

151 *The Hydrogenation of Δ^9 -Octadecenyl Δ^9 -Octadecenoate (Oleyl Oleate).*

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It has been known for many years that, when an ester of a long-chain polyethenoid acid is hydrogenated in presence of nickel, palladium, etc., catalysts, hydrogen is usually added selectively to one or other of the double bonds present. The investigations of Lebedev *et al.* (J., 1925, 127, 417; 1928, 823, 2190; 1929, 220; 1930, 321) showed that preferential hydrogenation also frequently results as a consequence of the extent to which different ethenoid carbon atoms are united with, for example, alkyl groups. More recently, further instances of selectivity have appeared in the hydrogenation of the mixed triglycerides of various natural fats. For example, the mixed palmito-oleo-(or linoleo-)glycerides of olive or cotton-seed oil (Hilditch and Jones, J., 1932, 805) or of pig depot fat (Hilditch and Stainsby, *Biochem. J.*, 1935, 29, 90) become converted into palmito-stearins before tristearin (from oleolinoleins, steardioleins, etc.) is produced in any quantity; and the progressive hydrogenation of rape oil triglycerides (mixed glycerides containing oleic, linoleic and erucic radicals) takes a somewhat different course from that of the corresponding mixture of methyl esters (*J. Soc. Chem. Ind.*, 1935, 54, 331T). We considered, therefore, that it would be interesting to examine the progressive hydrogenation of the ester of a monoethenoid higher fatty acid with the corresponding monoethenoid alcohol and chose for this purpose octadecenyl oleate, prepared by the esterification of purified oleic acid (from olive oil) with purified oleyl (Δ^9 -octadecenyl) alcohol (from sperm oil).

The ester was hydrogenated in presence of nickel on kieselguhr at 180° to four intermediate stages short of complete saturation, and the composition of the partly hydrogenated products was determined by oxidising them with potassium permanganate in acetone. Of the possible products of hydrogenation—*n*-octadecyl stearate, *n*-octadecyl oleate, *n*-octadecenyl stearate, and unchanged *n*-octadecenyl oleate—the first-named was isolated unchanged, after the oxidations, in a pure condition. The remainder were completely converted into acidic products, from which, after complete hydrolysis, it was at first hoped to recover quantitatively the *n*-octadecyl alcohol and stearic acid which were present. From the amounts of these three compounds the composition of each partly

hydrogenated ester could be determined. Actually, however, it was not found possible to obtain the stearic acid satisfactorily freed from traces of scission products (*n*-nonoic acid, 9-hydroxy-*n*-nonoic acid or azelaic acid), and only the proportions of *n*-octadecyl stearate, and of *n*-octadecyl alcohol which must have been present as oleate (or isooleate), were found capable of accurate determination. From these, however, the mean unsaturation (iodine value) of the partly hydrogenated ester being known, the proportions of the remaining components—*n*-octadecenyl stearate and unaltered *n*-octadecenyl oleate—were readily calculated.

The results obtained are in Table I, in which the extent of hydrogenation is expressed as a percentage of total saturation and determined from the iodine values of the hydrogenated esters (the *n*-octadecenyl oleate used had an iodine value of 94.7).

TABLE I.
Composition of Partly Hydrogenated n-Octadecenyl Oleate.

Hydrogenated ester. I.V.	% Hydrogenation.	<i>n</i> -Octadecyl stearate, %.	<i>n</i> -Octadecyl oleate, %.	<i>n</i> -Octadecenyl stearate, %.	<i>n</i> -Octadecenyl oleate, %.
64.6	32	12	22	18	48
52.3	45	24	22	20	34
37.4	61	40	19	22	19
20.0	79	65	13	14	8

These figures show that the course of the hydrogenation is largely non-selective; in this particular instance, however, the alcoholic ethenoid group is slightly more readily hydrogenated than the acidic ethenoid group. Formation of the fully saturated ester sets in from the commencement, and the relative proportions of saturated and monoethenoid esters present at each stage are not far from those which would be expected on the hypothesis that only one double bond was hydrogenated at each effective contact with the catalyst. The amounts of saturated ester (and therefrom of the half-saturated compounds and of unchanged ester) calculated on this basis for the four stages of hydrogenation given in Table I are compared with the observed figures in Table II.

