

STUDIES ON DEHYDRATED CASTOR OIL—PART II

EFFECT OF TEMPERATURE ON POLYMERIZATION AND ISOMERIZATION OF DEHYDRATED CASTOR OIL

by DIPTI KĀLYAN CHOWDHURY and B. K. MUKHERJI,
*Department of Applied Chemistry, University Colleges of
Science and Technology, Calcutta 9*

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In Part I of this investigation it had been clearly indicated that prolonging the period of heating at 250°C. after the first 60 minutes, initiates polymerization and there is also a slight increase in the content of conjugated isomers in the product. This increase in conjugated isomers has been found to be associated with a decrease in the non-conjugated dienoic acids in the product. This has not been reported by any previous worker.

von Mikusch (1940) carried out extensive investigations on the bodying of dehydrated castor oil and showed that the tendency to polymerize increased with increase in temperature and for the same temperature the rate of polymerization was more rapid than in linseed oil. He did not, however, record the influence of temperature and period of heating on the shifting of the double bonds from the non-conjugated to conjugated positions during bodying. It is obvious that both conjugated and non-conjugated dienes are involved during polymerization. It is also possible that prolongation of the heating period, after the dehydration is complete, may change the initial course of the reaction due to the accumulation of a large proportion of non-conjugated dienoic acid in the reaction product (about 60% after one hour ; initially 1 to 4%).

This increased concentration of the 9, 12 dienoic acid might well be expected to give a high speed of conversion of non-conjugated to conjugated isomers as indicated in Part I (*loc. cit.*).

Another fact to be considered is that the proportion of conjugated dienes is initially nil but goes up to between 18 and 28% during the first sixty minutes of heating (Part I; *loc. cit.*). The increased concentration of conjugated isomers will exert a prepondering influence on the speed of polymerization reaction. It is quite reasonable to assume, therefore, that if polymerization can be regulated the product will be enriched with conjugated isomers. This aspect of the problem has been investigated on the following lines.

EXPERIMENTAL

Cold-pressed raw castor oil was dehydrated at 250°C. with 1% NaHSO₄ and 1% KHSO₄ (on weight of oil) in the manner previously described (*vide* Part I). The heating was carried out for one hour ; the product was then rapidly chilled, and the catalysts remaining in suspension were removed. The prepared sample was divided into several portions which were respectively maintained at temperatures of 100°, 150°, 200°, 250°, and 300°C. for various periods in an atmosphere of nitrogen under partial vacuum. Samples were withdrawn from time to time in each case and were analysed for determining the following :

- (i) The molecular weight of the oil.
- (ii) Acid value of the oil.
- (iii) Viscosity of the oil.
- (iv) Per cent 9, 12 linoleic acid in the component mixed fatty acids.
- (v) Per cent 9, 11 linoleic acid in the component mixed fatty acids.

The analyses were carried out according to the methods already described (*vide* Part I). The results are given in Table 1. It has been observed that the higher the temperature and the longer the period of heating, the higher is the viscosity and the acid value of the product. The effects of temperature and period of heating on isomerization are best manifested at 200°C. and within that temperature range it is found that the proportion of conjugation reaches a maximum after the first sixty minutes and then tends to decrease. A possible explanation of this phenomenon is given. It has been noted that at lower temperatures neither polymerization nor isomerization assumes prominence while at higher temperatures, specially at 300°C., the former reaction proceeds so rapidly that the latter is outpaced.

DISCUSSION

It has been found that some dienoic acids are formed during heat bodying of oils which are not reactive (Paschke and Wheeler, 1949). Isomerization to a conjugated form is the first step in the heat bodying of non-conjugated oils, and is a slow reaction. Certain catalysts are known to greatly accelerate bodying of oils. The catalyst may also be effective in promoting the polymerization step.

Results in the given Table show the effect of temperature on isomerization and polymerization. It has been observed that the proportion of conjugated compounds diminishes after reaching a certain maximum. This diminution in conjugation is, perhaps, due to ring formation. 9, 12 linoleic esters combine with conjugated dienes, but the latter react with each other at a faster rate. This ring formation helps to bind together the glyceride molecules and the larger the number of glyceride molecules combined together, the bigger is the size of individual molecules. The increase in viscosity is a result of this polymerization.

