gram giving 0.0252 gram acid in 1/2 hr.) seemed extraordinary to the authors. It has been abundantly proven, however, that there are optimum temperatures for catalyzers in general, that is, temperatures allowing a maximum in the reaction along with a minimum of destruction to the catalyzer itself.

Many instances could be cited of the extraordinary influence of rise of temperature on the reaction velocity of catalytic actions, and particularly is this true of organic catalyzers (enzymes) within narrow margins of temperature. For instance, Tammann[1] has found that the temperature coefficient for emulsin on salicin between 60 and 70° was 12.3. What is true of enzymes is also true in a degree of cells, for broadly speaking these also are catalyzers, or rather systems of catalyzers. The organisms, then, may continue very rapidly to increase in activity until finally they die in hyper-activity. With this in mind, the increased velocity of sugar decomposition as higher temperatures were used becomes clear. This affords an explanation, too, of the occasional curdling of milk on pasteurizing, and gives further reasons for using a not too highly inoculated milk in such processes.

Conclusions.

1. The alkaline salts have no effect on the lactose in milk when it is heated at 85° for some time.

2. Perfectly concordant results can be obtained by the optical and gravimetric methods for lactose in pasteurized milk.

3. Concordance between the results by the optical and gravimetric methods can not be taken, as has been suggested, as evidence that the milk has not been pasteurized.

4. In bottle pasteurization it is impossible to heat the milk quickly enough to prevent appreciable amounts of lactose being decomposed, unless the milk has a very small bacteria count.

5. Some lactic acid organism or organisms work prodigiously at a temperature of 80-85°, though for a short time. They work more slowly but for a longer time at 60°.

6. The presence of a sediment containing calcium phosphate in pasteurized milk has been confirmed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MICHIGAN EXPERIMENT STATION.]

ORGANIC NITROGENOUS COMPOUNDS IN PEAT SOILS.

BY S. L. JODIDI.

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When we take into consideration that not less than one-seventh of the total area of the state of Michigan consists of swamp lands largely covered

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[1] *Z. physiol. Chem.*, 16, 323.

by peat and muck, which is more or less also true of New England, of the northwestern, western and middle states, and that their entire area in the Union is estimated to reach the imposing figure of 75,000,000 acres, we are impressed with the necessity of an investigation of peat soils with a view to learning as much as possible about their agricultural possibilities.

As far as could be learned from the literature within our reach, no systematic investigations of a similar nature have been conducted.

When we consider a soil from the standpoint of agricultural chemistry, one of the first things to demand attention is the so-called tripod of agriculture. This is natural enough, since many soils are deficient in one or more of the three essential elements: potassium, phosphorus and nitrogen.

Though the atmospheric ocean surrounding the earth contains countless millions of tons of nitrogen, it is, as such, of little avail, since the plants—with the exception of the legumes—are not able to utilize the free nitrogen of the air. It is the combined nitrogen only that is of agricultural value. Besides, there are a number of processes by which the nitrogen is liberated from the nitrogenous compounds and lost as plant food. The process of combustion, the denitrification through micro-organisms, and the reaction of nitrous acid upon organic nitrogenous compounds, the spontaneous decomposition of ammonium nitrite liberate[1] more or less free nitrogen.

True, some combined nitrogen in the shape of nitric acid and ammonia comes with atmospheric precipitations into the soil which is still more enriched with nitrogen through the activity of certain soil bacteria. But it is certain that, to-day, a much larger amount of nitrogen is removed from the soil than is returned to it by synthetic or other means.

In the peat bogs, nature has placed at the command of man soils with large quantities of combined nitrogen. From the data given below, it will be seen that Michigan brown peat—the most abundant type in that state—contains in round figures from 2.25 to 2.75 per cent. nitrogen in the oven-dried state. This percentage means that about four tons of nitrogen are contained in each acre-foot. Such a quantity of nitrogen, if it could be utilized, would be sufficient for continuous cropping during three-quarters of a century. As far as inorganic nitrogen is concerned, it was found that nitrates are not present in the brown peat deposits occurring in Michigan; also that the quantity of ammonia present is quite small, ranging from a few thousandths to a few hundredths of one per cent. Hence the nitrogen practically consists of organic bodies only. But of what nature are they? This question seems to be quite a complicated one when we consider that organic nitrogenous compounds ex-

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[1] O. Kellner and T. Yoshii, *Z. physiol. Chem.*, 12, 105–107 (1888).

ist in the shape of amines, acid amides, monamino and diamino acids, cyanides, indole derivatives, pyridine derivatives, etc., and that a good many of these bodies can be of aliphatic as well as of aromatic origin.

