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The crystal structure of methyl β-cellotrioside monohydrate 0.25 ethanolate and its relationship to cellulose II

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Abstract

The crystal structure of methyl β-cellotrioside (methyl *O*-β-D-glucopyranosyl-(1 → 4)-*O*-β-D-glucopyranosyl-(1 → 4)-β-D-glucopyranoside) complexed with water and ethanol, $C_{19}H_{34}O_{16} \cdot H_2O \cdot 0.25[C_2H_6O]$ was determined by combining Cu $K\alpha$ X-ray and synchrotron data collected at room temperature. The crystals have the monoclinic space group $P2_1$ with $Z = 8$ and unit cell parameters $a = 7.9978(11)$, $b = 76.38(4)$, $c = 8.9908(6)$ Å and $\beta = 116.40(1)°$. The structure, which was solved by direct methods and refined to a final R-factor of 0.067, contains four independent molecules of methyl β-cellotrioside with an extended conformation. They are arranged parallel to the long b axis of the unit cell, and organized in two pairs of antiparallel molecules. Each β-D-glucopyranosyl residue of the four independent molecules is in the $^4C_1$ pyranose conformation, and each (O-6) primary hydroxyl group has the *gt* conformation. The crystal structure of methyl β-cellotrioside has many points in common with that of cellotetraose hemihydrate as well as with the structure of cellulose II. Thus, it is likely that the precise atomic coordinates obtained in this study can be directly transposed to give an improved structure for cellulose II where, in particular, only the *gt* conformation would be present at the primary hydroxyl groups of both polysaccharide chains.

Keywords: Crystal structure; Crystal packing; Hydrogen bonding; Cellulose II structure; Methyl β-cellotrioside

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1. Introduction

There are two basic ways to solve the crystalline structure of a polymer. The first involves either the preparation of crystalline polymer fibers or that of micron-sized single crystals and the recording of their X-ray, or electron-diffraction diagrams. As the polymer crystals are usually very small, the number of reflections available, either from X-ray fiber diagram or from electron-diffraction patterns, is limited and one has to rely on extensive computer modelling to solve the corresponding polymer structure, which at best remains only a "probable" structure. The other approach consists of crystallizing a series of homologous oligomers of increasing degree of polymerization (dp). Beyond a given dp, the inner monomer residues adopt a conformation and a crystalline packing that are identical to those occurring in the parent crystalline polymer. The resolution of the crystal structure of such oligomers by conventional crystallography yields precise geometrical crystal data which can be used directly for the structural determination of the corresponding polymer from fiber diffraction patterns.

In the case of cellulose II—or cellulose recrystallized from solution—it has been established that the cellodextrins having a dp of four and higher give X-ray powder diffractograms that are similar to those of cellulose II [1–3]. Furthermore, powders of methyl β-cellotrioside, methyl β-cellotetraoside, and methyl β-cellopentaoside also give diffraction patterns having the cellulose II features [4]. Finally, the unit cell of cellotetraose [5] and that of methyl β-cellotrioside [6] display cell parameters perpendicular to the oligomer chain direction that are equivalent to those of cellulose II [7,8]. Solving the crystal structure of one or several of these cellodextrins should provide a model of the crystalline structure of cellulose II, the predominant crystal structure in man-made products based on reprecipitation of dissolved cellulose.

Since the initial submission of the present paper, a report from the group of Saenger [9] together with a communication from us [10] have provided a concordant molecular and crystal structure of cellotetraose hemihydrate. This structure consists of two antiparallel residues of cellotetraose where the conformation of the "up" and "down" molecules are somewhat different. In this report, we present the molecular and crystal structure of methyl β-cellotrioside. The conformation, packing and hydrogen-bonding parameters of this trisaccharide are compared with those of cellotetraose hemihydrate [9,10], together with the current structures of cellulose II [7,8].