TABLE II.

% Hydrogenation.	<i>n</i> -Octadecyl stearate.		<i>n</i> -Octadecyl oleate + <i>n</i> -octadecenyl stearate.		<i>n</i> -Octadecenyl oleate.	
	Calc.	Obsd.	Calc.	Obsd.	Calc.	Obsd.
32	10	12	44	40	46	48
45	20	24	50	42	30	34
61	37	40	48	41	15	19
79	62	65	34	27	4	8

The data in Table II (which are illustrated graphically in Figs. 1 and 2) show that the observed course of the hydrogenation approximates to that calculated from simple considerations of probability except in the following respects:

(a) The amount of fully saturated ester is slightly but consistently greater than would be expected; this is not surprising, since (notwithstanding vigorous agitation in the hydrogenation apparatus) it may be supposed that the chances of encounter between an ester molecule and a catalyst particle are somewhat greater in the case of a half-hydrogenated molecule leaving the catalyst surface, than in that of a di-unsaturated molecule which within the same period has escaped adsorption at the surface of a catalyst particle.

(b) Of the two monoethenoid groups present in the original ester, that in the alcoholic radical is slightly more readily attacked than that in the acid group. Compared with other recorded instances of hydrogenation of diethenoid derivatives, however, it may be said that there is relatively little selectivity in the hydrogenation of the Δ^9 -octadecenyl and Δ^9 -octadecenoic groups in the ester which we have studied.

EXPERIMENTAL.

The oleic acid employed was prepared from the mixed acids of olive oil, from which most of the saturated acids were first removed by crystallisation of the lead salts from alcohol. The

unsaturated acids recovered from the soluble lead salts were converted into lithium salts, which, after two crystallisations from 80% alcohol (Moore, *J. Soc. Chem. Ind.*, 1919, **38**, 322r), were almost free from linoleate. The acid recovered from the purified lithium oleate was converted into the methyl ester and fractionally distilled in a vacuum to remove the small proportion of palmitic acid which had escaped the lead salt-alcohol separation. The main fraction of the methyl oleate yielded on hydrolysis almost pure oleic acid.

The octadecenyl alcohol was prepared from alcohols obtained by the hydrolysis of sperm blubber oil. The alcohol, still contaminated with cetyl alcohol after fractional distillation in a vacuum, was kept at 0° for some time and the deposited solids were removed by filtration at 0°. It then had an iodine value of 90.7 (theo., 94.8).

The purified acid (247 g.) and alcohol (203 g.) were heated under 15 mm. pressure at 180° in presence of camphor- β -sulphonic acid (0.5 g.) for an hour after perceptible evolution of water vapour had ceased. The resulting ester (396 g.), from which unchanged acid had been removed, had saponification equivalent 534.0 and iodine value 94.7 (Calc. for $C_{36}H_{68}O_2$: saponification equiv., 532; iodine value, 95.5).

FIG. 1.

