

## STUDIES ON DEHYDRATED CASTOR OIL—PART I

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### INTRODUCTION

Since the pioneering work of Scheiber (1930) introducing castor oil, after dehydration, as a substitute for tung oil, extensive work has been carried out to find a suitable dehydration catalyst. During dehydration of castor oil ricinoleic acid is transformed into 9, 11- and 9, 12-linoleic acids. Commercial varieties of dehydrated castor oil contain appreciable amount of this 9, 11 isomer and so approach tung oil in drying properties. Tung oil, however, contains a conjugated triene acid, viz. elaeostearic acid, which is absent in D.C. oil. The absence of triple unsaturated fatty acids in dehydrated castor oil imparts to it an outstanding non-yellowing characteristic. The properties of tung oil have been compared with various natural drying oils by Priest and von Mikusch (1941). The drying time, rate of heat polymerization and water and alkali resistance of the varnish film of dehydrated castor oil is intermediate between that of linseed oil and tung oil. The films produced by it are softer than those obtained from linseed, perilla or tung oils but possess superior elasticity.

In the paints and varnish industry, dehydrated castor oil has achieved a place of its own along with the natural drying oils. Terrill (1950) has reported that the conjugated isomers in unbodied dehydrated castor oil generally amount to 30%. Priest and von Mikusch (1940) have shown that the conjugated isomers do not appreciably increase during bodying of the dehydrated oil. A high proportion of non-conjugated octadecadienoic acid is found to be present in dehydrated castor oil. The chemistry of the process of dehydration of castor oil is still ambiguous as a unanimous conclusion has not yet been reached regarding the mechanism of some of the essential steps involved.

The primary object of the previous investigators had been to obtain the maximum dehydration possible and, with this object in view, many empirical reaction conditions have been suggested. In most of the investigations claiming complete dehydration, the extent of dehydration has been ascertained by determining the hydroxyl value of the dehydrated oil. It has, however, been shown by Kappelmeier *et al.* (1948) that reactions other than the conversion of ricinoleic acid to linoleic acid take place during dehydration and so the procedure of using the observed hydroxyl value as a measure of dehydration should be denounced. The exact extent to which the various possible side reactions occur depends on the conditions employed and its absolute determination offers a rather difficult analytical proposition. The influence of the constituent fatty acids in castor oil, other than ricinoleic acid, on the course of dehydration has not been studied.

Very little work has also been done to improve the quality of the product by raising the proportion of conjugated to non-conjugated linoleic acid in the product. The introduction of spectrophotometric technique in fat chemistry has provided a convenient tool for estimating conjugated and non-conjugated fatty acids in the presence of each other, as also in the presence of saturated and substituted fatty acids. The present work was undertaken with a view to study the mechanism of

formation of conjugated isomers during dehydration of castor oil. To observe the influence of constituent fatty acids on polymerization, conjugation, and isomerization during the course of dehydration, samples of castor oil, containing varying proportions of ricinoleic, linoleic, oleic and saturated acids, were prepared by preferential solvent extraction of the seeds using ethanol, hexane, benzene and trichloro-ethylene as solvents. The different samples obtained were subsequently dehydrated under identical conditions as described below.

### EXPERIMENTAL

#### (i) Preparation of different samples of castor oil

Dried and crushed decorticated castor seeds in lots of 500 gm. were taken in a glass column having an inlet and outlet at the bottom and top respectively. The crushed castor seeds were placed in the column over a suitable perforated support; the upper surface of the charge was also covered with a perforated porcelain plate to prevent disturbance of the bed. 2,000 ml. of the solvent were used for each lot. The castor seeds were first extracted with a non-alcoholic solvent. The resulting solvent-oil mixture was recirculated until the concentration of oil in the solvent was constant. The castor seeds so extracted were then freed from the adhering solvent by evaporating off the latter under vacuum. The residual oil in the seeds was then extracted with absolute ethanol. The samples of oil were freed from the solvents by distilling off the latter under vacuum and were then analysed. The hydroxyl values of the oils and component fatty acids were determined by the method of West, Hoagland and Curtis (1934). Analysis of the mixed fatty acids according to the method of Kaufmann *et al.* (1939) showed that dihydroxy stearic acid was absent in all the samples.

