New York, N. Y., pp. 191-243, 1957.
14. H. Stack and M. Teichmuller, "The Chemistry and Petrography of Ion-Exchangers from Brown and Hard Coals," Brennstoff-Chem., **34,** 275-281 (1953).

BREAKING DORMANCY OF WILD OAT SEEDS WITH SOME PLANT EXTRACTS

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ABSTRACT

For some time we have studied the nature of dormancy in native wild oat (Avena fatua seeds. In our search for chemicals which might break dormancy in these seeds we have tried extracts from a number of different plants including various parts of the wild oat plant and its seeds.

In general extracts of wild oat material are either toxic, induce a more profound dormancy, or are mostly inactive. This is true of most other plant materials we have so far tested.

In September 1958, we discovered that aqueous extracts of fresh 10-day old wild oat seedlings appeared to break dormancy in a consistant manner. Subsequent studies indicate that other aged seedlings also are somewhat active. The magnitude of enhanced germination is comparable to that obtained with gibberellic acid or its salts, the only other plant substance we have found which will consistantly break dormancy of the wild oat seed.

Gibberellic acid or its potassium salt will break dormancy of wild seeds whether freshly harvested or seeds stored for some time. A concentration around 500 ppm is required for nearly complete germination of freshly harvested seeds, but as the seeds age the effective concentration is reduced to around 100 ppm.

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Beckering, Willis (Physical Chemistry), U. S. Bureau of Mines, Grand Forks. 1957.
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Bell, Gordon L. (Geology), Pingree. 1954.
Belter, John W. (Chemical Engineering), U. S. Bureau of Mines, Grand Forks. 1957.
Bergstrom, John R. (Geology), University. 1958.
Bieber, Loran L. (Biochemistry), Agricultural College. 1955.
Blake, Martin I. (Chemistry), Agricultural College. 1957.
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Bitzan, Edward F. (Chemistry), U. S. Bureau of Mines, Grand Forks. 1952.
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Bolin, Donald W. (Biochemistry), Agricultural College. 1946.
Bolin, F. M. (Veterinary Science), Agricultural College. 1948.
Bosch, Wouter (Chemistry), Agricultural College. 1948.
Bosch, Mrs. Wouter, (Chemistry), Agricultural College. 1949.
Brandt, Roger D. (Electrical Engineering), University. 1957.
Brezden, William (Chemistry), State Mill and Elevator, Grand Forks. 1945.
Broberg, Joel W. (Chemistry), Agricultural College. 1948.
Brookhart, Joseph W. (Geology), U. S. Geol. Survey, Grand Forks. 1957.
Brumleve, Stanley (Physiology), University. 1958.
Bruner, Gilbert H. (Cereal Technology), Agricultural College. 1956.
Bryant, Reece L. (Poultry Genetics), Agricultural College. 1948.
Brynsvold, Glen V. (Mechanical Engineering), University. 1958.
Buchanan, M. L. (Animal Husbandry), Agricultural College. 1950.
Buchwitz, Lyle F. (Physics), University. 1958.
Buegel, Hermann F. (Psychology), University. 1955.
Burr, Alex C. (Chemical Engineering), N. Dak. Research Foundation, Bismarck. 1940.
Busch, George W. (H. S. Science), Rugby. 1955.
Cardy, James D. (Pathology), University. 1950.
Carter, Jack F. (Agronomy), Agricultural College. 1950.
Callenbach, John A. (Entomology), Agricultural College. 1954.
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Christoferson, Lee A. (Neurological Surgery), Fargo. 1952.
Comita, Gabriel W. (Zoology), Agricultural College. 1954.
Coon, Ernest D. (Chemistry), University. 1923.
Cooley, A. M. (Chemical Engineering), University. 1938.
Corbus, Jr., Budd C. (Urological Surgery), Fargo. 1952.
Carnatzer, William E. (Biochemistry), University. 1952.
Cotrufo, Cosimo (Horticulture), Agricultural College. 1958.
Culmer, Ausmon E. (Orthopaedics), Grand Forks. 1958.
DeBoer, Benjamin (Pharmacology), University. 1952.
Delphia, John M. (Zoology), Agricultural College. 1958.
Denison, A. Rodger (Petroleum Geology), Amerada Corp., Tulsa. 1955.
Dillard, James R. (Gynecology), Fargo. 1954.
Dinusson, William C. (Animal Nutrition), Agricultural College. 1950.
Dixon, John C. (Electrical Engineering), University. 1955.
Dogger, James R. (Entomology), Agrcultural College. 1958.
Donat, Theodore L. (Medicine), Fargo. 1954.
Doubly, John A. (Bacteriology), Agricultural College. 1950.
Douglas, Raymond J. (Animal Husbandry), Agricultural College. 1950.
Downing, William L. (Biology), Jamestown College. 1952.
Dunbar, Ralph E. (Chemistry), Agricultural College. 1938.
Eastman, Irene (Chemistry), N. Dak. Research Foundation, Bismarck. 1956.
Edgerly, Charles G. M. (Dairy Husbandry), Agricultural College. 1955.

