574. *The Seed Fat of* Parinarium laurinum. *Part III.** *Catalytic Hydrogenation of Methyl Parinarate.*

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The hydrogenation of methyl parinarate at 100° in the presence of Raney nickel catalyst has been followed spectrophotometrically. It has been found that the primary reaction consists of the simultaneous addition of either two or three molecules of hydrogen, yielding non-conjugated methyl octadienoates (containing the unsaturated system $-CH{=}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH{=}CH-$) and methyl octadecenoates respectively. Only comparatively small amounts of conjugated methyl octadeca-dienoates and -trienoates are formed. The hydrogenation is extremely selective; very little methyl stearate is formed until all the parinarate, conjugated esters, and non-conjugated methyl octadienoates have been converted into methyl octadecenoates.

In the earlier papers of this series (*J.*, 1950, 12; 1951, 291) the constitution of the acids and glycerides of the seed fat of *Parinarium laurinum* has been described. It was shown that the mixed acids from the fat contained *ca.* 55% of parinaric acid (octadeca-9 : 11 : 13 : 15-tetraenoic acid †). Since the mechanism of hydrogenation of a conjugated tetraene does not yet appear to have been studied it was thought be of interest to prepare pure methyl parinarate and submit it to catalytic hydrogenation.

Methyl parinarate was hydrogenated at 100° in presence of Raney nickel as catalyst, fractions being removed at 20, 35, 50, 65, and 80% saturation. These fractions were analysed spectrophotometrically for methyl parinarate and conjugated methyl octadeca-dienoate and -trienoate as described in Part I. In Table I are recorded the extinction coefficients used in the calculations.

Table I.

Extinction coefficients used in calculations.

	$E^{1\%}_{1\,cm.}$ * at		
	234 mμ	270·5 mμ	305 mμ
Methyl parinarate	74·3	408	2630
Conjugated methyl octadecatrienoate	208	1780	—
Conjugated methyl octadienoate	1200	—	—

(* Expressed as acids.)

In Fig. 1 is shown the general effect of hydrogenation on the absorption spectrum of methyl parinarate. Clearly this indicates progressive removal of conjugated tetraenes with insignificant production of conjugated triene or conjugated diene esters.

* Part II, *J.*, 1951, 291. † Geneva system, $CO_2H = 1$.

Methyl stearate was determined in the later fractions by acetone–permanganate oxidation, and non-conjugated octadecadienoates and octadecenoates were determined from the amount of hydrogen which had been absorbed, allowance having been made for the other unsaturated esters present. It is not claimed that these results are of a high degree of accuracy, but it is impossible to use normal iodine-value methods for the measurements of the unsaturation of conjugated unsaturated systems, and even Toms's bromine absorption method (*Analyst*, 1928, **53**, 69) which gives theoretical values with methyl elæostearate yields results with methyl parinarate which are rather variable and low by about 25%. Fraction 5 in which the proportion of conjugated esters was negligible was calculated from the Wijs iodine value.

The results of these determinations are shown diagrammatically in Fig. 2 (cf. Table III). They indicate that the principal products of the hydrogenation in the initial stages are non-

FIG. 1.

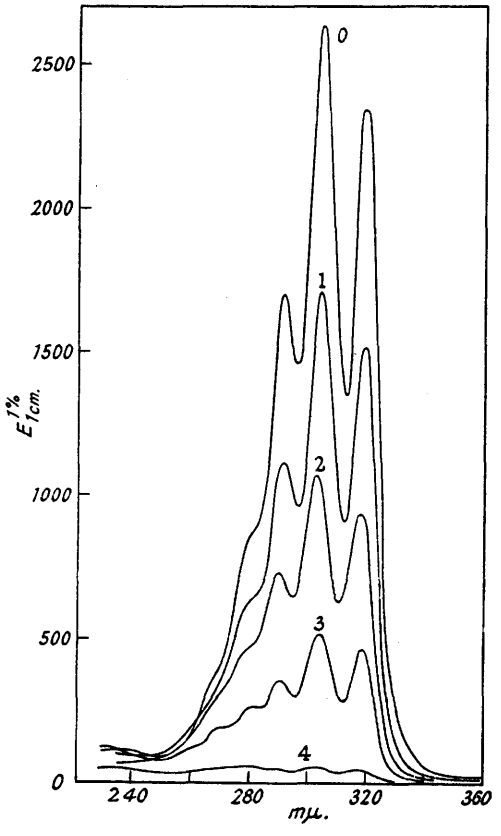
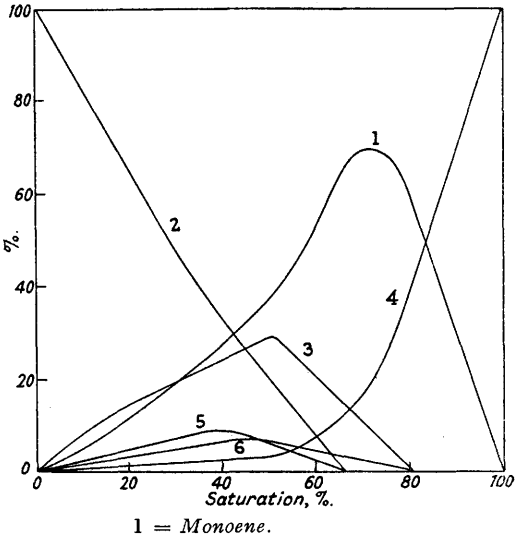


