HYDROGENATION OF OILS BY THE CONTINUOUS PROCESS.

PART III. ISOMERISATION OF ETHYL OLEATE BY NICKEL CARBONATE-KIESELGUHR CATALYST.

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INTRODUCTION.

In Part II (*This Journal,* **21A**, 285–293) the hydrogenation of olive and cottonseed oils by nickel carbonate-kieselguhr catalyst has been studied by us in a continuous process. The results in general showed a regular variation in the behaviour of the catalyst depending on the composition of the oil, especially in the temperature coefficients of the reaction. It was shown that the olein and the linolein in the oils were selectively hydrogenated 'at 150° and 125° respectively while the velocity of hydrogenation of both was high at 200°. The hydrogenation of ethyl oleate was studied with a view to verify the above findings.

The hydrogenation of ethyl oleate is of great interest from the standpoint of the formation of iso-oleic acid. Moore (*J.S.C.I.,* 1919, **38**, 321 T) who made an elaborate study of the problem of iso-oleic acid and its formation in hydrogenation, concluded that the acid was a mixture of isomers of different stability, elaidic acid being one of the main constituents. It was found that both the catalyst and the temperature play an important part in the formation of iso-oleic acid. Hilditch and Vidyarthi (*Proc. Roy. Soc.,* 1929, **122A**, 552–70) studied the partial hydrogenation of methyl oleate, palmitoleate and erucate. The evidence indicated that the isomeric acids produced during the hydrogenation, consisted of mixtures of acids in which the ethlenic linking is adjacent to the position occupied by the original compound and that these acids together with the original position isomerides are almost certainly present in both *cis-* and *trans-*forms in the hydrogenation product.

Lush (*J.S.C.I.,* 1923, **42**, 219 T) has shown that the formation of iso-oleic acid is least in the continuous process of hydrogenation when compared with the results obtained with the batch and the overflow methods. It was concluded that the lower percentage of iso-oleic acid is due to the greater availability of hydrogen to the catalyst in the continuous process.

In the present paper we have studied the hydrogenation of ethyl oleate using nickel carbonate-kieselguhr catalyst in a continuous process, and the relation between the iodine value and refractive index of the hydrogenated ethyl oleate, in order to determine the course of reaction from the measurement of refractive indices for which sufficient data were not available. The detection and estimation of iso-oleic acid is also a laborious process, particularly when a large number of samples were to be analysed. It was thought desirable to find out a method of analysis based upon physical characteristics such as the refractive index and the dispersion of the substance.

The customary method of determining the degree of hardness of the hydrogenated oils is to use the relationship between the iodine value and refractive index, the measurements of the refractive index being comparatively easy, reliable and very much quicker. An extensive amount of work was carried out by Sudborough, Watson and Athavale (*This Journal,* 1922, **5**, 47), and Sudborough and Watson (*ibid.,* 1924, **7**, 81) to determine the relation between the iodine values and refractive indices of some hardened vegetable oils. Most of the vegetable oils being solely mixtures of glycerides of stearic, oleic, linoleic and clupanodonic acids, it is highly probable that for any particular iodine value, the refractive index will be approximately constant and independent of the nature of the oil. The above authors found that most of the vegetable oils studied, gave curves which were linear and parallel to each other when the iodine value was below 50. For higher iodine values the curves bent away from the abscissa representing the iodine values, the results being explained on the assumption that the glycerides of more unsaturated acids which are reduced first, have a higher rate of change of refractive index with iodine value than the glyceride of oleic acid.

In the hydrogenation of oils, particularly in a batch process which was used by the above workers, changes, other than the mere saturation of double bonds, are possible, such as the formation of iso-oleic acid. Lush (*loc. cit.*) estimated the amounts of iso-oleic acids formed during the hydrogenation of cottonseed oil by the 'drip', 'overflow' and 'batch' methods and found that a sample hydrogenated by the batch process at 130° contained not less than 40% iso-oleic acid, the corresponding ratio of oleic to iso-oleic acid being 10: 15. A similar observation was made by Sie Ichi Ueno (*J. Soc. Chem. Ind. Japan,* 1925, **28**, 1235–9) who found that in the hydrogenation of sardine oil. some portions of the highly unsaturated fatty acids are changed into the iso-oleic acid in the first stage of hydrogenation and then to the saturated acids.

