8. *The Configuration of Naturally Occurring Mixed Glycerides. Part II. The Configuration of Some Monopalmito-glycerides from Various Natural Sources.*

By M. L. Meara.

The melting and transition points of palmitodistearin, produced by hydrogenation of glycerides originally present as palmito-oleostearins, palmitodioleins or palmito-oleolinoleins in cacao butter, cottonseed oil and pig back fat, and separated by fractional crystallisation, have been determined. In all cases the thermal data obtained coincided with those of β-palmitodistearin and were different from those of α-palmitodistearin (as determined by Malkin and his collaborators, J., 1939, 103, 577).

In continuation of the study of the configuration of naturally occurring glycerides, monopalmito-glycerides derived from cacao butter, cottonseed oil, and pig back fats have now been investigated.

Monopalmito-glycerides from Cacao Butter.—Hilditch and Stainsby (*J. Soc. Chem. Ind.*, 1936, **55**, 95T) determined the component glycerides of cacao butter by determining first the component acids of the fat, followed by a determination of the nature and amounts of fully saturated glycerides obtained on hydrogenating the fat to intermediate stages of saturation. A second method was then evolved, *viz.*, partial separation of the fat into its component glycerides by crystallisation from acetone, each fraction then being examined in a manner identical with the first method. From these investigations the authors were able to state that the specimen of cacao butter examined contained the following: oleopalmitostearin 52%, oleodistearin 19%, stearodiolein 12%, palmitodiolein 9%, oleodipalmitin 6%, and palmitodistearin 2%. Much of the trebly mixed glyceride was believed to be β-palmito-oleostearin, whereas oleo-disaturated glycerides were believed to have occurred mainly as the symmetrical isomers.

A selected fraction *A* (see below), rich in palmito-stearins, had been obtained from the fractional crystallisation of the fully saturated glycerides produced on hydrogenation of the cacao butter to an iodine value of 6·6, together with fractions *B*, *C*, *D*, m. p. 67·5°, 66·5°, 65·0°, sap. equiv. 288·5, 287·9, 287·8 (Calc. for palmitodistearin: 287·3). These fractions had been reserved and were the materials used in the present investigation.

Monopalmito-glycerides from Cottonseed Oil.—Hilditch and Maddison (*J. Soc. Chem. Ind.*, 1940, **59**, 162), applying the technique of low-temperature crystallisation from acetone solution to a specimen of cottonseed oil, thereby separated it into six fractions of different solubility and iodine value. One of these fractions with the following component acids (% wt.): myristic 2·6, palmitic 25·8, stearic 2·0, arachidic 1·1, tetradecenoic 0·1, hexadecenoic 1·1, oleic 24·9, linoleic 42·4, was found to consist almost wholly of mono-saturated di-unsaturated glycerides, for the most part palmito-oleolinolein and palmitodilinolein. Hydrogenation of a portion of this fraction, followed by crystallisation to remove myristo- and oleo-glycerides, gave the material used as the source of palmitostearin in this investigation.

Monopalmito-glycerides of Pig Back Fat.—In an investigation of the body fats of the pig, Hilditch and Stainsby (*Biochem. J.*, 1935, **29**, 94) prepared a series of fats progressively hydrogenated to iodine values of 35·8, 18·7, and 10·0. The non-fully-saturated portions of these fats were removed by oxidation, and the composition of the fully saturated residue determined. In each case this was found to consist principally of palmitodistearin, together with much smaller quantities of stearodipalmitin; crystallisation from ether gave yields of material of the order of 80% of the total palmitodistearin present, which was considered by Hilditch and Stainsby to be pure β-palmitodistearin and was therefore reserved for more complete investigation.

EXPERIMENTAL.

Specimens of palmitodistearin concentrates from the above sources were further crystallised from pure ether (40 ml. per g.) in the manner described in Part I (preceding paper). The same technique for the determination of transition and melting points was employed, it being found necessary, however, to keep a specimen at a particular transition point much longer, in the case of the saturated mixed triglycerides than in that of the unsaturated glycerides (Part I, *loc. cit.*), for it to become transformed into the next more stable modification. The values for transition and melting points of palmitodistearin from these sources are compared with those recorded for synthetic β- and α-palmitodistearin (Malkin and Meara, J., 1939, 103; Carter and Malkin, *ibid.*, p. 577) in the following table.

Melting and transition points of palmitodistearin from various sources.

	IV.	III.	II.	I.
Palmitodistearin from cacao butter (*A*)	50°	56°	64°	68°
,, ,, ,, ,, (*B*)	49—50	55	64	67·5
,, ,, ,, ,, (*C*)	48·5—49·5	55	63	66·5
,, ,, ,, ,, (*D*)	49	55	64	67·0
,, ,, cottonseed oil	50	56	64	67·7
,, ,, pig back fat (*A*)	49	55	64·5	67·5
,, ,, ,, ,, (*B*)	50	55—56	64	67·5
,, ,, ,, ,, (*C*)	49	55	63—66	67
Synthetic β-palmitodistearin	50	56	64	68
,, α- ,, ...	50	57	61	65

Discussion.—These values, obtained from hydrogenated naturally occurring glycerides, accord remarkably well with those recorded for the synthetic symmetrical (β) palmitodistearin. In view of the relative ease with which compounds of m. p. 67—68° have been obtained, and of the well-known difficulty attending the separation of mixtures of isomeric palmitostearins by crystallisation, these observations point definitely to the virtually exclusive occurrence of β-palmito-oleostearin and β-palmitodiolein in cacao butter, β-palmito-oleolinolein and β-palmitodilinolein in cottonseed oil, and β-palmito-oleostearin and β-palmitodiolein in pig back fat.

These results suggest that in all three fats (in which palmitic forms 20—30% of the total fatty acids) the palmitic group occupies the β- or symmetrical position in the mixed triglycerides, whether these are palmito-oleostearin or palmito-diunsaturated glycerides. It is hoped to extend these studies to include a more detailed investigation of the palmito-glycerides in a series of structurally related animal (pig, ox, and sheep) depot fats, and in some vegetable fats, *e.g.*, palm oils, in which palmitic acid is present in quantity.

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