XXX. THE DIRECT REPLACEMENT OF GLYCEROL IN FATS BY HIGHER POLYHYDRIC ALCOHOLS. PART I. INTERACTION OF OLEIN AND STEARIN WITH MANNITOL.

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GLYCEROL is required in abnormally large quantities during war and therefore just at such times as a shortage may be expected of oils and fats which are the essential raw materials in the manufacture of glycerol as at present practised. As the by-products in the manufacture have but a limited application as food-stuffs, various suggestions have been made with a view to extending this application and, among others, that of converting the fatty acids into ethyl and other esters has been considered. It is but a short step from this to the idea of esterifying the acids with polyhydric alcohols similar in type to glycerol and this again suggests the possibility of using sugars and their simpler derivatives for a like purpose. The latter line of inquiry appears especially promising inasmuch as many of the substances in this group are themselves valuable as food-stuffs.

We have been associated with Professor R. Robinson in considering the chemical aspects of such problems and in consultation with him decided to attempt a more direct solution than esterification of the preformed fatty acids.

It is well known that small quantities of acids or alkalis facilitate the exchange of alcohol residues in esters and accelerate the attainment of equilibrium in the resulting system. In those instances in which one of the products can be removed from the sphere of action a complete conversion of one ester into another may be effected.

It was anticipated that by bringing together, in presence of an acid or alkaline catalyst, a natural oil or fat and a polyhydric alcohol having a higher boiling point than glycerol the latter might be removed by distillation under reduced pressure.

Our first experiments were made with mannitol as the polyhydric alcohol and the catalyst used was sodium ethoxide, the alcohol arising therefrom being carried over with the glycerol formed during the reaction. The results justified our anticipations and although the products are not simple esters

of mannitol itself as we at first supposed, they resemble true glycerol fats in appearance and to some extent in taste and are reported by Professor W. D. Halliburton and Dr Drummond [1919] to be assimilated by rats to much the same extent as is olive oil.

Interaction of olive oil with mannitol. Formation of "Mannitol olive oil."

The olive oil used was a good commercial sample and had an acid value corresponding with 2.5 per cent. of free oleic acid.

100 g. of this oil was mixed in a Claisen distillation flask with 31 g. of pure mannitol and 1.5—2 per cent. of sodium ethoxide (freshly prepared by evaporating a solution of sodium in alcohol and heating gently until the mass appeared dry). One thermometer was kept with its bulb immersed in the mixture itself (the temperatures recorded by this are indicated hereafter by the letter T) and another with its bulb immersed in the issuing vapours in the exit tube of the flask (temperatures indicated by the letter t).

Experience having shown that on the small scale no harm resulted therefrom, the heating was usually carried out for convenience by direct contact with the flame of a Bunsen burner. Alcohol in small quantities appeared to be evolved first ($T = 87-90^\circ$, $t = 25-30^\circ$); later the mannitol crystals melted and two fluid layers were formed in the flask ($T = 140^\circ$) while considerable frothing ensued which continued as T rose to 215° . Here frothing subsided to some extent and as the heating went on the two fluid layers began to react, the upper one becoming turbid, and appearing to boil. Water, contaminated with a little oily or solid matter, distilled at this point ($t = 54^\circ$) and continued to do so as the temperature rose. A steady bubbling now took place (T steady at $236-240^\circ$ during 10—15 minutes; t about 52°), and the lower layer decreased in bulk. With further heating a thick fluid began to distil (t rose to 170° while T was raised to 270°) and the two layers in the flask merged into one. The heating was not pressed much further as some darkening in the product occurred if T was allowed to rise to 275° and very little more distillate was obtained.

Examination of distillate. This formed a thick viscid fluid on which floated a little oil; it was diluted with water, extracted with ether to free it from oily impurities and the aqueous solution was evaporated on the steam bath. A thick, viscid, sweet liquid remained (10 g.) which on distillation yielded 8 g. of a thick, almost colourless fluid, boiling at 179° at 14 mm. pressure. This was practically pure glycerol and was identified by conversion into the crystalline benzoate. As the amount of glycerol theoretically obtainable from the quantity of olive oil used is 10.4 g. it is evident that the yield was excellent in spite of losses inevitable in the manipulation of such comparatively small quantities of material.

