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THE PHYSICAL PROPERTIES OF  
TRIACYLGLYCEROLS  
IN RELATION TO MILKFAT

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ABSTRACT

Enantiomeric and racemic triacylglycerols (TGs) representative of the major structural classes in milkfat were synthesised and their polymorphism was characterised by differential scanning calorimetry (DSC) and infrared (IR) spectroscopy.

With butyric (B), oleic (O), palmitic (P) and stearic (S) acids as starting materials, 22 racemic TGs were prepared. The main TG classes were: 1) palmitoyl-stearoyl TGs (e.g. PSS), 2) 1-butyryl TGs (BPS), 3) 1-oleoyl TGs (OPS), 4) 2-oleoyl TGs (POS), 5) 1-butyryl-2-oleoyl TGs (BOS) and 6) 1,2-dioleoyl TGs (OOS). Three TGs containing elaidic acid (E) were also synthesised (BES, ESS and SES). In addition, enantiomers of three of the racemic TGs belonging to the 1-butyryl and 1-oleoyl classes were prepared (sn-SSB, -SSO and -PPO).

The polymorphic forms of each TG were classified as  $\alpha$ ,  $\beta'$  or  $\beta$  by comparison of their IR spectra with the spectra of the polymorphic forms of monoacid TGs. Solvent crystallised forms were also characterised by X-ray powder diffraction. Melting points of all polymorphs and heats of fusion of the least stable ( $\alpha$ ) and most stable forms were determined by DSC. However, the determination of the polymorphic assignment and heat of fusion of the intermediate forms was often uncertain because of the difficulty in obtaining a pure phase.

The principal findings were:-

- 1) Corresponding enantiomeric and racemic TGs exhibited similar polymorphic behaviour except that the  $\alpha$  forms of the enantiomers transformed more rapidly than those of their racemates.
- 2) For TGs in which one fatty acid was very different from the other two (e.g. BSS, OOS), the position of the unusual acid determined the chain packing of the stable form. If the acid was in a primary position, the TG was  $\beta'$ -stable (e.g. BSS, OSS, OOS), while if it was in the secondary position, the TG was  $\beta$ -stable (e.g. SOS, SBS).
- 3) There were close parallels between the stable forms of corresponding butyryl and oleoyl TGs (e.g. BSS, OSS; SBS, SOS; BOS, OOS), although in other respects their polymorphism had little in common. The stable forms of BSP and OSP showed anomalous thermal, diffraction and spectral data compared with the remaining 1-butyryl and 1-oleoyl TGs.
- 4) The results obtained for the 1-oleoyl, 2-oleoyl and 1,2-dioleoyl TGs were in general agreement with earlier reports, although some differences were noted in the transformation of OSP, OPS, SOS and POP.

Furthermore, previously undetected transitions were observed for all the oleoyl TGs, although these were minor. A new polymorph of OPP was also characterised. With the exception of POS, all monooleoyl TGs showed anomalous crystallisation behaviour.

- 5) The results for the polymorphism of the palmitoyl-stearoyl and elaidoyl-stearoyl TGs were also in accord with previous reports. The presence of a  $\beta'_2$  form was confirmed for all TGs except SPS and PSP. The heats of fusion of the  $\beta$  forms of SPS and PSP were comparable with those of their unsymmetrical counterparts, PSS and PPS, but the heats of fusion of their stable  $\beta'$  forms were much higher than those of  $\beta'$  SSS, PSS, PPS and PPP.

These findings are discussed in relation to the principles of close packing and their relevance to the phase behaviour of milkfat.

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## NOMENCLATURE

In general, the recommendations of the IUPAC-IUB Commission on Biochemical Nomenclature (1976; Lipids 12 (1977), 455) are followed for the nomenclature of lipids containing glycerol. However, the abbreviations MG, DG and TG are used for mono-, di- and triacylglycerol respectively. For the sake of brevity, TGs are specified by a three letter code in which the letters indicate the acyl group (B, butyryl; E, elaidoyl; L, lauroyl; O, oleoyl; P, palmitoyl and S, stearoyl) and the order of the symbols represents the position of the acyl group in the TG molecule. Enantiomeric TGs are distinguished by the prefix 'sn-', while TGs without a prefix are understood to be racemic. Thus sn-PPO represents 1,2-dipalmitoyl-3-oleoyl-sn-glycerol and POS (or SOP) represents rac-1-palmitoyl-2-oleoyl-3-stearoylglycerol.

The polymorphic forms of TGs are designated according to Larsson's modification (Larsson, 1966a) on Lutton's system of classification (Lutton, 1950). Where necessary, the chain multiplicity of a particular form is indicated by a suffix. Thus the term ' $\beta$ -2' represents a  $\beta$  form with a chain multiplicity of 2.