FIG. 2.



1 = *Monoene.*
2 = *Parinaric acid.*
3 = *Non-conjugated diene.*
4 = *Saturated.*
5 = *Conjugated triene.*
6 = *Conjugated diene.*

conjugated methyl octadecadienoates and octadecenoates formed by the simultaneous addition of either two or three molecules of hydrogen respectively. Only small amounts of conjugated dienoates and trienoates are formed. Comparatively little methyl stearate is formed until all the esters with two or more double bonds have been converted into methyl octadecenoates.

Three non-conjugated methyl octadecadienoates are theoretically obtainable by the hydrogenation of methyl parinarate (assuming, as is probable, that no double bond shift takes place on hydrogenation at 100° with Raney nickel) :

$CH_3 \cdot [CH_2]_3 \cdot CH{=}CH \cdot [CH_2]_2 \cdot CH{=}CH \cdot [CH_2]_7 \cdot CO_2Me$ (I.)
$CH_3 \cdot CH_2 \cdot CH{=}CH \cdot [CH_2]_2 \cdot CH{=}CH \cdot [CH_2]_9 \cdot CO_2Me$ (II.)
$CH_3 \cdot CH_2 \cdot CH{=}CH \cdot [CH_2]_4 \cdot CH{=}CH \cdot [CH_2]_7 \cdot CO_2Me$ (III.)

Ozonolysis of the hydrogenation fraction 2, which contained 20·6% of non-conjugated dienoates, yielded succinic acid, but no adipic acid, indicating that esters of the structures (I) and (II) were present.

Fractions 3 and 5 (50% and 80% saturation respectively) were submitted to acetone–permanganate oxidation and the recovered dibasic acids were separated by fractionation of their dimethyl esters with the results summarised below.

	Dibasic acids, % (mol.)			
Fraction	C_9	C_{11}	C_{13}	C_{15}
3	37	21	21	21
5	12	54	25	9

The high proportion of azelaic acid (C_9) formed from fraction 3 is due to the 20% of unchanged unhydrogenated methyl parinarate which it contains. These data enable the approximate proportion of hydrogen addition at the various double bonds to be estimated. If the small amounts of conjugated diene and triene esters present are ignored, it may be seen that undecanedicarboxylic acid must be formed either from the diene (II), or from the octadec-11-enoate formed either from (II), or directly from methyl parinarate by addition of 3 molecules of hydrogen. Similarly tridecanedicarboxylic acid is formed from methyl octadec-13-enoate, which may result either by simultaneous addition of 3 molecules of hydrogen to methyl parinarate or by partial hydrogenation of the diene (I). Pentadecanedicarboxylic acid can only be formed from octadec-15-enoic acid which must have been produced by the addition of 3 molecules of hydrogen to the 9, 11, and 13 double bonds. In the case of fraction 5, it is not possible to determine whether the high proportion of undecanedicarboxylic acid found is not in error owing to the difficulty of separating dibasic acids by fractional distillation.

It is interesting to compare the hydrogenation of methyl parinarate with that of methyl elæostearate (methyl octadeca-9 : 11 : 13-trienoate) which has been investigated by a number of workers, the most recent being Hilditch and Pathak (*Proc. Roy. Soc.*, 1949, *A*, **198**, 323), who confirmed the findings by Groot, Kentre, and Knol (*Rec. Trav. chim.*, 1947, **66**, 633) that the primary reaction is the simultaneous addition of two molecules of hydrogen to one molecule of elæostearate with the formation of considerable quantities of methyl octadeca-11-enoate. This reaction is quite analogous to the addition of two molecules of hydrogen to one molecule of methyl parinarate with the formation of the non-conjugated octadecadienoates (I) and (II).

