Crystal structure of a mixed chain diacylglycerol, 1-stearoyl-3-oleyl-glycerol

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Abstract Diacylglycerols composed of one saturated and one unsaturated chain make up the hydrophobic core of many biological membranes. We report here the first crystalline structure of such a mixed chain diacylglycerol. The mixed chain diacylglycerol, 1-stearoyl-3-oleyl-glycerol (1,3-SODG) was produced by solution isomerization of 1-stearoyl-2-oleyl-*sn*-glycerol. 1,3-SODG was isolated by flash chromatography and crystallized by slow evaporation in ethyl acetate at 4°C. The melting point was 42.5°C and the enthalpy was 18.0 kcal/mol. The crystal structure was determined to a final R factor of 0.127. Four molecules are present in the monoclinic unit cell: space group Cc, $a = 9.362(2)$, $b = 5.495(2)$, $c = 77.92(3)$Å, $\beta = 91.46(2)$, $V = 4007(4)$Å^3, $Z = 4$, $D = 1.032$ g/cm^3. The molecule forms an extended V-shaped conformation with the oleate and stearate chains coming off the two ends of the glycerol with an angle between their planes of 94°. The two chains pack separately in individual layers and do not interact. The hydrogen bonds between the free hydroxyl group on the glycerol-2 position and the carbonyl oxygen on the oleyl chain of an adjacent molecule are 2.78 Å in length and stabilize the glycerol layers. The stearoyl chain is roughly straight and packed in a triclinic parallel subcell. Both portions of the oleyl chain also pack in triclinic parallel packing. The torsion angle sequence along the double bond extending from the oleyl carbons C7 to C13 is tscsst (173°, -152°, -17°, -157°, -163°, -178°). This sequence is different from other monounsaturates. The torsion angle sequence around the glycerol region shows that the glycerol conformation is quite similar to the A conformer of racemic α monolaurin, and to 1,3-di-11-bromoundecanoyl glycerol, but completely unlike 1,2-diacyl-*sn*-glycerols. Thus the glycerol conformation appears to be driven by the hydrogen bond formation, which in turn determines whether chains interact or are segregated. In 1,3-diacylglycerols the two acyl chains point in different directions and are segregated. In 1,2-diacylglycerols the acyl chains lie side by side and must interact. When the two chains are quite different, then serious problems in packing occur, giving rise to disordered crystal packing. Probably as a result of the disordered chain packing in 1-stearoyl-2-oleyl-*sn*-glycerol (Di, L. and D. M. Small. 1993. *J. Lipid Res.* **34:** 1611–1623) we were not successful in growing adequate crystals suitable for crystallographic structure determination of this 1,2 mixed chain diacylglycerol.—**Goto, M., K. Honda, L. Di, and D. M. Small.** Crystal structure of a mixed chain diacylglycerol, 1-stearoyl-3-oleyl-glycerol. *J. Lipid Res.* 1995. **36:** 2185–2190.

Supplementary key words X-ray single crystal diffraction • molecular packing • torsion angles • conformation • membrane bilayers

Phospholipids make up the continuous phase of most biological membranes. Membrane phospholipids usually consist of a saturated chain and an unsaturated chain, esterified to glycerol, which in turn is esterified to a polar group such as phosphoryl choline. The interaction of the acyl chains in the membrane bilayer is of interest because the saturated and unsaturated chains have marked difficulty in packing together in crystalline states (1, 2). For instance, in mixtures of octadecane and 9-*cis*-octadecene, no mixing of these molecules occurs in the crystalline state (1). Although the crystal structures of some phospholipids and diacylglycerols, having saturated acyl or alkyl chains, have been solved (3), none have had mixed chains, particularly those biologically relevant molecules having both a saturated and a *cis*-unsaturated chain. In an attempt to understand the behavior of the diacylglycerol part of membranes, i.e., the hydrophobic core, we have tried to grow large crystals of 1-stearoyl-2-oleyl-*sn*-glycerol suitable for structure determination, but so far have not succeeded. We have, however, crystallized the mixed chain diacylglycerol 1-stearoyl-3-oleyl-glycerol and characterized its crystalline structure. This mixed chain diacylglycerol is a positional isomer of the diacylglycerol part of phospholipids in membranes, in that the chains are esterified to the 1 and 3 positions rather than the 1 and 2 positions. Nevertheless, it is of interest to see how the chains will pack in the crystalline state. The crystalline structure of simple anhydrous 1,2-diacyl-*sn*-glycerols (4–6) and their polymorphic behavior (7) has been studied in some detail. The most stable crystalline structure has β′ chain pack-