While the dienoic acids combine to form a dimer containing a single ring, it appears that the addition products form tri-unsaturated groups which may, to some extent, go further and form a structure containing two rings. Bradley and Johnston (1941) found that a third fatty acid group can combine and the conjugated group can add to one of the groups already combined to form a second ring. This reaction, perhaps, is a subsequent step to the first ring formation and, as it involves a termolecular reaction, its speed is slow and occurs at the later stages of bodying. In general, speeds of reaction can be accelerated by increasing the temperature. Results presented in the accompanying Table prove that while polymerization is not very appreciable at temperatures of 100°C. and 150°C., it increases considerably at 200°C. At 250°C. and 300°C. it proceeds very rapidly. The mechanism of polymerization is suggested below.

As regards the formation of 9, 11 linoleic acid at the cost of 9, 12 linoleic acid it has been found that particularly little or no increase in conjugation occurs when castor oil, previously dehydrated at 250°C. for 60 minutes, is held at temperatures of 100°C. and 150°C. for one hour. A temperature of 200°C. is an optimum for such a reaction; by maintaining the dehydrated oil at this temperature for 90 minutes conjugation could be increased by 8.6%. On prolonging the heating conjugation begins to decrease. At 250°C. the conjugation could be increased by 7.6% within 60 minutes after which period conjugation tends to decrease. At 300°C. the conjugation could be increased by only 4% after 60 minutes. Prolonging the period further than this results in destruction of conjugated structure and there is a rapid increase in polymerization. Data in the Table clearly indicate that the higher the

TABLE I
Effect of Temperature and Period of Heating on Polymerization and Isomerization of Dehydrated Castor Oil

Temp., °C.	Time in mins.	Mol. wt. of oil.	Visc. of oil. (a)	A.V. of oil. (b)	Analyses of m.f.a.		% composition of m.f.a.	
					Un-isomerized.	E ¹ % at 234 m μ . 1 cm.	Isomerized.*	% linoleic (conjugated).
100	0	938.2	1.6	2.7	242	824	20.2	65.6
	15	940.1	1.6	2.7	246	824	20.5	65.2
	30	940.5	1.7	2.8	244	824	20.3	65.4
	60	942.2	1.7	3.0	247	826	20.6	65.2
	90	944.3	1.7	3.1	245	826	20.4	65.4
	120	948.2	1.8	3.4	240	819	20.0	65.2
150	0	938.2	1.6	2.7	242	824	20.2	65.6
	15	941.5	1.7	2.8	250	827	20.8	65.1
	30	942.8	1.7	3.0	248	828	20.7	65.3
	60	944.6	1.8	3.1	252	822	21.0	64.9
	90	947.2	1.8	3.3	254	827	21.2	64.6
	120	950.5	1.9	3.5	252	823	21.0	64.5
200	0	938.2	1.6	2.7	242	824	20.2	65.6
	15	944.0	1.8	3.0	264	828	22.0	63.7
	30	947.1	2.1	3.4	302	846	25.2	61.7
	60	952.0	2.8	3.7	353	844	29.4	56.2
	90	956.2	3.0	3.9	346	843	28.8	56.9
	120	960.1	3.2	4.1	336	844	28.0	58.0

(a) Viscosity of the oil in poises at 25°C.

(b) Acid value of oil.

* Isomerized at 180°C. for sixty minutes.

