CLXI. AN UNUSUAL TYPE OF FATTY COMPOUND IN A PRODUCT OF ANIMAL ORIGIN.

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SOME time ago one of us [Funk, 1923] reported the presence of a fatty substance of M.P. 52° in all samples of caseinogen, except those which have been subjected to prolonged extraction with boiling alcohol. Extraction with ether apparently does not remove this substance to any extent. It was thought at first that this substance might be of biological importance, but specially conducted feeding experiments on rats proved that this was not so. However, on close investigation, the substance proved to be a rather peculiar combination of fatty acids. Neutral in nature, it could be regarded as a glyceride, but on saponification it yielded only a fatty acid, in slightly higher yield than the original substance taken. The fatty acid is probably one of the hydroxystearic acids, two molecules of which form an anhydride. On account of difficulty encountered in purification, and a rather low melting point for such a high-carbon acid, we consider it not impossible that our purest product is contaminated with the next homologue, hydroxyarachidic acid. From the analytical figures it is even possible that we are dealing with a mixed anhydride of these acids.

Erben [1900] has reported the isolation from the urine of a case of chyluria of a substance of M.P. 51.5° , which he regarded as a mixture of hydroxystearic acids. Lanocerin, according to Röhmann [1906], is an anhydride of lanoceric acid, a hydroxy acid.

EXPERIMENTAL.

Caseinogen is repeatedly extracted under a reflux condenser with boiling alcohol, and on cooling our fatty substance separates out. The combined yield reaches 1.5 %. On recrystallisation from alcohol, a small insoluble residue remains behind, and the substance is obtained in the crystalline state, with an indefinite melting point of about 49° . After repeated crystallisation from ether and ethyl acetate the substance melted at $55-55.5^{\circ}$ and solidified at 44.5° . The product is entirely neutral and is rather insoluble in cold alcohol. All analyses were made according to Pregl's¹ micro-methods.

¹ We take this opportunity to thank Prof. Pregl for his hospitality shown to one of us (C. F.) in his laboratory and to Mr W. H. F. Kuhlmann of Hamburg for a prompt delivery of one of his excellent micro-balances.

Two analyses gave 12.48 % H, 73.90 % C, and 12.05 % H, 74.45 % C. Calculated for anhydride of hydroxystearic acid $C_{36}H_{70}O_5$ (582.56), 74.15 % C and 12.11 % H.

A determination of the molecular weight was made according to the micro-method of Rast [1922]. Two determinations gave 580.5 and 630.

Saponification.

One gram of substance was saponified with 20 % alcoholic KOH. Yield of acid obtained 1.01 g. The product was recrystallised from 70 % alcohol and benzene to avoid esterification and gave colourless glistening plates, which melted at 57.5–58° and solidified again at 55.5°. The acid is much more soluble in alcohol than the anhydride. Determination of acidity gave higher figures than calculated, probably due to the interference of the hydroxy-group. For the preparation of the silver salt, the acid was dissolved in hot absolute alcohol and a boiling alcoholic silver nitrate solution was added. Some of the product separates out immediately, the rest on cooling. The crystals were filtered by suction, washed out with cold alcohol and then repeatedly with water.

Three analyses of the silver salt gave 26.36, 27.10 and 26.61 % Ag. Calculated for $C_{18}H_{35}O_3Ag$, 26.50 % Ag.

The free acid gave the following figures on combustion: C 71.96, H 12.16; C 71.76, H 12.30. Calculated for $C_{18}H_{36}O_3$ (300.29), 71.93 C and 12.08 H.

The molecular weight determination gave 302.

We could not identify the acid with any of the described hydroxystearic acids. The anhydride found in the caseinogen is unlikely to be formed secondarily, as prolonged boiling of the acid with alcohol did not yield any anhydride.

In studying the fats it seems to be worth while to pay attention to these anhydrides, which resemble very closely the ordinary glycerides of fatty acids.

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