Carbohydrate Research, 241 (1993) 89–98
Elsevier Science Publishers B.V., Amsterdam

Synthesis and X-ray crystallographic structure determination of methyl α-D-galactopyranoside 2,6-bis(sodium sulfate) · $2H_2O$

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(Received March 2nd, 1992; accepted August 19th, 1992)

ABSTRACT

The synthesis and molecular structure of methyl α-D-galactopyranoside 2,6-bis(sodium sulfate)·$2H_2O$, as determined by X-ray crystallography, are described. The sugar ring has the expected $^4C_1$ chair conformation; slight distortion may be due to the inclusion of sulfate groups. The sodium ions both exhibit octahedral co-ordination involving oxygen atoms from the monosaccharide hydroxyl groups, sulfate groups, and water molecules. The crystal packing includes an extended hydrogen-bonded network and is stabilised by co-ordination of the sodium ions.

INTRODUCTION

Galactopyranose 2,6-bis-sulfate units are found in various polysaccharide preparations from red algae, notably as the D-isomer in carrageenans[1,2]. In nu- and lambda-carrageenans, these units may be converted in vitro and in vivo into 3,6-anhydrogalactopyranose 2-sulfate units, the corresponding polysaccharides then being described as iota- and xi-carrageenan, respectively. These chemical changes are reflected in changes in conformation and in the physical properties of aqueous solutions of the polysaccharides, particularly an increase in gel-forming capability[2,3]. The physical properties are known to be dependent on polysaccharide conformation and on selective interaction of cations with sulfate groups. It has been proposed that the incorporation of 2,6-bis-sulfated units represents irregularities in the polysaccharide primary structures which prevent the formation of regular helices and so hinder gel formation[2]. The observed physical properties of car-

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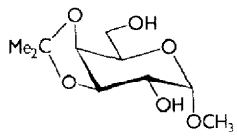
rageenans are therefore sensitive to the inclusion of 2,6-bis-sulfated units. The ability of carrageenans to form viscous solutions and hydrated gels has found many applications in the food industry[4].

The work now reported on methyl α-D-galactopyranoside 2,6-bis(sodium sulfate) (**3**) is part of a study of well-defined model compounds, which was undertaken to provide precise details of structural factors (such as hydrogen bonding and cation co-ordination) that may be important in interactions at the polymer level.



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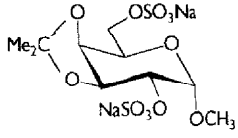

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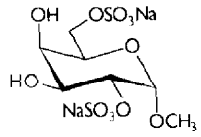

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Methyl α-D-galactopyranoside 2,6-bis(sodium sulfate) (**3**) was synthesised from the readily available methyl 3,4-*O*-isopropylidene-α-D-galactopyranoside (**1**). Sulfation of **1** with trimethylamine–sulfur trioxide in *N*,*N*-dimethylformamide (DMF) at 60°C yielded (90%) the bis-sulfate **2**. Treatment of **2** with aqueous 50% acetic acid under reflux then gave the required compound (**3**) in 94% yield.

EXPERIMENTAL

General methods.—Melting points were determined in capillary tubes with a Stuart melting-point apparatus and are uncorrected. TLC was performed on Silica Gel 60 (Merck) with detection by charring with H_2SO_4, and column chromatography was performed on silica gel (Merck 70–230). ^1H NMR spectra were recorded with a JEOL GX-400 spectrometer on solutions in D_2O [internal sodium 3-(trimethylsilyl)-1-propanesulfonate (δ 0) or acetone (δ 2.225)]. Optical rotations were determined with a Thorn type 243 automatic polarimeter at 24°C, using a 1-cm cell. Elemental analyses were performed by the analytical service of the Department of Chemistry, University of Leeds.