The hydrogenation of methyl parinarate is even more selective than that of methyl elæostearate, since for example at *ca.* 50% saturation only 3·5% of methyl stearate was formed from the former compared with 13·5% from methyl elæostearate.

Experimental.

Preparation of Methyl Parinarate.—The seed fat of *P. laurinum* (230 g.) was hydrolysed by boiling it for 30 minutes with 10% alcoholic potassium hydroxide (1 l.), and the product poured into a large amount of water. The acids were liberated from the soaps with sulphuric acid and extracted with ether as rapidly as possible to prevent oxidation. After removal of the ether, the mixed fatty acids (210 g.) were crystallised twice from light petroleum (b. p. 40—60°) (2·5 l.) first at −20° and then at 0°. The resultant crystals were recrystallised from ether at −20° and then at −15° and yielded parinaric acid (67·6 g.), m. p. 86°, sap. equiv. 274·8 (Calc. for $C_{18}H_{28}O_2$: 276).

The purified parinaric acid (48·0 g.) was esterified at room temperature with 500 ml. of methyl alcohol containing 0·5% of hydrogen chloride and yielded, after removal of free acid, white crystals of methyl parinarate (47·5 g.), m. p. 34—35°, n_D^{40} 1·5567, I.V. (Wijs on 0·1 g. for 30 minutes) 194·3; I.V. (Toms) 272·0, $E_{1\,cm.}^{1\%}$ at 305 mμ. 2630, at 270·5 mμ. 408, and at 234 mμ. 74·3.

Table II.

Fractions of hydrogenated esters.

No.	G.	Hydrogenated,* %	I.V. (Wijs)	I.V. (Toms)	n_D^{40}	$E_{1\,cm.}^{1\%}$ at (mμ.)† 234	270·5	305 ‡
0	44·3	0	194·3	272·0	1·5567	74·3	408	2630
1	4·84	20	176·2	259·9	1·5180	99·4	355	1711
2	4·73	35	156·3	198·5	1·4949	107·0	317	1048
3	14·76	50	128·5	166·4	1·4720	106·6	192	509
4	5·03	65	95·0	100·1	1·4510	50·8	53·7	47·1
5	15·07	80	50·4	47·5	1·4438	6·2	5·4	1·5
Total	44·43							

* Expressed as percentage of the volume of hydrogen required for complete saturation (14·02 l. at 19°/790 mm.). † Expressed as acids.

‡ Value at band head; actual positions of bands vary slightly.

TABLE III.

Composition of fractions.

No.	Hydrogenated, %	Parinaric acid	Conj. triene	Conj. diene	Non-conj. diene	Monoene	Satd.
0	0	100	—	—	—	—	—
1	20	65·0	4·7	3·7	14·7	11·9	—
2	35	39·0	8·5	5·1	20·6	26·0	—
3	50	19·3	6·3	6·7	29·0	35·3	3·4
4	65	1·8	2·6	3·7	15·4	64·5	12·0
5	80	0·1	0·3	0·5	—	59·3	39·8

TABLE IV.

(a) *Fractionation of methyl esters of water-soluble dibasic acids* L_1.

No.	G.	B. p./*ca.* 1 mm.	Sap. equiv.		Dibasic esters: C_9	C_{11}	C_{13}
1	0·119	<104°	104·6		0·119	—	—
2	0·265	104	104·9		0·265	—	—
3	0·278	104	104·3		0·278	—	—
4	0·258	104	104·9		0·258	—	—
5	0·282	100	107·2		0·282	—	—
6	0·332	80—100	110·7		0·261	0·071	—
7	0·118	100—116	114·0		0·064	0·054	—
8	0·038	110	115·5		0·016	0·022	—
9	0·134	Residue	133·3		—	0·024	0·110
Total	1·824			Total	1·543	0·171	0·110
				Ester, %	84·6	9·4	6·0
				Acid, %	84·3	9·5	6·2

(b) *Fractionation of methyl esters of water-insoluble dibasic acids* S_1.

