7. *The Configuration of Naturally Occurring Mixed Glycerides. Part I. The Configuration of Oleodistearin from Various Natural Sources.*

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The melting and transition points of oleodistearin, isolated from six seed fats of which it is a prominent constituent, have been determined. They are identical in each instance with those of β-oleodistearin and different from those of the unsymmetrical α-oleodistearin (the corresponding constants for the synthesised α- and β-oleodistearins have recently been determined by Daubert, Fricke, and Longenecker, *J. Amer. Chem. Soc.*, 1943, **65**, 2142, 2144; 1944, **66**, 289, 690).

The component glycerides of a large number of animal and vegetable fats have now been determined, for the most part by Hilditch and his co-workers, but there has been little definitive work to determine the positional configuration of these glycerides, mainly owing to the difficulty in isolating individual glycerides in a sufficient state of purity, and until comparatively recently the properties of synthetic mixed glycerides, needful for reference purposes, were not sufficiently characterised. The properties of the saturated symmetrical and unsymmetrical mixed glycerides have now been described by Malkin and his collaborators (J., 1939, 103, 577, 1141, 1518), and the corresponding unsaturated glycerides are now being synthesised and studied by Daubert, Longenecker, *et al.* (*loc. cit.*). From the available data it is therefore now possible to specify the configuration of a number of individual naturally occurring glycerides provided they be isolated in a state of sufficient purity.

The configuration of oleodistearin, which was amongst the first of the natural mixed glycerides to be isolated, forms the subject of the first paper of this series.

The reported m. p.'s of the majority of specimens of oleodistearin isolated from natural products lie between 42° and 44°, some authors reporting a transition point at 28—30°. An early synthesis of β-oleodistearin (Kreis and Hafner, *Ber.*, 1903, **36**, 276) by heating αα'-distearin with oleic acid under reduced pressure gave a low yield of oleodistearin, melting after crystallisation at 42°, and after fusion at 28—30°. A specimen isolated from cacao butter melted in similar circumstances at 44—45° and 27—28°, and from this these authors concluded that the substance isolated was the unsymmetrical isomer. Later knowledge of the component glycerides of cacao butter indicates that their material consisted of the symmetrical isomer contaminated with small amounts of fully saturated glycerides. Grün (*Ber.*, 1907, **40**, 1778) from oleic anhydride and αα'-distearin obtained a product which melted at 42°; after one year, however, it melted at 41° and 55°, and when cooled and reheated, at 42°. Amberger and Bromig (*Biochem. Z.*, 1922, **130**, 257) prepared α-oleodistearin of m. p. 42°, but were unable to prepare the symmetrical isomer. Hilditch and Saletore (*J. Soc. Chem. Ind.*, 1933, **52**, 101T), from the reaction between oleyl chloride and αα'-distearin, obtained a product which on oxidation gave what appeared to be a mixture of azelao-glycerides as judged from the m. p.'s of the fractions obtained by crystallisation, the main fraction melting at 62·5—63·5°. Oxidation of oleodistearin from *Allanblackia Stuhlmannii* gave a product of this m. p. which remained unchanged on admixture with some of the main fraction of synthetic material. Both symmetrical and unsymmetrical oleodistearin have now been synthesised by methods which have proved trustworthy in the synthesis of saturated mixed triglycerides of known composition, oxalyl chloride being used in the preparation of oleyl chloride, thus eliminating the use of thionyl chloride which gives oleyl chloride in low yields and doubtful purity (Daubert and Longenecker, *loc. cit.*).

The saturated–unsaturated mixed triglycerides resemble the saturated mixed triglycerides in exhibiting the same type of polymorphism as that described by Malkin and his collaborators (*loc. cit.*) for the saturated mixed triglycerides. Each glyceride is capable of existing in four forms, a vitreous form IV, two intermediate forms III and II, and the stable crystalline form I (in the American nomenclature), these forms corresponding to Malkin's vitreous, α-, β'-, and β-forms, respectively. The transition points of the three metastable forms and the m. p. of the stable forms are well defined and can be determined with comparative ease.

EXPERIMENTAL.

