TABLE II

Average-Collaborative Analyses—1956

	Sample 1		Sample 2		Sample 3	
	Analyst		Analyst		Analyst	
	1	2	1	2	1	2
Miner Method						
Collaborator 1	2.45	2.39	38.5	38.9	92.7	93.3
2	2.41	2.41	38.5	37.9	92.1	91.8
3	2.44	2.46	37.6	39.7	89.2	93.4
4	2.64	....	38.4	....	91.4	....
5	2.36	2.40	38.0	38.0	91.4	90.8
Extraction Method						
Collaborator 1	2.86	2.79	38.3	39.1	91.7	92.1
2	2.87	2.92	38.7	38.3	91.8	91.6
3	2.30	2.72	37.9	37.8	88.7	91.4
4	2.71	....	38.1	....	91.7	....
5	2.84	2.79	38.4	38.2	92.3	91.9
Partition Method						
Collaborator 1	2.91	2.74	38.4	39.2	91.8	91.1
2	2.86	2.80	38.8	38.8	92.4	92.9
3	2.23	2.81	38.8	38.9	89.1	92.9
4	2.90	....	39.1	....	93.0	....
5	2.90	....	39.2	38.5	92.9	92.6

TABLE III

Summary Indicating Over-all Precision—1956 Results

	Mean	Standard deviation	Coefficient of variation
Sample 1			
Miner Method	2.45	0.12	4.9
Extraction Method	2.80	0.17	6.1
Partition Method	2.80	0.18	6.4
Sample 2			
Miner Method	38.5	6.62	1.6
Extraction Method	38.4	0.41	1.1
Partition Method	38.8	0.41	1.1
Sample 3			
Miner Method	91.9	1.36	1.5
Extraction Method	91.5	1.15	1.3
Partition Method	92.2	1.12	1.2

2. *Extraction Method* (4). The sample is dissolved in chloroform, and the glycerol is removed by extraction with water. Periodic acid in an acetic acid-water solution is added. The periodic acid consumed by oxidation of the monoglyceride is determined from an iodimetric titration, using a sodium thiosulfate solution and starch indicator.
3. *Partition Method* (a modification of the extraction method developed in Swift and Company Research Laboratories). The sample is dissolved in chloroform; an equal volume of water is added, shaken, and allowed to separate into two phases; an aliquot of the chloroform solution is pipetted for the monoglyceride determination. The monoglyceride is determined in the same manner as in the extraction method.

A single sample was analyzed by the subcommittee in 1954, using the three methods under trial. The same sample was resubmitted to the subcommittee as an unknown in 1955 and 1956, and duplicate portions were also submitted as "knowns." The purpose of the "known" was to serve as a primary standard for over-all determination. The results obtained on this sample in three consecutive years appear in Table I.

Three additional samples were submitted to the subcommittee in 1955 and again in 1956. The latest results obtained on these samples appear in Table II.

All of the data were statistically processed by H. P. Andrews. The summary appearing in Table IV indicates the 95% probability limits for a number of analytical situations.

TABLE IV

Precision of the Partition Method at Various Monoglyceride Levels

% Monoglyceride present, approx.	2 x Standard deviation	Difference between		
		Single detn. by same analyst on different days	Single detn. by different analysts in the same labs.	Single analyses in different laboratories
3.0	±0.36	0.27	0.51	0.51
40.0	±0.8	0.6	1.2	1.2
90.0	±2.2	2.0	3.2	3.2

After due consideration the committee recommends the Partition Method on the basis of superior precision: more simple than the Extraction Method and more precise than the Miner Method.

REFERENCES

1. Malaprade, Bull. Soc. Chem. France, 4e *43*, 683 (1928); 5e *1*, 833 (1934).
2. Pohle, W. D., Mehlenbacher, V. C., and Cook, J. H., *22*, 115–119 (1945).
3. Handschumaker, Edward, and Linteris, L. L., Oil and Soap, *24*, 143 (1947).
4. Pohle, W. D., and Mehlenbacher, V. C., J. Am. Oil Chemists' Soc., *27*, 54–56 (1950).
5. Kruty, Margaret, Segur, J. B., and Miner, C. S., Jr., J. Am. Oil Chemists' Soc., *31*, 466–469 (1954).