The refractive indices of the individual isomers are not known but it may be reasonably believed that the refractive indices of the isomers formed by a mere shift of double bond may not be different from that of the ordinary oleic acid unless it is shifted right to the end of the chain. However, the fact that elaidic acid which forms the major part of iso-oleic acid, has a *much lower index* of refraction than oleic acid cannot be neglected while explaining the results. The higher rate of change of refractive index in the initial stage may, therefore, be due to the formation of elaidic acid.

Eijkman (*Rev. Trav. Chim. Pays. Bas.*, 1893, 12, 157–87) has measured the refractive indices and dispersions both of oleic and elaidic acid and has given the following values.

Elaidic acid (79·4°), $H_\alpha = 1\cdot43583$ $H_\beta = 1\cdot44425$ and $H_\beta - H_\alpha = \cdot00842$.

Oleic acid (78·4°), $H_\alpha = 1\cdot43752$ $H_\beta = 1\cdot44606$ and $H_\beta - H_\alpha = \cdot00854$.

Allowing for an approximate correction for temperature, the refractive index and dispersion of elaidic acid will be less by .00142 and .00012 respectively than that of oleic acid.

The refractive dispersion of a substance can be estimated correctly to one unit in the fifth place of decimal with a Pulfrich refractometer, and as the dispersion between the green and violet lines of mercury is more than between α and β hydrogen lines it should be possible to follow the isomeric changes in hydrogenation more accurately if the dispersions are measured in this region.

EXPERIMENTAL.

Ethyl oleate was prepared from oleic acid and had the following constants: B.P. 200° to 204°/4 mm. Refractive index at 40° for HG (546) 1.44619; for Hg (436) = 1.45498 and dispersion Hg (436)–Hg (546) as 0.008787; Iodine value (Hanus) 76.0. The iodine value is less by about 6 units than one calculated theoretically, indicating the presence of saturated compounds.

The iodine value was determined by Hanus' method while the refractive indices were measured on a Pulfrich refractometer at 40° C. The dispersion in each case was measured from the readings on the drum of the screw. The results are given in Table I and shown graphically in Fig. 1.

TABLE I.

Mixtures of ethyl oleate and ethyl stearate obtained by hydrogenation.

I.V. (Hanus)	n^{40}_{560} observed	Deviation from calculated value	$n^{40}_{(436)}$ observed	Deviation from calculated value	Dispersion $n_{(436)} - n_{(546)}$
76·0	1·44619	+ ·00147	1·45498	+ ·00176	·008787
65·9	1·44468	+ ·00002	1·45322	+ ·00095	·008543
64·1	1·44408	+ ·00051	1·45262	+ ·00053	·008535
56·7	1·44348	+ ·00059	1·45176	+ ·00044	·008278
53·3	1·44247	— ·00009	1·45092	— ·00012	·008441
39·5	1·44138	+ ·00012	1·44969	+ ·00016	·008311
37·8	1·44108	— ·00001	1·44934	— ·00001	·008262
30·1	1·44027	— ·00008	1·44849	— ·00006	·008213
14·9	1·43887	— ·00007	1·44693	— ·00004	·008063
1·4	1·43767	+ ·00003	1·44557	·00000	·007899

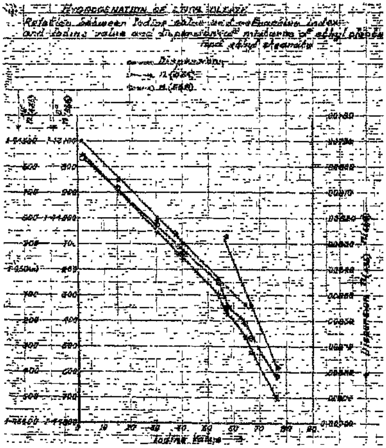

FIG. 1.

The figure shows an abrupt change in the refractive index when the iodine value has dropped by 25%, a corresponding change being also noticed in the dispersion when plotted against the iodine value.

The change in the refractive index with iodine number for samples having iodine numbers between zero and fifty-six can be represented by the equations

$$n^{40}_{(546)} = 1 \cdot 43750 + \cdot 000095 \times \text{I.V. and}$$

$$n^{40}_{(436)} = 1 \cdot 44542 + \cdot 000104 \times \text{I.V.}$$

The equations do not apply for samples having iodine values above fifty-six.

