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Carbohydrate Research 271 (1995) 137–150

CARBOHYDRATE RESEARCH

Molecular and crystal structures of 2,3,4,6,1′,3′,4′,6′-octa-*O*-acetyl-β-sophorose, methyl 2,3,4,6,3′,4′,6′-hepta-*O*-acetyl-β-sophoroside, and methyl 2,3,4,6,3′,4′-hexa-*O*-acetyl-6′-deoxy-β-sophoroside

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Received 31 October 1994; accepted 7 February 1995

Abstract

The molecular and crystal structures of 2,3,4,6,1′,3′,4′,6′-octa-*O*-acetyl-β-sophorose (β-sophorose octaacetate), methyl 2,3,4,6,3′,4′,6′-hepta-*O*-acetyl-β-sophoroside (methyl β-sophoroside heptaacetate), and methyl 2,3,4,6,3′,4′-hexa-*O*-acetyl-6′-deoxy-β-sophoroside (methyl 6′-deoxy-β-sophoroside hexaacetate) were determined by X-ray diffraction. All structures were obtained by the direct method and refined by the full-matrix least-squares procedure. The crystal data and final R values are as follows: β-sophorose octaacetate, $C_{28}O_{19}H_{38}$, monoclinic, $P2_1$, $a = 15.529(4)$, $b = 10.958(2)$, $c = 10.804(2)$ Å, $\beta = 107.73(3)°$, $D_{obsd} = 1.285$ g cm^{-3}, $D_{calcd} = 1.288$ g cm^{-3}, $Z = 2$, $R = 0.052$, $R_w = 0.052$; methyl β-sophoroside heptaacetate, $C_{27}O_{18}H_{38}$, orthorhombic, $P2_12_12_1$, $a = 20.992(5)$, $b = 27.642(7)$, $c = 5.730(2)$ Å, $D_{obsd} = 1.305$ g cm^{-3}, $D_{calcd} = 1.295$ g cm^{-3}, $Z = 4$, $R = 0.064$, $R_w = 0.066$; methyl 6′-deoxy-β-sophoroside hexaacetate, $C_{25}O_{16}H_{36}$, hexagonal, $P6_5$, $a = b = 15.136(2)$, $c = 23.534(4)$ Å, $D_{calcd} = 1.264$ g cm^{-3}, $Z = 6$, $R = 0.079$, $R_w = 0.064$. All the D-glucose residues have the $^4C_1$ pyranose conformation. These three molecules interact with their surrounding molecules by van der Waals forces, only.

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SSDI 0008-6215(95)00093-3

Conformational angles of ϕ and ψ at the β $(1 \rightarrow 2)$ glycosidic linkage of these compounds are similar to each other and close to the energetically minimum positions. All the primary acetate substituents at C-6 take a *gauche–gauche* conformation.

Keywords: β-Sophorose octaacetate; Methyl β-sophoroside heptaacetate; Methyl 6′-deoxy-β-sophoroside hexaacetate

1. Introduction

Conformational studies of macromolecules have been strongly supported by the systematic studies of crystal structures of related small molecules. Because of the difficulty of preparation, purification, and crystallization of oligosaccharides, the number of single-crystal analyses of these compounds has been limited. Acetylated derivatives of oligosaccharides crystallize more easily compared with the free-hydroxy carbohydrates in many cases. Consequently, a number of crystal structures of the acetate derivatives of mono-, di-, tri-saccharides have been reported [1–11]. Many of these

Table 1
Crystal data, details of the data collections, and structure determination and refinement data for β-sophorose octaacetate (**1**), methyl β-sophoroside heptaacetate (**2**), and methyl 6′-deoxy-β-sophoroside hexaacetate (**3**)

Data	1	2	3
Molecular formula	$C_{28}O_{19}H_{38}$	$C_{27}O_{18}H_{38}$	$C_{25}O_{16}H_{36}$
Molecular weight	678.6	650.6	592.5
Space group	$P2_1$	$P2_12_12_1$	$P6_5$
Crystal system	monoclinic	orthorhombic	hexagonal
Cell parameters			
a (Å)	15.529(4)	20.992(5)	15.136(2)
b (Å)	10.958(2)	27.642(7)	15.136(2)
c (Å)	10.804(2)	5.730(2)	23.534(4)
α (°)	90.0	90.0	90.0
β (°)	107.73(1)	90.0	90.0
γ (°)	90.0	90.0	120.0
Cell volume, V (Å^3)	1751(1)	3325(1)	4669(1)
Z	2	4	6
D_{calcd} (g cm^{-3})	1.288	1.295	1.264
D_{obsd} (g cm^{-3})	1.285	1.305	–
$2\theta_{max}$ (°)	130	120	120
Scan method	$2\theta - \omega$	$2\theta - \omega$	$2\theta - \omega$
Scan speed (°/min)	6	6	4
Scan width $\Delta\omega$(°)	$1.2 + 0.14 \tan \theta$	$1.2 + 0.14 \tan \theta$	$1.4 + 0.14 \tan \theta$
Unique reflections	3062	2887	1837
Unique reflections with $\lvert F_0 \rvert \geq n\sigma(F_0)$	2932(n = 3)	2233(n = 3)	1564(n = 2)
Final R value R	0.052	0.064	0.079
R_w	0.052	0.066	0.064

Table 2
Fractional coordinates and equivalent isotropic temperature factors (Å^2) of β-sophorose octaacetate (**1**), with estimated standard deviations in parentheses. $B_{eq} = 4/3 \times \{B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + 2(B_{12}ab + B_{23}bc + B_{31}ca)\}$