Oleodistearin has been isolated in quantity from the following seed fats by fractional crystallisation from acetone: *Allanblackia Stuhlmannii* (Hilditch and Saletore, *loc. cit.*), *Allanblackia floribunda* and *Allanblackia parviflora* (Meara and Zaky, *J. Soc. Chem. Ind.*, 1940, **59**, 25), *Palaquium oblongifolium* (Hilditch and Stainsby, *ibid.*, 1934, **53**, 197T), *Garcinia Indica* (Hilditch and Murti, *ibid.*, 1941, **55**, 16), and *Pentadesma butyracea* (Hilditch and Saletore, *ibid.*, 1931, **50**, 468T).

The oleodistearin from the above fats was recrystallised several times from pure redistilled B.G.S. acetone (15—25 ml. per g.), the flasks being well lagged with cotton wool and suspended in a room, the temperature of which was maintained as constant as possible. The deposited crystals were filtered off and dried in an desicdator for several days.

The m. p. of the stable crystalline form was obtained in a capillary tube in the normal way. The form III transition point was obtained by allowing the molten mass to solidify and redetermining the m. p. On keeping the specimen at this temperature for a short time, it solidified, and on raising the temperature of the bath it remelted at form II transition point. If this operation was carried out too slowly, the m. p. of the stable form was obtained, since form II had been converted into form I. The transition point of form II was checked by immersing the capillary tube with the specimen in form III into a beaker of water, the temperature of which was adjusted so that the specimen just melted, prolonged immersion causing it to change over again to form I. The transition point of form IV was obtained by immersing the capillary tube containing the molten specimen first in a freezing mixture and then in a beaker of water, the temperature being adjusted and the process repeated until the substance gave rise to a definite change in appearance, due either to expansion and filling up of the cracks caused by cooling or to melting followed by rapid re-solidification.

Transition and melting points of different specimens of oleodistearin.

	IV.	III.	II.	I.
From *Allanblackia floribunda*	23 —23·5°	29·5°	37·0°	43·3—43·6°
,, ,, *parviflora*	23 —24	29 —30	36·0	43·0—43·3
,, ,, *Stuhlmannii*	23 —24	29 —30	37·5	43·0—43·3
,, *Garcinia Indica*	23·5—24·5	29 —29·5	37·5	43·3—43·5
,, *Pentadesma butyracea*	23·5—24	29·3—29·6	37·0	43·5—43·8
,, *Palaquium oblongifolium*	22 —23	29 —29·5	37·5	43·0—43·5
Synthetic β-oleodistearin *	22·3	29·8	37—37·6	41·6
,, α- ,, *	?	?	?	38·5

* Daubert *et al.* (*locc. cit.*).

Discussion.—It is seen from the above data that the transition and melting points of all the specimens of oleodistearin examined lie very near to those given for synthetic β-oleodistearin, and that of form I differs markedly from that recorded for α-oleodistearin. This, taken in conjunction with the evidence available from oxidation of synthetic and naturally occurring β-oleodistearin, makes it conclusive that the oleodistearins so far examined occurring in the above seed fats consist entirely of symmetrical β-oleodistearin.

Little can yet be said in regard to the seeming paradox that, concurrently with a very pronounced tendency to elaborate glycerides of as mixed a character (*i.e.*, containing as many different acyl groups) as possible, the oleodistearin in this group of fats is restricted to one configurational form only. It may be pointed out, however, that the proportion of oleic acid in all the fats under consideration (cf. table below) is of a similar order, and that it is less than that of the saturated acids (of which stearic is the main component). Whether this feature is of any significance in determining the position taken by the oleic group in oleodistearin remains to be seen.

Component acids of the fats studied (*weight* %).

Seed fat.	Myristic.	Palmitic.	Stearic.	Oleic.	Linoleic.
Allanblackia floribunda	0·2	3·2	56·8	39·4	0·4
,, *parviflora*	—	3·5	52·7	43·8	—
,, *Stuhlmannii*	—	3·1	52·6	44·1	0·2
Garcinia Indica	—	2·5	56·4	39·4	1·7
Pentadesma butyracea	—	5·4	46·1	48·5	—
Palaquium oblongifolium	0·2	5·9	54·0	39·9	—

It is not practicable to define the configuration of the stearodiolein which accompanies oleodistearin in these fats until further refinements now under investigation can be added to the technique of separation of the lower-melting glycerides in a sufficient state of purity for thermal investigation.

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