If the reaction was merely a saturation of the double bond, the refractive index should vary linearly with iodine value. The comparatively larger drop in the refractive index in the initial stages of hydrogenation, indicates the formation of another compound, while the linear relationship between 0–56 iodine values suggests the formation of the stearate only.

A number of experiments were carried out at different temperatures and different rates of the flow of ethyl oleate over the catalyst and the refractive indices and dispersions of the samples were measured on the Pulfrich refractometer. The results are plotted in Fig. 2 which shows the dispersions of each of the samples against the refractive index.

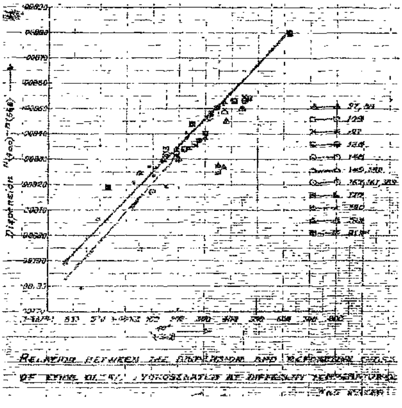

FIG. 2.

From the results shown in Fig. 1 it was expected that the refractive dispersion of a sample having a particular refractive index and consequently a particular iodine value, should be constant. Fig. 2, however, shows that the dispersions of samples having practically the same refractive index are considerably different, the variations in the dispersions being not due to any error in the measurements. In Fig. 3 the dispersion is plotted against the iodine value. It will be observed that the samples hydrogenated between 160° and 190° lie practically on a straight line.

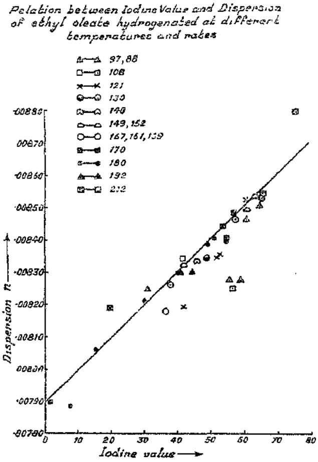

FIG. 3.

Below 160°, the dispersion of the sample is lower, lower the temperature of hydrogenation. The three samples hydrogenated at temperatures between 88° and 108° have a markedly low dispersion. Calculations showed that the deviation in the dispersion from the straight line relationship in the case of these samples was of the same order as the difference in the dispersions of oleic and elaidic acids. The formation of other isomers of oleic acid by a shift in the double bond will not produce appreciable changes in the refractive index and dispersion. It appeared, therefore, that the lower dispersion as observed in the three cases cited above, might be due to the formation of elaidic acid. According to the iodine value — refractive index relationship shown in Fig. 2 the above three samples contain approximately

25% of stearic acid, and if elaidic acid was formed, then, on separation of the solid and liquid fatty acids by the lead salt-ether method it was expected that the major portion of the fatty acids should separate as solid acids. Actual analysis of one of the samples, however, showed that it contained only 25% of solid acids having a m.p. of 62°–64° C. This shows that there is very little elaidic acid formed in the reaction. The lower dispersion therefore might be due to the formation of some other substance or isomer which may be present in the liquid acids.

Liquid fatty acids were therefore separated by the lead salt-ether method from three samples hydrogenated at 97°, 121° and 167° respectively. Refractive indices and dispersions of liquid acids were measured on Pulfrich refractometer and the values were compared with the corresponding values for the liquid acids separated from the original ethyl oleate (see Table II).

TABLE II.

Sample No.	Temp. of hydrogenation °C.	I.V.	n^{40}_{546}	Dispersion	% saturated acids	
					Observed	Calculated from I.V.
Original ethyl oleate	..	76	1·44619	·008787	0	0
1	97	57	1·44348	·008278	27·7	25·0
2	121	61	1·44368	·008522	34·3	19·7
3	167	37	1·44108	·008259	64·6	51·3

Properties of liquid fatty acids at 30° C.

	n_{546}	Dispersion
Original	1·46762	·009165
1	1·46775	·009097
2	1·46855	·009198
3	1·46709	·009000

Samples 1 and 2 had practically the same refractive index but the dispersions were very much different, while samples 1 and 3 had nearly the same dispersion but different refractive index. The considerable difference observed in the properties of liquid fatty acids separated from these samples and original ethyl oleate, indicates that there are isomers of oleic acid formed in the course of hydrogenation, the lead salts of which are soluble in ether.