For determining the content of linoleic acid in the mixed fatty acids, the oil was first saponified with alcoholic KOH solution and the resulting soap solution was scrupulously freed from unsaponifiable matters. The mixed fatty acids were liberated by mineral acid (HCl) and were recovered from the acidified liquid by extraction with di-ethyl ether. The mixed fatty acids were obtained from the ethereal solution in the usual manner by distilling off the ether under vacuum. The mixed fatty acids so obtained were analysed adopting the spectrophotometric technique of Hilditch, Morton and Riley (1945) as later modified by Hilditch, Patel and Riley (1951).

The non-saponifiable contents of the oils were determined in the usual manner. The iodine values of the oils and their mixed fatty acids were determined by Wij's method. The results are presented in Tables 1, 2 and 3. The hydroxyl value of the mixed fatty acids was accounted for by ricinoleic acid only. It will be seen from Table 3 that the benzene extract yields an oil with a fatty acid composition: 84.6% ricinoleic, 5.6% linoleic, 5.6% oleic and 4.2% saturated acids. The ethanol extract of the residual meal yielded an oil having the fatty acid composition: 97.5% ricinoleic, 0.8% linoleic, 1.3% oleic and 0.4% saturated acids. The extract in this case contains the highest proportion of ricinoleic acid in comparison with the alcohol extracts obtained from meals left after hexane or trichloro-ethylene extraction. It has thus been possible to prepare different samples of castor oil containing varying proportions of glycerides of different fatty acids. These samples have been used for studying the mechanism of dehydration of castor oil.

#### (ii) Dehydration of different samples of castor oil

Lots of 500 gm. of oil were used in each run. The oil was taken in a three-necked flask fitted with a mechanical stirrer operating through a stuffing box, an inlet for bubbling nitrogen gas, a thermometer and an outlet for the volatile gases released, this was connected to a vacuum pump *via* an intermediate vessel. The

TABLE 1

*Results of Solvent Extraction*

Solvent used.	% oil extracted.	% oil in residue. Extracted by absolute ethanol.
n-Hexane ..	54.06	45.94
Benzene ..	73.78	26.22
Trichloro-ethylene	46.80	53.20

TABLE 2

*Physico-Chemical Constants of the Extracted Oils*

	Iodine value (a)	Hydroxyl value	% non-sap. (b)	Ref. ind. at 25°C.	Mean mol. wt. (c)	Viscosity at 25°C. (in poises)
1. Hexane extract ..	85.0	152.4	1.4	1.4688	917.7	6.4
2. Residual oil after hexane extraction* ..	81.7	172.8	0.2	1.4718	931.2	7.1
3. Benzene extract ..	83.0	152.0	1.2	1.4692	922.8	6.4
4. Residual oil after benzene extraction* ..	81.7	175.0	0.1	1.4732	932.1	7.2
5. Trichloro-ethylene extract ..	86.4	150.0	1.1	1.4672	921.5	6.4
6. Residual oil after trichloro-ethylene ex- traction* ..	82.4	165.0	0.3	1.4702	922.5	6.9
7. Cold-pressed oil ..	83.1	160.1	0.8	1.4692	924.3	6.7

(a) Iodine value, Wij's 30 minutes.

(b) % non-saponifiable and unsaponified matter.

(c) Mean molecular weight determined by freezing point depression method.

\* The oil left in the meal was extracted with absolute ethanol.

vacuum used (24-25" Hg) was read off from a mercury manometer. The catalyst was a mixture of 1% NaHSO<sub>4</sub> and 1% KHSO<sub>4</sub> on the weight of oil. The temperature was maintained at 250°C. Samples were withdrawn from time to time for analysis. The molecular weight of the dehydrated oil was determined by the freezing point depression of a solution of the oil in benzene. The acid value was determined in the usual manner. The dehydrated oil was saponified in the usual manner and the non-saponifiable and unsaponified matters were removed from the soap solution by extraction with ether. The mixed fatty acids were then liberated with HCl and extracted with ether. The fatty acids were recovered in the manner previously described.

TABLE 3

*Analyses of the Mixed Fatty Acids of the Oils*

	I.V. (a)	H.V. (b)	$E_{1\text{cm.}}^{1\%}$ 180°C./60 mins. at 234 m $\mu$ .	% composition of mixed acids.			
				Ricin- oleic.	Lin- oleic.	Oleic.	Satura- ted.
1. Hexane ex- tracted ..	88.3	158.0	69	80.9	7.6	6.3	5.2
2. Residual oil after hexane ex- traction* ..	85.2	180.3	10	95.9	1.1	2.1	0.9
3. Benzene ex- tracted ..	87.2	159.1	51	84.6	5.6	5.6	4.2
4. Residual oil after benzene ex- traction* ..	85.6	183.2	7	97.5	0.8	1.3	0.4
5. Trichloro- ethylene extracted	88.9	157.5	63	83.8	7.0	5.3	3.9
6. Residual oil after trichloro- ethylene extrac- tion* ..	85.4	171.8	23	91.4	2.5	3.6	2.5
7. Cold-pressed oil .. ..	87.0	165.0	42	87.8	4.6	4.4	3.2

(a) Iodine value, Wij's 30 minutes.