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ing and a unit cell with monoclinic symmetry. The glycerol backbone lies roughly parallel to the plane of the bilayer and the two chains lie side by side in the crystal, while the free hydroxyl group in the 3 position hydrogen bonds to the *sn*-1 carbonyl oxygen of the adjacent molecule in the same layer. Some analogues of 1,3 diacylglycerols have been crystallized (8, 9), including diglyceride of 11-bromoundecanoic acid (8). This 1,3 diacylglycerol forms an extended structure with the two chains pointing in roughly the opposite directions. It packs in a monoclinic unit cell (space group C2/c): a = 9.36, b = 5.58, c = 54.53, b = 90.4°. Thus the 1 and 3 chains are segregated from one another and do not pack together in the same monolayer. As might be expected the 1-stearoyl-3-oleyl glycerol (1,3-SODG) also packed in a monoclinic cell, space group Cc, and the two chains are segregated, pointing roughly in opposite directions. The structures of a few saturated monoacylglycerols have been solved (10–13) including recently the β form of α-monolaurin (11) and the β′ form of optically active α-monostearin (12). Interestingly, one of the two conformers of α-monolaurin has a glycerol conformation very similar to 1,3-SODG.

EXPERIMENTAL

1-Stearoyl-3-oleyl glycerol (1,3-SODG) was obtained by converting 1-stearoyl-2-oleyl-*sn*-glycerol (1,2-*sn*-SODG) (purchased from NuChek Prep, Inc.) in ethyl acetate at room temperature. The yield of conversion is 50% in a week. The remaining material is 1,2-SODG. Pure 1,3-SODG (>99%) was obtained by flash chromatography (5% boric acid/silica gel, hexane/ethyl acetate = 95:5). The single crystals of 1,3-SODG were obtained in ethyl acetate by slow evaporation at 4°C. They were colorless thin plates. The crystalline material had a powder diffraction pattern showing triclinic parallel (β) subcell, a bilayer period of 38.7 Å, and melted at 42.5°C with an enthalpy of 18.0 kcal/mol.

A fairly good single crystal with dimensions of 0.35 × 0.2 × 0.03 mm^3 was used for X-ray analysis. Crystal data: monoclinic, space group Cc, a = 9.362(2), b = 5.495(2), c = 77.92(3)Å, β = 91.46(2), V = 4007(4)$Å^3$, Z = 4, D = 1.032 g/cm^3. All the X-ray data were obtained with an Enraf-Nonius CAD4 four-circle diffractometer by using graphite monochromated Cu-Ka radiation at room temperature. During data collection, three standard reflections were monitored to check crystal decay every hour. At the end of the data collection, the intensities of the standard reflections had dropped linearly to about 60% of their original values, and therefore, the intensities were corrected for the linear decay. A total of 3125 reflections were collected and 985 reflections $|Fo| \geq 3\sigma|Fo|$ were used for calculations. No correction was made for absorption. The structure was solved by MULTAN 84 applying RANTAN methods and successive Fourier methods. The structure was refined to R = 0.127 ($R_w = 0.122$ $w = 1/\sigma^2(Fo)$) by block-diagonal least-squares method using anisotropic temperature factors. While the hydrogen atoms attached to carbon atoms were located at their ideal positions, the one attached to an oxygen atom was obtained from the D-Fourier map and they were not refined.

The possibility of space group C2/c was considered but the intensity statistics indicated Cc as the correct space group. In the space group C2/c we could not resolve the chemically correct molecular features of 1,3-SODG and therefore discarded this possibility. The space group of the crystal of the 1,3-diglyceride of 11-bromoundecanoic acid was C2/c and Z = 4. That crystal structure, however, had disorder, due to the twofold axis of the molecule. Our structure did not have such disorder but has some thermal disorder.

RESULTS AND DISCUSSION

To our knowledge this is the first determination of a mixed chain diglyceride crystal structure containing a saturated (stearic acid) and an unsaturated fatty acid (oleic acid). The space group of 1,3-SODG is Cc. This implies that 1,3-SODG is a racemic mixture because in order to have a c-glide symmetry, there must be equal amounts of 2-R and 2-S 1,3-SODG in the unit cell. Even though we started with the chiral 1,2-*sn*-SODG, we got the racemic 1,3-SODG.