However, contemplations of a general nature will give us some idea as to the direction in which the problem under consideration can be attacked. It must be borne in mind that peat is a decomposition product of vegetable matter. Since the bulk of nitrogen in plants is commonly made up of proteins, which are contained in all plants, it is obvious that our attention must be directed first of all to the proteins and their decomposition products. However, in order to get some general conception as to the compounds or groups of bodies that may be present in peat, we must take into consideration the processes that take place in the plants when they cease to live. It is only protein in a dry state that is of a constant nature, but when subjected in a moist state to the influence of the ubiquitous bacteria—which is the case with protein in dead plants—it soon begins to decompose. The process of decomposition splits the complicated protein molecules into a considerable number of products. The following nitrogenous decomposition products have been discovered and identified by a great number of investigators:

Ammonia,[1] leucine,[2] tyrosine,[3] aminovaleric acid,[4] indole,[5] skatole,[6] indole acetic acid,[7] indole propionic acid,[8] putrescine,[9] cadaverine,[9] ptomaines generally, and others.

The nitrogenous decomposition products furnished by boiling the proteins with acids, *e. g.*, with hydrochloric acid, are as follows:

Ammonia,[10] histidine,[11] arginine,[11] lysine,[11] diamino-acetic acid,[12] glycocoll,[13] alanine,[13] aminovaleric acid,[13] leucine,[10] tyrosine,[10] aspartic acid,[10] glutamic acid,[10] cystine,[14] phenylalanine,[13] α-pyrrolidinecarboxylic acid,[13] oxyproline and humin substances.

Since peat has its origin from gradually decayed plants, and as far as nitrogen is concerned, chiefly from decayed proteins, it follows that the

[1] *Z. physiol. Chem.*, 22, 514–521 (1896–97).

[2] *Ibid.*, 22, 514 (1896–97).

[3] *Ibid.*, 2.

[4] E. und H. Salkowski, *Ber.*, 16, 1191.

[5] W. Kühne, *Ber.*, 8, 206.

[6] M. Nencki, *Z. physiol. Chem.*, 4, 371–372.

[7] *Z. physiol. Chem.*, 9, 8–22 (1885); *Ber.*, 13, 189; *Z. physiol. Chem.*, 27, 302 (1889); *Ber.*, 37, 1801 (1904).

[8] E. Salkowski, *Z. physiol. Chem.*, 27, 302 (1899); *Ber.*, 38, 2884 (1905).

[9] A. Ellinger, *Ber.*, 31, 3183.

[10] Hlasiwetz und Habermann, *Ann.*, 169, 150; also *J. prakt. Chem.*, [2] 7, 397.

[11] E. Schulze und E. Winterstein, *Z. physiol. Chem.*, 28, 459.

[12] Drechsel, *Ber. sächs. Ges. Wiss.*, 44, 115.

[13] Emil Fischer, P. A. Levene und R. H. Aders, *Z. physiol. Chem.*, 35, 70–79 (1902).

[14] K. A. H. Morner, *Z. physiol. Chem.*, 28, 595 (1899).

series of bodies representing the decomposition products of proteins through the action of micro-organisms is of special interest to us. However, it is not out of the question that we may find compounds present in the peat which are generally associated with the decomposition of proteins by mineral acids.

By considering the above two series of decomposition products more closely, we can readily see that the great majority of them belong to two classes of organic compounds, namely to the monamino acids—leucine, tyrosine, aminovaleric acid, aspartic and glutamic acid, etc.—and to the diamino acids—histidine, arginine, lysine and diamino acetic acid. Some of the monamino acids, *e. g.*, the aspartic and glutamic acid may originate from the amides, asparagine and glutamine, which are, as such, often contained in plants. Thus we logically come to the conclusion that the bulk of nitrogen in peat may be present in the shape of amides, monamino acids, and diamino acids.

We must not omit to mention here that it is reasonable to assume that the plants, through the decay from which the peat resulted, may have contained also nitrogenous bodies other than proteins, and further, that decomposition in nature, under the influence of its various agents, may be in some respects different from the decomposition in the laboratory of proteins proper, either by chemical means or through bacterial activity. The possible interaction of the decomposition products and the leaching in nature must also be taken into consideration. Consequently, the separation of the peat constituents into amides, diamino acids and monamino acids may not take place exactly in the same manner as it does with proteins. This should be kept in mind by viewing the data presented in Tables III and V.