Methyl 3,4-O-isopropylidene-α-D-galactopyranoside 2,6-bis(sodium sulfate) (**2**).—A mixture of **1** (1.6 g, 0.7 mmol) and trimethylamine–sulfur trioxide (2.8 g, 20 mmol) in dry DMF (50 mL) was heated at 60°C for 30 min and then cooled. Water (50 mL) was added, and the mixture was stirred at room temperature for 1 h and neutralised with an excess of sat aq $NaHCO_3$. The solvent was removed in vacuo, the residue extracted with MeOH, and the MeOH extract filtered and evaporated. Chromatography of the residue on silica gel (1:1 EtOAc–MeOH) afforded **2** (2.7 g, 90%); mp 220–225°C (dec) (recrystallised from 2-propanol); $[\alpha]_D^{22}$ +46° (*c* 2.0, H_2O). NMR (D_2O): ^1H, δ 5.110 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.431 (dd, 1 H, $J_{2,3}$ 8.0 Hz, H-2), 4.380 (dd, 1 H, $J_{5,6a}$ 4.3, $J_{6a,6b}$ 11.8 Hz, H-6), 4.358 (dd, 1 H, $J_{5,6b}$ 7.9 Hz, H-6b), 4.341 (dd, 1 H, $J_{4,5}$ 2.2, $J_{3,4}$ 3.3 Hz, H-4), 4.226 (dd, 1 H, H-3), 4.182 (ddd, 1 H, H-5), 3.452 (s, 3 H, OMe), 1.482 (s, 3 H, CMe_2), and 1.480 (s, 3 H, CMe_2); ^{13}C,

δ 111.75 (CMe_2), 98.09 (C-1), 76.82 (C-2), 74.40 (C-4), 74.32 (C-5), 68.01 (C-3), 66.33 (C-6), 56.39 (OMe), 27.92 and 26.33 (C-Me_2). Anal. Calcd for $C_{10}H_{16}O_{12}S_2Na_2$: C, 27.39; H, 3.65; S, 14.61. Found: C, 28.10; H, 3.15; S, 14.26.

Methyl α-D-galactopyranoside 2,6-bis(sodium sulfate) (**3**).—A solution of **2** in aq 50% acetic acid (30 mL) was heated under reflux for 1 h and then cooled. The solvent was evaporated in vacuo, the residue neutralised with sat aq $NaHCO_3$, and the solvent again evaporated. The residue was extracted with MeOH, the extract filtered, and the filtrate evaporated. Chromatography of the residue on silica gel (1:2 EtOAc–MeOH) yielded **3** (1.6 g, 94%); mp 280–285°C (dec) (from EtOH); $[\alpha]_D^{22}$ +22° (*c* 2.0, H_2O). NMR (D_2O): ^1H, δ 5.141 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.450 (dd, 1 H, $J_{2,3}$ 10.3 Hz, H-2), 4.250 (dd, 1 H, $J_{5,6a}$ 5.4, $J_{5,6b}$ 8.3 Hz, H-5), 4.175 (dd, 1 H, $J_{6a,6b}$ 11.8 Hz, H-6a), 4.172 (dd, 1 H, H-6b), 4.091 (bd, 1 H, $J_{3,4}$ 3.3, $J_{4,5} < 0.5$ Hz, H-4), 3.954 (dd, 1 H, H-3), and 3.436 (s, 3 H, OMe); ^{13}C, δ 98.27 (C-1), 76.07 (C-2), 69.92 (C-4), 69.23 (C-5), 68.28 (C-3), 68.00 (C-6), and 56.00 (OMe). Anal. Calcd for $C_7H_{12}O_{12}S_2Na_2 \cdot 2H_2O$: C, 19.35; H, 3.68; S, 14.74; Found: C, 19.96; H, 3.10; S, 14.56.

X-ray crystallography.—Crystals suitable for diffraction experiments were grown by slow concentration of an aq 2-propanol solution. Oscillation and Weissenberg photographs indicated a monoclinic lattice with space group $P2_1$. A crystal ($0.02 \times 0.03 \times 0.15$ mm) was sealed in a Lindemann glass capillary and set on an Enraf–Nonius CAD-4F diffractometer. Accurate unit-cell parameters were determined by least-squares fit by measurement of 40 reflections with $17° \leq \theta \leq 29°$. The crystal data are given in Table I. The intensity data were collected in the ω–2θ scan mode, using Nickel-filtered Cu$K\alpha$ radiation up to $\theta = 70°$ for a total of 3396 reflections of which 2633 were above the $3.0\sigma(I)$ cut-off level. The control reflection 504 was measured every hour of exposure time (85 measurements overall) with an averaged value of 760.1 counts and a standard deviation (of the

