The Crystal Structure of the β-Form of α-Monolaurin

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Synopsis. The crystal structure of the β form of α-monolaurin has been determined. The space group is $P2_1$, with a=9.2472(3), b=74.310(2), c=4.9523(1) Å, β=97.514 (3)°, and Z=8. Two types of molecular conformations of monolaurin exist in the crystal.

The α-monoglycerides have been shown by powder X-ray diffractions to exist in four crystalline forms, 1) α-form, 2) subα-form, 3) β′-form, and 4) β-form.[1] The β-form is a stable form at room temperature. Larsson found two different forms of the β-form and named them the β_1- and β_2- forms.[2] Both were monoclinic and had the same cell dimentions, but they differed in the absent reflections. He assigned the space group of $P2_1/m$ and Am for β_1 and β_2 respectively. He described the chain packing, but did not solve the structure of the glycerol parts.[2] The present authors obtained a single crystal of the β-form (β_1-form by Larsson's nomenclature) of α-monolaurin and undertook an X-ray crystal structure analysis.

Experimental and Structure Determination

The α-monolaurin was prepared by the Nihon Glyceride Co. Ltd. The β-form crystal was obtained by crystallization in a chloroform solution. The cell dimensions and diffraction intensities were measured on a Rigaku-Denki four-circle diffractometer by using graphite monochromated Cu-$K\alpha$ radiation at room temperature. 963 independent reflections with 2θ values up to 120° ($|F_o| \geqq 3\sigma(|F_o|)$) were used for the analysis. No correction was made for absorption. The systematic absences ($k=2n+1$ for $0k0$) and intensity statistics indicated $P2_1$ as the space group. The crystal data were as follows: $C_{15}H_{30}O_4$; monoclinic, $P2_1$; Z=8; a=9.2472 (3), b=74.310 (2), c=4.9523 (1) Å, β=97.514 (3)°; D_x=1.06 gcm^{-3}; mp=63.0°C. The structure was solved by MULTAN.[3] The hydrogen atoms except for the one near the end of the carbon chains were placed at the calculated positions. The structural parameters were refined by a block-diagonal least-squares method, using the UNICS III system.[4] The final refinement led to the R value of 0.070. The other possible space group $P2_1/m$ was found to be definitely incorrect because the R value did not decrease to less than 0.3.

Results and Discussion

The asymmetric unit contains four crystallographicaly independent molecules. They will hereafter be named the A_1, A_2, B_1, and B_2 molecules. Two pairs, A_1 and A_2, and B_1 and B_2, are enantiomers to each other. The numbering of atoms in the molecules is shown in Fig. 1, while the final atomic coordinates are given in Table 1.[5]

The difference in the conformation of monolaurin between A and B exists in the glycerol parts, as illustrated in Fig. 1. The dihedral angles φ (O2–C13–C14–O3) are 177° (A_1) and 175° (A_2) for the A molecules, and 62° (B_1) and −58° (B_2) for the B molecules. The dihedral angles φ (O3–C14–C15–O4) are −66° (A_1) and 60° (A_2) for the A molecules and 165° (B_1)

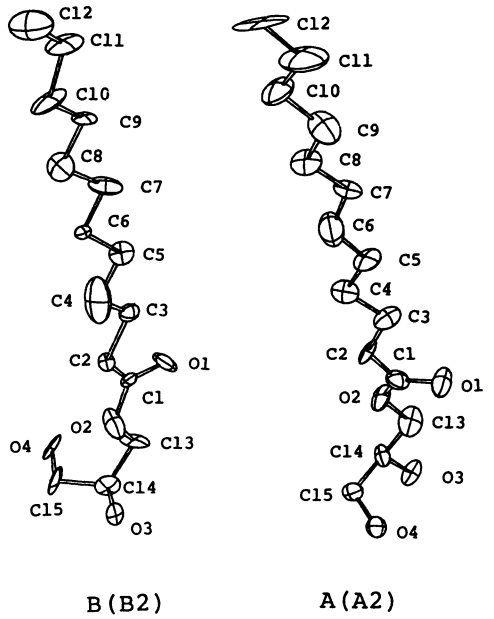

Fig. 1. ORTEP drawing along the C-direction and the numbering system of atoms.
The ellipsoids are drawn to enclose 40% probability.