Atom	x	y	z	B_{eq}
C-1	0.4903(1)	−0.0035(−)	0.1717(2)	4.42(6)
C-2	0.5308(1)	0.0275(3)	0.0644(2)	4.15(5)
C-3	0.6161(1)	−0.0459(3)	0.0748(2)	4.35(6)
C-4	0.6811(1)	−0.0432(3)	0.2122(2)	4.42(6)
C-5	0.6303(2)	−0.0745(3)	0.3086(2)	4.45(6)
C-6	0.6887(2)	−0.0710(4)	0.4484(2)	5.41(7)
O-1	0.4236(1)	0.0832(3)	0.1647(2)	4.85(4)
O-2	0.4649(1)	−0.0004(3)	−0.0583(1)	4.73(4)
O-3	0.6541(1)	0.0142(3)	−0.0158(1)	4.94(4)
O-4	0.7482(1)	−0.1373(3)	0.2259(2)	5.19(4)
O-5	0.5576(1)	0.0099(3)	0.2933(1)	4.71(4)
O-6	0.7299(1)	0.0489(3)	0.4751(2)	5.53(4)
CA-2	0.4471(2)	0.0863(4)	−0.1522(2)	5.56(7)
CA-3	0.6993(2)	−0.0523(4)	−0.0800(3)	5.75(8)
CA-4	0.8307(2)	−0.1059(4)	0.2152(3)	6.24(9)
CA-6	0.8108(2)	0.0556(4)	0.5641(3)	5.63(8)
CM-2	0.3798(2)	0.0397(4)	−0.2752(3)	7.48(10)
CM-3	0.7264(2)	0.0257(5)	−0.1753(3)	9.23(13)
CM-4	0.8905(2)	−0.2153(4)	0.2287(4)	8.85(12)
CM-6	0.8423(2)	0.1865(4)	0.5871(4)	8.32(12)
OA-2	0.4828(2)	0.1843(3)	−0.1382(2)	7.45(7)
OA-3	0.7157(2)	−0.1582(3)	−0.0626(2)	7.72(7)
OA-4	0.8490(1)	−0.0032(4)	0.1936(3)	9.31(9)
OA-6	0.8494(1)	−0.0308(3)	0.6201(2)	7.72(7)
C-1′	0.3533(2)	0.1632(4)	0.3138(2)	5.08(7)
C-2′	0.3581(1)	0.0532(3)	0.2292(2)	4.60(6)
C-3′	0.2681(2)	0.0335(3)	0.1274(2)	4.50(6)
C-4′	0.1914(2)	0.0329(4)	0.1867(2)	4.93(6)
C-5′	0.1959(2)	0.1480(4)	0.2646(3)	5.40(7)
C-6′	0.1206(2)	0.1630(4)	0.3269(3)	6.72(9)
O-1′	0.4317(1)	0.1622(3)	0.4230(2)	6.37(6)
O-3′	0.2741(1)	−0.0819(3)	0.0667(2)	5.39(4)
O-4′	0.1064(1)	0.0354(3)	0.0843(2)	6.33(5)
O-5′	0.2807(1)	0.1489(3)	0.3669(2)	5.73(5)
O-6′	0.1193(1)	0.0574(3)	0.4056(2)	6.64(5)
CA-1′	0.4863(2)	0.2595(5)	0.4416(4)	8.12(12)
CA-3′	0.2439(2)	−0.0873(4)	−0.0645(3)	6.48(9)
CA-4′	0.0600(2)	−0.0692(6)	0.0495(3)	8.27(13)
CA-6′	0.0606(2)	0.0644(4)	0.4750(3)	6.89(9)
CM-1′	0.5701(3)	0.2352(6)	0.5543(5)	12.03(18)
CM-3′	0.2582(4)	−0.2157(4)	−0.1080(4)	10.67(16)
CM-4′	−0.0260(3)	−0.0499(7)	−0.0559(4)	12.69(20)
CM-6′	0.0634(3)	−0.0446(4)	0.5571(3)	8.69(12)
OA-1′	0.4682(2)	0.3500(4)	0.3752(4)	11.37(12)
OA-3′	0.2119(2)	−0.0053(3)	−0.1307(2)	8.72(8)
OA-4′	0.0853(2)	−0.1631(4)	0.1020(3)	10.78(11)
OA-6′	0.0141(2)	0.1524(4)	0.4679(3)	11.18(11)

Table 3
Fractional coordinates and equivalent isotropic temperature factors (Å^2) of methyl β-sophoroside heptaacetate (**2**), with estimated standard deviations in parentheses. $B_{eq} = (4/3) \times \{B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + 2(B_{12}ab + B_{23}bc + B_{31}ca)\}$