TABLE I

Crystal data for methyl α-D-galactopyranoside 2,6-bis(sodium sulfate) dihydrate (**3**)

Molecular formula	$(C_7H_{12}O_{12}S_2)^{2-}(Na_2)^{2+} \cdot 2H_2O$
Molecular weight	434.30
Crystal system	Monoclinic
Space group	$P2_1$
Cell dimensions	
a (Å)	10.904(1)
b (Å)	5.511(1)
c (Å)	13.443(1)
β (°)	93.10(1)
Cell volume (Å^3)	806.7(1)
Z	2
F(000)	444
μ (Cu$K\alpha$) (cm^{-1})	36.3
D_c (g·cm^{-3})	1.789

TABLE II

Atomic co-ordinates and equivalent isotropic displacement coefficients (Å^2)

Atom	x/a	y/b	z/c	U_{eq} [a]
C-1	0.8308(8)	0.4983(-)	0.3073(6)	0.039(3)
C-2	0.7357(8)	0.5540(30)	0.2237(6)	0.040(3)
C-3	0.6597(8)	0.7806(33)	0.2436(6)	0.048(3)
C-4	0.6079(9)	0.7663(38)	0.3471(7)	0.061(4)
C-5	0.7088(8)	0.7025(32)	0.4250(6)	0.047(3)
C-6	0.6620(10)	0.6533(39)	0.5263(8)	0.059(4)
C-7	1.0141(9)	0.6537(40)	0.3870(8)	0.060(4)
O-1	0.9197(5)	0.6881(27)	0.3098(4)	0.049(2)
O-2	0.7984(5)	0.6060(26)	0.1319(4)	0.039(2)
O-3	0.5588(6)	0.8042(33)	0.1725(5)	0.070(4)
O-4	0.5180(7)	0.5883(37)	0.3523(5)	0.082(4)
O-5	0.7718(6)	0.4834(26)	0.3992(4)	0.045(2)
O-6	0.7684(5)	0.6549(27)	0.5952(4)	0.049(2)
S-2	0.8124(2)	0.3929(22)	0.0521(1)	0.034(1)
O-1S2	0.9037(5)	0.4984(25)	−0.0092(4)	0.043(2)
O-2S2	0.6926(5)	0.3667(27)	0.0003(5)	0.047(2)
O-3S2	0.8513(6)	0.1789(25)	0.1063(5)	0.049(2)
S-6	0.7497(2)	0.5904(22)	0.7078(1)	0.038(1)
O-1S6	0.8743(5)	0.6079(25)	0.7511(4)	0.043(2)
O-2S6	0.7018(7)	0.3473(27)	0.7093(5)	0.058(3)
O-3S6	0.6674(6)	0.7656(27)	0.7446(5)	0.055(2)
OW-1	0.8749(6)	0.0215(26)	0.8717(5)	0.048(2)
OW-2	0.5661(6)	−0.1717(26)	0.9597(5)	0.052(2)
Na-1	1.0067(3)	0.3626(22)	−0.1525(2)	0.042(1)
Na-2	0.6536(3)	0.1114(23)	0.8504(3)	0.050(1)

[a] $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$

distribution) of 18.6 (2.45%). Lorentz and polarization corrections were applied, but no absorption correction was made. The data were merged using the SHELXTL-Plus package[5] to give 1509 unique reflections, merging $R = 0.03$. The structure was solved by direct methods, which gave all non-H atoms, and the initial residual calculated for these atomic positions was 0.28. The structure was then refined isotropically ($R = 0.13$, unit weights) and anisotropically, minimising the function $\Sigma w(|F_o| - |F_c|)^2$ with $w = \sigma_2(F_o) - 1$ based on counting statistics. Attempts to locate H atoms in the difference Fourier map were only partially successful. The H atoms of the water molecules were not included in the refinement. Those of the galactopyranoside moiety were included in the later refinement with fixed $U_{iso} = 0.08$ Å^2. An extinction correction of the form $F_c = F_c/(1 + gF_c^2/\sin 2\theta)^{1/4}$ was used in the refinement. The final R was 0.065, and wR was 0.088 with a GOF of 0.99 and $g = 2.0 \times 10^{-5}$. The average and maximum shift-to-error ratios were 0.21 and 4.07(x/a of H6S), respectively, and the final difference Fourier map showed minimum and maximum peaks of −0.45 and 0.49 e · Å^{-3}. The atomic scattering factors used were those in the SHELXTL-Plus[5] package and are in the analytical form given in the International Tables for X-ray Crystallogra-