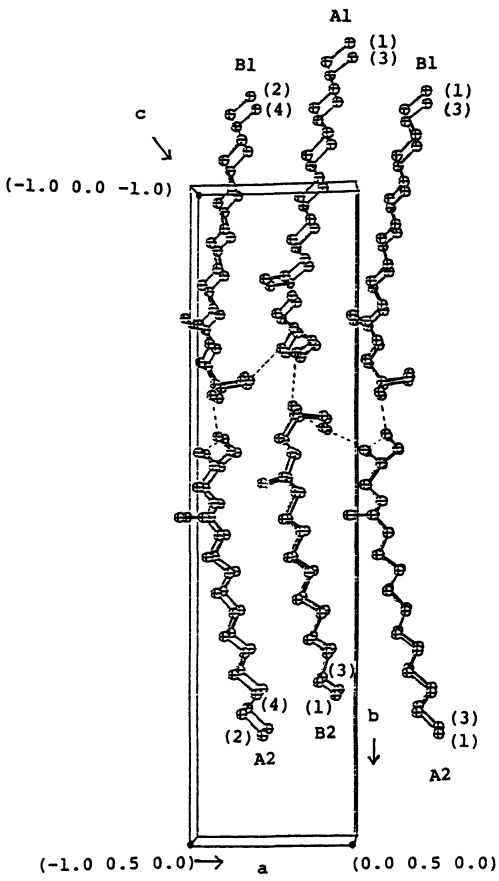

Fig. 2. Perspective view of the molecular packing (1) x,y,z (2) $x-1,y,z$ (3) $x,y,z-1$ (4) $x-1,y,z-1$.

TABLE 1. FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) AND THERMAL PARAMETERS FOR NON-HYDROGEN ATOMS
$B_{eq}=4/3\sum_i\sum_j\beta_{ij}a_ia_j$