Molecular geometry

The coordinates and isotropic temperature factors of the non-H atoms are given in **Table 1,** and the numbering of atoms is shown in **Fig. 1.** Bond lengths, bond angles, and selective torsion angles for the non-H atoms are given in **Table 2** and **Table 3,** respectively. **Figure 2** shows the packing of the molecules viewed along the b and a axes. The apparent decrease or increase in the bond lengths and angles are due to thermal disorder. The mean values of the chain C–C bonds and the C–C–C angles are 1.54 Å and 112°, respectively. These values are in agreement with those found for other long-chain structures (2). The least-squares planes through the stearoyl chain (C1S to C18S) and the oleyl chain (C1L to C18L) showed a maximum out-of-plane deviation of -0.24 and +0.46 Å, respectively. The torsion angle of the double bond C8–C9–C10–C11 is -17°. This value deviates some from the standard *cis* angle (0°), however the deviation may be due to the disorder among the adjacent carbon atoms.

TABLE 1. Atomic parameters

Atom	x	y	z	Beqv(Å^2)
C18S	0.568(6)	2.701(8)	-0.0964(8)	14.8(26)
C17S	0.460(6)	2.510(9)	-0.0873(7)	15.1(25)
C16S	0.527(4)	2.406(6)	-0.0725(4)	6.0(12)
C15S	0.419(4)	2.199(6)	-0.0645(5)	8.1(16)
C14S	0.498(4)	2.078(9)	-0.0477(8)	11.1(20)
C13S	0.397(2)	1.915(6)	-0.0383(5)	5.2(11)
C12S	0.475(3)	1.750(5)	-0.0245(4)	3.9(10)
C11S	0.362(4)	1.605(6)	-0.0135(6)	7.9(14)
C10S	0.446(3)	1.443(6)	0.0002(5)	4.7(10)
C9S	0.329(4)	1.301(6)	0.0096(4)	5.6(11)
C8S	0.408(2)	1.138(5)	0.0224(5)	4.3(10)
C7S	0.308(3)	0.973(7)	0.0326(6)	7.1(14)
C6S	0.389(2)	0.811(4)	0.0461(4)	2.2(7)
C5S	0.293(2)	0.674(5)	0.0554(4)	2.9(8)
C4S	0.374(2)	0.514(5)	0.0681(3)	2.2(7)
C3S	0.269(3)	0.366(7)	0.0805(4)	5.4(11)
C2S	0.350(3)	0.192(7)	0.0905(6)	7.1(14)
C1S	0.263(5)	0.021(11)	0.1012(9)	14.8(28)
O1S	0.134(2)	0.116(5)	0.1064(3)	7.2(8)
OG3	0.310(3)	-0.100(7)	0.1144(4)	11.7(13)
CG3	0.230(3)	-0.234(5)	0.1266(4)	3.6(8)
CG2	0.350(3)	-0.395(5)	0.1342(4)	3.6(8)
OG2	0.284(2)	-0.547(5)	0.1462(4)	8.7(10)
CG1	0.448(4)	-0.246(10)	0.1457(6)	11.6(20)
OG1	0.365(fix)	-0.107(4)	0.1594(fix)	5.5(7)
O1L	0.574(2)	0.086(5)	0.1690(4)	7.5(8)
C1L	0.437(2)	0.072(5)	0.1685(3)	2.6(7)
C2L	0.354(4)	0.166(9)	0.1817(4)	8.5(16)
C3L	0.435(4)	0.332(8)	0.1953(4)	7.9(15)
C4L	0.339(4)	0.498(11)	0.2042(6)	11.4(21)
C5L	0.423(4)	0.664(9)	0.2163(5)	8.8(16)
C6L	0.330(5)	0.791(11)	0.2302(6)	11.6(21)
C7L	0.399(4)	1.025(9)	0.2416(5)	8.4(15)
C8L	0.289(6)	1.171(17)	0.2539(9)	20.5(39)
C9L	0.390(5)	1.323(11)	0.2622(8)	14.5(27)
C10L	0.371(4)	1.403(9)	0.2771(5)	8.2(15)
C11L	0.233(4)	1.405(9)	0.2855(6)	9.9(17)
C12L	0.195(5)	1.558(8)	0.2989(6)	9.3(17)
C13L	0.071(3)	1.484(6)	0.3086(4)	5.6(11)
C14L	0.036(4)	1.686(8)	0.3228(6)	7.9(15)
C15L	-0.092(3)	1.573(6)	0.3319(6)	7.7(14)
C16L	-0.129(5)	1.775(16)	0.3468(9)	21.3(43)
C17L	-0.274(5)	1.667(12)	0.3573(9)	17.1(31)
C18L	-0.301(8)	1.877(23)	0.3717(12)	28.1(60)

