pholytic acid,[1] taking up the hydrobromic acid asymmetrically. The *d*-campholytic acid would, of course, give *l*-dihydrohydroxycampholytic acid in a similar manner. It is probable from this that the left form of the hydroxy acid is more stable than the expected isodihydrohydroxycampholytic acid and that a portion of the latter is transformed to the former by the action of the nitrous acid—or it may be that *d*-campholytic acid is formed as an intermediate product and that this adds water to form the *l*-dihydrohydroxycampholytic acid.

The study of these compounds will be continued.

URBANA, ILL.

[CONTRIBUTION FROM THE LABORATORY OF SOIL FERTILITY INVESTIGATIONS.]

SOME ACID CONSTITUENTS OF SOIL HUMUS.[2]

BY OSWALD SCHREINER AND EDMUND C. SHOREY.

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The complex character of the humus or organic matter of the soil need hardly be emphasized here, nor need the complexity of the so-called humic acid be again mentioned other than to remark that so many organic compounds, neutral, basic and acid, have been isolated therefrom in these researches that its claim to chemical unity is absolutely refuted and its non-existence proved. The present paper is a further contribution to the definit knowledge of the chemical nature of this organic soil complex and gives a description of several acids isolated therefrom. The isolation of other acid substances from soils, picolinecarboxylic acid, dihydroxystearic acid and agroceric acid, are reported in earlier papers.[3]

α-Monohydroxystearic Acid, $C_{18}H_{36}O_3$.—When the humus extract of a soil obtained by extraction with dilute alkali is acidified, a brown, flocculent precipitate of the so-called humus substances is formed. If this precipitate is separated by filtration, washed and treated while still moist with boiling 95 per cent. alcohol, a portion of the precipitate goes into solution. The amount of the humus precipitate so dissolved varies with the character of the soil treated, but the alcoholic solution obtained in this way is always dark-colored. On careful evaporation of this alcoholic solution, adding water to keep the volume constant until the alcohol is removed, there is formed a brown or reddish brown precipitate which can be separated by filtration. When so separated, washed and dried, it is in the form of resinous lumps or powder, varying in color, melting point and composition, with the soil from which it was obtained.

On extracting this resinous material with petroleum ether there is obtained an extract generally colorless or light-colored, which on evapora-

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[1] Noyes and Phillips, *Am. Chem. J.*, 24, 24, 291.

[2] Published by permission of the Secretary of Agriculture.

[3] THIS JOURNAL, 30, 1295, 1599 (1908); Bureau of Soils, U. S. Dept. Agr. *Bull.* 53, (1909).

tion of the petroleum ether leaves a residue which may vary from an oily, semi-solid mass to a waxy solid. This residue is generally wholly soluble in hot alcohol. From this alcoholic solution there sometimes separates on cooling a white or yellowish microcrystallin mass or powder which in the case of one soil has been identified as α-hydroxystearic acid.

The soil from which this compound was obtained was a sample of Elkton silt loam, a type covering a considerable area in Maryland. This soil is almost white in color, high in clay and silt and contains 0.53 per cent. organic carbon and 0.066 per cent. nitrogen. The sample examined was one of several hundred pounds obtained from the eastern shore of Maryland.

This soil when treated with 2 per cent. sodium hydroxide solution yields an extract much darker than might be expected from a soil so light in color. From this brown alkaline extract there is precipitated on acidifying with sulphuric acid a brown, flocculent mass. On separation of this by filtration, washing and treating with boiling 95 per cent. alcohol, there is obtained an alcoholic solution nearly as dark in color as the original alkaline extract. The precipitate formed by evaporation of the alcohol and addition of water was, after filtration, washing and drying, a brown mass easily pulverized.

Extraction of this brown powder with petroleum ether and evaporation of the solvent left an oily, semi-solid, light-yellow mass, which was completely soluble in hot 95 per cent. alcohol. On cooling, this alcoholic solution there separates a yellow, microcrystallin powder, which after separation by filtration, washing with cold alcohol, dissolving again in hot alcohol, and repeating the separation several times, can be obtained free of color and of constant melting point.