Ederstrom, Helge E. (Physiology), University. 1953.
Eisenhard, Robert M. (Geology), N. Dak. Geological Survey, Grand Forks. 1958.
Ellman Robert C. (Chemical Engineering), U. S. Bureau of Mines, East Grand Forks, Minnesota. 1957.
Enloe, Joseph R. Jr. (Petroleum Engineering), Amerada Petrol. Corp., Williston. 1957.
Elder, James L. (Chemical Engineering), U. S. Bureau of Mines, Grand Forks. 1957.
Erickson, Roland I. (Mining), University. 1953.
Eveleth, D. E. (Veterinary Science), Agricultural College. 1944.
Estensen, Ernest V. (Psychology), Agricultural College. 1951.
Facey, Vera (Botany), University. 1948.
Fleetwood, Charles W. (Chemistry), Agricultural College. 1948.
Flor, Harold H. (Plant Pathology), Agricultural College. 1943.
Fordyce, Ira V. (Chemistry), AGSCO Chemicals Inc., Grand Forks. 1950.
Fossum, Giulford O. (Civil Engineering), University. 1957.
Fowkes, Walter W. (Chemical Engineering), U. S. Bureau of Mines, Grand Forks, 1957.
Frank, Richard E. (Chemistry), University. 1949.
Frear, D. Stuart (Agricultural Biochemistry), Agricultural College. 1958.
Frederickson, Ronald L. (Chemistry), Abbott Laboratories, North Chicago, Ill. 1951.
Freeman, Andrew L. (Electrical Engineering), Grand Forks. 1955.
Freeman, Philip G. (Chemistry), U. S. Bureau of Mines, Grand Forks. 1958.
French, Harley E. (Anatomy), Dean Emeritus, University. 1911.
Fromm, Herbert J. (Biochemistry), University. 1955.
Frost, Clyde M. (Chemistry), U. S. Bureau of Mines, Grand Forks. 1957.
Galysh, Fred T. (Pharmacy), Agricultural College. 1957.
Gantner, Ida E. (Biology), Grand Forks H. S., Grand Forks. 1957.
Garske, Jay T. (Geology), N. Dak. Geological Survey, Grand Forks. 1958.
Giles, Ray N. (Petroleum Engineering), Standard Oil Co., Mandan. 1954.
Geiszler, Gustav N. (Agronomy), Agricultural Experiment Station, Minot. 1950.
Gough, Francis J. (Plant Pathology), Agricultural College. 1958.
Graham, Charles M. (International Medicine), Grand Forks. 1951.
Grimes, Ruby M. (Mathematics), Agricultural College. 1946.
Gronhovd, Gordon H. (Mechanical Engineering), U. S. Bureau of Mines, Grand Forks. 1957.
Gustafson, Ben G. (Chemistry), University. 1939.
Hamre, Christopher J. (Anatomy), University. 1950.
Hansen, Dan E. (Geology), University. 1954.