Atom	*x*	*y*	*z*	B_{eq}
C-1	0.6625(3)	0.7481(2)	0.3400(11)	4.34(14)
C-2	0.7175(2)	0.7161(2)	0.4151(10)	3.72(13)
C-3	0.7296(3)	0.6764(2)	0.2356(10)	3.97(13)
C-4	0.6682(2)	0.6495(2)	0.1749(10)	3.72(13)
C-5	0.6161(3)	0.6858(2)	0.1121(12)	4.65(15)
C-6	0.5526(3)	0.6616(2)	0.0695(14)	5.69(19)
O-1	0.6501(2)	0.7789(1)	0.5270(7)	4.75(10)
O-2	0.7757(2)	0.7441(1)	0.4183(7)	4.61(10)
O-3	0.7734(2)	0.6438(1)	0.3482(7)	4.33(9)
O-4	0.6769(2)	0.6223(1)	−0.0370(6)	4.36(9)
O-5	0.6082(2)	0.7189(1)	0.3029(8)	4.84(10)
O-6	0.5330(2)	0.6366(2)	0.2769(9)	6.18(13)
CA-2	0.8041(4)	0.7525(2)	0.6277(12)	5.85(20)
CA-3	0.8227(3)	0.6255(2)	0.2301(15)	6.02(20)
CA-4	0.6967(3)	0.5754(2)	−0.0195(11)	4.34(15)
CA-6	0.4739(3)	0.6166(3)	0.2894(17)	7.13(25)
CM-2	0.8691(3)	0.7745(3)	0.5927(17)	7.84(25)
CM-3	0.8650(3)	0.5946(3)	0.3796(18)	8.71(27)
CM-4	0.7052(3)	0.5528(2)	−0.2558(11)	6.06(19)
CM-6	0.4575(4)	0.5930(3)	0.5139(18)	8.63(28)
OA-2	0.7770(3)	0.7432(2)	0.8073(9)	8.39(18)
OA-3	0.8307(2)	0.6342(2)	0.0265(12)	8.84(18)
OA-4	0.7064(2)	0.5558(1)	0.1645(8)	5.22(11)
OA-6	0.4408(2)	0.6195(2)	0.1160(12)	9.88(21)
C-1′	0.5657(3)	0.8279(2)	0.6834(12)	4.90(16)
C-2′	0.6119(3)	0.8207(2)	0.4770(11)	4.30(14)
C-3′	0.6551(2)	0.8644(2)	0.4544(10)	3.76(12)
C-4′	0.6163(2)	0.9104(2)	0.4348(11)	3.93(13)
C-5′	0.5727(3)	0.9136(2)	0.6470(11)	4.30(14)
C-6′	0.5313(3)	0.9579(2)	0.6536(14)	5.36(17)
O-1′	0.5215(2)	0.7911(1)	0.6829(9)	6.51(13)
O-3′	0.6929(2)	0.8582(1)	0.2474(6)	4.20(9)
O-4′	0.6585(2)	0.9513(1)	0.4433(7)	4.48(9)
O-5′	0.5317(2)	0.8724(1)	0.6463(7)	4.80(10)
O-6′	0.4963(2)	0.9602(1)	0.4374(8)	5.40(11)
CA-3′	0.7582(3)	0.8633(2)	0.2679(14)	4.90(17)
CA-4′	0.6590(3)	0.9828(2)	0.2642(14)	5.86(19)
CA-6′	0.4542(3)	0.9970(2)	0.4138(15)	5.93(20)
CM-1′	0.4831(4)	0.7907(3)	0.8961(16)	8.00(25)
CM-3′	0.7902(3)	0.8508(2)	0.0464(12)	5.88(18)
CM-4′	0.6985(4)	1.0267(2)	0.3199(14)	7.93(23)
CM-6′	0.4190(3)	0.9945(3)	0.1865(13)	8.05(25)
OA-3′	0.7821(2)	0.8752(2)	0.4473(9)	6.99(14)
OA-4′	0.6294(3)	0.9767(2)	0.0895(10)	9.63(20)
OA-6′	0.4472(2)	1.0265(2)	0.5647(11)	8.13(16)

conformations have been also analyzed by semiempirical potential energy methods to get a better understanding of the observed conformations. [12]

In this paper, we report on the molecular and crystal structures of 2,3,4,6,1′,3′,4′,6′-octa-*O*-acetyl-β-sophorose [β-sophorose octaacetate (**1**)], methyl 2,3,4,6,3′,4′,6′-hepta-

Table 4
Fractional coordinates and equivalent isotropic temperature factors (Å^2) of methyl 6′-deoxy-β-sophoroside hexaacetate (**3**), with estimated standard deviations in parentheses. $B_{eq} = (4/3) \times \{B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + 2(B_{12}ab + B_{23}bc + B_{31}ca)\}$

Atom	x	y	z	B_{eq}
C-1	0.7226(7)	0.7215(7)	0.5489(-)	4.7(4)
C-2	0.6123(8)	0.6938(7)	0.5559(6)	5.3(4)
C-3	0.5546(7)	0.6318(7)	0.5058(5)	4.3(3)
C-4	0.6001(7)	0.6945(7)	0.4518(5)	4.5(3)
C-5	0.7130(7)	0.7295(7)	0.4499(5)	4.7(4)
C-6	0.7673(7)	0.7940(7)	0.3983(5)	5.2(4)
O-1	0.7782(4)	0.7806(4)	0.5957(4)	4.7(2)
O-2	0.5690(5)	0.6343(4)	0.6068(5)	5.5(3)
O-3	0.4495(5)	0.6052(5)	0.5116(5)	5.8(3)
O-4	0.5530(4)	0.6264(4)	0.4031(4)	5.5(2)
O-5	0.7613(4)	0.7877(4)	0.5000(4)	4.7(2)
O-6	0.7497(5)	0.8814(5)	0.3954(4)	6.5(3)
CA-2	0.5395(7)	0.6704(8)	0.6502(5)	5.7(4)
CA-3	0.3810(9)	0.5076(10)	0.5269(7)	7.7(5)
CA-4	0.4897(8)	0.6461(10)	0.3673(6)	6.9(5)
CA-6	0.7119(8)	0.8978(10)	0.3482(6)	6.8(5)
CM-2	0.4935(8)	0.5981(8)	0.6968(5)	6.5(4)
CM-3	0.2748(8)	0.4910(10)	0.5405(7)	11.1(7)
CM-4	0.4588(9)	0.5736(8)	0.3156(6)	9.0(5)
CM-6	0.6964(9)	0.9885(9)	0.3548(6)	9.4(6)
OA-2	0.5527(6)	0.7571(5)	0.6482(5)	8.3(3)
OA-3	0.4036(6)	0.4419(6)	0.5289(6)	11.2(4)
OA-4	0.4730(7)	0.7121(7)	0.3749(5)	12.6(5)
OA-6	0.6966(7)	0.8444(7)	0.3080(5)	10.9(5)
C-1′	0.9408(7)	0.8716(8)	0.6386(6)	5.7(4)
C-2′	0.8657(6)	0.7706(7)	0.6101(5)	4.5(3)
C-3′	0.8306(7)	0.6823(8)	0.6540(5)	5.3(4)
C-4′	0.9196(9)	0.6800(8)	0.6783(6)	6.7(5)
C-5′	0.9954(9)	0.7853(10)	0.7020(6)	7.9(5)
C-6′	1.1003(9)	0.7934(9)	0.7225(7)	11.2(6)
O-1′	0.9783(5)	0.9503(4)	0.5997(4)	5.0(3)
O-3′	0.7668(5)	0.5886(4)	0.6209(4)	5.9(3)
O-4′	0.8845(6)	0.6088(6)	0.7267(5)	8.1(3)
O-5′	1.0225(5)	0.8583(5)	0.6581(5)	6.7(3)
CA-3′	0.6789(8)	0.5050(9)	0.6428(7)	7.9(5)
CA-4′	0.8614(11)	0.5116(10)	0.7238(8)	10.5(7)
CM-1′	1.0331(7)	1.0504(6)	0.6249(6)	5.9(4)
CM-3′	0.6275(8)	0.4252(8)	0.5983(6)	8.1(5)
CM-4′	0.8220(10)	0.4528(9)	0.7767(6)	10.9(7)
OA-3′	0.6589(5)	0.5113(6)	0.6919(5)	7.8(3)
OA-4′	0.8723(7)	0.4824(7)	0.6764(6)	10.8(5)