Another interesting fact is that the refractive index of the liquid acids from sample No. 2 is higher while that of the liquid acids from sample No. 3 is lower than the refractive index of the liquid acids from original ethyl oleate. The increase in the refractive index in one case and its decrease in the other case suggests that the double bond in the ordinary oleic acid migrates in either direction according as the shift of the position of the double bond increases or decreases the refractive index.

The percentages of solid acids in these samples (*cf.* Table II) were higher than those calculated from the iodine values while the melting points of the solid portions varied from 60–64°, showing that the solid portions were contaminated with 10 to 30% of iso-oleic acid.

Measurements of the refractive index and dispersion of ethyl oleate hydrogenated at different temperatures thus indicate (1) the formation of the isomers of oleic acid by the migration of the double bond in either direction from the position it occupies in ordinary oleic acid, having different refractive index and dispersion from that of ordinary oleic acid and yielding lead salts which are soluble in ether, and (2) the formation of appreciable quantities of iso-oleic acid, the lead salt of which is insoluble in ether.

These conclusions are in harmony with the results of Vidyarthi and Hilditch (*loc. cit.*) who have shown that 8–9 and 10–11 oleic acids are formed in the partial hydrogenation of methyl oleate, in addition to other solid iso-oleic acids. Moore (*loc. cit.*), however, believed that the iso-oleic acid was mostly 11–12 oleic acid. All these authors are, however, in agreement with the view that no isomeric oleic acids are produced unless hydrogenation is actually progressing, and they believe that the isomeric acids are formed as a result of dehydrogenation of the freshly formed saturated compounds.

After the completion of our work, Waterman and van Vlodrop (*Recvil Des Travaux Chimiques Des Pays-Bas*, 1938, Tome 57, No. 6, 629) published a paper on the 'Transformation of esters of unsaturated fatty acids with hydrogenation catalysts in the absence of hydrogen'. These authors heated olive oil and ethyl oleate in presence of nickel catalyst at 250–300°. The products obtained had a higher refraction and yielded solid fatty acids (m.p. 43° C.), which had a low value for the 'iodine equilibrium constant'. From these results they concluded that isomerisation to elaidic acid took place.

When experiments were carried out by us at higher temperatures, we actually observed decomposition of the oil. It appears to us that the increase in the refractive index observed by the above authors can be easily accounted for by the amount of the free acidity in the oil which rose from 5 to 14, as the difference in the refractive index of the free fatty acid and its esters is of the order of 0.02. On the other hand, if we expect that elaidic acid is formed, the refractive index of the product ought to have been lower than that of the ethyl oleate, as pointed out in this paper previously. Regarding the melting point, the following values are given in the literature for the isomeric oleic acids.

	Acid	M P.	Reference
2–3	Oleic	61	(1) Lewkowitch, *Chemical Technology and Analysis of Oils, Fats and Waxes,* Vol. I, pp. 192–96.
3–4	Oleic	57	
4–5	Oleic	53	
6–7	Oleic	34	(2) Myddleton and Barry, *Fats—Natural and Synthetic,* 1924, pp. 17–18.
6–7	Elaidic	52	
9–10	Oleic	14	
9–10	Elaidic	44·5	(3) Holde, *Kohlen Wasserstoffole und Fette,* 1933, pp. 626–27.
10–11	Oleic	45	
11–12	Oleic	39	

From these results it is clear that the high melting point cannot decide the formation of elaidic acid.

Regarding the iodine equilibrium constant, the measurements of iodine adsorption by some of the structural isomers of oleic acids are known to have abnormally low values. For example, in the case of 2–3 acid it has been found that iodine adsorption does not exceed beyond 46% even after 70 hours. The low iodine equilibrium constants cannot, therefore, be the criterion in deciding that elaidic acid is formed. The possibility that acids formed by the shift in the double bond can also occur as geometrical isomers which may have a low iodine equilibrium constant cannot be overlooked.