TABLE III

Molecular geometry of (3)

Bond distances (Å)			
C-1–C-2	1.52(1)	C-6–O-6	1.45(1)
C-2–C-3	1.53(2)	O-1–C-7	1.44(1)
C-3–C-4	1.53(1)	O-2–S-2	1.60(1)
C-4–C-5	1.52(1)	O-6–S-6	1.58(1)
C-5–C-6	1.50(1)	S-2–O-1S2	1.45(1)
C-1–O-1	1.43(1)	S-2–O-2S2	1.46(1)
C-2–O-2	1.47(1)	S-2–O-3S2	1.44(2)
C-3–O-3	1.42(1)	S-6–O-1S2	1.45(1)
C-4–O-4	1.39(2)	S-6–O-2S6	1.44(2)
C-1–O-5	1.43(1)	S-6–O-3S6	1.43(1)
C-5–O-5	1.44(2)		
Bond angles (°)			
C-2–C-1–O-1	107.9(6)	C-1–O-1–C-7	112.5(9)
C-2–C-1–O-5	109.2(4)	C-2–O-2–S-2	118.9(7)
O-1–C-1–O-5	111.1(4)	C-1–O-5–C-5	113.9(7)
C-1–C-2–C-3	113.0(6)	C-6–O-6–S-6	118.1(6)
C-1–C-2–O-2	109.2(6)	O-2–S-2–O-1S2	100.4(5)
C-3–C-2–O-2	105.7(9)	O-2–S-2–O-2S2	106.0(4)
C-2–C-3–C-4	110.3(1.0)	O-2–S-2–O-3S2	107.3(4)
C-2–C-3–O-3	111.4(9)	O-6–S-6–O-1S6	101.7(3)
C-4–C-3–O-3	107.6(7)	O-6–S-6–O2S6	106.8(5)
C-3–C-4–C-5	110.3(7)	O-6–S-6–O-3S6	107.3(5)
C-3–C-4–O-4	112.3(8)	O-1S2–S-2–O-2S2	113.4(4)
C-5–C-4–O-4	106.9(9)	O-1S2–S-2–O-3S2	115.0(4)
C-4–C-5–C-6	113.3(8)	O-2S2–S-2–O-3S2	113.3(6)
C-4–C-5–O-5	111.5(8)	O-1S6–S-6–O-2S6	113.0(7)
C-6–C-5–O-5	104.9(9)	O-1S6–S-6–O-3S6	114.2(5)
C-5–C-6–O-6	106.1(8)	O-2S6–S-6–O-3S6	112.8(5)
Torsion angles (°)			
Endocyclic		Exocyclic	
O-5–C-1–C-2–C-3	54(1)	O-1–C-1–C-2–O-2	51(1)
C-1–C-2–C-3–C-4	−51(1)	O-2–C-2–C-3–O-3	71(1)
C-2–C-3–C-4–C-5	50(1)	O-3–C-3–C-4–O-4	52(2)
C-3–C-4–C-5–O-5	−55(1)	O-4–C-4–C-5–C-6	−50(2)
C-4–C-5–O-5–C-1	61(1)	C-5–O-5–C-1–O-1	60(1)
C-5–O-5–C-1–C-2	−59(1)	C-4–C-5–C-6–O-6	−166(1)
		O-5–C-5–C-6–O-6	72(1)
Sulfate groups		Methyl group	
C-1–C-2–O-2–S-2	97(1)	C-2–C-1–O-1–C-7	180(1)
C-3–C-2–O-2–S-2	−141(1)	O-5–C-1–O-1–C-7	60(1)
C-5–C-6–O-6–S-6	−176(1)		
C-2–O-2–S-2–O-1S2	−166(1)		
C-2–O-2–S-2–O-2S2	76(1)		
C-2–O-2–S-2–O-3S2	−45(1)		
C-6–O-6–S-6–O-1S6	179(1)		
C-6–O-6–S-6–O-2S6	61(1)		
C-6–O-6–S-6–O-3S6	−61(1)		