The method applied for the separation of the organic nitrogenous bodies in peat soils was essentially the one employed in protein chemistry with slight modifications. A definite volume of the sulphuric acid or the hydrochloric acid extract of peat, corresponding to, say, 0.05 gram nitrogen was, after cooling, carefully neutralized with cream of magnesia, of which some excess was used. The ammonia obtained by distillation gave the amount of nitrogen corresponding to the amides present in the peat.

The residue from distillation with magnesia was dissolved in dilute sulphuric acid so as to have approximately a five per cent. acid solution, then phosphotungstic acid solution added in some excess and allowed to stand for at least twenty-four hours. The precipitate containing the diamino acids was then filtered out, washed with water containing from two and one-half to five per cent. sulphuric and the same amount of phosphotungstic acid. The filter, together with the diamino acid precipitate, was transferred to a flask and the diamino nitrogen estimated according to Kjeldahl's method.

The filtrate and washings from the diamino acids, containing the monamino acids, were filled up with distilled water to a definite volume, usually to 500 cc., of which 100 cc. or 200 cc. were oxidized by the Kjeldahl method. The amount of ammonia found by distillation and calculated to the total volume gave the percentage of nitrogen corresponding to the monamino acids.

Instead of directly determining the amount of monamino nitrogen by Kjeldahl's method, which is difficult to accomplish in an exact way, the sum of the percentages of amido nitrogen and diamino nitrogen can be subtracted from the total quantity of nitrogen extracted from the peat. The difference evidently represents the monamino nitrogen.

Experimental Part.

Prior to starting experiments with the object in view of finding out the various organic nitrogenous compounds contained in peat soils, it was thought advisable to establish their composition by elementary analysis. This was also suggested by the fact that the literature, as far as we know, contains very few complete analyses of American peat soils, at least as far as the organic constituents are concerned. The brown peat sample,[1] the analyses of which are given below, is one that is typical for Michigan. It was taken from three to four feet below the surface or about the usual water-line in that peat deposit. It was made up of fibrous remains of sedges and, in the upper layers, of small shrubs and similar plants. It represents a well-decomposed, fibrous, brown peat. In order to have the peat sample in a state suitable for analytical purposes, it was dried in an electric drying oven at a temperature of from 40 to 60°, and then put through a 20-mesh sieve.

Calculated to water-free basis, the analysis gave:

C, 55.06; H, 5.21; N, 2.74; S, 0.35; Ash, 6.62; O (by difference), 30.02.

In order to be able to separate the nitrogenous bodies present in peat soils, it was necessary first of all to find a suitable solvent for the extraction of these compounds. It was soon found that the quantity of nitrogenous substances which could be extracted with water was small. Moderately dilute hydrochloric and sulphuric acids proved to be the most suitable solvents for the purpose we had in view. Since only a small part of the peat soils could be dissolved in these acids, the suggestion was plausible that a number of factors, like the amount and concentration of the acids, temperature and duration of digestion, as well as the fineness of the samples, might have an influence upon the percentage of nitrogenous bodies that could be extracted. The experi-

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[1] All of the peat samples referred to in this paper were very kindly furnished by Dr. Chas. A. Davis, of the United States Geological Survey.

ments, the results of which are contained in Table I, have fully confirmed this supposition. Before presenting the results, however, we shall briefly describe the manner in which the peat was extracted with the various reagents. A definite amount of peat was transferred to a flask, then sulphuric or hydrochloric acid previously diluted with distilled water was added. The contents of the flask were shaken to a uniform mass, heated to the boiling point and kept boiling under a reflux condenser for a certain number of hours. Or, instead of boiling with reflux condenser, the flask containing the peat with the reagents was put into an autoclave where it was kept under a constant pressure. The boiled mass was then filtered and washed with boiling water. The peat remaining on the filter was then transferred to a flask, distilled water added, boiled for a few minutes, sucked off, washed with hot water, and these operations repeated another time. Filtrate and washings were evaporated and filled up to a definite volume, usually to 500 or 1000 cc., of which 100 or 200 cc. were taken for nitrogen determinations by the Kjeldahl method. The nitrogen found was calculated to the original volume. Results of this experiment will be found in Table I, under method (*a*).

Since the repeated boiling and washing with hot water, as well as the filtrations, require considerable time, this method was modified in a number of cases as follows: After digestion of the peat for a specified length of time, either under reflux condenser or in the autoclave, the flask content was cooled to room temperature and filled up to a definite volume with distilled water. After shaking, it was filtered through a dry filter, and two portions of the filtrate were taken for nitrogen estimations by Kjeldahl's method. The nitrogen thus found was calculated to the volume of the liquid minus the volume occupied by the peat. The results of this experiment will be found in Table I, under method (*b*). That these two methods differ to a degree in their results may be partly due to the high absorptive power of peat for ammonia and other nitrogenous substances.