D. S. BOLLEY
R. A. MARMOR
O. S. PRIVETT
S. J. RINI
R. C. WALKER
W. D. POHLE, chairman

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Studies on Castor Oil. II. Hydrogenation of Castor Oil[1]

B. SREENIVASAN,[2] N. R. KAMATH, and J. G. KANE, Department of Chemical Technology, University of Bombay, Bombay, India

THE HYDROGENATION OF CASTOR OIL, also of methyl ricinoleate, has been studied by several investigators (2, 6–13, 15, 20–23). In spite of wide variations in conditions of hydrogenation with respect to type and amount of catalyst, temperature and pressure, practically all the investigators have assumed that the products formed will be essentially esters of 12-hydroxy stearic acid and/or stearic acid; only the relative proportions will be dependent on the external factors. Thus a) at low temperatures and low pressures the rate of hydrogenation is slow; b) at low temperatures and low pressures, saturation of the double bond is the predominant reaction; c) at high temperatures and low pressures, dehydroxylation is marked; and d) at high temperatures and high pressures, decomposition reactions predominate. These conclusions are based mainly on the chemical constants of the hydrogenated product and, in particular, on the iodine and acetyl or hydroxyl values. Only in certain cases have attempts been made to confirm the above conclusions by separating some of the constituent fatty acids. Thus Grün and Woldenberg (5) and Thoms and Deckert (19) isolated 12-hydroxy stearic acid from hydrogenated methyl ricinoleate and hydrogenated castor oil, respectively.

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[1] Part of the thesis submitted for the Ph.D. degree at the University of Bombay.

[2] Present address: Lipides Laboratory, Department of Physiological Chemistry, Ohio State University, Columbus, O.

Gupta and Aggarwal (6) hydrogenated castor oil at 250°C. and 75 p.s.i., using 2% of a commercial nickel catalyst for 20 hrs., and obtained a product of low acetyl and iodine values, from which they were able to isolate stearic acid in 60% yield.

While saturation of the double bonds and hydrogenolysis of the hydroxyl of the ricinoleic acid chain are undoubtedly the major reactions that occur when castor oil or methyl ricinoleate is hydrogenated, it must be pointed out that a number of other reactions can occur even under comparatively mild conditions. These reactions include conjugated hydrogenation, dehydration, shifting of the double bond and isomerization, cyclization, estolide formation, hydrolysis, polymerization, and polycondensation. If these reactions do occur, the reaction products will definitely show different iodine and acetyl values without any hydrogenation. Besides, as has been already pointed out in part I of this work (17), these values are truly representative only under certain rigid conditions and for glycerides containing specific component fatty acids. Sudborough *et al.* (18) and Toyama and Ishikawa (20) have observed that hydrogenated castor oils give erratic iodine values because of the presence of monohydroxy stearic acid.

There is a need to have an unambiguous method for determining the fatty acid composition of hydrogenated castor oil, particularly the intermediate products, so as to determine the type of reactions that occur during hydrogenation. The method described in part I (17) of this work for determining the fatty acid composition of castor oil should prove to be convenient for this purpose.

In the present investigation castor oil has been hydrogenated, using two different preparations of nickel catalyst (Raney nickel and dry reduced nickel) in two different proportions (0.1 and 1.0%) at various temperatures (80° to 240°C.) for different periods (2 to 10 hrs.). The course of hydrogenation under these conditions has been studied by analyzing periodical samples for their acid values, iodine values, hydroxyl values, and melting points. A few representative samples have also been analyzed for their fatty acid composition by the technique reported in Part I.

In addition, castor oil has been hydrogenated with Raney nickel in the presence of ethyl alcohol, at room temperature (25–30°C.) under comparatively low pressure (40 p.s.i.). Essentially under these conditions saturation of the double bond occurs, indicating that these are the most favorable conditions for the preparation of the glycerides of 12-hydroxy stearic acid. On the other hand, if a product which is essentially tristearin is required to be produced from castor oil, the desired conditions of hydrogenation will have to be determined. It may be added that, from the point of view of the prevailing conditions in India, a tristearin obtained from castor oil should prove to be an economically attractive proposition.

Experimental

The three lots of castor oil were the same as those previously studied. Their constants and compositions have been already reported (17).

Catalyst. a) *Raney nickel.* This was prepared from Ni-Al alloy powder according to the procedure of Covert and Adkins (3). The catalyst was stored under absolute alcohol.

b) *Dry-reduced nickel.* Nickel carbonate was precipitated in the presence of "Hyflo-super-cell" (Celite), from a boiling solution of nickel nitrate by sodium carbonate. The precipitate was washed free of water solubles, dried, and stored. The proportion of support was so adjusted that the completely reduced catalyst contained about 20% Ni. Requisite quantities of this supported catalyst were reduced according to the procedure of Covert *et al.* (4) and used directly for hydrogenation.