Examination of residue. The fluid remaining in the flask was dissolved in ether and shaken with water, the whole being treated drop by drop with

acetic acid until a permanent slight acidity towards litmus was attained. The ethereal solution was separated and shaken several times with water to remove sodium salts together with any glycerol and mannitol or its anhydrides which might be present, though in point of fact when the foregoing procedure was followed the aqueous fluids yielded only very small quantities of residue, mainly sodium acetate, so that practically no free glycerol or mannitol was present.

After a preliminary drying over sodium sulphate and evaporation of the ether, the residual oil was more fully dried by heating it in a vacuum at 200–220° for several hours while a continuous stream of air was passed through it.

The product is an oil with a brownish yellow colour and a very faint odour. In taste and fluidity it is not dissimilar to olive oil. When kept for some weeks it gradually becomes somewhat cloudy and this effect appears to be due to deposition of a fine powder (stearates?) which may be removed by filtration. Professor Halliburton kindly undertook the examination of the properties of this oil when used as a food and a report on the subject appears elsewhere in this *Journal* [Halliburton and Drummond, 1919].

We have formed definite views on the chemical character of the oil only after consideration not only of its percentage composition and the amount of free and combined acid, but also of free hydroxyl, which was determined by means of magnesium methyl iodide in amyl ether.

By the interaction of mannitol and glyceryl oleate there may be formed a number of oleates in which from one to six of the hydroxyls of mannitol are esterified, as well as a series of wholly or partially esterified derivatives of mannitan and of isomannide, compounds which are derived from mannitol by loss of one and two molecules of water respectively. The percentages of carbon and hydrogen in many of these esters hardly admit of their being used to distinguish the esters from one another in a mixture, even if the entire absence of any esters of glycerol could be regarded as quite certain. On the other hand the percentages of combined acid, calculated as oleic acid, and especially of the free hydroxyl in the several possible esters vary very considerably as is shown in the following table from which some esters have been omitted because their composition differs so widely from that of the "mannitol olive oil" that they could only be present there if at all in quite small proportions.

While it seems possible that several or all of the above esters are present to some small extent in "mannitol olive oil" a careful examination of the table will show that in every instance but two there is at least one characteristic figure for each which differs widely from the one found experimentally. The two exceptions are the di-oleates of mannitan and isomannide.

Compositions of various esters of Oleic Acid.

Compound	Mol. wt. and formula	% OH	% combined acid	% C	% H
(1) Mannitol penta-oleate	$C_{99}H_{174}O_{11}$ (1502)	1.13	93.8	76.69	11.58
(2) Mannitol tetra-oleate	$C_{78}H_{142}O_{10}$ (1238)	2.7	91.1	75.6	11.47
(3) Mannitol tri-oleate	$C_{60}H_{110}O_9$ (974)	5.22	86.85	73.92	11.29
(4) Mannitol di-oleate	$C_{42}H_{78}O_8$ (710)	9.57	79.43	70.98	10.98
(5) Mannitan tri-oleate	$C_{60}H_{108}O_8$ (956)	1.77	88.49	75.31	11.29
(6) Mannitan di-oleate	$C_{42}H_{76}O_7$ (692)	4.91	81.5	72.83	10.98
(7) Isomannide di-oleate	$C_{42}H_{74}O_6$ (674)	0	83.68	74.77	10.97
(8) Isomannide mono-oleate	$C_{24}H_{42}O_5$ (410)	4.01	68.78	70.24	10.24
Olive oil	$C_{57}H_{104}O_6$ (884)	0	95.7	77.36	11.76
Found in "mannitol olive oil"	—	2.17	83.65	72.82	10.77

Interaction of mannitol with stearin. Formation of "Mannitol stearin."

