

### 150. *The Configuration of Naturally Occurring Mixed Glycerides. Part III. The Configuration of the Major Component Glycerides of Piqui-a Fruit-coat Fat.*

By M. L. MEARA.

Piqui-a fruit-coat fat has been separated by crystallisation into mono-oleo- and dioleo-glycerides. The mono-oleo-glycerides have been shown to consist of  $\beta$ -oleodipalmitin, no unsymmetrical isomer having been found. Low-temperature crystallisation of the dioleoglycerides followed by crystallisation of the hydrogenated derivatives has shown that both symmetrical and unsymmetrical palmitodioleins and palmito-oleolinoleins occur in this fat.

THE fruits of the piqui-a (*Caryocar villosum*) contain fatty matter in both the kernel and the mesocarp. The characteristics of these fats have been described by Georgi (*Malayan Agric. J.*, 1929, 17, 166) and a fuller examination of the component acids and glycerides has been reported by Hilditch and Rigg (*J. Soc. Chem. Ind.*, 1935, 54, 109r), who showed that the fats were quantitatively similar and unusually rich in palmitic acid, the component fatty acids of the fruit-coat fat being myristic, 1.8; palmitic, 47.3; stearic, 1.7; oleic, 47.3; linoleic, 1.9% (mol.). Oxidation of a portion of the fat with permanganate in acetone gave 2% of fully saturated glycerides, indicating that the fat conforms closely to the "evenly distributed" type of seed fats, differing from palm oil, which, at this palmitic acid content, would contain 7—10% of fully saturated glycerides. From this Hilditch and Rigg deduced that piqui-a fruit-coat fat consisted chiefly of oleodipalmitins and palmitodioleins together with small amounts of minor components.

Another portion of the fruit-coat fat was hydrogenated and the product systematically crystallised from benzene. Tristearin was shown to be absent, indicating the absence of triolein in the fat. Difficulty was encountered in the separation of pure palmitodistearin, and Hilditch and Rigg concluded that this was due not only to the presence of more steardipalmitin than in fats such as hydrogenated cotton-seed oil (where this difficulty had not arisen), but also to the probable presence of both  $\alpha$ - and  $\beta$ -palmitodistearins and steardipalmitins. This view received considerable support from a similar examination of a partially hydrogenated specimen (iodine value, 7.0).

Because of this anomaly and of the fact that piqui-a fruit-coat fat must be one of the simplest mixtures of mixed triglycerides occurring in a natural fat, a portion of the specimen used in the earlier investigation of Hilditch and Rigg has been re-investigated in the manner recently described by Meara (Parts I and II of this series, *J.*, 1945, 22, 23).

#### EXPERIMENTAL.

Piqui-a fruit coat fat (saponification equiv. 281.6, iodine value 47.8) was neutralised by shaking an ethereal solution with 10% aqueous potassium carbonate solution, followed by washing and removal of the solvent. The fat (200 g.) was then exhaustively crystallised from acetone and from ether until a series of crystalline fractions was obtained which on further recrystallisation gave no further change in iodine value. In this way 5 fractions (A—E) of iodine value 30.2, 30.1, 29.9, 29.9, and 30.2, respectively, were

obtained. Each fraction was investigated separately in case, if both symmetrical and unsymmetrical oleodipalmitins occurred in this fat, their partial separation might have been effected during the exhaustive crystallisation. After a final slow recrystallisation from acetone, the transition and melting points of each fraction were determined (Table I) in the manner described in Part I (*loc. cit.*).

[The nomenclature used by Daubert *et al.* for the polymorphic forms has been adopted in the tables which follow (cf. Part I, 1945, 22). The forms IV, III, II, I correspond respectively to Malkin's vitreous,  $\alpha$ ,  $\beta'$ , and  $\beta$ .]

TABLE I.

*Transition and melting points of oleodipalmitin.*

Fraction.	Weight (g.).	IV.	III.	II.	I.
A .....	20.0	13.5—14°	17.5—18°	35°	36.8—37°
B .....	10.0	13—14	17—18	35	36.8—37
C .....	14.1	12.5—14	17—18	34—35	36.5—37
D .....	27.1	12.5—13.5	17—18	34—35	36.5—37
E .....	12.2	13—14	17—18	35	36.7—37
Synthetic $\beta$ -oleodipalmitin *	.....	12.0	20.8	30.4	35.2
„ $\alpha$ - „ *	.....	18.5	29.8	—	34.5

\* Daubert *et al.*, *J. Amer. Chem. Soc.*, 1944, **66**, 690; *Oil and Soap*, 1945, **22**, 113.