According to our experiments the conditions which are favourable for the formation of elaidic acid appeared to be the low activity of the catalyst which obtains at low temperatures (100–20°) and an insufficient supply of hydrogen at temperatures at which the catalytic activity of hydrogenation is fairly high (180°).

Hydrogenation of Ethyl Oleate.—The hydrogenation of ethyl oleate was carried out at different temperatures and rates using nickel carbonate-kieselguhr catalyst. The refractive indices of the samples for the violet line were measured on the Pulfrich refractometer and the percentage conversion was calculated from the iodine value-refractive index relationship (Fig. 1). The yields and the apparent velocity coefficients (K) were calculated in the manner described in Parts I and II (*This Journal*, 1938, **21A**, 95–109; 285–293). The results are given in Table III.

TABLE III.

Expt. No.	Temp. °C.	Rate grams/hr.	Yield	K	Expt. No.	Temp. °C	Rate grams/hr.	Yield	K
1	180	24·3	2187	56·0	19	121	90·0	1755	19·5
2	180	42·3	3338	68·3	20	121	34·2	1094	13·2
3	180	67·2	4058	62·3	21	86	94·5	1843	20·5
4	180	124·4	4105	49·8	22	97	80·7	1169	12·6
5	167	51·0	2550	35·3	23	108	30·4	821	9·6
6	159	50·4	2621	37·0	24	108	49·2	1329	15·5
7	149	51·0	2295	30·5	25	108	130·0	1690	18·1
8	140	49·9	1996	25·5	26	120	102·6	1406	15·1
9	130	48·0	1762	22·0	27	130	96·6	1323	14·3
10	121	44·7	1386	16·6	28	140	92·0	1610	17·7
11	108	19·6	878	11·7	29	152	90·0	1840	20·7
12	108	48·0	1124	14·1	30	161	82·0	2050	23·6
13	97	36·9	941	10·9	31	171	77·6	1940	22·3
14	88	36·0	810	9·2	32	180	92·3	3249	40·0
15	192	69·3	3222	43·3	33	192	70·6	2838	36·3
16	192	37·8	2238	33·9	34	180	126·0	3590	42·2
17	212	50·1	3713	67·9	35	212	116·5	3495	41·5
18	121	36·3	1633	21·8					

The first four experiments at 180° were carried out with the idea to determine the relation between the apparent velocity coefficients and the rates. The results indicate that the velocity rises with an increase in the rates in the initial stages and then drops down on increasing the rates further.

Experiments from Nos. 5 to 17, and 18 to 35 were carried out particularly to study the effect of temperature on the velocity of hydrogenation at a fixed rate of the flow of ethyl oleate over the catalyst. The values of K calculated for rates of 50 and 100 grams per hour are plotted against the temperature in Fig. 4 which shows two maxima in the curves at 150° and 180° respectively and a high velocity coefficient at 210°.

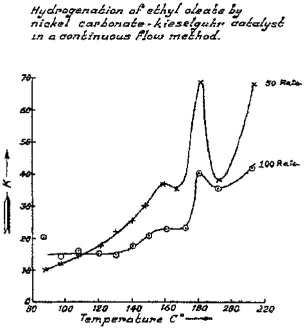

FIG. 4.

The two maxima at 150° and above 210° are in conformity with the conclusions reached from the study of hydrogenation of different oils as described in Part II. The high maxima at 180° in the hydrogenation of ethyl oleate was not observed even in the case of olive oil which contains approximately 85% of oleic acid. The reaction appears to be selective in the sense that a simple molecule like ethyl oleate is hydrogenated more readily than tri-olein at this temperature.

The greater deviations in the dispersion of the samples hydrogenated between 88° and 108° indicate that it is not the process, but the low activity of the catalyst, that is responsible for the formation of iso-oleic acids.

SUMMARY.

The measurements of iodine values, refractive indices and dispersions of the hydrogenated ethyl oleate showed that the iodine values varied linearly with refractive index only after the former had dropped down by about 25%, the variation of the refractive index with iodine value in the initial stages being comparatively greater. The dispersions of the hydrogenated products, were considerably different for the samples having either the same refractive index, or the same iodine value, and depend on the temperature of hydrogenation, marked deviations being observed in the case of samples hydrogenated at low temperatures. It is concluded that isomers of oleic acid are formed in the reaction owing to the low activity of the catalyst for hydrogenation at lower temperatures.

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