(b) Hydroxyl value.

\* The oil left in the meal was extracted with absolute ethanol.

The mixed fatty acids of the products were obtained and their hydroxyl values were determined as in the case of the original oil and the proportion of ricinoleic acid in these were calculated on the assumption that this acid accounts for the hydroxyl value.

To estimate the proportion of conjugated linoleic acid, about 0.1 gm. of the mixed fatty acids was dissolved in aldehyde-free ethanol. The extinction coefficient at 234m $\mu$  of this alcoholic solution, after dilution, was observed with the help of a Beckman Spectrophotometer.

For estimating the proportion of non-conjugated linoleic acid the extinction coefficient at 234m $\mu$  of an alcoholic solution of the mixed fatty acids, isomerized at 180°C. for one hour with caustic potash-glycol reagent, was determined. For calculating the percentage of conjugated and non-conjugated linoleic acids the following figures for the extinction coefficients of pure conjugated and non-conjugated linoleic acids were used :

$E_{1\text{cm.}}^{1\%}$  of un-isomerized conjugated dienoic acid at 234m $\mu$  → 1,200

$E_{1\text{cm.}}^{1\%}$  of conjugated dienoic acid isomerized at 180°C./60 mins. at 234m $\mu$  → 1,140

$E_{1\text{cm.}}^{1\%}$  of non-conjugated linoleic acid isomerized at 180°C./60 mins. at

234m $\mu$  → 906.

The results are presented in Tables 4, 5 and 6.

TABLE 4  
Dehydration at 250°C. of Cold-pressed Castor Oil

Time in minutes.	I.V. of oil (Wij's). (a)	Mol. wt. of oil. (b)	Viscosity of oil. (c)	A.V. of oil. (d)	Analyses of m.f.a. of dehydrated oil.			% composition of m.f.a.		
					H.V. (e)	E <sup>1</sup> % Icm. (*)	E <sup>1</sup> % Icm. (†)	Ricinoleic.	9, 11-linoleic. (f)	9, 12-linoleic. (g)
0	83.1	924.3	6.7	0.2	165	3	42	87.8	nil	4.6
15	87.2	921.2	5.5	0.4	151	47	113	80.5	3.9	7.6
30	118.5	924.5	4.6	1.1	63.9	103	526	34.0	8.6	47.2
45	136.5	928.6	2.9	1.8	24.2	175	747	12.9	14.6	64.2
60	140.2	938.2	1.6	2.7	10.9	242	824	5.8	20.2	65.6
90	135.9	948.3	2.5	3.5	8.6	289	844	4.6	24.1	62.3
120	128.3	960.3	3.6	4.4	7.7	334	868	4.1	27.8	60.8

(a) Iodine value of oil, Wij's 30 minutes.  
 (b) Molecular weight of oil (determined by freezing point depression).  
 (c) Viscosity of oil in poises.  
 (d) Acid value of oil.  
 (e) Hydroxyl value of the mixed fatty acids of oil.  
 (\*) E<sup>1</sup>% Icm. of mixed fatty acids isomerized at 180°C. for 60 minutes at 234m $\mu$ .  
 (†) E<sup>1</sup>% Icm. of un-isomerized mixed fatty acids at 234m $\mu$ .  
 (f) 9, 11-linoleic acid (conjugated).  
 (g) 9, 12-linoleic acid (non-conjugated).

TABLE 5  
Dehydration at 250°C. of Hexane Extracted Castor Oil

Time in minutes.	I.V. of oil. (a)	Mol. wt. of oil. (b)	Viscosity of oil. (c)	A.V. of oil. (d)	Analyses of m.f.a. of dehydrated oil.			Composition of m.f.a.		
					H.V. (e)	E <sub>1cm.</sub> <sup>1%</sup> (*)	E <sub>1cm.</sub> <sup>1%</sup> (†)	Ricin- oleic.	9, 11- linoleic. (f)	9, 12- linoleic. (g)
0	85.0	917.7	6.4	0.5	152	2	69	80.9	nil	7.6
15	89.1	918.2	5.2	0.7	141.4	26	124	75.2	2.2	10.9
30	109.4	922.5	4.2	1.5	80.7	60	420	42.9	5.0	40.2
45	128.3	926.9	2.6	2.1	33.9	97	654	18.0	8.1	62.2
60	130.6	928.7	1.5	3.1	13.5	220	777	7.2	18.4	62.6
90	125.6	938.5	2.3	3.6	9.6	264	803	5.1	22.0	60.9
120	120.2	949.9	3.3	4.7	8.5	290	814	4.5	24.2	59.2

(a), (b), (c), (d), (e), (f), (g), (\*), (†) same as in Table 4.