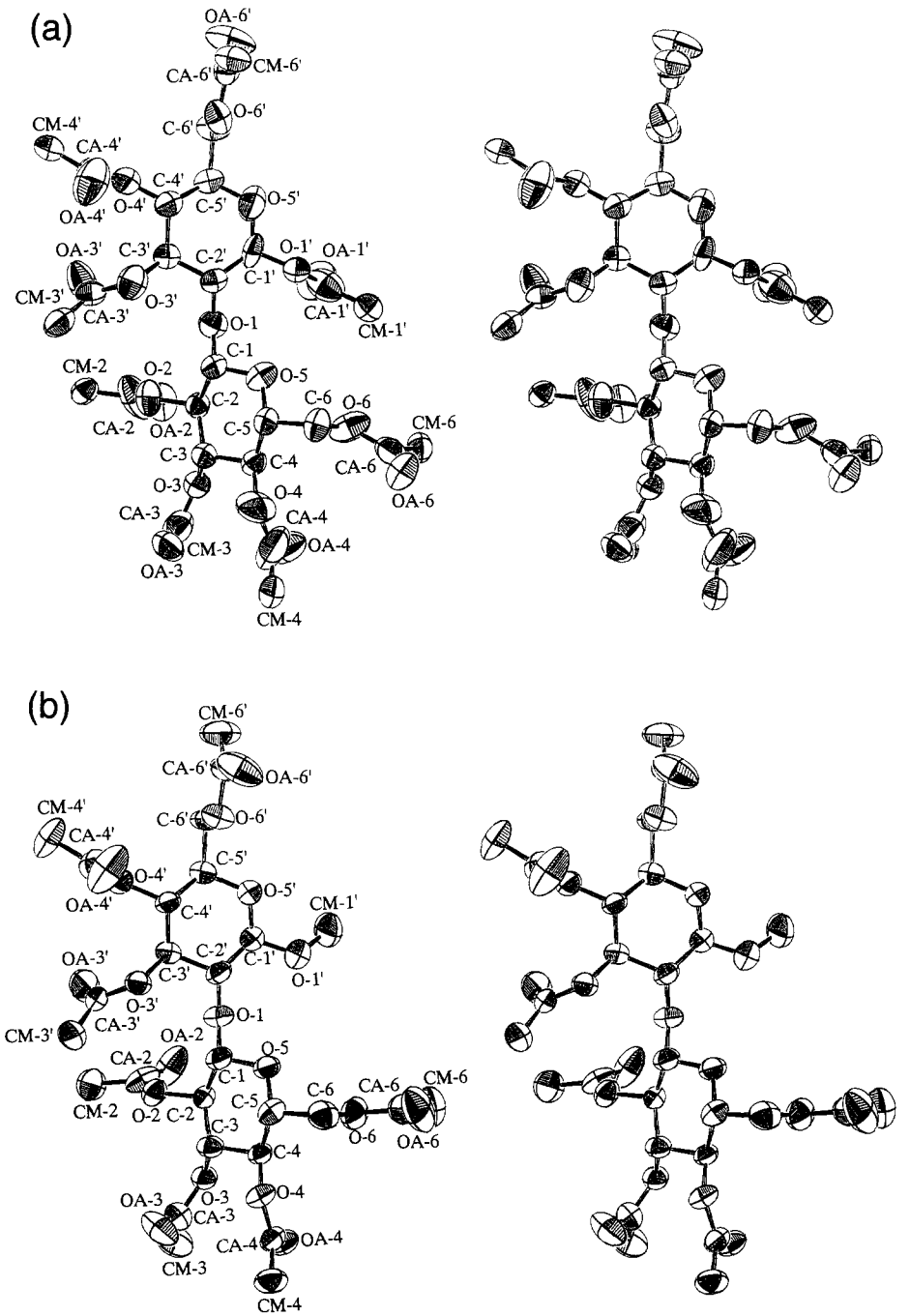

Fig. 1. Stereoscopic views of (a) β-sophorose octaacetate (**1**), (b) methyl β-sophoroside heptaacetate (**2**), and (c) methyl 6′-deoxy-β-sophoroside hexaacetate (**3**) (drawn with ORTEP [22]). The 30% probability thermal ellipsoids are shown for the carbon and oxygen atoms. The upper ring is the glycosidic residue.