The substance so obtained melts at 84–85°, is soluble with difficulty in cold alcohol, readily in hot alcohol, cold ether or petroleum ether. It crystallizes usually in small irregular leaflets, but can be crystallized from alcohol by very slow cooling, in six-sided plates. It forms salts with alkalies soluble in water and can be obtained from such solution unchanged by acidifying and extracting with ether.

The analysis of this compound gave the following:

Calculated for $C_{18}H_{36}O_3$: C, 72.00; H, 12.00.
Found: C, 72.09; H, 12.17.

This composition corresponds with that of the monohydroxystearic acids, two of which are known, designated α and β, respectively, and having the formula $C_{18}H_{36}O_3$. The properties of the acid isolated from the soil fix it as the α acid. The α acid is much less soluble in alcohol than the β acid and the β acid, moreover, forms an anhydride on heating with strong hydrochloric acid, which is not the case with the α acid nor the acid from the soil. The melting points of the α and β acids are so nearly the same that this property cannot be used to distinguish between them. The melting point of the pure α acid artificially prepared remained unchanged on mixing with the acid from the soil. This fact, together with the composition found and sparing solubility in alcohol and failure to form an anhydride, is sufficient to establish the identity of the acid from the soil as α-monohydroxystearic acid.

α-Hydroxystearic acid is easily made in the manner described by Sadomsky.[1] When stearic acid is treated with red phosphorus and bromine, α-bromostearic acid is formed. On heating this with alcoholic potash the potassium salt of α-hydroxystearic acid is formed and on acidifying the aqueous solution of this salt the acid is set free and can be extracted with ether.

α-Hydroxystearic acid is not known to occur in any natural animal or vegetable product and up to the present has been isolated from only one soil.

Two hydroxy acids of the fatty series have been isolated from soils, but neither are known as natural products. These are α-hydroxystearic acid and the dihydroxystearic acid previously described.[2] Both must be looked on at present as the products of the action of microörganisms, probably fungi, on some of the organic matter known to be of plant or animal origin.

While at present little is known of the processes by which these compounds are formed in the soil and little can be said that is not of a speculative nature, it may be of interest at this point to note the laboratory methods by which hydroxy acids are formed. Three general methods are known by which the hydroxy acids are formed from the corresponding acid. These are: Making a halogen substitution product and treating this with silver oxide and water; making an amino derivative and treating this with nitrous acid; and making a sulphonic acid derivative and treating it with caustic potash.

In attempting to find a parallel between these reactions and the processes likely to take place in the soil, the second method seems to be the only one that offers any foundation for a theory. It is known that amino compounds result from the decomposition of more complex nitrogenous compounds and may possibly be formed or built up by the action of ammonia, which is commonly formed in soils. Nitrous acid, as the result of denitrification or as the first stage in the change of ammonia into nitrates, is formed in nearly all soils and would supply the reagent required in the second stage of the reaction.

In addition to these purely chemical methods of formation, there are to

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[1] *Ber.*, 24, 2388 (1891).

[2] Bureau of Soils, U. S. Dept. Agr., *Bull.* 53, (1909). THIS JOURNAL, 30, 1599 (1908).

be considered the biological formations by fungi or bacteria, but this would lead somewhat afield from the purposes of the present article.

While α-hydroxystearic acid is not known as a natural product, it must be remembered that natural fats and oils are usually complex mixtures of glycerides and that the chemistry of such glycerides as occur in these products in small amounts is very incomplete. More complete chemical knowledge of the natural fats and oils may show the presence of α-monohydroxystearic acid. The method of its laboratory preparation does not suggest any possible parallelism in the soil as was the case when the origin of dihydroxystearic acid was under discussion.