Mannitol and stearin were mixed and heated in a vacuum with a little sodium ethoxide under much the same conditions as in the experiments where olive oil instead of stearin was used. The non-volatile residue was dissolved in chloroform, in which it dissolved more freely than in ether, and the resulting solution was treated with acetic acid and water as described in the preceding experiments. The washed and dried product was solid at ordinary temperatures. It was easily soluble in cold chloroform, hot petroleum (B.P. 80—100°), hot ethyl acetate, acetone or benzene. It dissolved in hot alcohol but was nearly insoluble in the cold. It separated from acetone on cooling as a granular powder melting at 67—72°.

Advantage was taken of the solid character of this product to do what was not possible in the case of the material from olive oil, namely to separate it into two main fractions by crystallisation from acetone. It was anticipated that if there were present any appreciable quantities of impurities markedly different in character from the main mass, evidence of this would be obtained by analysis of different fractions. In point of fact however no appreciable difference was found.

It is also interesting to observe that if the molecular proportion of mannitol to stearin used in the original reaction is increased from 1.5 to 2.25, the product is not appreciably altered in percentage composition and it seems probable that any excess of mannitol passes over with the glycerol during the heating with stearin in the first process or is washed out afterwards.

In the following table are exhibited the four characteristic data for the series of stearic esters derived from mannitol and its dehydration products.

Compositions of various esters of Stearic Acid.

Compound	Mol. wt. and formula	% OH	% combined acid	% C	% H
(1) Mannitol penta-stearate	$C_{96}H_{184}O_{11}$ (1512)	1.12	93.91	76.19	12.16
(2) Mannitol tetra-stearate	$C_{78}H_{150}O_{10}$ (1246)	2.72	91.1	75.12	12.03
(3) Mannitol tri-stearate	$C_{60}H_{118}O_9$ (980)	5.2	86.93	73.47	11.83
(4) Mannitol di-stearate	$C_{42}H_{82}O_8$ (714)	9.52	79.55	70.58	11.48
(5) Mannitan tri-stearate	$C_{60}H_{114}O_8$ (962)	1.76	88.56	74.83	11.85
(6) Mannitan di-stearate	$C_{42}H_{80}O_7$ (696)	4.88	81.6	72.41	11.49
(7) Isomannide di-stearate	$C_{42}H_{78}O_6$ (678)	0	83.9	74.32	11.50
(8) Isomannide mono-stearate	$C_{24}H_{44}O_5$ (412)	4.12	68.93	69.9	10.67
Stearin	$C_{57}H_{110}O_6$ (890)	0	95.73	76.85	12.36
Found in "mannitol stearin"	—	2.2	82.44	73.1	11.26

What was true of the original "mannitol olive oil" is equally true, *mutatis mutandis*, of "mannitol stearin," which from the above therefore appears to consist mainly of the di-stearates of mannitan and isomannide. We have to record with regret that we have not yet been able to obtain direct evidence of the presence of mannitan and isomannide residues in either product and feel doubtful whether an examination of the products of hydrolysis would lead to very conclusive results.

SUMMARY.

1. By distillation of olein or stearin with mannitol under reduced pressure in presence of a little sodium ethoxide, nearly the whole of the glycerol present in the original fatty compound is expelled.

2. The maximum yield of glycerol is reached when the proportion of fat to mannitol corresponds with two molecules of fat to three of mannitol.

3. The other main products are in both cases water with a little alcohol and a substance which is similar in many properties to the original fat.

4. The composition of the product, whether made with the above proportions of fat and mannitol or with excess of mannitol, corresponds with that of a mixture of the di-oleates (or di-stearates) of mannitan and isomannide. This closely corresponds with the observations mentioned under (2) above.

Professor J. C. Irvine has very kindly confirmed the description we submitted to him of our original mode of preparing glycerol and "mannitol olein" from olive oil. The extension of the work with sugars (and their derivatives other than mannitol) has been left in his hands.

This investigation was carried out for the Food Investigation Board (Dept. of Scientific and Industrial Research) who defrayed the expenses involved.

REFERENCE.

Halliburton and Drummond (1919). *Biochem. J.*, 13, 301.