As a whole, the stearic acid part can be considered to be a plane (maximum out-of-plane deviation of -0.24 Å at C15). The torsion angle sequence along the oleate chain shows considerable distortion. Proceeding from CL7 to CL13 (Fig. 1) the sequence is *trans* (173°), *skew* (-152°), *cis* (-17°), *skew* (-157°), *skew* (-163°), *trans* (-178°). Considering the oleic acid part, as a whole, the least-square plane through C1L to C18L showed maximum deviation of +0.46(C8L) and can be considered to be almost a plane. Accordingly, the molecule is V-shaped (Fig. 2B) and the dihedral angle between the planes of the two parts is 94°. The OG3 to CG2 parts of the glycerol are contained in the plane of the stearic acid. The glycerol atoms OG1 to CG2 are contained in the plane of the oleic acid part of the molecule as seen in Fig. 2B. Thus the oleate and stearate planes intersect at the central glycerol carbon, CG2.

Molecular packing

Figure 2 shows the packing of 1,3-SODG molecules viewed along the two short unit cell axes (a and b). The unit cell contains four molecules, which are symmetry-related by a c-glide and a C-center. Similar to saturated, symmetric 1,3-diglycerols (8, 9), the molecule is in a V-shaped conformation. The dihedral angle between the stearoyl and the oleyl planes is 94°. The stearoyl chain and the oleyl chain are segregated. The oleyl chain packs in one layer, the stearoyl chain in the other, which results in a mixed bilayer arrangement, with no mixing of stearoyl and oleyl chains in one layer. In the glycerol region, the molecules are linked by hydrogen bonds 2.78

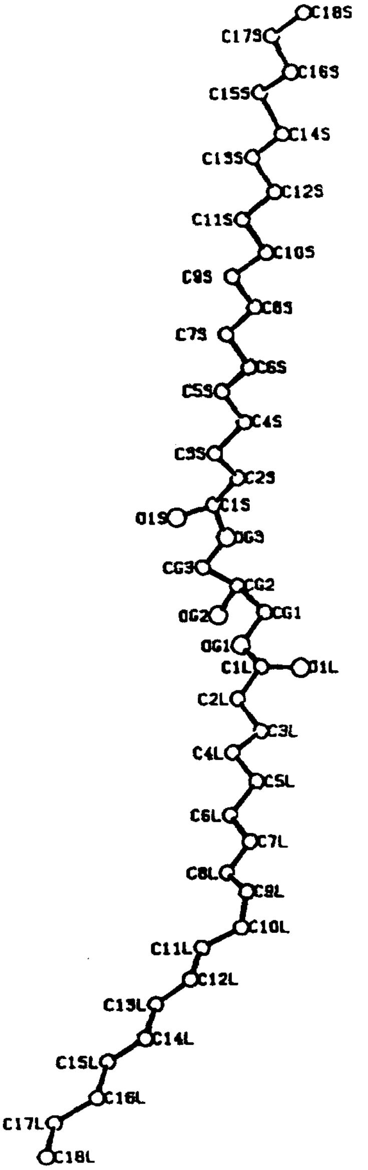

Fig. 1. Molecular conformation and numbering of atoms of 1,3-SODG.

TABLE 2. Bond distances and bond angles

a) Bond distances (Å)