ATOM	X	Y	Z	B_{eq}/Å^2	ATOM	X	Y	Z	B_{eq}/Å^2
C12A1	42(61)	-805(8)	-23255(99)	15.0	C12A2	5074(55)	4068(5)	-19487(84)	14.7
C11A1	-1253(57)	-677(7)	-23294(112)	14.1	C11A2	3848(58)	3922(6)	-18573(120)	13.8
C10A1	-837(32)	-490(6)	-22136(61)	6.7	C10A2	4630(33)	3791(6)	-16377(69)	8.7
C 9A1	-1968(40)	-372(7)	-20976(74)	8.0	C 9A2	3280(37)	3647(6)	-16395(66)	7.9
C 8A1	-1229(36)	-202(7)	-20022(62)	7.6	C 8A2	3828(34)	3498(6)	-14104(50)	5.4
C 7A1	-2412(29)	-51(5)	-19493(51)	5.5	C 7A2	2598(27)	3381(5)	-13523(37)	3.2
C 6A1	-1793(36)	95(6)	-17194(54)	4.1	C 6A2	3114(44)	3215(8)	-12113(87)	9.5
C 5A1	-2942(28)	228(6)	-16806(47)	5.0	C 5A2	2016(34)	3073(6)	-11031(58)	5.7
C 4A1	-2357(32)	381(5)	-14959(47)	4.5	C 4A2	2714(33)	2930(6)	-9174(50)	4.6
C 3A1	-3452(26)	520(5)	-14321(50)	4.1	C 3A2	1402(31)	2811(5)	-8745(51)	4.8
C 2A1	-2756(33)	647(6)	-12261(64)	6.2	C 2A2	2024(28)	2652(5)	-6892(50)	3.3
C 1A1	-3939(45)	765(7)	-11466(70)	7.6	C 1A2	1079(35)	2518(6)	-6111(63)	4.2
C13A1	-4505(31)	1021(6)	-8273(65)	4.2	C13A2	613(36)	2294(3)	-3040(42)	5.6
C14A1	-3539(27)	1122(5)	-6306(48)	3.0	C14A2	1532(29)	2135(5)	-1740(56)	3.4
C15A1	-2427(37)	1227(5)	-8074(59)	5.1	C15A2	2577(30)	2025(5)	-3228(56)	3.6
O 1A1	-5077(28)	783(5)	-11962(52)	8.7	O 1A2	-307(22)	2516(5)	-7182(43)	6.0
O 2A1	-3546(23)	898(5)	-9337(45)	6.1	O 2A2	1578(21)	2415(5)	-4159(43)	4.7
O 3A1	-4305(21)	1270(5)	-4960(38)	6.2	O 3A2	547(19)	2032(5)	-497(29)	3.8
O 4A1	-3265(21)	1324(5)	-10231(39)	5.2	O 4A2	1886(18)	1920(4)	-5269(35)	4.0
C12B1	4263(49)	-498(8)	-17481(81)	12.4	C12B2	-725(50)	3782(7)	-21703(71)	10.0
C11B1	3024(39)	-383(6)	-16036(67)	7.9	C11B2	-1742(42)	3692(6)	-20332(69)	8.1
C10B1	3685(38)	-207(7)	-15012(81)	8.8	C10B2	-1260(41)	3485(6)	-19822(74)	7.5
C 9B1	2577(42)	-74(6)	-13826(76)	8.1	C 9B2	-2384(32)	3396(5)	-18262(50)	3.2
C 8B1	2983(30)	108(6)	-12882(60)	5.2	C 8B2	-1686(30)	3211(6)	-17293(65)	6.2
C 7B1	2094(30)	217(5)	-10958(69)	5.9	C 7B2	-3072(34)	3114(5)	-16194(57)	5.2
C 6B1	2478(32)	405(6)	-10572(58)	6.3	C 6B2	-2432(26)	2925(5)	-14861(47)	2.7
C 5B1	1596(30)	491(6)	-8442(62)	4.7	C 5B2	-3669(29)	2816(6)	-13726(64)	4.4
C 4B1	1976(34)	679(7)	-7824(68)	5.3	C 4B2	-2959(37)	2627(6)	-12700(64)	4.1
C 3B1	981(29)	790(6)	-6391(54)	3.7	C 3B2	-4029(29)	2539(5)	-10896(46)	3.1
C 2B1	1629(38)	961(7)	-5402(73)	6.1	C 2B2	-3303(33)	2343(6)	-10306(59)	3.0
C 1B1	674(29)	1072(7)	-3563(63)	4.7	C 1B2	-4096(30)	2233(6)	-8654(64)	4.5
C13B1	676(30)	1350(6)	-1084(62)	4.2	C13B2	-4371(39)	1944(6)	-6473(71)	5.0
C14B1	1574(33)	1517(6)	-1270(56)	2.9	C14B2	-3473(36)	1762(6)	-6179(58)	4.3
C15B1	3114(33)	1490(6)	0(52)	3.8	C15B2	-1809(34)	1776(6)	-5149(61)	5.5
O 1B1	-219(23)	1019(5)	-2519(46)	6.0	O 1B2	-5356(22)	2273(5)	-7570(46)	5.4
O 2B1	1328(22)	1218(5)	-3036(48)	4.9	O 2B2	-3611(23)	2054(5)	-8132(50)	6.0
O 3B1	1480(24)	1606(5)	-4036(41)	4.5	O 3B2	-3519(20)	1710(5)	-8923(32)	2.9
O 4B1	3193(27)	1449(5)	2778(43)	6.9	O 4B2	-1858(20)	1859(5)	-2472(34)	4.2

and 171° (B_2) for the B molecules. The dihedral angles φ (O2–C13–C14–C15) are 64°, −69°, −52°, and 54° for the A_1, B_1, A_2, and B_2 molecules respectively. Therefore, the A and B molecules take a *trans-gauche* and a *gauche-trans* conformation respectively. The molecules are linked by hydrogen bonds, the average hydrogen-bond distance being 2.68 Å. The packing of the molecules in the crystal is shown in Fig. 2.

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5) The lists of the structure factors, the atomic parameters for the hydrogen atoms, and the anisotropic thermal parameters for the non-hydrogen atoms are deposited at the Office of the Chemical Society of Japan. (Document No. 8515).