[CONTRIBUTION FROM THE LABORATORY OF SOIL FERTILITY INVESTIGATIONS.]

PARAFFIN HYDROCARBONS IN SOILS.[1]

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The paraffin hydrocarbons represent the simplest form of organic compounds and are widely distributed in nature. The lowest member of this group, methane or marsh gas, CH_4, is a constant product of the decomposition of organic matter under certain conditions. Higher members of the group, liquid and solid, occur as mixtures very widely distributed in the earth's crust as petroleum, asphalt, or similar deposits and also in mineral resins. The occurrence of paraffin hydrocarbons in plants is not very common and so far as observed is confined to a few members of the group and to a few species of plants. The large deposits in the earth's crust cannot, then, be attributed to the accumulation of unchanged plant residues; and a great many theories have been propounded to account for these deposits, most of them based on some transformation of organic material.

In spite of the fact that these hydrocarbons are of rather rare occurrence in plants and are seldom added to soil in plant débris, the wide distribution of extensive deposits of such compounds and the occurrence also of mineral resins and shales from which hydrocarbons can be obtained in the rocks from which soils are formed might lead one to expect to find some trace of these compounds in the soil. The question is also raised by this consideration whether some of the processes by which hydrocarbons have been formed from more complex organic compounds may not take place in the soil and escape recognition because the conditions are not favorable for the accumulation of these products in the soil. The production of the simplest paraffin hydrocarbon, methane, is known to take place in soil organic matter when submerged under water, as in swamps. The production here is supposed to be due to the activity of anaërobic microörganisms, but it is not known that absolutely anaërobic conditions are essential to this production or that methane may not be formed in small quantities in ordinary soils. Methane is present in the gases from the combustion of fuel, even when excess of oxygen is available and it has been found in the combustion of organic compounds in elementary analysis that some of the carbon may be present in the products of combustion as methane instead of carbon dioxide, and this when the combustion was carried on in pure oxygen. It may be, therefore, that in the decomposition of organic matter the formation of methane rather than carbon dioxide depends on the structure or constitution of a portion of the material decomposed and similarly more complex members may also be split off

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

One paraffin hydrocarbon has been isolated from a soil and while in this particular case there is nothing to indicate that it may not be an unchanged plant residue, the isolation is of interest not only in accounting for a small portion of the organic matter, but also in that it opens up the question of a possible connection between the processes that go on in the soil and the processes by which paraffin hydrocarbons have been formed in nature.

Hentriacontane, $C_{31}H_{64}$.—A peaty soil from North Carolina containing 27 per cent. organic carbon, when extracted with boiling 95 per cent. alcohol yields a dark-colored extract from which on cooling a light yellow microcrystallin substance separates. This material was separated by filtration and the alcohol removed from the filtrate by evaporation, the volume being kept constant by the addition of water. There was formed a reddish-brown precipitate, which after separation and washing was in the form of a brown resinous powder. Extraction of this with boiling petroleum ether yielded a light-colored solution, which after removal of the petroleum ether left a light yellow, oily residue. This was saponified with alcoholic potash, the alcohol removed and the soap dried and extracted with petroleum ether. On evaporation of the petroleum ether the residue was a light-colored, waxy mass completely soluble in a relatively large volume of hot alcohol. On cooling the alcoholic solution thus obtained, there was a separation of a feathery microcrystallin substance which was collected, washed and purified by recrystallizing several times from alcohol.

As thus obtained, the compound was a hard, waxy mass, melting at 68° and having a specific gravity of 0.780 at its melting point. It was soluble in ether and petroleum ether, difficultly soluble in hot and very little soluble in cold alcohol. It was unacted on by fuming nitric acid at room temperature and did not absorb bromine.

The elementary composition as well as its resistance to nitric acid shows it to be a hydrocarbon and its behavior toward bromine that it must be a saturated compound. The melting point indicates hentriacontane. While it is difficult to obtain paraffin hydrocarbons in a condition of absolute purity, an elementary analysis gave the following figures:

	Found.	Calculated for $C_{31}H_{64}$.
Carbon	84.14	85.22
Hydrogen	15.11	14.78

Hentriacontane is a member of the paraffin series found in the paraffin residue of some petroleums. It has also been found in beeswax together with another member of the same series, heptocosane, $C_{27}H_{56}$.[1] It occurs

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[1] Schwalb, *Ann.*, **235**, 117 (1886).

also in some plants, having been found in the leaves of *Gymnema sylvestre*,[1] in tobacco leaves,[2] and in East India ko-sam seeds, *Brucea sumatrana*.[3] With this information regarding its occurrence as a natural product and in the absence of any information regarding the possibility of its formation from other soil organic matter, this paraffin hydrocarbon may be regarded as an unchanged plant residue.

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CONVENIENT ATTACHMENTS FOR A MELTING-POINT APPARATUS.

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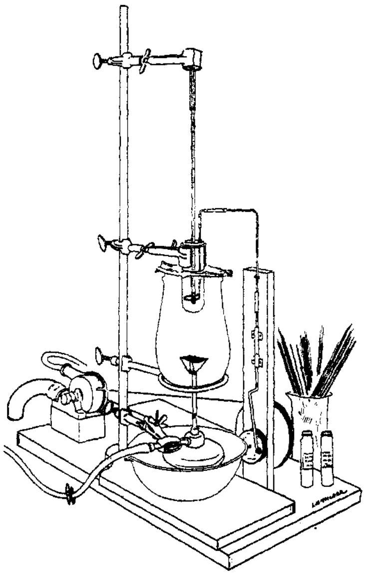
In a bulletin[4] of the Hygienic Laboratory entitled "A Study of Melting-Point Determinations," Dr. Geo. A. Menge describes a simplified form of melting-point apparatus which he found, after numerous experiments, to embody all the essential features required for the practical and reasonably accurate determination of melting points. In using the apparatus it was specified that the bath be constantly stirred during the determination and that the heat be applied in such a manner that the rate of rise of the temperature remain constant (3 degrees per min.) over a range of 20° immediately preceding the temperature of melting and at a slower constant rate ($^1/_2$ degree per min.) while the compound was melting. To accomplish this it was necessary to operate the stirrer continually with one hand and the Bunsen burner with the other. Although this cannot be called a difficult feat for most persons it was apparent that a certain amount of skill and practice would be required on the part of some individuals. It was on this account, therefore, that it appeared desirable to devise attachments to operate the stirrer automatically and



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[1] Power and Tutin, *Pharm. J.*, [4] 19, 234 (1904).

[2] Thorpe and Holmes, *J. Chem. Soc.*, 79, 982 (1901).

[3] Power and Lees, *Pharm. J.*, [4] 17, 183 (1903).

[4] *Bull.* 70, Hygienic Laboratory, U. S. P. H. and M.-H. Service, Washington, October, 1910.