C18S-C17S	1.63(9)	C17S-C16S	1.43(6)	C16S-C15S	1.65(5)
C15S-C14S	1.62(6)	C14S-C13S	1.50(6)	C13S-C12S	1.57(4)
C12S-C11S	1.59(5)	C11S-C10S	1.59(5)	C10S-C9S	1.55(5)
C9S -C8S	1.52(4)	C8S -C7S	1.52(4)	C7S -C6S	1.56(5)
C6S -C5S	1.39(4)	C5S -C4S	1.51(5)	C4S -C3S	1.61(4)
C3S -C2S	1.43(5)	C2S -C1S	1.51(7)	C1S -O1S	1.38(6)
C1S -OG3	1.29(7)	OG3 -CG3	1.43(4)	CG3 -CG2	1.54(4)
CG2 -OG2	1.41(4)	CG2 -CG1	1.50(5)	CG1 -OG1	1.54(5)
OG1 -C1L	1.38(3)	C1L -C2L	1.40(5)	C1L -O1L	1.28(3)
C2L -C3L	1.58(6)	C3L -C4L	1.47(6)	C4L -C5L	1.52(6)
C5L -C6L	1.57(7)	C6L -C7L	1.68(7)	C7L -C8L	1.63(9)
C8L -C9L	1.41(10)	C9L -C10L	1.26(8)	C10L-C11L	1.47(6)
C11L-C12L	1.39(7)	C12L-C13L	1.46(6)	C13L-C14L	1.61(6)
C14L-C154(5)	1.54(5)	C15L-C16L	1.65(9)	C16L-C17	1.71(8)
C17L-C18L	1.63(13)				

b) Bond angles (°)

C18S-C17S-C16S	110(4)	C17S-C16S-C15S	109(3)
C16S-C15S-C14S	108(3)	C15S-C14S-C13S	111(3)
C14S-C13S-C12S	113(2)	C13S-C12S-C11S	111(2)
C12S-C11S-C10S	109(3)	C11S-C10S-C9S	105(2)
C10S-C9S -C8S	106(3)	C9S -C8S -C7S	113(2)
C8S -C7S -C6S	113(2)	C7S -C6S -C5S	111(2)
C6S -C5S -C4S	110(2)	C5S -C4S -C3S	113(2)
C4S -C3S -C2S	110(2)	C3S -C2S -C1S	115(3)
C2S -C1S -O1S	114(4)	C2S -C1S -OG3	126(4)
O1S -C1S -OG1	104(4)	C1S -OG1 -CG1	128(3)
OG1 -CG1 -CG2	99(2)	CG1 -CG2 -OG2	105(2)
CG1 -CG2 -CG3	110(3)	OG2 -CG2 -CG3	102(3)
CG2 -CG3 -OG3	112(3)	CG3 -OG3 -C1L	118(2)
OG3 -C1L -O1L	122(2)	OG3 -C1L -C2L	112(3)
O1L -C1L -C2L	122(3)	C1L -C2L -C3L	116(3)
C2L -C3L -C4L	113(3)	C3L -C4L -C5L	110(3)
C4L -C5L -C6L	114(4)	C5L -C6L -C7L	119(4)
C6L -C7L -C8L	116(4)	C7L -C8L -C9L	98(5)
C8L -C9L -C10L	122(5)	C9L -C10L-C11L	124(4)
C10L-C11L-C12L	125(4)	C11L-C12L-C13L	116(4)
C12L-C13L-C14L	110(3)	C13L-C14L-C15L	102(3)
C14L-C15L-C16L	104(3)	C15L-C16L-C17L	107(5)
C16L-C17L-C18L	103(6)		

Å long, between the free hydroxyl group OG2 and the carbonyl oxygen on the oleyl chain (see Fig. 2A). The hydrocarbon chains are packed in a triclinic subcell (T//). The torsion angles around the glycerol ester part of the molecule as described by the notation of Sundaralingam (14) are compared to monoglycerides and 1,3 di-11-bromo-undecanoyl glycerol in **Table 4.** The conformation of molecule is rather similar to the A conformer of *rac*-monolaurin β-form (11) and to 1,3-bromo di-undecanoin (8).

TABLE 3. Selected torsion angles (°)

C4S -C3S -C2S -C1S	-173(3)	C3S -C2S -C1S -O1S	-29(6)
C3S -C2S -C1S -OG3	-159(5)	C2S -C1S -OG3 -CG3	169(4)
O1S -C1S -OG3 -CG3	35(6)	C1S -OG3 -CG3 -CG2	161(4)
OG3-CG3 -CG2 -OG2	-178(2)	OG3 -CG3 -CG2 -CG1	74(3)
CG3 -CG2 -CG1 -OG1	53(4)	OG2 -CG2 -CG1 -OG1	-58(4)
CG2 -CG1 -OG1 -C1L	-168(3)	CG1 -OG1 -C1L -O1L	-17(4)
CG1 -OG1 -C1L -C2L	-174(3)	OG1 -C1L -C2L -C3L	168(3)
O1L -C1L -C2L -C3L	11(5)	C1L -C2L -C3L -C4L	157(4)
C6L -C7L -C8L -C9L	173(4)	C7L -C8L -C9L -C10L	-152(5)
C8L -C9L -C10L-C11L	-17(9)	C9L -C10L-C11L-C12L	-157(5)
C10L-C11L-C12L-C13L	-163(4)	C12L-C13L-C14L-C15L	-178(3)

Looking from atom 2 to atom 3, the clockwise rotation of bond 3-4 with reference of bond 2-1 is given.

