Polymorphism of Palmitoyl and Stearoyl Dioleins

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Abstract

Polymorphism has been explored for the pairs of homologs 1) 2-palmitoyl diolein (OPO) and 2-stearoyl diolein (OSO), and 2) 1-palmitoyl diolein (POO) and 1-stearoyl diolein (SOO). The symmetrical compounds show α, β'-2 and stable β-3 forms; the unsymmetrical compounds show α (presumed) and stable β'-3 forms.

Introduction

THE STRUCTURALLY RELATED pairs of triglycerides 1) symmetrical 2-palmitoyl diolein (OPO) and 2-stearoyl diolein (OSO) and 2) the isomeric unsymmetrical palmitoyl diolein (POO) and 1-stearoyl diolein (SOO) are components of natural fats, the symmetrical isomers occurring in lard and the unsymmetrical isomers in many vegetable fats. The solidification behavior of these compounds has been explored as was previously done with corresponding disaturated glycerides (1–3).

Experimental

From well-purified (99.8%) oleic acid, 1,3-diolein was prepared via triolein with added glycerol by a combination of methods developed in this laboratory (4). The diglyceride was esterified by familiar procedures with palmitoyl or stearoyl chloride (each from fatty acids of purity > 98%) to obtain the desired triglycerides, which were crystallized 4 times from acetone and once from hydrocarbon solvent (Skelly B). Iodine values on the products were somewhat below theory, but not sufficiently, it is believed, to cause important modification of their phase behavior: OPO-57.3 (theory, 59.2), OSO-55.8 (theory, 57.3).

From well purified monopalmitin and monostearin (purity > 98%) and oleic acid, POO and SOO were prepared by reaction of the oleoyl chloride with the monoglyceride. The products were twice crystallized from acetone at 0C to give POO of IV-58.6 (theory, 59.2) and SOO of IV-56.5 (theory, 57.3).

Preliminary results on POO and SOO were obtained on small samples in Nylon capillaries made available through the courtesy of H. E. Longenecker and B. F. Daubert, then of the University of Pittsburgh where the samples were prepared (5).

Thermal and diffraction data were obtained by procedures previously described (6). "Rapid complete melting points" were obtained on the metastable phases and "regular complete melting points" on the stable phases. Flat film x-ray diffraction patterns were obtained on all higher melting forms, but only for OSO could a distinctive pattern for the lowest melting form be obtained, at −20C, due to the fleeting existence of the OPO, POO and SOO polymorphs. Samples from compounds synthesized in this laboratory were prepared either as "rod pellets" or as "rods" in thin-walled 1 mm O.D. Pyrex glass capillaries. The preliminary POO and SOO samples were treated entirely within their nylon capillaries. Samples were maintained in a cold block during diffraction when necessary. The source of x-rays was a General Electric XRD-1 unit employing CuKα radiation (nickel-filtered) and a 0.025 in. pinhole system. Sample to film distance was normally 5 cm, but was 10 cm for determination of long spacings. Data appear in Table I.

Preparation of Phases

The various polymorphic forms were prepared as follows:

Lowest Melting Form for each compound—Melt, chill (below clouding point)

Symmetrical Compounds

β'—OPO, melt, hold 15 min at −7C.
OSO, melt, hold 20 min at 3C.
β —OPO, crystallize from Skelly B at 10C; or melt, chill, hold 1 day at −6C, 9 days at 4C.
OSO, crystallize from Skelly B at 20F.; or melt, chill, hold 1 day at 4C, 9 days at 21C.

Unsymmetrical Compounds

β'—Melt, solidify between α melting point and complete melting point. (These forms were obtained at the University of Pittsburgh by crystallization from ether.)

Discussion

There is considerable similarity in the behavior of homologous pairs, e.g., OPO and OSO, with respect to both thermal and difffraction behavior. The single point of important variance is the substantially greater melting point difference observed between β'-2 and β-3 for OPO as compared with OSO; it is not out of the question that this variance is due to difficulties with melting points of the somewhat fleeting intermediate forms; on the other hand a real difference may be based on some different relationship between O and P chains from that between O and S chains.

The symmetrical compounds are trimorphic with α, β'-2 and β-3 forms. The unsymmetrical compounds are dimorphic with α (presumed) and β'-3 forms. The low temperature forms are fleeting and difficult to explore by x-ray diffraction.

A comparison of symmetrical OPO and OSO with unsymmetrical POO and SOO shows many similarities to features observed in comparison of POP and SOS with PPO and SSO. In each comparison the symmetrical compounds are higher but only a little higher melting and show stable β-3 phases as compared with stable β'-3 phases for the unsymmetrical compounds; in each case more polymorphic states are exhibited by the symmetrical than by the unsymmetrical pair.

TABLE I
Physical Data on Dioleoyl Triglycerides

	Low melting form	β'-2	β'-3	β-3
		Thermal data (° C)		
OPO	−11.5	5.5?		21.0(18.7, Ref. # 7)
OSO	1.0	20.5?		25.4
POO	−13±2(−13.2, Ref. # 8)		19.5(18–19, Ref. # 5 15.8, Ref. # 8)	
SOO	2.5±1(−1.5, Ref # 8)		24.5(22.5–23.5, Ref. # 5 22.9, Ref. # 8)	
		Diffraction data (Å) (Long spacings)		
OPO	......	43.4		63.0
OSO	47–50	45.6		64.4
POO	......		64.1	
SOO	......		66.0	

(Short spacings)

Symmetrical compounds: (α, for OSO—4.16S); β'-2—4.30S+, 3.91S; β-3—5.40M+, 4.58VS, 3.93W+, 3.79M, 3.66M
Unsymmetrical compounds: β'-3—4.47M+, 4.26S, 4.05M, 3.85S
VS—Very Strong, S—Strong, M—Medium, W—Weak

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