Hydrogenation Procedure. About 200–300 g. of the oil were hydrogenated in a three-neck flask equipped with a mechanical stirrer through the middle neck. A thermometer, a hydrogen inlet tube, and a tube for removing samples were introduced through the two side-necks. Samples of the hydrogenated oil were removed at certain intervals and analyzed. Hydrogenations under pressure were carried out in Parr laboratory hydrogenation apparatus.

TABLE I

Hydrogenation of Castor Oil[a] at Atmospheric Pressure and Various Temperatures

Catalyst—Raney Nickel 0.1%

Expt. No.	Temp. °C.	Time Hours	Iodine Value Wijs 30–33°C.	Hydroxyl Value	Melting Point °C.
1	160	4	72.5	155.6	46.5
		6	67.6	155.6	55.6
		8	62.5	155.6	63.0
2	180	4	69.4	151.1	51.5
		6	64.2	142.8	55.5
		8	57.9	137.5	63.5
3	200	4	67.2	146.7	52.0
		6	58.2	136.6	58.5
		8	50.4	131.2	63.0
4	220	4	58.0	127.6	52.0
		6	48.5	111.9	59.5
		8	38.8	104.0	62.0
Catalyst—Raney Nickel 1.0%					
5	80	8	68.0	162.7	—
6	100	8	67.3	154.5	—
7	140	4	55.7	142.7	61.5
		6	41.3	130.4	71.0
		8	27.2	126.0	78.0
8	160	4	38.3	127.6	74.0
		6	20.8	117.1	78.0
		8	13.3	117.2	78.5
9	180	2	52.5	122.5	58.0
		4	24.7	106.5	75.5
		6	12.5	101.2	70.5
		8	8.5	97.1	68.5
10	200	2	50.4	103.1	56.5
		4	18.2	78.2	67.5
		6	10.0	68.3	67.0
		8	7.0	65.2	65.0
11[b]	220	2	44.6	77.8	58.0
		4	14.0	55.1	55.7
		6	12.4	40.3	52.0
		8	10.6	36.2	52.0
12[b]	240	4[d]	65.3(c)	89.5	37.0
		6[d]	56.6(c)	58.6	39.5
		8	50.3(c)	32.5	40.5
13[e]	220	8	84.9	153.1	—
Catalyst—Dry Reduced Nickel, 1.0%					
14	140	4	60.7	130.7	51.0
		6	49.7	109.4	56.0
		8	33.7	97.2	66.0
15	180	4	17.9	64.1	64.5
		6	5.7	62.0	65.0
		8	4.8	59.8	65.0
16[b]	220	4	65.6	69.0	57.0
		6	39.3	44.5	65.0
		8	22.5	34.6	67.0

[a] Average values as reported in part I (17): Iodine value Wijs 30–33°C., 84.3; hydroxyl value—163.0.

[b] Marked changes in acid values with time were noted in these experiments only:

Expt. No.	Acid values			
	2 hrs.	*4 hrs.*	*6 hrs.*	*8 hrs.*
11	3.3	4.1	4.4	4.4
12	7.3	11.3	13.7	15.1
16	3.1	5.2	6.7	6.7

[c] Iodine values by the Woburn method.

[d] $E^{1\%}_{1\,cm.}$ 234 mμ values for these two samples before and after isomerization were 10.4, 8.8 and 17.2, 13.4, respectively.

[e] Blank experiment, using nitrogen instead of hydrogen.

The various hydrogenation runs together with analytical values of the various samples of hydrogenated castor oil are given in Tables I, II, and III. In Table IV are given iodine values of hydrogenated castor oil and its derivatives, obtained by different procedures.

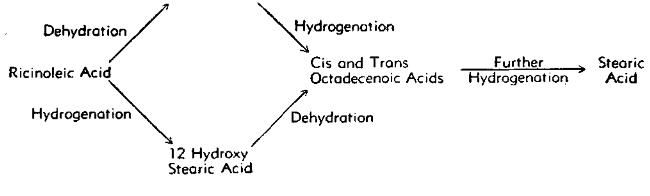
A number of typical hydrogenated castor oil samples were resolved into hydroxy and nonhydroxy portions by the technique described in Part I (17). Data on this resolution are given in Table V. The methyl esters of the above typical samples were analyzed for their total unsaturation (Wijs I.V. method at 15–20° C.), dienoic acids content (spectrophotometrically), and dihydroxy stearic acid content (periodic acid oxidation of the fully hydrogenated methyl esters). Independent estimation of the latter acid was necessary in order to obtain the 12-hydroxy stearic acid by difference. The methods of estimation and calculation were essentially the same as described in Part I (17). The analytical data and the fatty acid compositions of the various samples have been given in Table V.