In the earlier literature of the hydroxystearic acids there is some confusion of nomenclature, as well as disagreement regarding their constitution. The β acid described by Saytzeff[1] was designated as the α acid by Geitel.[2] The designations α and β acid seem to have been primarily used to distinguish isomers, the constitutions of which were not known. The constitution, as now accepted and established by Shukov and Shestakov[3] is not in harmony with the common meaning of α and β designations. In the simple hydroxy fatty acids the term α is applied to that acid having the hydroxyl group next the carboxyl group; for example, α-hydroxypropionic acid (lactic) is represented thus: $CH_3.CHOH.COOH$; the term β is applied to that acid having the hydroxyl on the second carbon atom; for example, β-hydroxypropionic acid (hydracrylic) is represented thus: $CH_2OH.CH_2COOH$. The constitution of the α and β-hydroxystearic acids is represented as follows: α acid, $CH_3(CH_2)_6CH.OH(CH_2)_9COOH$; β acid, $CH_3(CH_2)_7CH.OH(CH_2)_8COOH$. In neither case is there α or β structure. The authors in discussing these formulas used the designations: 1.11 for the α acid, and 1.10 for the β acid, 1 being the carbon atom of the carboxyl group and 10 and 11 the carbon atoms counting from 1 to which the hydroxyl group was attached. Since, however, these acids are still generally described and referred to in the literature as α and β, these terms have been used in this paper with this explanation.

Paraffinic Acid, $C_{24}H_{48}O_2$.—The cold alcoholic solution from which α-hydroxystearic acid has separated in the manner just described is yellow in color and evaporation of the alcohol leaves a semi-solid, oily mass. On standing some time crystals form in this mass, but the nature of the material was such that they could not be separated without great loss and so this was not attempted. The oily mass was dissolved again in alcohol and an alcoholic solution of lead acetate added. This gave a yellow precipitate which was separated by filtration, washed with alcohol,

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[1] *J. prakt. Chem.* (2), 35, 369 (1887).

[2] *Ibid.* (2), 37, 53 (1888).

[3] *Ibid.* (2), 67, 414 (1903).

suspended in alcohol and treated with hydrogen sulphide. After separation from the lead sulphide the alcoholic solution was allowed to evaporate slowly, leaving a somewhat waxy mass of leaflets. This mass was purified by dissolving again in alcohol and repeating the operation of precipitation with lead acetate and finally drying on a porous plate. The body so obtained was light yellow in color and melted at 45–48°. Analysis gave the following figures:

Calculated for $C_{24}H_{48}O_2$: C, 78.20; H, 13.00.
Found: C, 78.40; H, 13.29.

This composition, the melting point and physical properties correspond with paraffinic acid, $C_{24}H_{48}O_2$, described by Pouchet[1] as obtained by the action of fuming nitric acid on paraffin.

The research of Pouchet on which alone the existence of paraffinic acid rests is, as published, inconclusive as to its being a definit chemical compound. The quantity of this substance obtained from the soil was insufficient for any extended research and so far the character of the compound obtained from paraffin has not been studied except that the following facts were established. Paraffin was treated with fuming nitric acid in the manner described by Pouchet and a compound obtained having the properties and composition stated by him. Elementary analysis of this substance gave the following figures:

Calculated for $C_{24}H_{48}O_2$: C, 78.2; H, 13.0.
Found: C, 78.1; H, 13.3.

The properties and composition of this compound corresponded with those of the substance obtained from the soil and there is little doubt that whatever may be the nature of the two substances, they are identical. With this understanding, the name paraffinic acid is applied to the soil compound. This body has so far been obtained from but one soil, the Elkton silt loam already described. A number of soils have been examined that gave at the point where paraffinic acid was obtained in the case of the Elkton silt loam a precipitate with alcoholic lead acetate, but the quantity of material has been either too small for identification or has had other properties and composition.

Very little can be said regarding the possible origin of paraffinic acid in the soil. Several solid hydrocarbons of the paraffin series have been shown to occur in plants and may therefore be a part of the organic matter added to the soil. Oxidation of these in the soil might give rise to the substance found.

It may be noted in this connection that it is well established that paraffin can be oxidized in the laboratory, but usually by rather vigorous treatment. Gill and Mensel[2] found that on treating paraffin with dilute

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[1] *Bull. soc. chim.*, 23, 111 (1875).

[2] *Zeit. Chem.*, 1869, 65.

nitric acid or chromic acid it was oxidized to cerotic acid, $C_{27}H_{54}O_2$, acetic acid and succinic acid. Pouchet in the research referred to found succinic acid in addition to paraffinic acid, but no cerotic acid.