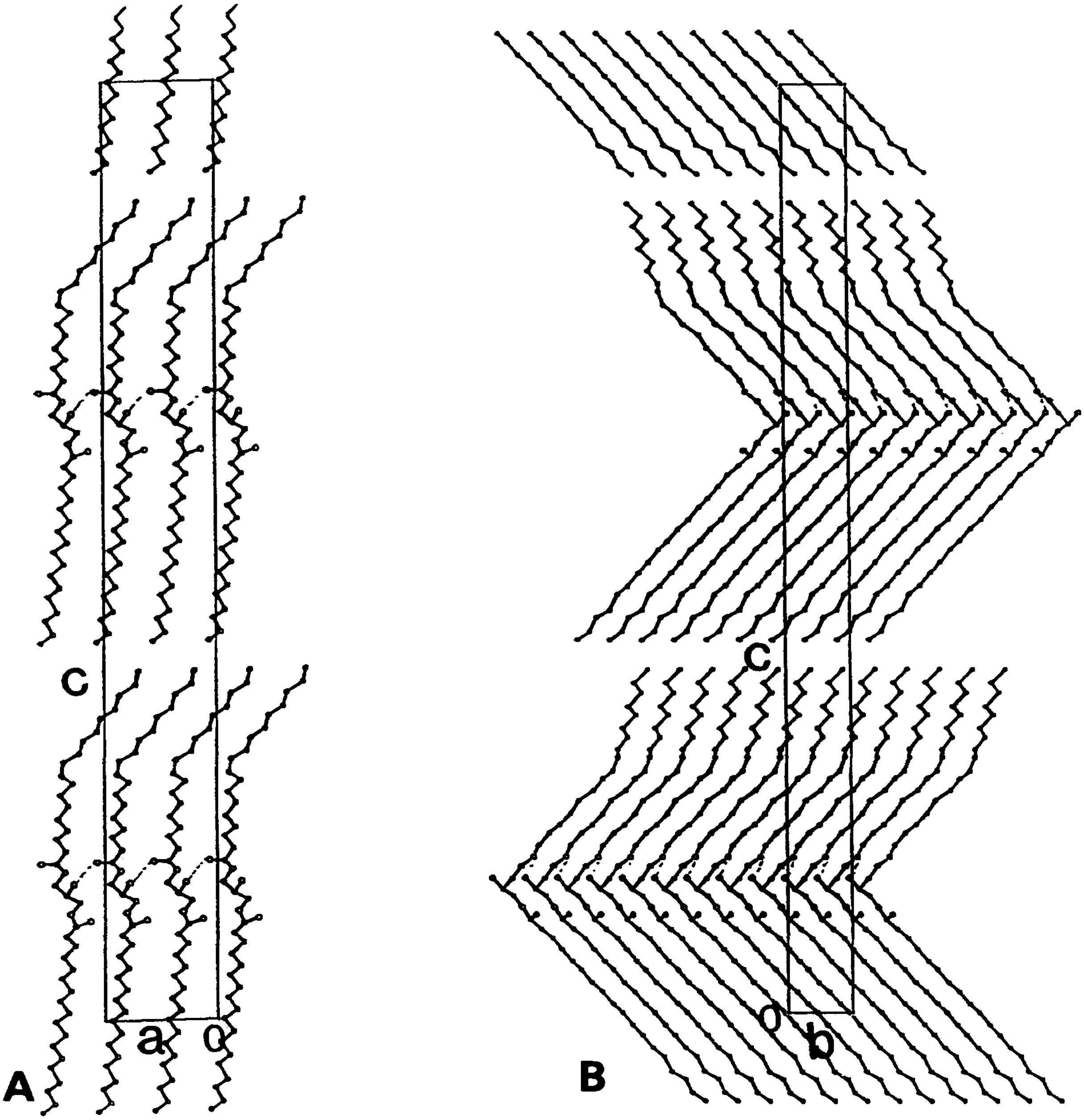

Fig. 2. Molecular packing of 1,3-SODG A) down the b axis and B) down the a axis. H-bonds are shown as dotted lines.