Discussion

The double bond and the hydroxyl group of ricinoleic acid are the two centers which are affected during hydrogenation. The extent of this influence and its dependence on the conditions of hydrogenation are clearly brought out by the values given in Table I. Increasing the time or the temperature of hydrogenation or the amount of catalyst decreases both the iodine and hydroxyl values but increases the melting point. Although these values reflect only the over-all resultant effect of several reactions, they would, if considered along with some more data as given in Table V, throw considerable light on the course of hydrogenation under different conditions.

During hydrogenation it was observed that droplets of water tended to condense on the cooler parts of the reaction flask in most of the experiments, showing thereby that the hydroxyl group of ricinoleic acid was undergoing some reaction. Water formation could be caused by etherification, estolide formation, dehydration, or hydrogenolysis. It is unlikely that etherification reactions are occurring under these conditions specially with a secondary hydroxyl group. Hydrogenolysis is known to occur to a limited extent only even under very drastic conditions of high temperature and high pressure (1, 14, 16). Estolide formation demands initial splitting of the glycerides and subsequent esterification of the hydroxyl groups of the hydroxy acids, in which case the product should have significant acid value and a lower hydroxyl value than its methyl esters. Since most hydrogenated products do not satisfy these requirements, it is reasonable to conclude that the chief reaction responsible for water formation is dehydration. Thus, on this basis, hydrogenation of ricinoleic acid to form stearic acid can be represented schematically as in Chart I.

CHART I



The presence of dienoic acids in the products at a stage when the linoleic acid of the original oil can be reasonably considered to have been hydrogenated and any increase in the content of nonhydroxy acids over the original amount can be taken as indications that dehydration is occurring. The composition of the hydrogenated oils will depend largely on the relative rates of the reactions shown in Chart I under the various conditions tried. These points are brought out in the discussion that follows.

Raney Nickel 0.1%. At the lowest temperature studied, *viz.,* 160°, reduction in iodine value is small and the hydroxyl value is practically unaffected. Temperatures of the order of 220° are required to cause appreciable decrease in both iodine and hydroxyl values. The hydroxyl values of the glycerides (experiments 2 and 4, Table I) and methyl esters (Table V) are of the same order, indicating the absence of estolides. There is a progressive increase in melting points with the time of reaction. It is however to be noted that all the final eight-hour samples have almost similar melting points in spite of marked differences in their chemical constants.

Comparison of the composition of raw castor oil and of sample 2 (Table V) shows considerable decrease in ricinoleic acid and the presence of an appreciable quantity of 12-hydroxystearic acid. However ricinoleic acid and 12-hydroxystearic acid amount to only 73.2%, showing that the balance of 12.5% (85.7–73.2) have become nonhydroxy acids. This is supported by an increase in the total amount of nonhydroxy acids. This rise in the content of nonhydroxy acids and the presence of a small but significant amount of conjugated dienoic acid show that dehydration has occurred. The amount of ricinoleic acid converted into 12-hydroxy stearic acid is much higher than that into nonhydroxy acids, a fact which means that hydrogenation of ricinoleic acid is proceeding at a faster rate than dehydration at 180°. In Sample 4 linoleic acid has disappeared, ricinoleic acid content is reduced farther, saturated nonhydroxy acids have increased to 30%, and the nonhydroxy monoethenoic acids are of the same order as in sample 2. The proportions of 12-hydroxy stearic acid and nonhydroxy acids derived from ricinoleic acid are close to each other, indicating that at 220° dehydration and hydrogenation of ricinoleic acid are proceeding at about the same rate and also that the hydrogenation of the acids produced by dehydration has increased. It is likely that considerable amounts of *trans* acids (both hydroxy and nonhydroxy) are produced under the various conditions studied, and this aspect was not investigated because of lack of both necessary equipment and infrared data on hydroxy acids. It is evident that, with 0.1% Raney nickel, even at 220° one cannot get products of low iodine and hydroxyl values in a reasonable time.

Raney Nickel 1.0%. With the increase in the amount of catalyst the rate of hydrogenation is appreciable even at 140°. It reaches a maximum at 200° and distinctly drops off at 240°. On the other hand, the increase in the rate of dehydration is small and its optimum appears to be about 240°. Though products of iodine value, about 10 are obtained at lower temperatures. The hydrogenation of castor oil at 220° for 8 hours, using 1.0% Raney nickel, appears to be best for getting products of maximum nonhydroxy acids, chiefly stearic acid, and a low content of hydroxy acids (experiment 11, Table V). At 240°