In glancing at the table, one can see at once that the concentration of the acid and the duration of digestion have the greatest influence, whereas the quantity of the reagents used has only a slight influence upon the percentage of nitrogenous bodies that can be extracted from the peat. Thus, comparing the experiments 1 and 2, 4 and 8, 6 and 7, where, with the exception of the time of digestion, all the conditions were the same, we find that the percentage of nitrogenous substances extracted rises with increased hours of digestion. Also we notice, by comparing experiments 3 and 4, having equal hours of digestion, that, although the amount of acid used in the latter is considerably smaller than in 3, yet the percentage of extracted nitrogen is about 12 per cent. higher, showing the predominant influence of the concentration of the sulphuric acid. The same

TABLE I.—QUANTITY OF NITROGEN EXTRACTED FROM PEAT UNDER VARIOUS CONDITIONS.

		Reagent used.						Nitrogen extracted.			
									Method (a).		
No. of exp.	Grams of oven-dried peat.	H_2SO_4, grams.	H_2O, grams.	Strength of acid (per cent. by wt.).	Ratio of weight of reagent to weight of oven-dried peat.	Hours digested.	Method of digestion.	Method (b). Per cent. of total N in peat.	Gram.	Per cent. of total N in peat.	Per cent. of oven-dried peat.
1	4.7415	60.8	118.0	33.3	38	28	Boiling under reflux condenser,	50.47	0.06605	50.84	1.39
2	4.7415	60.8	118.0	33.3	38	10	Boiling under reflux condenser,	43.09	0.05616	43.23	1.19
3	4.7415	85.5	337.0	20.0	90	28	Boiling under reflux condenser,	39.22	0.06171	47.50	1.30
4	4.7415	142.5	150.0	47.5	63	28	Boiling under reflux condenser,	55.41	0.07750	59.65	1.63
5	4.7415	121.6	236.0	33.3	77	25	Treated in autoclave, 7/8 atm. pressure,	51.12	.....	...	....
6	9.4830	128.3	250.0	33.3	41	32	Boiling under reflux condenser,	...	0.14545	55.98	1.53
7	9.4830	128.3	250.0	33.3	41	35	Boiling under reflux condenser,	...	0.14690	56.54	1.55
8	9.4830	285.0	300.0	47.5	63	30	Boiling under reflux condenser,	...	0.16090	61.92	1.70
9	28.449	286.9	300.0	47.5	21	72	Boiling under reflux condenser,	...	0.49842	63.94	1.75
10	28.449	...	300.0	....	11	16	Boiling under reflux condenser,	3.73	.....	...	....
11	28.449	...	500.0	....	18	10	Treated in autoclave, 7/8 atm. pressure,	5.77	.....	...	....
12	28.002[1]	199.5	388.0	33.3	21	60	Boiling under reflux condenser,	...	0.34601	58.56	1.24
13	28.002[2]	199.5 HCl	388.0	33.3	21	60	Boiling under reflux condenser,	...	0.35928	60.81	1.28
14	9.4830	136.2	222.3	38.0	38	30	Boiling under reflux condenser,	...	0.14549	55.99	1.53

[1] For this experiment a black peat was used which passed through a 20-mesh sieve.

[2] Black peat passing through an 80-mesh sieve.

conclusion can be drawn from experiments 1 and 3. What is true of the sulphuric acid is also true of the hydrochloric acid, which extracts about the same percentage of nitrogen as does the sulphuric acid under the same conditions. Thus experiments 4, 8 and 14, with the same or about the same hours of digestion, show that the 47 per cent. sulphuric acid extracted more nitrogen than the 38 per cent. hydrochloric acid, whereas from experiments 1 and 14 it follows that the hydrochloric acid of a higher concentration was able to extract more nitrogen than the sulphuric acid of a lower concentration.

The experiments 10 and 11 show how small an amount of nitrogenous bodies can be extracted from the brown peat by means of water. This also holds true for other types of peat, for instance, for black peat as well as for weathered brown peat.

That from a peat in a finer state of division more nitrogen can be extracted than from a coarser peat is plainly seen from experiments 12 and 13, conducted under exactly the same conditions with the exception of the fineness to which the respective peat samples were reduced. From this it follows further that the percentages of nitrogen extracted from the brown peat and given in Table I should be considered as minimum figures, since all the experiments, with the exception of 13, were made with peat which passed a 20-mesh sieve.

TABLE II.—NITROGEN EXTRACTED BY REPEATED DIGESTION WITH ACID.

