$C_3H_5.C_6H_4OCH_3$, oil of cloves, eugenol, $C_3H_5C_6H_3(OCH_3)OH$, and oil of parsley, apiole, $C_3H_5C_6H(OCH_3)_2:O_2:CH_2$.

From the point of view of the origin of this radical in soil organic matter its occurrence in woody tissue is most important. Benedict and Bamberger[1] determined the methoxyl in a large number of woods and found it to be fairly constant, the methoxyl calculated as $CH_3$ was usually between two and three per cent., the extremes being 1.99 and 3.21 per cent., and they suggested this determination as a method of arriving at the quantity of wood cellulose in a mixture such as paper. It has been found that methoxyl is always a constituent of the lignocellulose or so-called compound cellulose of higher plants but the quantity in grasses, shrubs, etc., varies much more than in woods.

With these three sources of methoxyl compounds in mind it is clear that in the death and decay of vegetation all soils are having added to them organic material containing this radical. The fact that the quantity of methoxyl in soils varies and bears no relation to the total organic matter is no doubt due in part to variation in the composition of the vegetation that is the source of the organic matter, but the fact that it persists or forms in one soil and disappears in another of the same general type indicates that the processes of decay are quite different in different soils.

The methoxyl group then constituting but a small, and perhaps unimportant, part of the soil organic matter, by its presence or absence, or when present, by its proportion to the total organic matter, demonstrates one form of variation of soil organic matter. This or any other variation when found in soils of the same type and supplied with organic material from the same general source must be regarded as proof of some fundamental difference in the chemical, physical or biological factors that decide in what way a complex organic compound shall break down or decay when added to a soil.

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[CONTRIBUTION FROM THE LABORATORY OF SOIL FERTILITY INVESTIGATIONS.]

# GLYCERIDES OF FATTY ACID IN SOILS.[2]

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The oils, fats and waxes are widely distributed in plants and animals and it follows that considerable quantities of these materials get into the soil and form the material from which soil organic matter is made. From the evidence at hand in the form of substances isolated from soils, it is clear that in some soils, at least, these compounds persist unchanged.

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[1] *Monatsh. Chem.*, 11, 260 (1890).

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

The isolated substances represent esters in the form of glycerides and higher alcohols.

The presence of unchanged plant glycerides in the soil is of interest in view of the number of substances of a fatty nature which have already been isolated from soils. In discussing the possible origin of dihydroxystearic acid in the soil, it was pointed out that oleic acid in the form of a glyceride was a nearly universal plant constituent and that it was possible that dihydroxystearic acid might be formed from it in the soil in somewhat the same way as in the laboratory.[1] Cholesterol-like compounds seem to occur frequently in soils[2] and oleic acid or olein may have some relation to the occurrence of this group, inasmuch as Lifschütz[3] has shown that cholesterol compounds may be formed by the oxidation of oleic acid.

The glyceride described in this paper was obtained from the Elkton silt loam as the final step in the treatment which resulted in the isolation of α-hydroxystearic acid and paraffinic acid. So far all soils examined in this manner give at this stage an oily, semi-solid mass similar in appearance to that obtained from the Elkton silt loam. In only a few cases, however, has sufficient material been obtained to establish its identity as a glyceride.

*Glycerides of Fatty Acids.*—When the alcoholic filtrate from the lead precipitate of paraffinic acid obtained in the isolation of this compound in the manner described in a previous paper[4] is freed from lead by hydrogen sulfide and the alcohol evaporated, there is left an orange-colored oil which remains clear and liquid at room temperature, but becomes turbid on cooling, crystallin material finally separating. This oil on examination proved to be a mixture of glycerides of fatty acids as are most natural oils.

The oil obtained in the manner just described is slightly acid to litmus and has an odor not unlike that of olive oil. Its specific gravity at 26° is 0.935. On saponification with alcoholic potash and evaporation of the alcohol, a soap was obtained completely soluble in water. When the soap solution was acidified with sulfuric acid the fatty acids were set free and extracted by shaking with ether. The mixture of fatty acids obtained on evaporating the ether was a fatty, semi-solid mass from which crystallin leaflets separated on standing. This mass immediately after removal of the ether had an odor suggesting capric acid, but this disappeared in a short time, leaving a tallow-like odor. On shaking the mixed fatty acids with equal parts of nitrosylsulfuric acid and water, a solid mass was obtained on standing, thus showing the presence of oleic acid. The

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

[2] THIS JOURNAL, **31**, 116 (1909).

[3] *Z. physiol. Chem.*, **55**, 1 (1908).

[4] THIS JOURNAL, **32**, 1674 (1910).

original glyceride behaved in the same manner, indicating the presence of oleic acid or olein in the oil. The presence of oleic acid or at least of some unsaturated acid was confirmed by the fact that the acid mixture when dissolved in carbon tetrachloride decolorized bromine without setting free hydrobromic acid.

In the water solution left after acidifying the soap solution and extracting with ether, the presence of glycerol was shown by the usual tests. The acid liquid was evaporated nearly to dryness and mixed with a small quantity of potassium hydrogen sulfate and the mass so obtained heated in a test tube provided with a stopper and delivery tube which dipped beneath the surface of a few cubic centimeters of water in a second tube. The presence of acrolein in the second tube, as a result of the distillation of glycerol, was established by the characteristic odor and by the generation of a pink color when treated with fuchsin-aldehyde reagent.[1]

The fact then that the oil obtained from the soil is a glyceride is established first by the changed character of the material after saponification and second by the presence of glycerol in the saponification products. It is, of course, possible that there is some free acid present in the oil, but the indications are that such must be small, if any. That the oil is a mixed glyceride is established by the complex character of the fatty acids obtained on saponification, a semi-solid mass from which crystallin material separated, oleic acid also being present.

When the soap solution resulting from the saponification of this oil is dried and extracted with petroleum ether and the ether evaporated, there is obtained a small quantity of unsaponified material. This forms a soft, waxlike mass insoluble in water, but soluble in soap solution. This material gave the Liebermann's cholesterol reaction strongly, but it was not possible to obtain from it any definit crystals of any cholesterol compound.

The oil obtained from the soil is, therefore, a glyceride of fatty acids containing a small quantity of unsaponifiable material and possibly a small quantity of free acid. As such then it corresponds in all particulars with natural glycerides, especially the vegetable oils.

The presence of glycerides similar to natural oils in the soil can perhaps best be explained on the ground that they are unchanged plant residues which have resisted decomposition. Nearly all plants at some stage of their development contain glycerides and they may also be built up by microörganisms as with other plants. They are probably not formed by purely chemical reactions such as are likely to take place in the soil.

BUREAU OF SOILS, WASHINGTON.

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[1] A solution of fuchsin decolorized with sulphur dioxide.