TABLE II

Stepwise Hydrogenation of Castor Oil
Catalyst Used—Raney Nickel

Experiment No.	Catalyst %—Time in hours			Temperature °C.	Hydrogenated product		
	1st stage	2nd stage	Total		Acid value	Iodine value Wijs (15–20°C.)	Hydroxyl value
17	1.0–4	—	1.0–4	200	4.5	16.8	72.0
	1.0–4	1.0–2	2.0–6		5.0	4.0	63.8
	1.0–4	1.0–4	2.0–8		5.2	2.2	48.5
18	2.0–2	—	2.0–2	200	4.1	10.9	64.6
	2.0–4	—	2.0–4		4.9	3.5	58.5
	2.0–4	2.0–2	4.0–6		5.4	1.7	37.0
	2.0–4	2.0–4	4.0–8		5.7	1.1	29.5 (45.4)[a]
19	2.0–2	—	2.0–2	200	—	—	—
	2.0–2	0.0–2	2.0–4	240	6.4	16.1	40.5
	2.0–2	0.0–4	2.0–6	240	6.8	8.9	20.1
	2.0–2	0.0–6	2.0–8	200	6.9	6.1	26.4 (38.2)[a]
20	1.0–4	—	1.0–4	220	6.4	23.0	62.1
	1.0–4	0.0–2	1.0–6	240	8.2	11.1	36.1
	1.0–4	0.0–4	1.0–8	240	8.4	6.5	28.4
	1.0–4	0.0–5	1.0–9	200	8.5	5.3	27.4 (39.8)[a]
21	1.0–4	—	1.0–4	220	6.4	16.4	54.8
	1.0–4	1.0–2	2.0–6	220	7.2	5.7	35.9
	1.0–4	1.0–4	2.0–8	220	7.5	3.4	25.1
22	2.0–2	—	2.0–2	220	5.4	35.8	60.4
	2.0–2	0.0–2	2.0–4		7.3	12.9	36.4
	2.0–2	0.0–4	2.0–6		7.4	5.5	25.4
	2.0–2	0.0–6	2.0–8		7.6	2.4	21.4
	2.0–2	0.5–2	2.5–10		7.6	2.4	17.6
	2.0–2	0.5–4	2.5–12		7.9	2.0	12.7 (46.0)[a]
23	2.0–8	—	2.0–8	220	—	—	—
	2.0–8	0.5–4	2.5–12		5.6	2.0	17.5 (38.6)[a]
24	2.0–4	—	2.0–4	220	—	—	—
	2.0–4	0.5–4	2.5–8		5.4	2.0	20.3
	2.0–4	0.5–2	2.5–10		5.6	1.6	20.0

[a] Hydroxyl values of methyl esters.

the samples show higher iodine values with considerable proportions of dienoic acids (Table 1, Experiment 12, 4- and 6-hr. samples) affording more evidence for dehydration during the hydrogenation of castor oil. Considerable splitting has occurred as shown by the high acid values of the samples.

The melting points of the various products apparently show a peculiar behavior. At the lower temperatures (experiments 7 and 8) the melting point increases with the time of reaction and parallels a rapid decrease in iodine values, which is also true in the early stages of reaction (up to 4 hrs. with 9 and 10) at 180° and 200°, respectively. This rise in melting point is obviously caused by the rise in the content of 12-hydroxy-stearic acid (m.p. 84°), as shown by the fairly high hydroxyl values of these samples. This means that under these conditions hydrogenation of ricinoleic acid is more pronounced than dehydration. When dehydration with the consequent production of nonhydroxy acids becames more marked, the melting point drops off. This is brought out best in experiment 11, where the progressive decrease in melting point is paralleled by considerable decrease in both iodine and hydroxyl values. It is thus likely that at 220° dehydration and hydrogenation of the resulting unsaturated acids are proceeding at a faster rate than simple hydrogenation of ricinoleic acid.

The hydroxyl values of the glycerides of samples 7 and 9 (Table I) and methyl esters (Table V) are about the same, showing the absence of estolide formation while with 11 there is evidence for a small amount of estolides.

With sample 9 there is a definite increase in the contents of both saturated nonhydroxy acids and hydroxy acids as compared to 2, indicating that at 180° increase in the amount of catalyst has favored saturation of the double bond. Although the conversion of ricinoleic acid into nonhydroxy acids has increased, yet it is of the same order as with 0.1% at 220° (Table V, Experiment 4). This obviously results from the fact that the rate of dehydration of the saturated hydroxy acid, 12-hydroxy stearic acid, is very low at 180°. Similar comparisons of the compositions of experiments 4 and 11 reveal considerable increase in the conversion of ricinoleic acid into nonhydroxy acids and in the content of saturated nonhydroxy acids while there is a definite decrease in the content of unsaturated nonhydroxy acids. These observations point out that at 220° the increase in the amount of catalyst has markedly increased the rates of dehydration of hydroxy acids and the hydrogenation of the resulting unsaturated acids, thus confirming the point made earlier.