A portion of each fraction was hydrogenated at 100° in the presence of Raney nickel, hydrogen being readily and quantitatively absorbed at this temperature, which is low enough to inhibit any tendency to acyl migration (now known to occur to some small extent in the presence of nickel on kieselguhr at 180°; cf. Atherton and Hilditch, *J.*, 1941, 527). The steardipalmitins obtained were crystallised from ether and their transition and melting points determined, the respective values (Table II) being identical within experimental error, and identical with the now well-authenticated values for  $\beta$ -steardipalmitin.

TABLE II.

*Transition and melting points of the steardipalmitins.*

	IV.	III.	II.	I.
A—E .....	48—49°	59—60°	65°	67.7—68°
Synthetic $\beta$ -steardipalmitin *	49	59	65	68
„ $\alpha$ - „ †	46.5	55	59.5	62.5

\* Malkin and Meara, *J.*, 1939, 103.

† Carter and Malkin, *J.*, 1939, 577.

The liquid fractions, iodine values 62.1 and 58.0, which consisted mainly of palmitodiolein with some palmito-oleolinolein and traces of triolein, were crystallised separately from acetone at low temperatures to give 3 main fractions, F, G, and H (weights 36.5, 17.7, and 16.7 g.; iodine values 59.5, 59.7, and 70.0 respectively). These were hydrogenated and exhaustively crystallised from ether.

From H a small quantity of material, m. p. 70—72°, was obtained, indicating the presence of a trace of tristearin, m. p. 71°, but this was not further investigated. The bulk of the remaining material had m. p. 64—65° unchanged by further recrystallisation. Transition and melting points of this fraction were then determined and are recorded in Table III.

Crystallisation of G gave a small yield of material, m. p. 67—67.2°, consisting mainly of  $\beta$ -palmitodistearin together with a fraction, m. p. 64.5—66.5° not significantly changed by further recrystallisation. Satisfactory transition points could not be obtained for this fraction.

Crystallisation of F gave a main fraction, m. p. 67—68°, and a small yield of material, m. p. 63—64°. More detailed thermal data for these fractions are given in Table III.

TABLE III.

*Transition and melting points of palmitodistearins.*

Fraction.	IV.	III.	II.	I.
F (mainly) .....	49—50°	55—56°	63—64°	67—68°
F (small quantity) .....	48	55—56	59—60	63—64
G „ „ .....	50	55	62.5—63.5	67—67.2
G (mainly) .....	44—48	52—55	—	64.5—66.5
H (mainly) .....	48	56	60	64.5—65
Synthetic $\beta$ -palmitodistearin *	50	56	64	68
„ $\alpha$ - „ *	50	57	61	65

\* Malkin and co-workers (*loc. cit.*).

## DISCUSSION.

It is evident from Tables I and II that the oleodipalmitin occurring in piqui-a fruit-coat fat consists wholly of the symmetrical isomer. While the observed values in Table I are identical within experimental error they are not in complete accord with those obtained by Daubert *et al.* but resemble much more those of the  $\beta$ - than those of the  $\alpha$ - (unsymmetrical) isomer.

The data for the derived stearodipalmitins (Table II) agree remarkably well with those for synthetic  $\beta$ -stearodipalmitin.

Thermal data for products of hydrogenation of the palmitodioleins present in piqui-a fruit-coat fat could only be determined after a much more rigorous crystallisation of the hydrogenated material. Table III, summarising the data obtained, indicates that fraction F consisted mainly of symmetrical palmitodistearin together with a small quantity of the unsymmetrical isomer. From fraction G a small quantity of pure symmetrical palmitodistearin was obtained, but the bulk of this fraction appeared to be a difficultly resolvable mixture of the two isomers. Fraction H, however, appeared to consist almost entirely of the unsymmetrical isomer.

Thus both  $\alpha$ - and  $\beta$ -palmitodistearins occurred in the hydrogenated material from these fractions, a moderate separation of the parent dioleins having been obtained in the low temperature crystallisation of the more soluble portions of the original fat. Although the conditions of crystallisation and hydrogenation precluded any strictly quantitative estimate of the proportions of the various glycerides isolated, it is considered that the amounts of the unsymmetrical and symmetrical palmitodioleins in fractions F, G, and H were probably of the same order.

This investigation has therefore partially confirmed the earlier work of Hilditch and Rigg (*loc. cit.*) who, not having first separated mono-oleo- from dioleo-glycerides, were led by their results to postulate the probable occurrence of both  $\alpha$ - and  $\beta$ -mono-oleodipalmitins and palmitodioleins. It is also seen that, if they can be isolated in a sufficiently high degree of purity, thermal examination either of the individual glycerides or of their hydrogenated products is sufficient to determine their structure, without the necessity of resorting to X-ray crystal analysis, as has been suggested by Daubert *et al.* (*J. Amer. Chem. Soc.*, 1946, **68**, 167).

The author wishes to thank Professor T. P. Hilditch for his advice and criticism during this investigation.

THE UNIVERSITY, LIVERPOOL.

[Received, October 2nd, 1946.]

---