					Nitrogen extracted.		
No. of experiment.	Digestion.	Amount of oven-dried peat. Grams.	Strength of H_2SO_4 (per cent. by weight).	Hours digested.	Grams.	Per cent. of total nitrogen.	Per cent. of oven-dried peat.
1	1st	4.7415	33.3	10	0.05616	43.23	1.19
1	2nd		33.3	11	0.01300	10.01	0.27
1	3rd		33.3	29	0.01248	9.61	0.26
1	4th		33.3	32	0.00710	5.47	0.15
					Total,	68.32	1.87
2	1st	7.5864	25.4	10	0.09507	45.74	1.25
2	2nd		33.3	15	0.01803	8.67	0.24
2	3rd		25.0	22	0.01184	5.70	0.16
					Total,	60.11	1.65
3	1st	4.7415	33.3	28	0.06605	50.84	1.39
3	2nd		33.3	29	0.01360	10.47	0.29
3	3rd		29.1	42	0.00842	6.48	0.18
					Total,	67.79	1.86
4	1st	9.4830	33.3	32	0.14545	55.98	1.53
4	2nd		33.3	49	0.01155	4.45	0.12
					Total,	60.43	1.65

But, on the other hand, even boiling for several days with quite strong acid did not dissolve out all the nitrogen contained in the peat. Since the separation of different organic, nitrogenous bodies into groups can be accomplished only in an acid solution, the question as to whether it is possible to extract all the nitrogen from peat by means of acids was of considerable importance. To definitely decide this question, a few peat samples were boiled for a number of hours with fairly strong acid, filtered and thoroughly washed with hot water. The peat was re-extracted several times, being thoroughly washed with hot water after each extraction. The filtrates and washings, after each digestion, were filled up to a definite volume and the nitrogen estimated according to Kjeldahl's method. Table II contains the results obtained through repeated digestions.

In reviewing the results of Table II, we can readily see that the total amount of nitrogen extractable from peat can be increased a few per cent. by repeated digestion, although even in the latter case it was not possible to obtain all the nitrogen in solution, 68.32 being the highest percentage of nitrogen extracted with acid. However, taking into consideration experiments 12 and 13, of Table I, as well as experiment 1 of Table II, we are justified in saying that at least 70 per cent. of the nitrogen can be obtained in solution if the digestion with acid is performed with a brown peat that has passed through an 80-mesh sieve. But the question as to whether it is possible to extract all the nitrogenous bodies from peat by digesting with acid must be answered in the negative, at least this is true under the conditions given in Tables I and II.

Separation of the Organic Nitrogenous Bodies into Different Groups.

As already mentioned, practically all the nitrogen contained in the brown peat is of organic nature. The quite small amount of ammonia present as such in the peat is, it should be remembered, also represented in the total amount of ammonia obtained by distilling the acid-treated peat with magnesium oxide. Hence, we must subtract the ammonia present as such in the fresh peat from this total amount of ammonia in order to find the ammonia corresponding to the amides only. Table III shows the percentage of the different nitrogenous groups contained in the brown peat.

From Table III it can readily be seen that the strong acid (47.5 per cent.) gave about six per cent. more nitrogen in solution than the weaker acid, and that this nitrogen was chiefly amido nitrogen, and monamino nitrogen. When we consider the nitrogen in solution as 100 and reduce to this basis the data in Table III, we get the figures contained in Table IV.

The percentage of monamino nitrogen given in this table was found by difference from one hundred. This percentage was usually higher

TABLE III.—AMOUNT AND PERCENTAGE OF NITROGEN CONTAINED IN THE DIFFERENT GROUPS IN BROWN PEAT.

				Nitrogen extracted.			Ammoniacal nitrogen originally contained in peat.		
No. of expt.	Oven-dried peat. Grams.	Total nitrogen in peat. Gram.	Strength of H_2SO_4. Per cent. by weight.	Gram.	Per cent. of total nitrogen in peat.	Per cent. of oven-dried peat.	Gram.	Per cent. of total nitrogen in peat.	Per cent. of oven-dried peat.
1	9.483	0.25983	33.3	0.14545	55.98	1.53	0.00417	1.60	0.044
2	9.483	0.25983	33.3	0.1469	56.54	1.55	0.00360	1.39	0.038
3	9.483	0.25983	47.5	0.16020	61.65	1.69	0.00360	1.39	0.038
4	28.449	0.77950	47.5	0.49842	63.94	1.75	0.01252	1.61	0.044
Av.,	....	......	....	.....	59.53	1.63	.....	1.50	0.041