It is of interest to note the decrease in dihydroxystearic acid, which is considerable—1.0% in contrast to 0.1% catalyst.

A blank experiment (experiment 13, Table I) carried out in a current of nitrogent instead of hydrogen under otherwise comparable conditions (experiment 11) showed negligible change in iodine value with a slight decrease in hydroxyl value. It is apparent that, even at 220°, nickel is not an effective dehydration catalyst.

Dry-Reduced Nickel 1.0%. With this catalyst the results obtained are different than with Raney nickel under comparable conditions (compare experiments 14, 15, and 16 with 7, 9, and 11, respectively, Tables I and V). At 140° there is a greater conversion of ricinoleic acid into nonhydroxy acids, and the amount of saturated nonhydroxy acids is also higher, with a consequently lower proportion of 12-hydroxy stearic acid. Therefore dehydration and hydrogenation are occurring to a marked extent with this catalyst even at such a low temperature. These general tendencies are more pronounced at 180° when ricinoleic acid has almost disappeared. The lower content of 12-hydroxy

TABLE III

Hydrogenation of Castor Oil in Solution with Raney Nickel (at 40–42 p.s.i. and 30–33°C.)

Experiment No.	Oil g.	Ethyl alcohol (95%) ml.	Catalyst %	Time hrs.	I.V. Wijs 30–33°C.	Hydroxyl value[b]	m.p. °C.
25	100	Nil	1.0	8	82.9	163.5	—
26	100	75	1.0	8	66.1	163.3	61.5
27	75	75	1.0	8	55.7	163.7	69.5
28	75	100	1.0	8	48.4	163.4	73.5
29	50	100	5.0	8	20.3	163.4	82.0
30	50	100	3.0 + 3.0 } 6	5 + 5 } 10	8.4[a]	163.1	82.5

[a] Wijs, 15–20°C.

[b] Average hydroxyl value for original castor oil—163.0.

stearic acid reveals that dehydration of this acid is also occurring to a greater extent. The higher proportion of saturated nonhydroxy acids indicate an increased rate of hydrogenation of the double bond. In contrast, at 220°, the product after eight hours of hydrogenation contains a significant amount of ricinoleic acid, appreciable amounts of oleic and iso-oleic acids, and a small amount of dienoic acid while the conversion of ricinoleic acid into nonhydroxy acids is about the highest. These points demonstrate that the dehydration of the hydroxy acids has proceeded at a faster rate than the hydrogenation of consequent unsaturated acids or ricinoleic acid. At the three temperatures studied the dry-reduced catalyst is superior to Raney nickel with respect to both hydrogenation and dehydration. The content of dihydroxy stearic acid is reduced but not to the same extent as it is with Raney nickel. The hydroxyl values of glycerides and methyl esters of samples 14 and 15 (Tables I and V) are about the same, and therefore no estolide formation has taken place. In contrast, at 220° (experiment 16), a small difference is noted, which indicates that estolide formation has occurred to a small extent at this temperature. With dry-reduced catalyst, conditions represented by experiment 15 are good enough for obtaining a product with a high content of saturated nonhydroxyl acids with the added advantage of a lower temperature.

Stepwise Addition of Catalyst. From Table I it is seen that under the optimum conditions used, both the iodine and hydroxyl values reach limiting values of 5 and 35, respectively. Increasing the temperature beyond the optimum has been found to have a retarding effect on hydrogenation. Therefore larger amounts of catalyst as well as longer periods of hydrogenation were used to see the effect on the two values. It is noted from Table 2 that by adding the catalyst in one lot up to 2% or in stages up to 4%, or increasing the time of reaction to 12 hrs., the iodine value is reduced to about 1, but the hydroxyl value is not reduced to the same extent. The recorded hydroxyl values of the hydrogenated samples are not truly representative as there is evidence of estolide formation [*Vide:* difference in the hydroxyl values of the glycerides and their methyl esters (Table II, last column)]. In addition, some splitting takes place.

Hydrogenation in Solution. The results given in Table III show that a) the addition of alcohol enhances greatly the saturation of the double bond, b) large portions of the catalyst added in two stages help in reaching low iodine values, and c) no reaction occurs at the hydroxyl group, thus permitting the production of the maximum quantity of 12-hydroxy stearic acid.