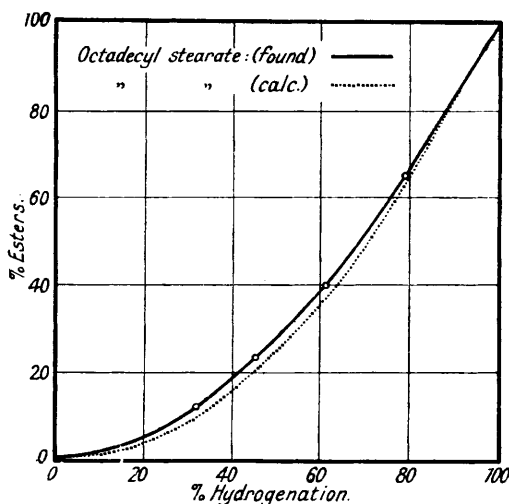
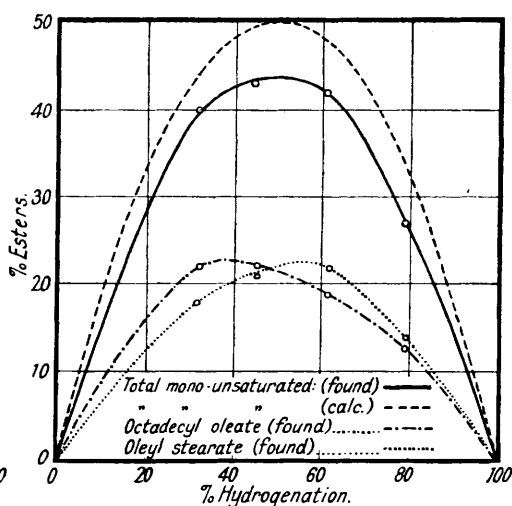


FIG. 2.



The ester was hydrogenated, in quantities of 80 g., a nickel-kieselguhr catalyst being used at 180° in an agitation apparatus connected with hydrogen inlet and exit meters in order to obtain products of the desired iodine values (cf. Table I).

The proportions of octadecyl stearate and of octadecyl oleate in the partly hydrogenated esters were determined by the following procedure. The ester (50 g.) was dissolved in acetone (500 g.) and oxidised under reflux by the addition of powdered potassium permanganate until the iodine value of the recovered neutral (unoxidised) product was below 1. After removal of all acidic products of oxidation there was thus obtained the octadecyl stearate which had been formed during hydrogenation. The whole of the alkaline (carbonate) aqueous extracts and washings obtained in this process were carefully hydrolysed with excess of caustic potash and then extracted with ether in order to recover any octadecyl alcohol thus liberated. This portion of the saturated alcohol must have been present as oleate and from its weight the corresponding weight of its oleic ester follows.

Similarly, after the extracted aqueous liquor from the preceding had been acidified, it was originally hoped to determine the stearic acid present; but, as already mentioned, a good quantitative separation of this acid from the mixture of azelaic, nonoic and hydroxynonoic acids also present was not satisfactorily achieved. Sufficient data were already available, however, to determine the proportions of the remaining components. The iodine value of the mixture of these was calculated from that of the original hydrogenated ester and its observed contents of saturated ester and of octadecyl oleate (iodine value 47.6), and from this iodine value the amounts of octadecenyl stearate (iodine value 47.6) and of octadecenyl oleate (iodine value 94.7) were, in turn, calculated. The octadecyl stearate obtained from the four products

melted, after crystallisation from acetone, at 58·5—59°; the octadecyl alcohol recovered from the acidic products of oxidation melted in each case (after crystallisation from alcohol) at 58°.

Some details of these analyses are in Table III.

TABLE III.

Composition of Partly Hydrogenated Esters.

Iodine value of esters	64·6	52·3	37·4	20·0
Wt. oxidised (g.).....	50·58	24·68	51·11	51·21
Octadecyl stearate isolated (g.)	6·05	5·87	20·51	33·59
" alcohol " (g.)	5·50	2·72	4·79	3·35
whence octadecyl oleate (g.)	10·87	5·38	9·47	6·62
Octadecenyl stearate } Iodine value				
+ " oleate } (calc.)	81·7	77·0	69·2	64·4
	g.	%.	g.	%.
Octadecyl stearate	6·05	12	5·87	24
" oleate.....	10·87	22	5·38	22
Octadecenyl stearate	9·29	18	5·05	20
" oleate.....	24·37	48	8·38	34
			11·44	22
			9·69	19
				3·92
				8

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