TABLE IV

Geometry of the sodium co-ordination [a]

Type	Bond length (Å)	Type	Bond angles (°)
Na-1 · · · O-1S2$^{(I)}$	2.40(1)	O-1S2$^{(I)}$ · · · Na-1 · · · O-1S6$^{(I-c)}$	87.8(4)
Na-1 · · · O-1S6$^{(I-c)}$	2.32(1)	O-1S2$^{(I)}$ · · · Na-1 · · · O-2$^{(II+2a-b)}$	120.6(3)
Na-1 · · · OW-1$^{(I-c)}$	2.40(2)	O-1S6$^{(I)}$ · · · Na-1 · · · O-1$^{(II+2a-b)}$	88.3(3)
Na-1 · · · O-3S2$^{(II+2a)}$	2.39(1)	O-1$^{(II+2a-b)}$ · · · Na-1 · · · O-2$^{(II+2a-b)}$	64.8(3)
Na-1 · · · O-1$^{(II+2a-b)}$	2.49(1)	OW-1$^{(I-c)}$ · · · Na-1 · · · O-3S2$^{(II+2a)}$	157.0(3)
Na-1 · · · O-2$^{(II+2a-b)}$	2.56(1)		
Na-2 · · · OW-1$^{(I)}$	2.47(8)	OW-1$^{(I)}$ · · · Na-2 · · · O-3S6$^{(I-b)}$	79.4(4)
Na-2 · · · OW-2$^{(I)}$	2.38(1)	OW-1$^{(I)}$ · · · Na-2 · · · O-2S2$^{(I+c)}$	84.0(3)
Na-2 · · · O-2S6$^{(I)}$	2.38(1)	O-3S6$^{(I-b)}$ · · · Na-2 · · · O-3$^{(II+a-b+c)}$	110.2(4)
Na-2 · · · O-3S6$^{(I-b)}$	2.38(2)	O-2S2$^{(I+c)}$ · · · Na-2 · · · O-3$^{(II+a-b+c)}$	88.7(4)
Na-2 · · · O-2S2$^{(I+c)}$	2.47(1)	O-2S6$^{(I)}$ · · · Na-2 · · · OW-2$^{(I)}$	164.4(4)
Na-2 · · · O-3$^{(II+a-b+c)}$	2.56(1)		

[a] Symmetry code: (I) x, y, z; (II) $-x$, $1/2+y$, $-z$.

TABLE V

Geometry of the hydrogen-bonding pattern and short contacts [a]

Acceptor · · · H-Donor	A · · · D(Å)	H-D(Å)	A · · · H(Å)	< (A · · · H-D) (°)
O-3–H-O-3 · · · OW-2$^{(I+b-c)}$	2.87(1)	0.61(14)	2.41(14)	134(15)
Short contacts				
O-4 · · · O-2S6$^{(II+a+c)}$	2.87(2)			
O-4 · · · O-3S6$^{(II+a-b+c)}$	2.94(2)			
O-1S2 · · · OW-1$^{(II+2a+c)}$	2.97(1)			
O-2S2 · · · OW-2$^{(I+b-c)}$	2.93(2)			
O-2S2 · · · OW-2$^{(II+a+c)}$	2.92(1)			
O-1S6 · · · OW-1$^{(I+b)}$	2.79(2)			

[a] For the symmetry codes, see Table IV.

phy[6]. The final positional parameters of the non-H atoms are given in Table II, the description of the internal geometry is shown in Table III, and the co-ordination of the sodium ions and the hydrogen-bond geometry are given in Tables IV and V, respectively *.

