The Crystal Structure of the β'_1 Form of Optically Active α-Monostearin

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(Received September 5, 1987)

Synopsis. The crystal structure of the β'_1 form of (*R*)-α-monostearin has been determined. The space group is $P2_12_12_1$, with a=4.943(1), b=8.858(2), c=101.05(1)Å, and Z=8. The two independent molecules in the title compound have different conformations.

The polymorphism of the α-monoglycerides has been reported mainly in racemic forms.[1] The modifications named the sub-α, α, β', and β forms (β_1, β_2) have been known.[1,2] The β_1 form is a stable form and the structure has been determined in α-monolaurin.[3]

The pioneer work on the optically active α-monoglycerides was carried out by Larsson. Four modifications, the α, β'_1, β'_2, and β forms were found. He described the lattice constants and the space groups of two β' forms of monostearin, but did not solve their structures.[2] Recently Iwahashi et al. reported the thermodynamic behavior, infrared and NMR spectra of optically active monoglycerides.[4] The present authors obtained a single crystal of the β'_1 form of (*R*)-α-monostearin and undertook an X-ray crystal structure analysis.

Experimental and Structure Determination

The (*R*)-α-monostearin was obtained from Fluka AG-(Switzerland). The phase of the β'_1 form can be made from solvents as precipitates and is considered the stable form at room temperature. A crystal for the X-ray work could be obtained by slow evaporation at 20 °C from a acetone-chloroform mixed solution (1 : 1 volume ratio). A crystal with dimensions of 0.3×0.3×0.1 mm^3 was used. The unit cell parameters and intensities were measured on a Rigaku-Denki AFC-4 four-circle diffractometer by using graphite monochromated Cu $K\alpha$ radiation (λ=1.54184 Å). 4020 independent reflections within the range of $5°<2\theta<120°$ were collected by the $2\theta/\omega$ scan mode, with a scan width ω of $0.7+0.35\tan\theta$, and a scan speed of 4° min^{-1}. The standard reflections, monitored every 50 reflections showed no decline. 1855 independent reflections with $|F_o|\geq 3\sigma(|F_o|)$ were used for the analysis. The 1 0 0 reflection (F_o=15.5) was observed. Attempts to refine the structure in the $P2P2_1P2_1$ space group remained unsatisfactory. Therefore, it was concluded that the existence of the 1 0 0 reflection might be due to some disorders in the lattice, and so this reflection was excluded from the reflection data. Crystal data: $C_{21}H_{42}O_4$, M=358.6, orthorhombic, $P2_12_12_1$, a=4.943(1), b=8.858(2), c=101.05(1) Å, cell volume=4424.2(11) Å^3, Z=8, D_c=1.08 g cm^{-3}, μ=5.76 cm^{-1}. The structure could be solved by MULTAN 84.[5] The hydrogen atoms of the carbon chains were placed at the calculated positions. The structural parameters were refined by a block-diagonal least-squares method, using scattering factors from the International Tables for X-ray Crystallography (1974).[7] Anisotropic thermal parameters were assumed for the non-hydrogen atoms, and isotropic parameters for the hydrogen atoms. All the calculations except MULTAN 84 were carried out in a Facom M-380 Computer, using the UNICS III system.[7] The final refinement led to the R value of 0.110 (W=1.0). The maximum and minimum heights on the final difference Fourier map were 0.28 and −0.32 e Å^{-3} respectively; no other significant features were observed.

Results and Discussion

The numbering of the atoms in the molecules is shown in Fig. 1, while the final atomic coordinates are given in Table 1.[8]

The asymmetric unit contains two crystallographically independent molecules, which differ in the conformation of their glycerol parts. They will hereafter be named A and B. The differences in conformation are illustrated in Fig. 1, while the dihedral angles are shown in Table 2, together with the case of racemic α-monolaurin. The larger temperature factors of the O1A and O1B atoms might be due to the disorder.