The molecular packing is very different from 1,2 diacylglycerols (4, 5). In these molecules the chain in the primary position bends at the carbonyl so that it forms a hairpin shape and lies next to the *sn*-2 chain. The chains are packed in an orthorhombic perpendicular (β′) conformation. The -OH on the free glycerol hydroxyl (*sn*-3) is hydrogen-bonded to the carbonyl oxygen on the adjacent molecules' *sn*-1 acyl chain, so that the glycerol lies perpendicular to the chain axes and parallel to the bilayer plane. In this hairpin conformation the two chains pack together even when the two chains are different. Thus 1-stearoyl-2-oleyl-*sn*-glycerol (1,2-SODG) forms a series of bilayer structures with the oleate lying next to the stearate (15). This results in an uncomfortable packing and the formation of many crystalline forms of similar free energies (15). The most stable bilayered form of 1,2-SODG (β′) melts at 25.7° with a low enthalpy (ΔH = 11.9 kcal/mol) and entropy (ΔS = 39.8 cal/°k/mol). In contrast, 1,3-SODG is more stable and melts at 42.5° with an enthalpy of 18 kcal/mol and entropy of 56.9 cal/°k/mol. The fact that all the 1,3-diacylglycerols have their chains separated in this V formation and the 1,2-diacylglycerols have a hairpin conformation with chains lying side by side probably relates to the formation of specific H-bonds in the glycerol region to stabilize the glycerol conformation.

TABLE 4. Selected torsion angles of 1-stearoyl-3-oleyl-glycerol compared to other acyl glycerols

		α-Monostearin (D)		α-Monolaurin (rac)				
	This Work	A	B	A1	B1	A2	B2	1,3-BrDiG
θ 1: OG1–CG1–CG2–CG3	52	172	-55	-52	61	69	-60	64
θ 2: OG1–CG1–CG2–OG2	-58	-67	78	66	165	-59	-171	-68
θ 3: CG1–CG2–CG3–OG3	74	-68	-166	-63	-68	52	53	64
θ 4: OG2–CG2–CG3–OG3	-178	171	61	-177	62	-174	-58	-163
α 1: CG2–CG1–OG1–C1L	-168							-174
α 2: CG1–OG1–C1L–C2L	-174							180
α 3: OG1–C1L–C2L–C3L	168							176
γ 1: CG2–CG3–OG3–C1S	161	-153	177	-179	-171	154	-176	-174
γ 2: CG3–OG3–C1S–C2S	169	7	171	171	-171	-171	-179	-178
γ 3:OG3–C1S–C2S–C3S	-159	171	171	-177	165	165	-176	179

Monostearin, ref. 12; monolaurin (rac), ref. 11; 1,3-BrDiG (1,3-di-11-bromoundecanoyl glycerol) ref. 8.

Thus the hydroxyl in the 2 position H-bonded to the oleyl carbonyl forces the chains to extend away from the glycerol in the 1,3 isomers, while the hydroxyl in the primary position H-bonded to the other primary position forces the glycerol to lie parallel to the layer plane and allows the chains to come together and lie side by side. If intramolecular H-bonds are replaced by H-bonding to some other molecule, for instance water, then the glycerol conformation changes to orient the -OH toward the water interface. This occurs with 1,2-diacyl-*sn*-glycerols at the air–water interface (16, 17) and aqueous bilayer interface (18). At the air–water interface 1,3 diacylglycerols also change conformation so that the -OH orients towards the water and the two chains lie side by side (16). Further, if the free -OH is esterified and H-bond formation is prevented, for instance in the formation of a triacylglycerol, then at least two other glycerol conformations can be obtained depending on chemical nature of the triacylglycerol (19, 20).

We wish to thank Dr. Kouzou Kozawa and Professor Tokiko Uchida (Science University of Tokyo) for their help in calculating with MULTAN 84. Supported by USPHS grants nos. HL07291 and HL26335 (D. M. Small, P. I.). We wish also to thank Elizabeth Martin for help in preparing the manuscript.

Manuscript received 20 April 1995 and in revised form 14 July 1995.

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