RESULTS AND DISCUSSION

Molecular geometry.—A perspective view of **3** together with the numbering scheme is shown in Fig. 1. The C–C and C–O bond lengths, and the C–C–C,

* The observed and calculated structure factors, H atom co-ordinates, and anisotropic thermal parameters of the non-H atoms have been deposited with, and may be obtained from, Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, Netherlands. Reference should be made to No. BBA/DD/521/*Carbohydr. Res.*, 241 (1993) 89–98..

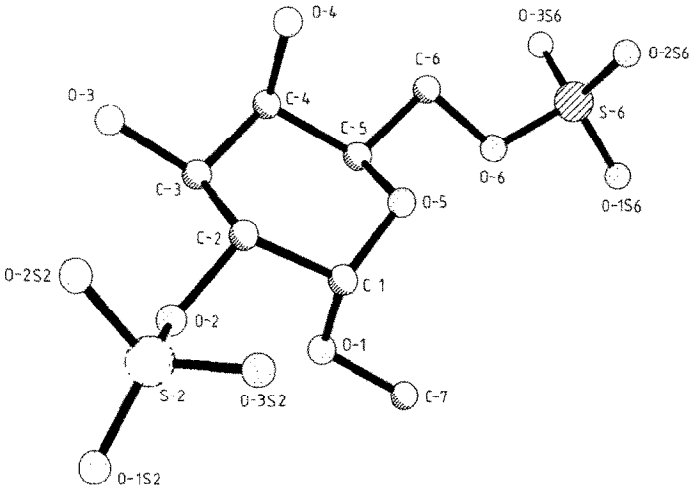

Fig. 1. Perspective view and atom labelling of methyl α-D-galactopyronoside 2,6-bis(sodium sulfate) (3).

C–C–O, and C–O–C valence angles (see Table III) conform to the tabulated values for pyranoses[7–9] and their values are well within the range observed in the crystal and molecular structures of sulfated carbohydrates known so far: methyl α-D-galactopyranoside 2-(sodium sulfate)[10], methyl α-D-galactopyranoside 3-(sodium sulfate)[10], methyl α-D-galactopyranoside 4-(sodium sulfate)[10,11], methyl α-D-galactopyranoside 4-(potassium sulfate)[10], β-D-glucopyranose 6-(potassium sulfate)[12], and sucrose octakis(potassium sulfate)[13]. In the sulfate groups, the bridging S-2–O-2 and S-6–O-6 distances are long [1.60(1) and 1.58(1) Å, respectively], and the three other S–O distances of the S-2 and S-6 sulfate groups, average 1.45(1) and 1.44(2) Å, respectively, are between the non-bridging S–O values found in SO_4^{2-} and C–SO_2–O–C, average 1.472(13) and 1.423(8) Å, respectively[7]. In the sulfated monosaccharides[10–12], the bridging [average 1.59(2) Å] and non-bridging [average 1.44(1) Å] S–O distances are similar. The C-2–O-2 and C-6–O-6 bonds in **3** are 1.47(1) and 1.45(1) Å, respectively, and this lengthening, which is also present in the C–O bonds of the monosulfated monosaccharides[10–12] [average 1.46(2) Å], is apparently caused by the sulfation. The substitution with sulfate results also in the opening of the C–O–S angle at the point of attachment of the sulfate moiety, 118.9(7) and 118.1(6)°, respectively, for the S-2 and S-6 sulfate groups of **3**. This compares satisfactorily with the average value of 119.0(2.0)° for sulfated monosaccharides[10–12]. The O–S–O angles show a wide range of values, from 100.4(5) to 115.0(4)° for S-2 and from 101.7(3) to 114.2(5)° for S-6. These are similar to the range of values for other monosulfated monosaccharides[10–12] [100.6(2) to 115.5(3)°]. The galactopyranose ring adopts a slightly distorted $^4C_1$ chair conformation, Q = 0.55(1) Å, $\theta = 3.5(1.5)°$, and $\phi = -174(24)°$, as described by the Cremer and Pople[14] puckering parameters. In methyl α-D-galactopyranoside 3-(sodium sulfate)[10] [Q = 0.60(1) Å, $\theta = 10.5(4)°$, $\phi = -93(2)°$], methyl α-D-galactopyranoside