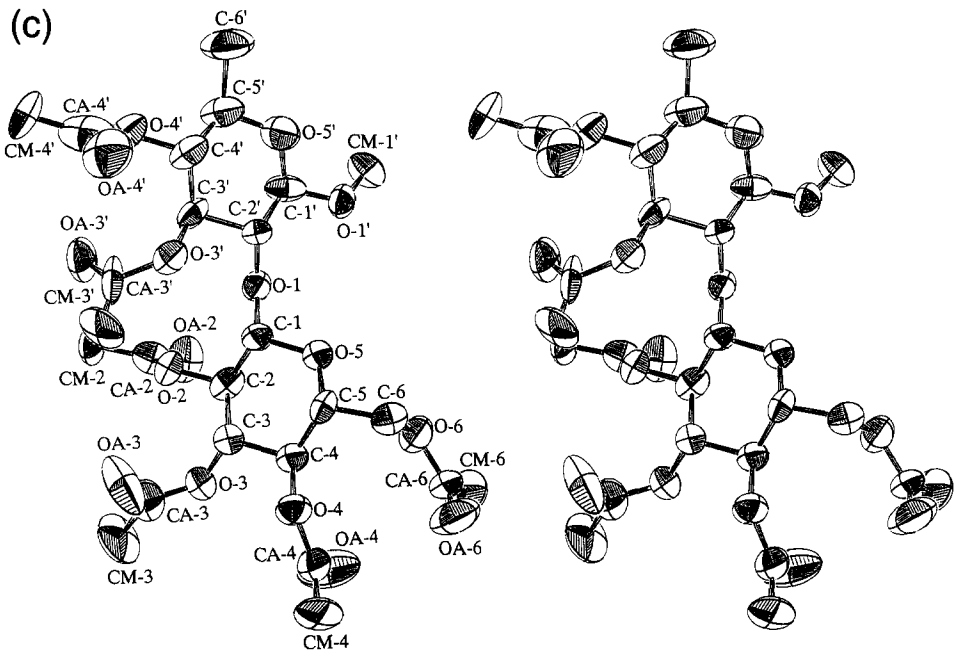

Fig. 1 (continued).

O-acetyl-β-sophoroside [methyl β-sophoroside heptaacetate (**2**)], methyl 2,3,4,6,3′,4′-hexa-*O*-acetyl-6′-deoxy-β-sophoroside [methyl 6′-deoxy-β-sophoroside hexaacetate (**3**)], which are acetylated disaccharides with (1 → 2)-linked β-D-glucopyranosyl residues. Sophorose is a simple repeating unit of cyclic (1 → 2)-β-D-glucans produced by gram-negative bacteria. These glucans are thought to play an important role in adapting the bacteria to changes in environmental osmotic pressure by regulating the osmotic balance between the cytoplasm and the periplasmic space [13]. The introduction of acetate substituents to the sophorose removes the possibility of intermolecular hydrogen bonds observed in the structure of α-sophorose [14]. The linkage angles so obtained (ϕ and ψ) were compared with those of α-sophorose [14].

2. Experimental

X-ray experiments. — Specimen crystals were obtained from their ethanolic solution by slow evaporation of the solvent. The X-ray intensities were measured by a four-circle diffractometer (RASA 5R-II, Rigaku Corporation) with graphite-monochromatized Cu-K_α radiation ($\lambda = 1.5418$ Å). The crystal data, the details of the data collection, and structure determination and refinement data are given in Table 1. Unit-cell parameters were determined by the least-squares fit from measurements of 20 reflections with 2θ range of 50–60°.

The densities of the crystals were measured by the floatation method using a mixture of carbon tetrachloride and hexane.

Solution and refinement of the structures. — The structures were solved by the direct method with SHELX-86 program [15] for compound **1** and using the SAPI-85 program [16] for compounds **2** and **3**. The locations of all nonhydrogen atoms are revealed by

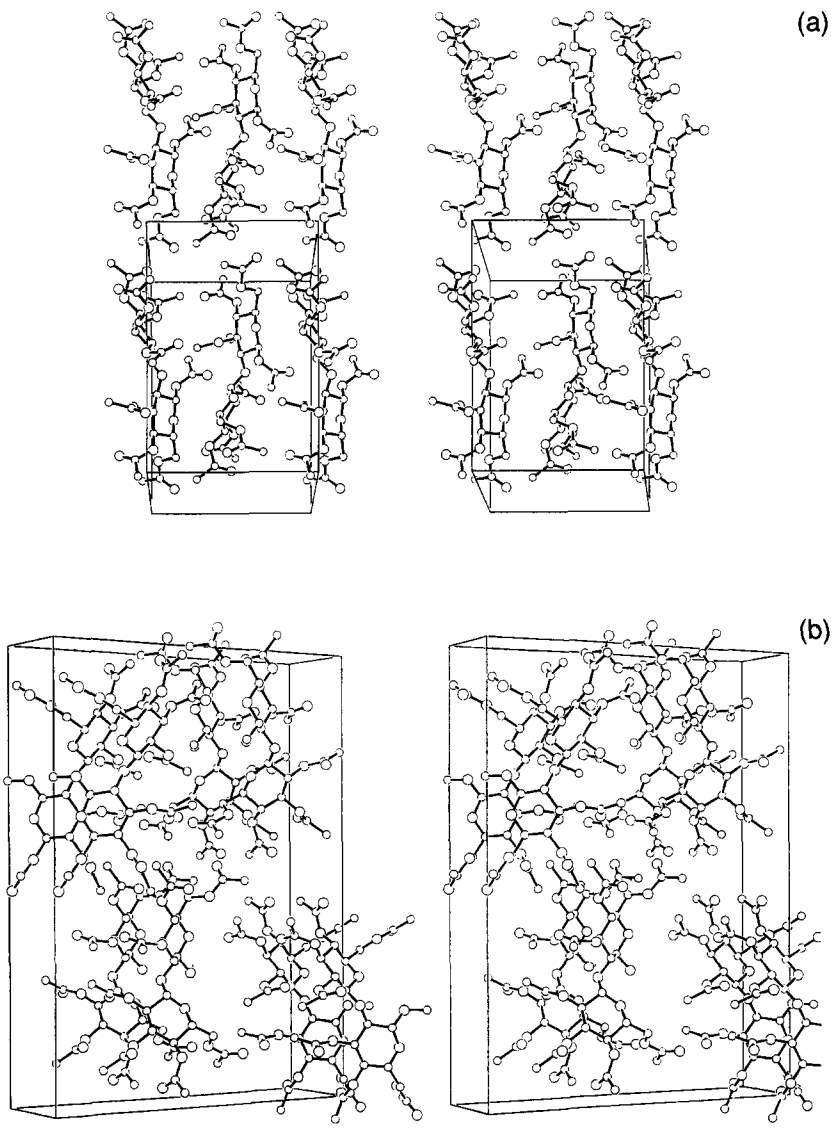

Fig. 2. Stereodrawings of the molecular packing of (a) β-sophorose octaacetate (**1**), (b) methyl β-sophoroside heptaacetate (**2**), and (c) methyl 6′-deoxy-β-sophoroside hexaacetate (**3**) (drawn with ORTEP [22]). Hydrogen atoms are not included.