TABLE IV

Comparative Iodine Values of Some Hydrogenated Products

No.	Product	Wijs, 30 min.		Bromometric, 60 min. 30–33°C.	
		30–33°C.	15–20°C.	Uncorrected	Corrected
1	Hydrogenated castor oil	28.2	17.6	70.2	17.3
2	Acetylated product of No. 1 above	19.2	14.2	19.9	11.4
3	Methyl ester of No. 1 above	27.8	17.3	61.4	17.3

The fatty acid composition of sample 30, Table V, has about the same proportions of hydroxy and nonhydroxy acids as the parent oil, thus confirming the points made above that no reaction has occurred at the hydroxyl group.

TABLE V

Analysis, Resolution, and Composition of Methyl Esters of Samples of Hydrogenated Castor Oil

Expt. No.	Analysis of methyl esters		$E^{1\%}_{1\,cm.}$ 234 mμ		Resolution of esters		I.V. Wijs 15–20°C. non-hydroxy esters	Composition of methyl esters						Ricinoleic converted into non-hydroxy acids[b] %
	Hydroxyl value	Iodine value Wijs 15–20°C.	Nonisomerized	Isomerized	Hydroxy %	Non-hydroxy %		Saturated nonhydroxy, %	Oleic and isoleic,%	Dienoic, %	Ricinoleic, %	12-Hydroxy stearic, %	Di-hydroxy stearic, %	
Raw[a] castor oil	163.0	82.6	5.8	33.1	87.8	12.2	—	3.3	5.4	3.5	85.7	—	2.0	—
2	135.8	49.1	6.6	7.4	74.8	25.2	52.3	10.7	13.6	0.9	31.9	41.3	1.6	12.5
4	103.4	25.5	3.2	3.2	56.3	43.7	27.2	29.8	13.9	—	16.8	37.6	1.9	31.3
7	125.8	17.0	2.4	3.9	69.0	31.0	26.2	21.5	9.5	—	11.1	56.9	1.0	17.7
9	97.2	4.1	—	—	53.5	46.5	8.0	42.1	4.4	—	0.5	52.2	0.8	33.0
11	40.5	2.8	—	—	22.0	78.0	2.3	75.9	2.1	—	1.2	20.4	0.4	64.1
14	96.2	17.3	2.3	3.0	53.0	47.0	20.2	35.9	11.1	—	9.6	42.3	1.1	33.8
15	58.7	1.6	—	—	31.5	68.5	1.4	67.4	1.1	—	0.8	29.3	1.4	55.6
16	38.8	13.6	2.8	6.5	21.0	79.0	10.9	69.7	8.6	0.7	6.1	13.3	1.6	66.3
30	162.4	7.9	—	—	88.3	11.7	16.0	9.5	2.2	—	7.4	78.2	2.7	—

[a] Average of values reported for the three samples of castor oil in Part I (17) presented for purposes of comparison.

[b] Calculated thus: 85.7 —(% 12 hydroxy stearic acid in hydrogenated sample)—(%ricinoleic acid in hydrogenated sample).

Estimation of Unsaturation. It has been shown in Part I of this work (17) that the Standard Wijs method employed at 15–20°C. gives an accurate measure of the total unsaturation of the methyl esters of castor oil and can be used in calculating the fatty acid composition. A comparative study of the iodine values of hydrogenated castor oil, its mixed methyl esters, and acetylated hydrogenated castor oil has shown (Table IV) that the same method can be applied with certainty to the methyl esters of hydrogenated castor oil. This has therefore been employed in calculating the fatty acid composition of various samples of hydrogenated castor oil, as given in Table V. The high uncorrected iodine value by the bromometric method shows that substitution predominates in hydrogenated castor oil. In such an oil there is an excess of hydroxyl groups over double bonds with the result that a greater quantity and higher concentration of halogens are available for side reactions than in castor oil.

Summary

1. Products of low iodine value (<10.0) and hydroxyl value (35–40) can be readily obtained by hydrogenating castor oil at atmospheric pressure and at temperatures of the order of 220°, using 1.0% Raney nickel.

2. Dehydration of ricinoleic acid and subsequent hydrogenation of the resulting double bond as also simple saturation of ricinoleic acid are the main reactions occurring during the hydrogenation of castor oil under ordinary conditions.

3. Increase in the amount of catalyst favors more the hydrogenation of double bond at lower temperatures and both dehydration and hydrogenation at about 220°, which seems to be the optimum temperature for the maximum conversion of ricinoleic acid into nonhydroxy acids with both Raney and dry-reduced nickel at atmospheric pressures.

4. Higher proportions of catalyst, addition of catalyst stepwise, and higher temperature of hydrogenation cause considerable splitting and estolide formation.

5. When hydrogenation is carried out at room temperature, under a pressure of 40 p.s.i. with alcohol as solvent, a product rich in monohydroxy stearic acid is obtained.