The packing of the molecules in the crystal is shown in Fig. 2. In the packing of the hydrocarbon chains, every second hydrocarbon plane is approximately perpendicular to the other chain planes. This packing is common in fatty acids or paraffin crystals (named O⊥

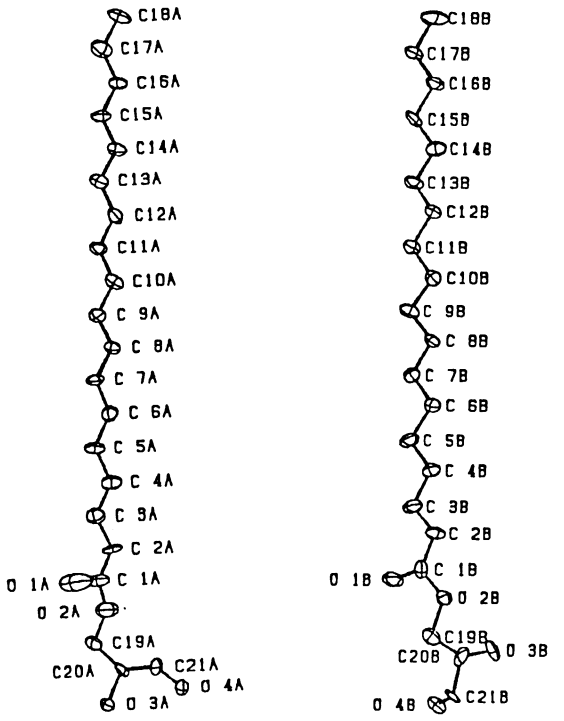

Fig. 1. ORTEP drawing and the numbering systems of atoms. The ellipsoids are drawn to enclose 40% probability.

Table 1. Fractional Atomic Coordinates ($\times 10^4$) and Thermal Parameters for Non-hydrogen Atoms
$B_{eq}=4/3\ \sum_i\sum_j a_i a_j$

Atom	X	Y	Z	B_{eq}/A^2
C1A	4486(41)	10106(21)	8092(2)	4.6(6)
C2A	5889(40)	8883(20)	8166(2)	4.0(5)
C3A	4494(41)	8730(20)	8304(2)	4.2(5)
C4A	5838(40)	7401(21)	8380(2)	4.3(6)
C5A	4437(39)	7243(19)	8522(2)	3.9(5)
C6A	5711(41)	5923(19)	8600(2)	4.0(5)
C7A	4258(47)	5686(20)	8736(2)	4.7(6)
C8A	5842(34)	4330(17)	8805(2)	2.8(5)
C9A	4661(40)	4125(18)	8942(2)	3.8(5)
C10A	5804(33)	2755(17)	9017(2)	3.4(5)
C11A	4655(44)	2552(18)	9157(2)	4.2(5)
C12A	5707(44)	1184(18)	9229(2)	4.4(6)
C13A	4427(49)	969(19)	9373(2)	5.1(6)
C14A	5685(36)	−401(18)	9440(2)	3.4(5)
C15A	4665(41)	−602(19)	9580(2)	4.0(5)
C16A	5838(36)	−1959(18)	9650(2)	3.3(5)
C17A	4832(46)	−2141(20)	9793(2)	5.2(6)
C18A	5855(50)	−3530(21)	9861(2)	6.1(7)
C19A	4668(44)	11685(18)	7904(2)	4.4(6)
C20A	5553(40)	11275(15)	7763(2)	3.4(5)
C21A	4205(44)	9955(18)	7704(2)	4.6(6)
O1A	2743(48)	10946(23)	8132(2)	12.5(9)
O2A	5646(34)	10456(15)	7983(1)	6.6(5)
O3A	5020(25)	12593(10)	7679(1)	3.2(3)
O4A	5287(28)	9508(11)	7585(1)	4.1(4)
C1B	368(41)	14936(18)	8082(2)	4.1(5)
C2B	−816(39)	13852(20)	8172(2)	4.0(5)
C3B	451(48)	13785(22)	8302(2)	5.2(6)
C4B	−696(47)	12510(21)	8385(2)	5.0(6)
C5B	647(45)	12314(22)	8522(2)	4.9(6)
C6B	−707(41)	10936(19)	8594(2)	4.0(5)
C7B	528(40)	10719(18)	8730(2)	3.6(5)
C8B	−477(41)	9360(19)	8806(2)	4.1(5)
C9B	824(36)	9194(18)	8947(2)	3.8(5)
C10B	−347(47)	7785(19)	9011(2)	4.7(6)
C11B	874(35)	7571(18)	9152(2)	3.4(5)
C12B	−430(41)	6225(17)	9230(2)	3.8(5)
C13B	691(42)	5985(17)	9361(2)	4.1(5)
C14B	−582(50)	4645(21)	9431(2)	5.6(7)
C15B	895(39)	4399(18)	9571(2)	4.2(6)
C16B	−368(44)	3059(21)	9647(2)	4.9(6)
C17B	913(37)	2835(18)	9785(2)	3.7(5)
C18B	−343(59)	1537(25)	9861(2)	7.8(8)
C19B	1007(41)	15879(19)	7845(2)	4.4(6)
C20B	−329(47)	15486(17)	7725(2)	4.5(6)
C21B	390(37)	16605(16)	7609(2)	3.5(5)
O1B	2517(34)	15676(17)	8100(1)	7.7(6)
O2B	−494(25)	14899(13)	7949(1)	4.0(3)
O3B	−155(29)	13969(11)	7688(1)	5.1(4)
O4B	3314(26)	16536(12)	7609(1)	4.3(4)

