

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 $\alpha\alpha'$ -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 $\alpha\alpha'$ -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**, 101r), from the reaction between oleyl chloride and $\alpha\alpha'$ -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.