Hansen, Miller (Geology), N. Dak., Geological Survey. 1952.
Harak, Arnold E. Chemistry), U. S. Bureau of Mines, Grand Forks. 1958.
Haraldson, Harold C. (Geology), Calgary, Alberta. 1952.
Harman, Charles M. (Mechanical Engineering), University. 1957.
Harris, Rae H. (Agricultural Biochemistry), Agricultural College. 1938.
Hart, Harry B. (Chemistry), Jamestown College. 1929.
Hartt, Kenneth (Physics), University. 1957.
Harwood, Theodore H. (Internal Medicine), University. 1954.
Haunz, Edgar A. (Internal Medicine), Grand Forks. 1951.
Hazen, Arlon G. (Agricultural Engineering), Agricultural College. 1950.
Helgeson, E. A. (Botany). Agricultural College. 1936.
Henderson, J. Donald (Physics), University. 1945.
Hetland, Philip R. (Physics), Agricultural College. 1957.
Higgins, Edith C. (State Seed Department), Agricultural College. 1950.
Hill, A. Glenn (Mathematics), Agricultural College. 1946.
Hoeppner, Jerome J. (Chemistry), U. S. Bureau of Mines, Grand Forks. 1949.
Hoffman, Charles A. (Biology), Teachers College, Minot. 1958.
Holland, Neal S. (Horticulture), Agricultural College. 1955.
Holland, Robert C. (Anatomy), University. 1957.
Holmes, Richard R. (Chemistry), University. 1953.
Horner, Oscar (Vertebrate Ecology), Agricultural College. 1954.
Hultz, Fred S. (Agriculture), President, Agricultural College. 1950.
Humphrey, William R. (Geology), Agricultural College. 1958.
Hundley, John L. (Physics), University. 1930.
Jacobs, Francis A. (Biochemistry), University. 1955.
Jensen, Christian (Dairy Husbandry), Agricultural College. 1927.
Johansen, Robert H. (Horticulture), Agricultural College. 1955.
Johnson, Stanley S. (Civil Engineering), University. 1958.
Keefer, Darlye E. (Psychology), University. 1953.
Keller, Wesley E. (Mining), Truax-Traer Coal Co., Minot. 1958.
Kennedy, Gene O. (Geology), Amerada Petroleum Corp., Williston. 1957.
Kirby, Joseph R. (Civil Engineering), Highway Dept., Bismarck. 1955.
Kjerstad, C. L. (Philosophy and Psychology), University. 1937.
Klosterman, Harold J. (Agricultural Chemistry), Agricultural College. 1952.
Klovstad, George S. (Chemistry), Teachers College, Minot. 1957.
Knoblich, Jerome M. (Chemistry), Jamestown College. 1958.
Knudson, Walter L. (Biolgoy), School of Forestry, Bottineau. 1951.