	Amido nitrogen.			Diamino nitrogen.			Monamino nitrogen.		
No. of expt.	Gram.	Per cent. of total nitrogen in peat.	Per cent. of oven-dried peat.	Gram.	Per cent. of total nitrogen in peat.	Per cent. of oven-dried peat.	Gram.	Per cent. of total nitrogen in peat.	Per cent. of oven-dried peat.
1	0.03570	13.74	0.376	0.00814	3.13	0.086	0.09744	37.51	1.03
2	0.03627	13.95	0.382	0.00828	3.19	0.087	0.09875	38.01	1.04
3	0.04694	18.06	0.495	0.00543	2.09	0.057	0.10423	40.11	1.10
4	0.14278	18.32	0.502	0.02681	3.44	0.094	0.31631	40.57	1.11
Av.,	.....	16.02	0.439	.....	2.96	0.081	.....	39.05	1.07

than the one directly found by Kjeldahlizing the filtrate from the phosphotungstic acid precipitate. For instance, in experiment 2 the percentage of monamino nitrogen directly found was only 62.83 and in experiment 3 it was 64.25 per cent. instead of 67.22 and 65.06, respectively. The chief reason why the direct determination usually gives too low a percentage of the monamino acids lies in the difficulty of a complete oxidation of the nitrogenous bodies in the presence of an excess of phosphotungstic acid.

TABLE IV.

	Per cent. of nitrogen in solution as				
Number of experiment.	Ammoniacal nitrogen originally contained in peat.	Amido nitrogen.	Diamino nitrogen.	Monamino nitrogen.	Total nitrogen in solution.
1	2.87	24.54	5.59	67.00	100
2	2.45	24.69	5.64	67.22	100
3	2.24	29.31	3.39	65.06	100
4	2.51	28.65	5.38	63.46	100
Average,	2.52	26.80	5.00	65.68	100

An attempt was made to isolate in substance and, if possible, to identify the diamino and monamino acids present in the peat. For this purpose a brown peat from Chelsea, Michigan, was used, of the same type as the one previously described. Its analysis, calculated to peat free of water and ash, gave: C, 60.03; H, 5.73; N, 2.38.

With this brown peat the following experiments were made:

To 54.94 grams of air-dried peat corresponding to 50 grams of oven-dried peat, a mixture of 150 grams concentrated sulphuric acid and 300 grams of water was added, then heated to the boiling point, and kept boiling under reflux condenser for 14 hours. During the boiling, development of hydrogen sulphide was noticed. (Hydrogen sulphide was detected when another sample of peat was digested with hydrochloric acid.) The flask content was filtered, the peat remaining on the filter was transferred to a flask, boiled with water, filtered and washed with hot water. These operations were repeated three times. Filtrate and washings were evaporated, filled up to 1000 cc., and two Kjeldahl determinations made to determine the amount of extractable nitrogenous bodies. The peat extract was then treated with a hot solution of barium hydroxide in order to remove nearly all the sulphuric acid. The barium sulphate was filtered out, boiled with water three times, and each time sucked off and thoroughly washed. Filtrate and washings were somewhat concentrated and then treated with magnesium oxide on a water bath until all ammonia was removed. Barium hydroxide solution was then added in excess; the precipitate, consisting chiefly of magnesium hydroxide and barium sulphate, was filtered out and then extracted three times with hot water. Filtrate and washings were then united and sulphuric acid added in some excess to remove the baryta. The filtrate containing the organic nitrogenous bodies was treated according to the method given by A. Kossel for the separation and identification of histidine and arginine as silver compounds. The result was a negative one.

The resulting filtrate from the above procedure was acidulated with sulphuric acid and treated with hydrogen sulphide. The new precipitate consisting of barium sulphate and silver sulphide was filtered out, extracted with hot water, the filtrate and washings were somewhat concentrated and sulphuric acid was added so as to make the solution contain five per cent. It was then treated with phosphotungstic acid. A precipitate was obtained which was washed with a five per cent. sulphuric acid and then treated with barium hydroxide to remove the phosphotungstic acid. The filtrate was freed from barium by means of carbon dioxide, evaporated nearly to dryness, taken up with hot water and filtered. The filtrate, when evaporated nearly to dryness, consisted of a few drops of a brown sirup. This, treated with picric acid, gave a yellow precipitate too small in quantity for identification.

The filtrate from phosphotungstic acid precipitate, supposed to contain monamino acids, was treated with barium hydroxide to remove the phosphotungstic acid and then treated with carbon dioxide to remove the excess of barium hydroxide. The filtrate from barium carbonate showed the Millon reaction. It was natural enough to think of tyrosine. On the other hand, it must be taken into consideration that nearly all benzene derivatives in which one hydrogen atom is replaced by the hydroxyl group give the same reaction. Considering the relation of peat to protein decomposition products, phenol, ortho- or paracresol or tyrosine were possible.