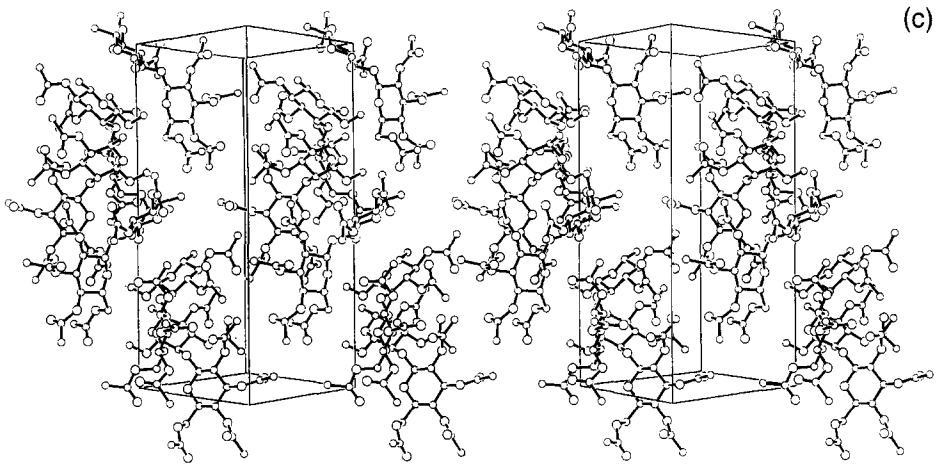

Fig. 2 (continued).

following the Fourier method, and these were refined isotropically by the full-matrix least-squares procedure. The difference Fourier map calculated after anisotropic refinement showed hydrogen atoms attached to the glucopyranose rings. Hydrogen atoms of the methyl moieties, however, could not be located. After additional refinement including these hydrogen atoms with equivalent temperature factors (B_{eq}) of the corresponding parent atoms, final R values of 0.052, 0.064 and 0.079 were obtained for compounds **1**, **2** and **3**, respectively. The final atomic parameters of these compounds are given in Tables 2–4, respectively. The atoms in the acetate moieties have been labeled CA, CM, and OA. These abbreviations stand for the carbonyl carbon atom, the methyl carbon atom, and the carbonyl oxygen atom, respectively. The positions of hydrogen atoms, anisotropic temperature factors, and observed and calculated structure factors have been deposited [†].

The atomic scattering factors were taken from the International Tables for X-ray Crystallography [17]. Computations were performed on an A-70 minicomputer with the help of the CRYSTAN program in a RASA-5RII system (Rigaku Corporation).

Conformational analysis. — The potential energy was calculated by considering van der Waals interactions and electrostatic interactions between nonbonded atoms, torsion energies [18], and the *exo*-anomeric effect. The van der Waals interactions were evaluated by using the Lennard–Jones 6–12 potential function with the parameters proposed by Scott and Scheraga [19]. For the electrostatic interactions, the parameters proposed by Scheraga and co-workers [20] were used. For evaluation of the energy associated with the exo-anomeric effect, a formula suggested by Tvaroska [21] was used. Using the molecular structures obtained in this study, the angles ϕ and ψ were varied

[†] Atomic coordinates, bond lengths and bond angles for these structures have been deposited with the Cambridge Crystallographic Data Centre. The coordinates may be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

Table 5
Comparison of torsion angles, with estimated standard deviations in parentheses for β-sophorose octaacetate (**1**), methyl β-sophoroside heptaacetate (**2**), and methyl 6′-deoxy-β-sophoroside hexaacetate (**3**), and α-sophorose [14] (**4**)