Koenker, William E. (Economics), University. 1958.
Kohanowski, N. (Geology), University. 1949.
Koons, Melvin E. (Bacteriology), Public Health Lab., University. 1943.
Koth, Arthur W. (Metallurgy), University. 1939.
Kress, Warren D. (Geography), Agricultural College. 1958.
Kruschwitz, Earl H. (Physics), Valley City. 1947.
Kube, Wayne R. (Chemical Engineering), U. S. Bureau of Mines, University. 1949.
Laird. Wilson M. (Geology), University. 1941.
Lana, Edward P. (Horticulture), Agricultural College. 1957.
Langford, Larkin H. (Animal Husbandry), Agricultural College. 1950.
Larson, Edith E. (Biology), University. 1947.
Lawson, Edward C. (Mechanical Engineering), University. 1955.
Lerfald, Gordon M. (Physics), University. 1958.
Lindseth, Joseph M. (Agriculture), Teachers College. Dickinson. 1955.
Lium, Elder L. (Civil Engineering), University. 1953.
Lockhart, William C. (Poultry Husbandry), Agricultural College. 1955.
Loomis, Fred H. (Cereal Chemistry), Loomis Laboratories, Grand Forks. 1947.
Love, Janet (Botany), Agricultural College. 1958.
Lundy, John S. (Anesthesiology), Mayo Clinic Rochester, Minn. 1940.
Lunseth, John H. (Pathology), University. 1958.
McBride, Woodrow H. (Mathematics), University. 1958.
McMillan, William W. (Chemistry), N. Dak. Research Foundation, Fordville. 1947.
MacDonald, John H. (Biology), Teachers College, Dickinson. 1951.
MacDonald, Wittmer (Basic Science), Teachers College, Minot. 1958.
MacKichan, Ruth B. (Mathematics and Astronomy), University. 1958.
Magill, John W. (Biological Chemistry), Agricultural College. 1958.
Magnusson, Adelynn M. (Chemistry), University. 1951.
Manning, Francis P. (Medicine), Union Laboratories. Minot. 1958.
Manz, Oscar E. (Ceramic Engineering), University. 1953.
Marwin, Richard M. (Bacteriology), University. 1949.
Mason, Harry (Physics), Jamestown College. 1951.
Matson, Charles F. (Biochemistry), Veteran's Adm., Fargo. 1957.
Meighan, John N. (Mathematics), Teachers College, Dickinson. 1958.
Meintzer, Roger B. (Biological Chemistry), Agricultural College. 1958.
Meldrum, Alan H. (Petroleum Engineering), University. 1957.
Middleton, Herman F. (Geology), Amerada Petroleum Corp., Williston. 1957.
Miller, Wilford L. (Biology), State Game & Fish Dept., Bismarck. 1955.
Minnear, F. L. (Chemistry), Agricultural College. 1954.
Mogen, Clinton A. (Soils), Soil Conservation Service. Fargo. 1955.
Moir, David R. (Botany), Agricultural College. 1954.
Moore, Cyril C. (Chemistry), Teachers College, Minot. 1948.
Moran, W. H. (Chemistry), University. 1931.
Mulkern, Gregory B. (Entomology), Agricultural College. 1958.
Murphy, H. E. (Chemistry), Teachers College, Dickinson. 1928.
Naismith, Donald P. (Mechanical Engineering), University. 1958.
Nallaperumal, Ulaganathan (Chemical Engineering), University. 1958.
Newgard, Vernon H. (Histo-chemistry), University. 1958.
Norum, E. B. (Soils), Agricultural College. 1948.
Nungesser, William C. (Physiology), University. 1954.
Nedom, H. A. (Petroleum Engineering), Amerada Petroleum Corp., Tulsa, Okla. 1957.
Oakey, John A. (Civil Engineering), Agricultural College. 1954.
Oehler, Mrs. Alma (Nutrition), State Mill and Elevator, Grand Forks. 1945.
Olmstead, Edwin G. (Internal Medicine), University. 1958.
Olson, Ordell P. (Agronomy), Agricultural College. 1955.
Omodt, Hollis W. (Soils), Agricultural College. 1958.
Oppelt, Walter H. (Fuels), Bureau of Mines, University. 1949.
O'Reilly, Edward J. (Chemistry), University. 1955.
Orseth, Melvin M. (Electrical Engineering), University. 1958.
Owen, Shubel D. (Education-Agricultural), Agricultural College. 1958.
Overbo, Gerhard O. (Physics), Teachers College, Valley City. 1947.
Owens, Paul R. (Floriculture), Owens Floral Co., Grand Forks. 1945.
Parsons, Jesse L. (Bacteriology), Agricultural College. 1951.
Peterson, Norman C. (Chemistry), Agricultural College. 1957.
Peterson, Robert H. (Organic Chemistry), Agricultural College. 1951.
Pike, George M. (Hydraulic Engineering), U. S. Geol. Survey, Grand Forks. 1957.
Posin, D. Q. (Physics), Agricultural College. 1950.
Porter, Charles B. (Surgery), Grand Forks. 1951.
Porter, Robert B. (Chemical Engineering), U. S. Bureau of Mines, Grand Forks. 1957.
Potter, Loren (Botany), Agricultural College. 1948.
Promersberger, William J. (Agricultural Engineering) Agricultural College. 1958.