Table 2. Dihedral Angles (φ/°)

	Racemic		Active	
	A2	B2	A	B
O2−Cn−Cn+1−Cn+2	−52(3)	53(3)	68(2)	167(1)
O2−Cn−Cn+1−O3	174(2)	−58(3)	−171(2)	−61(2)
O3−Cn+1−Cn+2−O4	60(3)	171(3)	67(2)	−78(2)

Racemic α-monolaurin (β_1) n=13.
Active α-monolaurin (β'_1) n=19.

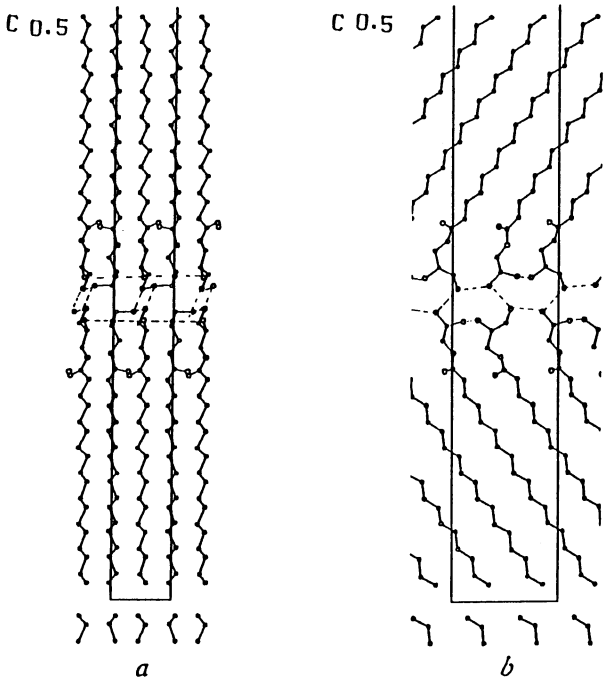

Fig. 2. Molecular arrangement. a) Viewed along the b axis. b) Viewed along the a axis.

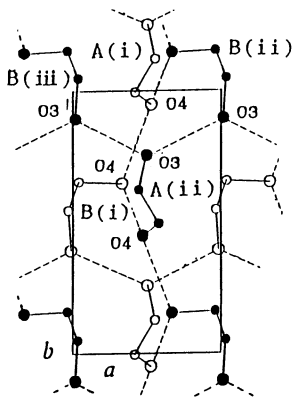

Fig. 3. Illustration of the hydrogen bond net work viewed along the c-axis. O3A(ii)-O3B(ii) 2.68(2)Å, O3A(ii)-O3B(iii) 2.84(2), O4A(i)-O4B(ii) 2.74(2), O4A(i)-O4B(i) 2.82(2). Symmetry code; A(i) $x,y+1,z$; B(ii) $1-x,y-1.5,1.5-z$; B(i) $x,y-1,z$; B(iii) $1-x,y-1.5,1.5-z$; A(ii) $1-x,y-0.5,1.5-z$. Upper layer atoms ●, Lower layer atoms ○.

packing). The dimensions of the subcell are; a_s=7.42 Å, b_s=4.94 Å, and c_s=2.54 Å. These are nearly the same as those of the B and C forms of fatty acids.[9,10] The molecules are linked by the hydrogen bonds shown in Fig. 3. Only the hydroxyl groups participate in the hydrogen-bond system. The average hydrogen-bond distance is 2.77 Å.

We are indebted to Dr. Toshio Sakurai and Miss Kimiko Kobayashi of the Institute of Physical and Chemical Research for the UNICS III programs used in this work; we also wish to thank Dr. Kazumasa Honda of National Chemical Laboratory for help with the experimental work.

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