	1	**2**	**3**	**4**
Glycosidic torsion angles (°)				
O-5–C-1–O-1–C-2′(ϕ)	−81.2(3)	−79.1(6)	−94.7(10)	−78.9(10)
C-2–C-1–O-1–C-2′(ϕ')	162.0(2)	164.1(7)	151.0(8)	161.6(5)
C-1–O-1–C-2′–C-1′(ψ)	130.0(2)	139.7(5)	152.8(11)	98.0(10)
C-1–O-1–C-2′–C-3′(ψ')	−111.5(5)	−101.3(7)	−90.7(11)	−139.8(6)
Glycosidic bridge angle (°)				
C-1–O-1–C-2′(τ)	116.3(3)	116.3(5)	113.9(8)	113.7(5)
Intracyclic torsion angles (°)				
O-5–C-1–C-2–C-3	53.9(3)	56.1(8)	65.7(17)	52.9(9)
C-1–C-2–C-3–C-4	−48.2(4)	−50.8(6)	−59.6(14)	−47.4(6)
C-2–C-3–C-4–C-5	49.3(2)	50.7(6)	55.7(9)	51.2(7)
C-3–C-4–C-5–O-5	−57.5(4)	−56.2(5)	−57.9(23)	−59.4(11)
C-4–C-5–O-5–C-1	66.8(3)	65.6(6)	65.7(8)	67.2(8)
C-5–O-5–C-1–C-2	−64.0(3)	−65.1(12)	−69.0(10)	−64.2(6)
O-5′–C-1′–C-2′–C-3′	54.3(2)	55.8(11)	58.6(18)	57.5(9)
C-1′–C-2′–C-3′–C-4′	−49.7(2)	−54.6(8)	−56.1(9)	−60.1(10)
C-2′–C-3′–C-4′–C-5′	53.7(3)	56.4(6)	53.3(17)	58.0(10)
C-3′–C-4′–C-5′–O-5′	−61.4(4)	−60.6(7)	−56.2(18)	−55.7(8)
C-4′–C-5′–O-5′–C-1′	68.1(4)	66.5(10)	65.7(10)	56.7(5)
C-5′–O-5′–C-1′–C-2′	−64.2(5)	55.8(9)	−66.6(9)	−56.6(9)
Exocyclic torsion angles (°)				
O-5–C-5–C-6–O-6(χ_5)	−65.3(4)*g* −	−59.3(10)*g* −	−66.8(8)*g* −	61.5(9)*g*
C-4–C-5–C-6–O-6	56.3(4)*g*	60.4(11)*g*	54.9(8)*g*	−178.6(8)*t*
O-1–C-1–C-2–O-2	−70.7(3)	−72.4(9)	−61.3(16)	−70.8(10)
O-2–C-2–C-3–O-3	72.5(4)	73.0(6)	60.0(9)	69.7(10)
O-3–C-3–C-4–O-4	−79.7(5)	−80.6(11)	−69.8(12)	−68.0(6)
O-4–C-4–C-5–C-6	63.6(4)	67.4(8)	64.8(25)	61.0(12)
O-5′–C-5′–C-6′–O-6′($\chi_{5'}$)	−65.5(6)*g* −	−66.1(8)*g* −	—	−66.1(11)*g* −
C-4′–C-5′–C-6′–O-6′	55.2(3)*g*	54.3(8)*g*	—	54.6(10)*g*
O-1′–C-1′–C-2′–O-1	−75.0(4)	−69.5(8)	−68.4(17)	57.8(8)
O-1–C-2′–C-3′–O-3′	73.2(4)	67.9(11)	71.4(10)	58.5(6)
O-3′–C-3′–C-4′–O-4′	−71.5(5)	−68.4(9)	−75.1(10)	−64.5(13)
O-4′–C-4′–C-5′–C-6′	60.1(4)	61.9(7)	69.7(18)	67.0(7)
C-1–C-2–O-2–CA-2(χ_2)	130.5(3)	113.3(12)	114.7(15)	—
C-2–C-3–O-3–CA-3(χ_3)	−147.2(3)	−137.4(5)	−104.3(30)	—
C-3–C-4–O-4–CA-4(χ_4)	98.7(4)	92.0(7)	113.9(10)	—
C-5–C-6–O-6–CA-6(θ_6)	−149.6(4)	172.6(9)	−125.8(16)	—
O-5′–C-1′–O-1′–CA-1′($\chi_{1'}$)	−122.0(4)	—	—	—
O-5′–C-1′–O-1′–CM-1′	—	−73.2(8)	−76.6(9)	—
C-2′–C-3′–O-3′–CA-3′($\chi_{3'}$)	−133.8(4)	−128.6(10)	−142.8(15)	—
C-3′–C-4′–O-4′–CA-4′($\chi_{4'}$)	100.4(5)	122.0(10)	96.4(15)	—
C-5′–C-6′–O-6′–CA-6′($\theta_{6'}$)	174.5(4)	177.6(9)	—	—

systematically at 5° intervals. The coordinates of hydrogen atoms of the methyl moieties were located at the geometrically calculated positions with the C–H bond length of 1.1 Å and H–C–H bond angle of 109.5°.

3. Results and discussion

Stereoscopic views of molecules **1**, **2** and **3** are presented in Fig. 1 as ORTEP plots [22]. The bond lengths and bond angles have been deposited (see previous footnote). All bond lengths and angles are similar to those found in other carbohydrates [23].

Glycosidic linkage. — The relative orientation of contiguous pyranosides is usually described by the torsion angles around the glycosidic bonds, C-1–O-1 and O-1–C-2′, and they are denoted as the conformational angles $\phi = \Theta$(O-5–C-1–O-1–C-2′) and $\psi = \Theta$(C-1–O-1–C-2′–C-1′). Another important parameter is the bridge angle τ = C-1–O-1–C-2′. These torsion and bridge angles are compared with those in α-sophorose [14] (Table 5). Like other disaccharides, a comparison of the natural and acetylated sophorose shows that the angle ϕ is much less disturbed than the angle ψ. This is interpreted as a manifestation of *exo*-anomeric effect [24].

Ring torsion angles. — Torsion angles about various skeletal bonds of the pyranose rings are given in Table 5. Like other glucose residues in many single-crystal structures, the expected $^4C_1$ conformation was found for all the six residues.

Molecular packing. — Crystal structures of the compounds **1**, **2** and **3** are shown in Fig. 2. The molecules are held in the crystals by van der Waals force, only. No short atomic contacts are observed.

Although the molecular structures of these compounds are very similar, these crystals belong to different space groups and have specific packing features. Especially, the packing structure of compound **3** belongs to the hexagonal space group $P6_5$ that is rare in single crystals. In the crystal structure of the compound **1**, the D-glucopyranose rings are stacked along the *b* axis and parallel to the *ac*-plane, while the rings are stacked along *c* axis and parallel to the *ab*-plane in that of **2**. In the case of **3**, the ring of the glycosidic residue is perpendicular to the *c* axis, while one of glycosyl residue is parallel to the *c* axis (Fig. 2).

Conformational analysis. — Figure 3 shows conformational contours for ϕ and ψ angles of compounds **1**, **2** and **3**. With respect to the relative energy minimum, isoenergy contours were drawn with the 1 kcal mol^{-1} interval. All reconnaissance measurements of these conformational energy surfaces delineated two low-energy regions. The ϕ and ψ values obtained are included in two local minimum-energy regions for all three compounds.

As in the other acetylated carbohydrate derivatives [1–11], the secondary acetate groups have a conformation in which the carbonyl oxygen atom nearly eclipses the axial hydrogen atom at the corresponding carbon atom of pyranose ring.