No.	G.	Sap. equiv.		Dibasic esters: C_9	C_{11}	C_{13}	C_{15}	C_{18}Satd.
1	0·174	118·5		0·040	0·134	—	—	—
2	0·338	123·4		—	0·301	0·037	—	—
3	0·289	130·9		—	0·098	0·191	—	—
4	0·303	128·4		—	0·156	0·147	—	—
5	0·334	131·6		—	0·097	0·237	—	—
6	0·496	140·9		—	—	0·311	0·185	—
7	0·552	152·0		—	—	—	0·538	0·014
8	0·443	167·7		—	—	—	0·349	0·094
9	0·379	248·0		—	—	—	0·077	0·302
Total	3·308		Total	0·040	0·786	0·923	1·149	0·410
			Ester, %	1·2	23·8	27·9	34·7	13·6
			Acid, %	1·1	23·0	27·3	34·4	14·2

(c) *Combined results of ester fractionations.*

Dibasic acid	L_1 (32·9%)	S_1. (67·1%)	Total, %	Dibasic acids, % (mol.)
Azelaic acid	27·7	0·8	28·5	37·4
Undecanedioic	3·1	15·4	18·5	21·1
Tridecanedioic	2·1	18·3	20·4	20·6
Pentadecanedioic	—	23·1	23·1	20·9
C_{18}-satd.	—	9·5	9·5	—

Hydrogenation.—Methyl parinarate (44·3 g.) was hydrogenated at 100° with Raney nickel (*ca.* 2 g.) (Pavlic and Adkins, *J. Amer. Chem. Soc.*, 1946, **68**, 1471) in a three-necked 250-ml. round-bottomed flask, fitted with a mechanical stirrer (1300 r.p.m.) operating through a packed gland, and with a tube reaching to the bottom of the flask so that samples could be withdrawn without the hydrogenation being stopped. Before the experiment was begun, the apparatus was evacuated and filled with hydrogen; the progress of the reaction was followed by supplying the hydrogen to the reaction vessel from a graduated gas-container.

Examination of Hydrogenation Fractions.—Ozonolysis of fraction 2. The mixed acids (3·50 g.) from fraction 2 were dissolved in methyl acetate (40 ml.) and ozonised at −30°. The solvent was distilled off under reduced pressure, and the resultant ozonides were hydrolysed by refluxing them with water (100 ml.) for 90 minutes and then oxidised with 30% hydrogen peroxide (5 ml.) for 30 minutes. The cooled solution was filtered and the filtrate evaporated to dryness. The residue (0·28 g.) was twice recrystallised from ether and sublimed twice. The sublimate, m. p. 150—160°, was recrystallised from

water several times and yielded succinic acid (0·05 g.), m. p. 178—180° undepressed when admixed with authentic succinic acid (m. p. 182°).

Acetone–permanganate oxidation of fraction 3. Fraction 3 (13·18 g.) was oxidised in solution in acetone (140 ml.) with potassium permanganate (70 g.). There were recovered: unoxidised esters (methyl stearate) 0·47 g., I.V. 4·5; dibasic acids 6·46 g.; steam-volatile monobasic acids 1·99 g.

Examination of dibasic acids. The dibasic acids (6·46 g.) were separated by crystallisation from 400 ml. of water into two fractions; insoluble fraction S_1 4·30 g., soluble fraction L_1 2·11 g. Both fractions were esterified separately with methyl alcohol containing 0·5% of sulphuric acid and fractionated through a micro-fractionation column (Table IV).

Acetone–permanganate oxidation of fraction 5. Fraction 5 (14·05 g.) was oxidised in solution in acetone (140 ml.) with potassium permanganate (70 g.). There were recovered: methyl stearate 5·71 g., I.V. 1·0; dibasic acids 4·63 g.; and steam-volatile monobasic acids 2·20 g.

TABLE V.

Fractionation of the dimethyl esters of dibasic acids.

				Dibasic esters:			
No.		B.P./*ca.* 1 mm.	Sap. equiv.	C_9	C_{11}	C_{13}	C_{15}
1	0·453	<122°	116·7	0·159	0·294	—	—
2	0·532	122—130	117·8	0·146	0·386	—	—
3	0·584	130—140	119·2	0·106	0·478	—	—
4	0·534	140—130	122·5	—	0·513	0·021	—
5	0·461	130	126·2	—	0·312	0·149	—
6	0·699	140	132·2	—	0·175	0·524	—
7	0·257	140	137·7	—	—	0·223	0·034
8	0·123	140	141·8	—	—	0·069	0·054
9	0·134	140	143·4	—	—	0·060	0·074
10	0·073	140 Falling	143·5	—	—	0·032	0·041
11	0·258	Residue	157·5	—	—	—	0·258
Total	4·108		Total	0·511	2·158	1·078	0·461
			Ester, %	10·0	52·5	26·3	11·2
			Mol., %	11·7	54·4	24·5	9·4

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