Randall, Robert N. (Wildlife Management), U. S. Fish and Wildlife Service, Bismarck. 1954.
Ranz, Robert (Chemistry), University. 1957.
Rathmann, Franz H. (Chemistry), Agricultural College, 1955.
Redmond, Charles E. (Soils), Agricultural College. 1955.
Reid, Russell (Natural Science), State Museum, Bismarck. 1940.
Richards, Stephen H. (Wildlife Management), Agricultural College. 1954.
Reiten, Palmer J. (Mechanical Engineering), University. 1957.
Riedesel, Mildred (Home Economics), University. 1955.
Riley, Kenneth W. (Chemistry), Marietta, Ohio. 1936.
Robinson, Hugh M. (Botany), State Teachers College, Valley City. 1948.
Robinson, Roy N. (Physics), Public Schools, Minot. 1951.
Rogers, Riley (Pharmacy), Agricultural College. 1958.
Rognlie, Philip A. (Mathematics), University. 1946.
Rolzinski, J. J. (Biology), Junior College, Devils Lake. 1950.
Roth, Kingsley W. (Geology), Amerada Petroleum Corp., Denver, Colorado. 1957.
Rudesill, James T. (Chemistry), Agricultural College. 1958.
Russell, Seth (Sociology), Agricultural College. 1958.
Sailki, A. K. (Pathology), University. 1949.
Sandal, Paul C. (Plant Breeding), Agricultural College. 1955.
Sands, F. H. (Chemistry), Agricultural College. 1946.
Saugstad, Stanley (Entomology), Minot. 1939.
Schermeister, Leo J. (Pharmacy), Agricultural College. 1957.
Schnell, Richard D. (Zoology), Agricultural College. 1955.
Schneider, Clifford F. (Geology), U. S. Geol. Survey, Grand Forks. 1957.
Schooler, Arnold B. (Cytology), Agricultural College. 1957.
Scott, George M. (Cereal Chemistry), Agricultural College. 1952.
Sebens, William P. (Agriculture), State Soil Cons. Comm., Bismarck. 1948.
Severson, D. E. (Chemical Engineering), University. 1949.
Shoesmith, Lloyd (Soils), Agricultural College, 1950.
Shumard, Raymond F. (Parasitology), Agricultural College. 1954.
Sibbitt, L. D. (Cereal Technology), Agricultural College. 1946.
Silverman, Louis B. (Pediatrics), Grand Forks Clinic, Grand Forks. 1957.
Sleeper, Bayard P. (Bacteriology), Agricultural College. 1952.
Smith, Glenn S. (Plant Breeding), Agricultural College. 1930.
Snook, Teodore (Anatomy), University. 1954.
Sommerfeldt, Therom G. (Soil Science), Agricultural College. 1958.
Spier, Jack J. (Pathology), St. John's Hospital, Fargo .1952.
Splies, Robert G. (Organic Chemistry), University. 1958.
Staley, Raymond C. (Mathematics), University. 1946.
Stallings, Harris D. (Library), Agricultural College. 1951.
Starcher, George W. (Mathematics), President, University. 1954.
Stevens, O. A. (Botany), Agricultural College. 1910.
Stewart, Donald L. (Chemistry), Am. Cryst. Sugar Co., E. Grand Forks, Minn. 1943.
Stoa, Theodore E. (Agronomy), Agricultural College. 1950.
Stockdale, Thomas E. (Petroleum Refining), Standard Oil Co., Mandan. 1954.
Sullivan, John W. (Biochemistry), Agricultural College. 1954.
Summers, Lawrence (Chemistry), University. 1951.
Svore, Jerome H. (Sanitary Engineering), Columbia Basin Inter-Agency Comm., Portland, Oregon. 1943.
Thompson, John C. (Mathematics), Teachers College, Dickinson. 1948.
Timian, Roland G. (Plant Pathology), Agricultural College. 1954.
Towse, Donald F. (Geology), Dickinson. 1952.
Treumann, William B. (Chemistry), Agricultural College. 1946.
Turelle, Joseph W. (Agronomy), U. S. Soil Conservation Service. Bismarck. 1954.
Turn, Jenny (Bacteriology), Agricultural College. 1957.
Turner, Robert C. (Medicine), Grand Forks. 1958.
Van Heuvelen, W. (Chemistry), State Health Dept., Bismarck. 1945.
Vasey, Edfred H. (Soils), Agricultural College. 1958.
Vennes, John W. (Bacteriology), University. 1957.
Vergeer, Teunis (Physiology), University. 1954.
Vick, James A. (Physiology), University. 1955.
Vincent, Muriel C. (Pharmacy), Agricultural College. 1957.
Waldron, Howard L. (Mining Engineering), University. 1957.
Walster, H. L. (Director of Experiment Station, Dean Emeritus), Agricultural College, 1920.
Wardner, G. A. (Chemistry), University. 1958.
Watkins, John B. (Veterinary Medicine), Grand Forks. 1954.
Weck, Herman I. (Chemical Engineering), Standard Oil Refinery, Mandan. 1957.
Weisser, Wilbur O. (Mathematics), State Teahcers College, Dickinson. 1957.
Whalin, Edwin A. (Physics), University. 1955.
Wheeler, Jeanette N. (Biology), University. 1957.
Wheeler, George C. (Biology), University. 1924.
Whitman, Warren C. (Botany), Agricultural College. 1950.