On adding iron chloride to the filtrate from barium carbonate, no violet or blue color reaction was noticed. Addition of bromine water did not cause any precipitate. These two negative reactions showed that the filtrate under consideration did not contain either phenol or cresol. The non-volatility of the substance in question spoke in favor of tyrosine; however, identification of the tyrosine by means of the microscope or Piria's test could not be accomplished, since the tyrosine was not obtained in substance. This will be comprehended when we state that altogether only 0.43 gram nitrogen was originally in the shape of organic compounds, of which a part was lost through a number of operations mentioned above, and that the remaining nitrogen was very likely present in the shape of various monamino acids.

Weathered Brown Peat.

It was of interest to learn whether the peat undergoes changes, and if so of what nature, when subjected to atmospheric influences. For this purpose a sample of brown peat was taken which had been weathering for two or three years on the surface of the bog. The analysis of this peat reduced to the water-free basis, gave: C, 54.35; H, 5.56; N, 2.69; S, 0.34; ash, 3.79; oxygen (by difference), 33.27.

The nitrogen of the peat was separated into the different groups. The results are given in the table below:

TABLE V.—AMOUNT AND PERCENTAGE OF NITROGEN CONTAINED IN THE DIFFERENT GROUPS IN WEATHERED BROWN PEAT.

				Nitrogen extracted.			Ammoniacal nitrogen originally contained in peat.		
No. of expt.	Oven-dried peat.	Total nitrogen in peat.	Strength of acid. Per cent. by weight.	Gram.	Per cent. of total nitrogen in peat.	Per cent. of oven-dried peat.	Gram.	Per cent. of total nitrogen in peat.	Per cent. of oven-dried peat.
1	9.596	0.25813	H_2SO_4 33.3	0.15735	60.96	1.64	0.00048	0.186	0.005
2	9.596	0.25813	HCl 38.0	0.17394	67.38	1.81	0.00048	0.186	0.005
Av.,					64.17	1.72		0.186	0.005

TABLE V (*Continued*).

	Amido nitrogen.			Diamino nitrogen.			Monamino nitrogen.		
No. of expt.	Gram.	Per cent. of total nitrogen in peat.	Per cent. of oven-dried peat.	Gram.	Per cent. of total nitrogen in peat.	Per cent. of oven-dried peat.	Gram.	Per cent. of total nitrogen in peat.	Per cent. of oven-dried peat.
1	0.03773	14.62	0.393	0.0	0.0	0.0	0.11914	46.15	1.24
2	0.04058	15.72	0.423	0.0	0.0	0.0	0.13288	51.48	1.38
Av.,	....	15.17	0.408	...	0.0	0.0	....	48.81	1.31

By calculating the data in Table V to the nitrogen in solution as a basis, we get the following table:

TABLE VI.

	Nitrogen in solution as				
Number of experiment.	Ammoniacal nitrogen originally contained in peat.	Amido nitrogen.	Diamino nitrogen.	Monamino nitrogen.	Total nitrogen in solution.
1	0.30	23.99	0.0	75.71	100
2	0.28	23.33	0.0	76.39	100
Average,	0.29	23.66	0.0	76.05	100

When we compare Tables V and VI with Tables III and IV, we can readily see that certain changes took place in the nitrogenous groups by virtue of the agencies active in the weathering process. In the first place we notice that whereas in the brown peat, prior to the weathering process, the percentage of ammoniacal and amido nitrogen was 0.041 and 0.439, it changed to 0.005 and 0.408, respectively, in the weathered peat. Thus, through the weathering, a total decrease of 0.067 per cent. of ammoniacal and amido nitrogen took place, through leaching or some other cause. This may account for the fact that while the brown peat had 2.52 per cent. of ammoniacal and 26.80 per cent. of amido nitrogen, the weathered brown peat had 0.29 per cent. and 23.66 per cent., respectively, calculated to the nitrogen in solution as basis. This, as well as the disappearance of the diamino nitrogen in the weathered peat, must have necessarily increased the percentage of monamino acids in the weathered peat. It should, however, be borne in mind that, while the estimations of ammoniacal and amido nitrogen give accurate results, the determination of diamino nitrogen is not quite satisfactory. This influences, of course, the monamino nitrogen, since the latter is calculated by difference.