The conformation of the primary acetate substituent at C-6 is described by the torsion angles of $\chi_5 = \Theta$(O-5–C-5–C-6–O-6) and $\theta_6 = \Theta$(C-5–C-6–O-6–CA-6). According to the terminology proposed by Sundaralingam [25], this conformation is *gauche–gauche* (abbreviated *gg*). The major conformational differences for **1**, **2** and **3** occur at θ_6.

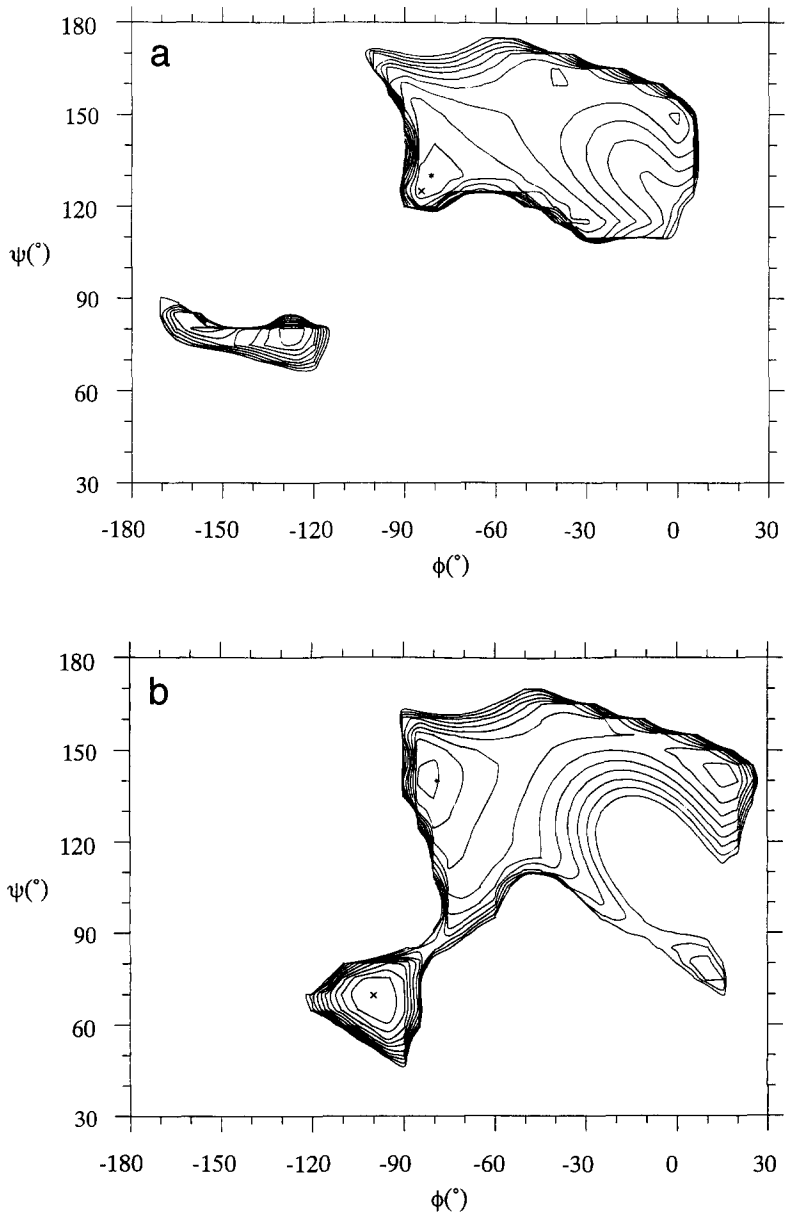

Fig. 3. Energy diagrams computed (a) for β-sophorose octaacetate (**1**), (b) for methyl β-sophoroside heptaacetate (**2**), and (c) for methyl 6′-deoxy-β-sophoroside hexaacetate (**3**) in terms of (ϕ, ψ) angles. Contours were drawn by interpolation of energies computed at 5° for ϕ and ψ. The * indicates the observed position from the X-ray structure analysis, whereas × indicates the minimum-energy position.

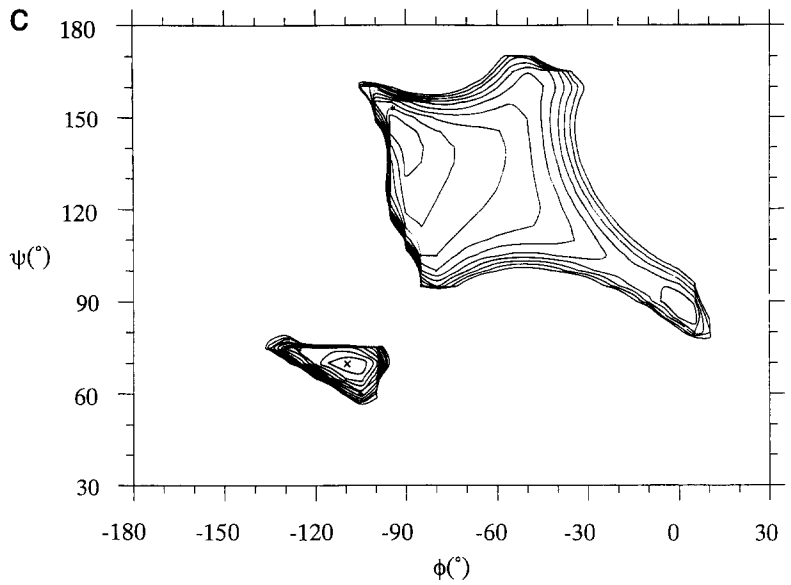

Fig. 3 (continued).

These conformations fall into the theoretically predicted range of conformations for acetyl groups in glucosaccharides [12]. Only one kind of the conformation about χ_5 is observed (Table 5).

Acknowledgments

This work was supported in part by a grant from the Special Coordination Funds of the Science and Technology Agency for Promoting Science and Technology.

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