6. True unsaturation of hydrogenated castor oil is measured by the Wijs method at 15–20°C.

REFERENCES

1. Adkins, H., and Wojcik, B., J. Am. Chem. Soc., *55*, 1293–1294 (1933).
2. Brochet, A., Compt, rend., *176*, 513–515 (1923).
3. Covert, L. W., and Adkins, H., J. Am. Chem. Soc., *54*, 4116–4117 (1932).
4. Covert, L. W., Connor, R., and Adkins, H., J. Am. Chem. Soc., *54*, 1651–1663 (1932).
5. Grün, A. O., and Woldenberg, M., J. Am. Chem. Soc., *31*, 490–506. (1909).
6. Gupta, S. S., and Aggarwal, J. S., J. Sci. Ind. Res. (India), *11B*, 303–304 (1952).
7. Hertelendi, L., Magyar. Chem. Folyoirat, *47*, 49–75 (1941).
8. Jurgens, T., and Meighen, W., Chem. Umschau, *23*, 99–102, 116 (1916).
9. Kaestner, F., and Heinrich, H., Food, *10*, 196 (1941).
10. Nord, F. F., Z. angew. Chemie, *32* (1), 305 (1919).
11. Normann, W., Z. deut. Oel Fette-Ind., *46*, 193–195 (1923).
12. Palfray, L., Bull. Soc. Chim., *7*, 439–445 (1940).
13. Paquot, G., and Richet, H., Oleagineux, *3* (1), 26–28 (1948).
14. Schmidt, O., Berischte, *64B*, 2051–2053 (1931).
15. Shinozaki, Y., and Kagawa, S., J. Agr. Chem. Soc. Japan, *13*, 12–17 (1937).
16. Shinozaki, Y., and Kubo, H., *ibid.*, *13*, 18–22 (1937).
17. Sreenivasan, B., Kamath, N. R., and Kane, J. G., J. Am. Oil Chemists' Soc., *33*, 61–66 (1956).
18. Sudborough, J. J. Watson, H. E., and Athawale, D. Y., J. Ind. Inst. Sci., *5*, 47–69 (1922).
19. Thoms, H., and Deckert, W., Pharm. Monatshefte, *1*, 147 (1920).
20. Toyama, Y., and Ishikawa, T., J. Soc. Chem. Ind. Japan, Suppl. binding, *39*, 300–302 (1936).
21. Ueno, S., J. Soc. Ind. Japan, Suppl. binding, *39*, 150–151 (1936).
22. Vol'fson, E., and Levit, M., Maslob. Zhirov. Delo., *13* (4), 30–31 (1937).
23. Warburton, G. H., Rep. Prog. Appl. Chem., *4*, 298 (1919).

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Reactions of Unsaturated Fatty Alcohols. III. Viscosity and Molecular Weight Studies on Some Vinyl Ether Polymers[1]

L. E. GAST, W. J. SCHNEIDER, and H. M. TEETER, Northern Utilization Research Branch,
Agricultural Research Service, U. S. Department of Agriculture, Peoria, Illinois

RECENT WORK AT THIS LABORATORY on the preparation and polymerization of vinyl alkyl ethers derived from fatty alcohols has resulted in the initiation of molecular weight studies on these materials. Although several of the higher vinyl ether polymers have been known for a number of years, no molecular weight information appears to have been published. Investigators working with the higher alkyl vinyl ether polymers have referred to viscosity measurements to get comparisons of the degree of polymerization of their products. It seemed to us that a relationship between molecular weight and intrinsic viscosity for the higher alkyl vinyl ethers would be valuable. This paper reports the results of our studies on stearyl, soybean, and linseed vinyl ether polymers.

Molecular Weight Studies

In a previous paper of this series (9) preliminary experiments on the polymerization of vinyl ethers prepared from stearyl alcohol and several unsaturated fatty alcohols were described. Molecular weight data obtained by boiling-point elevation studies in benzene gave molecular weights ranging from 1,000–5,000. However the method was not considered satisfactory for our purposes because improved polymerization conditions were giving polymers of higher molecular weight and the relatively small boiling-point elevation in benzene reduced the accuracy of the determination. Isothermal distillation methods for determining molecular weights seemed a possible solution. The method of Parrette (6), using a modified Signer tube agitated by a rocking device, was tried, but attainment of equilibrium was too slow for our purposes. Cyclohexane has a rather large molal depression constant ((K_f)), and since our polymers were readily soluble in this solvent, a cryoscopic method was worked out. The apparatus used was simple in design and was similar to the conventional apparatus used for this work (1). A Beckman thermometer was used to measure freezing-point depressions. Constant stirring was accomplished by coupling an automobile

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