4-(sodium sulfate)[10,11] [Q = 0.57(1) Å, $\theta = 11.2(4)°$, $\phi = -92(2)°$], and β-D-glucopyranose 6-(potassium sulfate)[12] [Q = 0.58(1) Å, $\theta = 9.4(5)°$, $\phi = 116(3)°$], the chair conformation is more distorted. In methyl α-D-galactopyranoside 2-(sodium sulfate)[Q = 0.57(1) Å, $\theta = 3.2(2)°$, $\phi = -115(4)°$] and methyl α-D-galactopyranoside[15] [Q = 0.56(1) Å, $\theta = 4.6(1)°$, $\phi = -99(7)°$], the distortions are comparable. The sulfate group at position 6 is in a staggered conformation with respect to the ester bond. The conformation along the C-5–C-6–O-6 sequence is *gauche–trans–trans*. At position 2, the bridging S–O bond is eclipsed with the C-2–H-2 bond, which

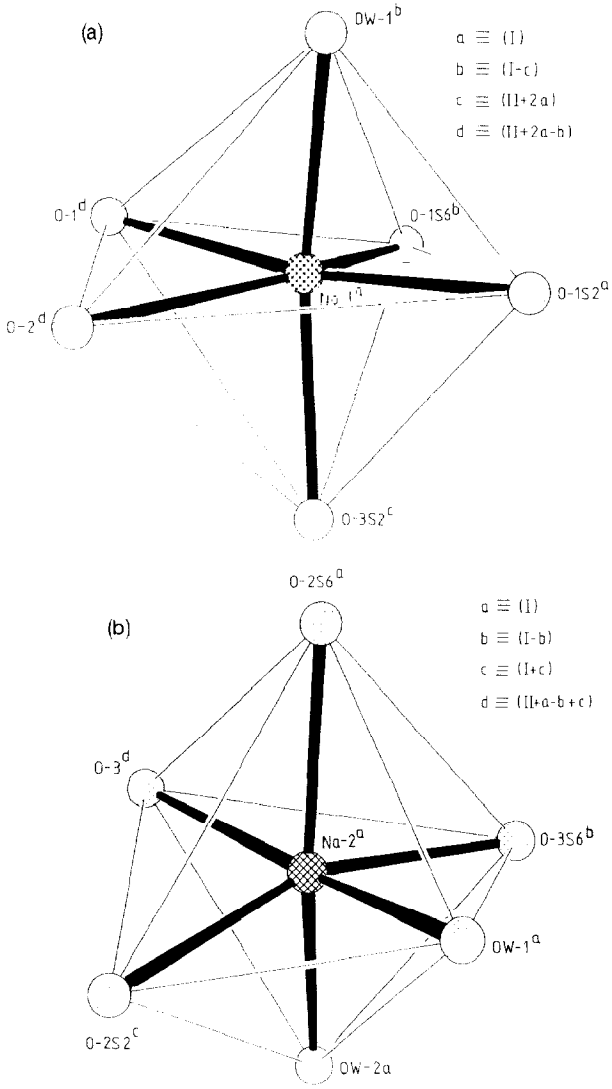

Fig. 2. Six-fold co-ordination of the Na-1 (a) and Na-2 (b) sodium ions in **3**. For the symmetry codes, see Table IV.

reduces steric repulsion of the sulfate group with the MeO-1 and HO-3 groups. For the same reason, the sulfate group deviates significantly (average 15.2°) from the ideal staggered conformation with respect to the C-2–O-2 ester bond. Similar spatial arrangements of the sulfate groups have been found in the crystal structures of methyl α-D-galactopyranoside 2-(sodium sulfate)[10] and β-D-glucopyranose 6-(potassium sulfate)[12]. The O–C bond of MeO-1 is oriented *gauche–trans* with respect to O-5 and C-2, respectively.