Lignoceric Acid, $C_{24}H_{48}O_2$.—When a soil high in organic matter is carefully heated in a closed tube, there is obtained a dark-colored, tarry distillate, which in some cases sets on cooling to a semi-solid, crystallin mass.

A peat soil containing 27 per cent. of organic carbon treated in this way gave a distillate of this character in considerable quantity. The semi-solid mass on washing with cold alcohol was freed from much of its color with little loss of solid matter. The material so washed was completely soluble in hot alcohol from which it separated on cooling in microcrystallin form. On repeating this solution and separation several times the material was obtained nearly free of color. Treatment at this stage with cold petroleum ether removed the remaining color and a small quantity of oily matter. The body after this purification melted at 80–81°, was soluble in ether and hot alcohol, little soluble in cold alcohol and insoluble in water. Its elementary composition was found to correspond to the formula, $C_{24}H_{48}O_2$.

Calculated for $C_{24}H_{48}O_2$:	C, 78.2;	H, 13.0.
Found:	C, 78.1;	H, 13.2.

The compound dissolved in aqueous alkalies and was set free from such solution unchanged on addition of a mineral acid. The properties, melting point and composition indicate the identity of this compound as lignoceric acid first described and obtained by Hell and Hermanns[1] from the solid residue or "paraffin" of beechwood tar. It is also found[2] as a glyceride in peanut oil.

It is generally assumed that the lignoceric acid found in wood tar is the result of decomposition effected by the method of treatment and that it does not occur as such in the wood. In the case of the soil, however, certain observations indicated that this might not be the case. It was observed that if the soil was heated to a high temperature or the heating done rapidly the yield of solid matter in the distillate was very small. When the heating was done carefully and the temperature raised only to the point where a distillate could be obtained, the solid product seemed to be the result of distillation directly from the soil and when the operation was carried on in a glass tube such distillation could actually be observed, the melted distillate collecting on the upper, cooler side of the tube and being driven forward as heat was applied, just as water would be. It was also found that the purified lignoceric acid obtained from the soil

[1] *Ber.*, 13, 1713 (1880).

[2] Kreiling, *Ber.*, 21, 880 (1888).

in the manner described could by careful heating be distilled with little or no decomposition.

With the object of extracting the lignoceric acid from the soil if it existed as such, the soil was treated with boiling 95 per cent. alcohol, the extract filtered hot and allowed to cool. On cooling, a voluminous precipitate separated from the dark-colored extract. This was separated by filtration and purified by dissolving several times in hot alcohol from which it separated on cooling and finally by washing with cold petroleum ether. The compound so obtained corresponded in all properties with that obtained by distillation. It melted at 80–81° and elementary analysis gave the following figures:

Calculated for $C_{24}H_{48}O_2$: C, 78.2; H, 13.0.
Found: C, 78.2; H, 13.8.

The identity of the two compounds obtained from the soil by distillation and by extraction with hot alcohol is thus established. It follows that lignoceric acid exists in the soil as such.

Regarding the source of the lignoceric acid in the soil there are two possibilities suggested by our knowledge of the compound. It is, as has been already stated, present in peanut oil as a glyceride and may be a component of other vegetable oils and be somewhat widely distributed in plants in small amounts, in which case it might occur in the soil as a residue of the decomposition of such glycerides.

Lignoceric acid is obtained by the distillation of wood, presumably through the decomposition of woody tissue. It is possible that similar decomposition through the agency of microörganisms may take place in the soil.

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PENTOSANS IN SOILS.[1]

BY EDMUND C. SHOREY AND ELBERT C. LATHROP.

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Carbohydrates, represented by sugars, starch and compound celluloses, make up by far the greater portion of the organic substance of plants and so form the greater portion out of which soil organic matter is made. The extreme susceptibility of these substances to fermentation or decomposition by microörganisms renders them, probably, the most unstable organic material added to soils. Sugars and starch are used by a great variety of bacteria and fungi as food and no doubt disappear as such long before the cell tissues break up and become part of the soil. The cell wall and fibrovascular tissues are made up for the most part of a complex compound containing a carbohydrate or cellulose radical. These resist

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[1] Published by permission of the Secretary of Agriculture.