TABLE 6  
Dehydration at 250°C. of Residual Oil (Extracted by Ethanol) after Benzene Extraction

Time in minutes.	I.V. of oil. (a)	Mol. wt. of oil. (b)	Viscosity of oil. (c)	A.V. of oil. (d)	Analyses of m.f.s. of dehydrated oil.			% composition of m.f.s.		
					H.V. (e)	E <sup>1</sup> % <sub>1cm.</sub> (*)	E <sup>1</sup> % <sub>1cm.</sub> (†)	Ricinoleic.	9, 11-linoleic. (f)	9, 12-linoleic. (g)
0	81.7	923.1	7.2	0.3	183.2	nil	7	97.5	nil	0.8
15	91.2	930.0	6.1	0.6	158.0	67	138	84.0	5.6	8.2
30	124.0	934.5	5.2	1.2	77.1	154	532	41.0	12.9	42.5
45	144.2	940.6	3.1	1.7	32.0	246	782	17.0	20.5	60.5
60	148.2	950.9	1.8	2.9	13.3	341	888	7.1	28.4	62.3
90	140.2	961.2	2.9	3.1	9.8	389	917	5.2	32.4	60.5
120	132.1	975.2	4.1	3.9	9.2	408	928	4.9	34.0	59.6

(a), (b), (c), (d), (e), (f), (g), (\*), (†) same as in Table 4.

## DISCUSSION

It will be evident from the data that maximum dehydration is almost reached within the first sixty minutes of the reaction and that further prolongation of heating period leads to polymerization of the product with simultaneous drop in iodine values.

It has been observed (*vide* Tables 2 and 3) that the viscosity of the oil increases with increasing ricinoleic acid content of the oil. This can be explained by the fact that the 'drag' or association of the hydroxyl groups on the fatty acid chains is responsible for the viscosity.

It is also observed that the hydroxyl value of the mixed fatty acids from the dehydrated product never reaches zero but tends to attain a limiting value between 8 to 10 even under severe conditions. The mixed fatty acids liberated from the dehydrated oil contain some unconverted ricinoleic acid, though the amount of the latter is insignificant. It is evident from the results presented in Tables 3, 4 and 5 that the higher the percentage of ricinoleic acid in the oil, the greater is the degree of polymerization. The proportion of dienoic acids in the original oil does not affect the degree of polymerization to such an extent. This suggests that the di-unsaturated acids, as obtained by the dehydration of ricinoleic acid, play a more important rôle in bringing about the polymerization reaction than the dienoic acids originally present.

This phenomenon suggests that the dienoic acid produced by the dehydration of ricinoleic acid is structurally different from the ordinary dienoic acid. The major portion of the dienoic acids produced during dehydration is of the non-conjugated form. It cannot, therefore, be suggested outright that polymerization is entirely dependent on the proportion of conjugated isomers in the product.

The principal chemical reaction involved in the dehydration of castor oil, viz. the splitting off of the OH group in ricinoleic acid together with a neighbouring hydrogen atom, is too well known to need any elaboration; controversy arises, however, regarding the position of the carbon atom in the fatty acid chain which supplies the hydrogen atom.

The original view, which is still held by Scheiber (1949), is that a hydrogen on the eleventh carbon atom is involved and formation of conjugated octadecadienoic acid is exclusively due to this. Priest and von Mikusch (1940), however, concluded on the basis of diene values that non-conjugated isomers predominate in the product. The present investigation also confirms the latter observation (*vide* Tables 4, 5 and 6).

Assuming on the basis of physico-chemical data (cf. T. P. Hilditch: *The Chemical Constitution of Natural Fats*, 2nd Edition, Chapman and Hall, London, 1947, pp. 401-402) that the double bonds in oleic, linoleic and ricinoleic acids have the *cis* structure, it may be stated that the following two conjugated and two non-conjugated linoleic acid isomers having a *cis*-double bond between the 9th and 10th carbon atoms are produced as a result of dehydration,

- 9-*cis*, 11-*cis* octadecadienoic acid.
- 9-*cis*, 11-*trans* octadecadienoic acid.
- 9-*cis*, 12-*cis* octadecadienoic acid.
- 9-*cis*, 12-*trans* octadecadienoic acid.