Co-ordination of the sodium ions.—The structure of **3** contains two independent sodium ions. Both Na-1 and Na-2 ions show a six-fold oxygen co-ordination involving distorted octahedra (see Table IV and Fig. 2). The Na-1 ion is surrounded by MeO-1 oxygen, O-2 ester oxygen, three sulfate groups (two S-2 oxygens and one S-6 oxygen), and one water molecule OW-1, whereas the Na-2 ion is surrounded by O-3 hydroxyl, three sulfate groups (one S-2 oxygen and two S-6 oxygens), and two water molecules OW-1 and OW-2. The Na-1–O and Na-2–O distances average 2.43(8) and 2.44(7) Å, respectively, and fall in the expected range of Na–O distances for sodium ions having co-ordination number six[16]. Three symmetry-related anions participate in the co-ordination shell of each of the sodium ions. Six-fold sodium co-ordination has been found in both the methyl α-D-galactopyranoside 2- and 4-sulfate structures[10,11], whereas, in methyl α-D-galactopyranoside 3-(sodium sulfate)[10], a seven-fold co-ordination has been observed. In the crystal structure of the α-D-glucose · NaCl complex[17,18], the only example in the literature where hydroxyl groups from carbohydrates occupy the entire co-ordination shell of a Na ion, the octahedral co-ordination is significantly distorted.

Crystal packing.—The crystal packing, projected along the *b* axis (Fig. 3), is dominated by the co-ordination of the sodium ions and hydrogen bonds involving the oxygen atoms of the sulfate groups, each oxygen atom of the hydroxyl groups,

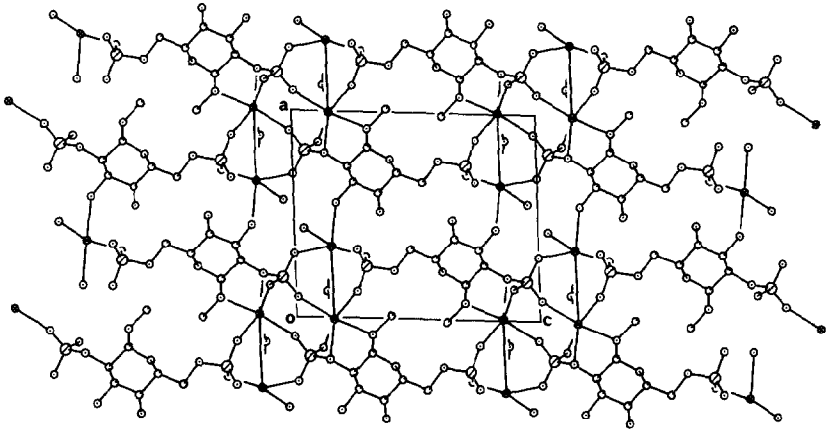

Fig. 3. View of the unit cell of **3** along the *b* axis.

and the two water molecules (Table V). Layers extending on the $a \cdot c$ plane at $b = 0.0$ and 0.5 are stabilised by the co-ordination of the two sodium ions and the hydrogen bond involving the O-3 hydroxyl oxygen and the OW-2 water molecule. The D-galactopyranose ring is almost parallel to the layer. The water molecule OW-1 is on an edge shared by both the Na-1 and Na-2 octahedra and joins, via hydrogen bonds, the oxygens of the S-2 and S-6 sulfate moieties belonging to symmetry-related layers. The water molecule OW-2 donates two hydrogen bonds to oxygens of the S-2 sulfate group belonging to symmetry-related layers. An interesting feature of the hydrogen bond network concerns the O-4 hydroxyl oxygen which donates a bifurcated bond to O-2S6 and O-3S6 oxygens of the S-6 sulfate moiety belonging to symmetry-related layers. All of these interactions constitute important cohesive elements along the b axis.

ACKNOWLEDGMENTS

We thank the A.F.R.C. (A.R.) and S.E.R.C. (E.A.Y.) for financial support, and Dr. I.J. Colquhoun (I.F.R., Norwich) for recording the NMR spectra. The provision of financial support by grants of the Italian National Research Council special ad hoc programme "Chimica Fine II" subproject 3 (to D.L.) is gratefully acknowledged.

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