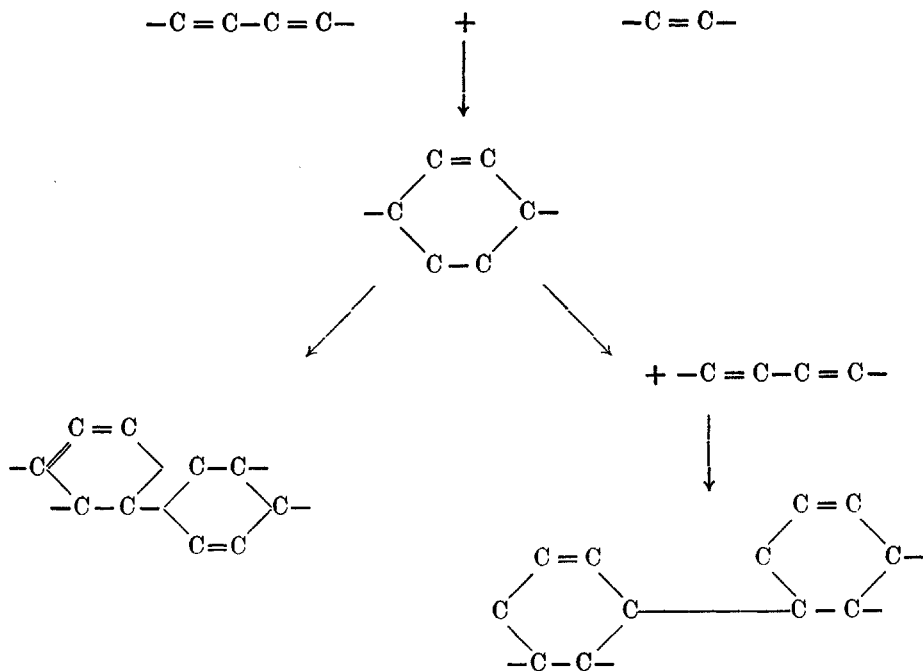
TABLE I—contd.

Temp., °C.	Time in mins.	Mol. wt. of oil.	Visc. of oil. (a)	A. V. of oil. (b)	Analyses of m.f.a. E ₁ % at 234 mμ.		% composition of m.f.a.	
					Un-isom- erized.	Isomerized.*	% linoleic (conjugated).	% linoleic (non-conju- gated).
250	0	938.2	1.6	2.7	242	824	20.2	65.6
	15	946.1	1.8	3.2	262	824	21.0	64.6
	30	948.3	2.3	3.6	289	844	24.1	62.8
	60	960.3	3.3	4.7	334	868	27.8	60.8
	90	964.3	3.6	4.9	313	862	26.1	61.2
	120	968.0	4.1	5.2	307	854	25.6	62.0
300	0	938.2	1.6	2.7	242	824	20.2	65.6
	15	960.1	2.2	3.4	246	825	20.5	65.2
	30	956.3	3.6	3.9	264	824	22.0	63.2
	60	966.2	5.8	5.1	290	831	24.2	61.2
	90	972.5	7.2	5.5	277	829	23.1	62.5
	120	983.8	10.5	6.1	258	828	21.5	64.3

(a) Viscosity of the oil in poises at 25°C.

(b) Acid value of oil.

* Isomerized at 180°C. for sixty minutes.



temperature, the higher is the acid value of the product. This probably results from decomposition of fat by pyrolysis. Moreover, a substance, saponifiable with difficulty, has been found to be formed during heating of the dehydrated oil at 300°C.

SUMMARY

An attempt has been made to regulate the polymerization of dehydrated castor oil during bodying and to enrich the product with conjugated isomers. It has been found that at 250°C. and above, polymerization predominates over isomerization and that the optimum temperature for the formation of 9, 11 linoleic acid at the expense of 9, 12 linoleic acid is 200°C. So by maintaining the product after dehydration stage at 200°C. for 90 minutes, it has been possible to increase its conjugated isomer content by 3.6%.

REFERENCES

- Bradley, T. F., and Johnston, W. B. (1941). Purification of methyl linoleate by molecular distillation. *Ind. Eng. Chem.*, **33**, 86-89.
- Paschke, R. F., and Wheeler, G. A. (1949). Thermal polymerization of drying oils. Paint, Varnish & Plastics Division, A.C.S., Atlantic City.
- von Mikusch, J. D. (1940). Bodying of dehydrated castor oil. *Ind. Eng. Chem.*, **32**, 1061-69.

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