That the *cis*-double bond already present in the ricinoleic acid is, as a rule, not eliminated during dehydration is proved by the fact that *trans*, *trans*, 9, 11 octadecadienoic acid (melting point 54°C.), which is found in the distillation product of ricinoleic acid (Mangold, 1894), is not produced to any appreciable extent when castor oil or ricinoleic acid is dehydrated. von Mikusch identified *cis-trans* isomers of ordinary linoleic acid in dehydrated castor oil by treatment with excess of aq. alkali. Similar treatment of fixed oils containing linoleic acid does not produce



this isomer. From further investigation, von Mikusch (1949 and 1951) concluded that the *cis-trans* isomer of ordinary linoleic acid could only be produced by dehydrating castor oil and this isomer is responsible for the formation of solid conjugated acid during alkali isomerization. It is thus apparent that this *cis-trans* isomer of linoleic acid is an important factor during polymerization. The mechanism of dehydration of castor oil may now be pictured as follows.

The removal of water molecule from ricinoleic acid gives rise to three products : (i) 9, 11 conjugated linoleic acid, (ii) 9-*cis*, 12-*cis* non-conjugated linoleic acid, (iii) 9-*cis*, 12-*trans* non-conjugated linoleic acid, of which the last is rapidly polymerized and the other two are left in non-polymerized state ; the conjugated variety (i) has, of course, a tendency to undergo polymerization, but this is less than that of the *cis-trans* variety (iii).

It may also be concluded from data presented in Tables 4, 5 and 6 that the higher the content of ricinoleic acid in the initial sample the higher will be the proportion of 9-*cis*, 12-*trans* linoleic acid in the product and the higher will be the degree of polymerization. It is further revealed that the primary function of the catalyst is to effect the dehydration of ricinoleic acid and that the isomerization of the non-conjugated compounds to conjugated ones is more or less remote. After this dehydration the dienoic acids produced have a tendency to undergo the following changes, viz. (i) conversion into the conjugated isomer, and (ii) polymerization. The latter tendency seems to be more pronounced after the first sixty minutes of the reaction (*vide* Tables 4, 5 and 6). It is also interesting to note that prolonging the heating at 250°C. beyond sixty minutes results in conversion of non-conjugated dienes to conjugated dienes in addition to polymerization that has already been referred to.

The proportion of the non-conjugated dienes in the reaction mass after the first sixty minutes of the heating is about 60%, while only 1 to 4% of the same is initially present. The increased concentration of this component affects the speed of conversion of non-conjugated to conjugated dienes and so the reaction is led to yield a higher proportion of the conjugated variety to maintain the equilibrium constant. Further, at this reaction temperature the double bonds migrate in either direction from or towards the next double bond. Certain catalysts are known to greatly accelerate bodying of oils. A catalyst may be effective in promoting polymerization, but isomerization to a conjugated form is the first step in the heat bodying of oils.

## SUMMARY

In average samples of dehydrated castor oil, 30% conjugated isomers and a high proportion of non-conjugated octadecadienoic acid are found to be present. The mechanism of formation of conjugated isomers and the influence of the constituent fatty acids on conjugation, isomerization and polymerization during the process of dehydration and subsequent bodying have been investigated. For this purpose, samples of castor oil containing varying proportions of constituent fatty acids have been prepared by preferential solvent extraction of the seed meal. Spectrophotometric technique of analysis has been employed for estimation of conjugated and non-conjugated fatty acids. It has been suggested that the 9-*cis*, 12-*trans* non-conjugated linoleic acid, which is one of the products of dehydration during the first 60 minutes of treatment, plays a more important rôle in bringing about polymerization reaction than the conjugated dienoic acids originally present and also formed during the course of reaction. It is also concluded that the higher the content of ricinoleic acid in the original sample, the larger is the proportion of the conjugated dienes in the product and higher the degree of polymerization. While heating dehydrated castor oil it has been observed that the tendency towards polymerization is pronounced after the first 60 minutes of heating at 250°C.; some conversion of non-conjugated dienes to conjugated dienes is also marked during this period. During the first one hour period of heating at 250°C., the proportion of conjugated dienes in the product goes up to between 18-28%, the accumulation of which influences the speed of polymerization reaction.

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