Considering the changes in the weathered peat, the assumption was justified that the solubility of the nitrogenous substances in the peat must have changed. From Table I it was evident that the solubility in water of the nitrogenous bodies contained in the brown peat is very small. It was of interest to learn the solubility in water of the weathered brown peat. For this purpose a few grams of peat were transferred to a flask, a definite amount of water added, mixed, digested, then filled up usually to 500 cc., mixed, filtered, through a dry filter, and two portions of 200 cc. each taken for Kjeldahlization. The nitrogen thus found was recalculated to the total volume. Table VII shows the results of these experiments:

TABLE VII.—THE SOLUBILITY IN WATER OF THE NITROGENOUS BODIES IN WEATHERED BROWN PEAT.

					Nitrogen extracted.		
Number of experiment.	Oven-dried peat. Grams.	Distilled water. Grams.	Hours digested.	Method of digestion.	Gram.	Per cent. of total nitrogen in peat.	Per cent. of oven-dried peat.
1	4.798	400.0	10	Autoclave at $^3/_4$ to $^7/_8$ atm. pressure,	0.01172	9.08	0.25
2	2.8788	300.0	16	Boiling under reflux condenser,	0.00685	8.85	0.24
3	4.798	500.0	60	Shaken 10 minutes each hour, room temperature,	0.00300	2.32	0.06

From these experiments it follows that the solubility in water of the nitrogenous compounds in the weathered brown peat increases with the rise of temperature. This was also the case with the brown peat as dug from the bog, as can be seen from experiments 10 and 11, in Table I, and holds true also for the black peat. In other words, the solubility in water of the nitrogenous compounds in the various types of Michigan peat is in certain limits a function of the temperature. This being the case, we can further assume that the peats digested at higher temperature and pressure in a suitable autoclave will give a larger amount of water-soluble compounds than was obtained, for instance, in experiment 1, Table VII. That digestion at a higher temperature gives a higher percentage of water-soluble nitrogenous compounds is very likely due, in part, to hydrolysis of the nitrogenous bodies present in the peat.

By comparing Tables IV and VI it is readily seen that only about ten per cent. of the nitrogen in acid solution (and still less of the total nitrogen in the peat) has changed during weathering during two or three years, and that, in addition, the changes of the nitrogenous bodies did not go far enough to be converted, for instance, into ammoniacal nitrogen.

Conclusions.

While the data in hand do not warrant conclusive deductions as to the agricultural value of peat soils, for which further investigation will be necessary, the results obtained and given in this paper permit of drawing the following conclusions:

1. There are no nitrates in the types of Michigan peat soil examined.
2. The amount of ammonia is small, ranging from a few thousandths to a few hundredths of one per cent., this representing the nitrogen available immediately as plant food. In the case of the brown peat, the amount of ammonia is sufficient to meet the needs of one or two crops, as is evident from the following: There are in an acre-foot in round numbers 170 tons of oven-dried peat, with 0.041 per cent. ammoniacal nitrogen, making 0.0697 ton or 139.4 pounds nitrogen as ammonia.
3. Practically all the nitrogen in the peat is of organic nature.
4. The bulk of the organic nitrogen, namely from two-thirds to three-quarters calculated upon the nitrogen in solution, by boiling with acids, is present in the form of monamino acids, about one-quarter in the form of amides and the rest of the nitrogen represents diamino acids.
5. Through weathering, the organic nitrogenous bodies present in the brown peat change quite slowly.

REVIEW.

SOME RECENT ADVANCES IN ORGANIC CHEMISTRY.

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By L. H. Cone.

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Among the advances in organic chemistry during the last few years which have been remarkable for the difficulty of the experimental work involved are those which have been made at the border line between pure organic and physiological or biochemistry. These have deservedly attracted very wide attention.

Proteins.—Naturally one thinks first of Fischer's already classic work on the proteins when biochemistry is brought under discussion. This work has been steadily continued and polypeptides have been prepared of every naturally occurring amino acid, with the exception of five, which are very difficult to obtain or for which special methods will have to be worked out. The number of polypeptides isolated from the partial hydrolysis of proteins has constantly increased and five of these so isolated have been found to be entirely identical with those previously prepared synthetically in the laboratory.[1] Thus Fischer's theory of the protein constitution has been steadily strengthened. A discussion of the impetus which this theory has given to the more scientific study of problems of digestion, of assimilation, and of ferment action, lies without the province of this review, but a casual glance at the physiological literature will show the valuable service which the theory is rendering.

Early in the study of the polypeptides it became apparent that in order to obtain any large number of derivatives of the hydroxyamino acids some method would have to be devised for the temporary protection of the hydroxyl group so that hydroxyamino acid chlorides could be pre-

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[1] "Abderhalden-Physiologische Chemie," 2nd Edition, p. 258 (1908).