Wiidakes, William (Agronomy), Agricultural College. 1946.
Wills, Bernt L. (Geography), University. 1949.
Witmer, Robert B. (Physics), University. 1925.
Yeager, Vernon L. (Anatomy), University. 1957.
Young, Duane E. (Natural Sciences), Teachers College, Minot. 1958.
Young, Ralph A. (Agronomy), Agricultural College. 1954.
Youngs, Nelson A. (Otolaryngology), Grand Forks. 1957.
Youngs, Roger W. (Chemistry), U. S. Bureau of Mines, Grand Forks. 1957.
Youngs, Vernon (Chemistry), School of Forestry, Bottineau. 1955.
Zubriski, J. C. (Soil Physics), Agricultural College. 1955.

CORPORATE SUSTAINING MEMBERSHIPS

American State Bank of Minot, Minot, North Dakota. 1958.
First Federal Savings and Loan Association, Grand Forks, North Dakota. 1958.
First National Bank, Grand Forks, North Dakota. 1958.
First National Bank, Minot, North Dakota. 1958.
Minot Federal Savings and Loan Association, Minot North Dakota. 1958.
North Dakota Farmers Union, Jamestown, North Dakota. 1958.
Red River National Bank, Grand Forks, North Dakota. 1958.
Valley Bank, Grand Forks, North Dakota. 1958.
Truax-Traer Coal Company, Minot, North Dakota. 1957.

NEW MEMBERS

Ballantyne, Frederick L. (National Science), Minot.
Carlson, Kenneth T. (Chemistry), Mayville.
Hager, Alice M. (National Science), Minot.
Kannowski, Paul B. (Biology), University of North Dakota.
McCabe, Edward (Pharmacy), University of North Dakota.
Melhouse, LaClair A. (Mathematics), Minot.
Moyer, Fred J. (Botany), Mayville.
Smith, Aird C. (Mathematics), Minot.
Tilly, Lawrence J. (Biology), Jamestown.
Zimmerman, Don C. (Biochemistry), North Dakota Agricultural College.

ASSOCIATE MEMBERS

Higgins Potato Co., East Grand Forks, Minnesota.
Lee and Ferguson Pharmacy, East Grand Forks, Minnesota.
H. H. Westlie, Minot.