2. Experimental

Crystallization and crystal selection.—Methyl β-cellotrioside, prepared by enzymatic synthesis [11], was a gift from C. Lancelon from this laboratory. Hexagonal platelet crystals were grown by slow diffusion of EtOH in a water–EtOH solution. Initially, the crystals of methyl β-cellotrioside were too small for conventional X-ray measurements. However, we succeeded in growing one crystal that was large enough to be submitted to X-ray diffraction. This crystal with the dimensions $0.43 \times 0.33 \times 0.04$ mm^3 was mounted on a glass fiber with the platelet base perpendicular to the fiber axis.

X-ray data collection was achieved using an Enraf–Nonius CAD4 diffractometer equipped with a graphite monochromator and operated with Cu $K\alpha$ radiation. The other crystals had dimensions of only ca. $0.14 \times 0.09 \times 0.005$ mm^3, i.e. too small for conventional X-ray measurements, but large enough for synchrotron radiation data collection.

Data collection with the ENRAF Nonius CAD4 diffractometer.—Unit-cell dimensions were obtained as part of the alignment process by a least-squares fit to the setting of 25 well centred reflections. These parameters, as well as other relevant crystallographic data, are presented in Table 1. X-ray diffraction data were collected at room temperature using a $\omega/2\theta$ scan mode. The intensities of four reference reflections, measured every 2 h, decreased by ca. 8% of their initial value during the total data collection. The data were corrected for Lorentz and polarization effects and an absorption correction was applied. The data reduction and absorption correction were performed with SDP programs [12]. A summary of the crystal data and structure refinement is presented in Table 1.

In the data collection, it was found that a number of reflections had an asymmetric background as a result of a large crystallographic axis ($b = 76.4$ Å) and a short distance of 173 mm between the crystal and the detector. This phenomenon is responsible not only for a R(int) figure that takes the high value of 0.130, but also for a number of overlaps along the b^* axis. Thus, the systematic absences along this axis could not be established with certainty and therefore the space group could not be ascertained.

Data collection at the European Synchrotron Radiation Facility (ESRF).—In order to confirm the space group, a short data collection was achieved at ESRF on the beam line 2(ID11) [13]. Monochromatic radiation with a wavelength of 0.6199 Å was used and diffraction data were recorded to $\theta = 38°$ during successive oscillations of the crystal. The data collection was achieved on image plate detectors positioned at 303 mm from the crystal. The plates were scanned with a Molecular Dynamic Phosphor Imager 400E. The data were corrected using the program FIT2D [14] to correct the distortion of the detector. The sets of intensities recorded in each plate were then scaled and corrected for Lorentz and polarization using the DENZO (Copyright Zbyszek Otwinowski) program which was also used to index the patterns and refine the unit-cell parameters. The extinctions of $0k0$ for $k = 2n + 1$ were verified up to $k = 34$. In this collection, a R(int) of 0.074 was obtained from a total of 3399 reflections with 1387 unique reflections.

Determination and refinement of the structure.—The structure was solved by direct methods using the SHELXS-86 program [15]. Fourier synthesis, based on the phases produced for the set with the highest combined figure of merit, showed the location of all non-hydrogen atoms of the four independent methyl β-cellotrioside molecules (**a**, **b**, **c** and **d**). Consecutive cycles of full matrix least-squares refinement and difference Fourier synthesis with the SHELXL-93 program [16] revealed the positions of four water molecules and one ethanol molecule with some disorder. The positions and the anisotropic thermal factors of all non-hydrogen atoms of methyl β-cellotrioside molecules were refined. The hydrogen coordinates of the carbohydrate residues were computed and kept fixed but their isotropic thermal factors were refined. Hydrogen atoms of the hydroxyl groups were positioned at the maximum electron density around the circle, which represents the loci of possible hydrogen positions for a fixed O–H

Table 1
Crystal data and structure refinement data for methyl β-cellotrioside at room temperature [a]

Empirical formula	$C_{19}H_{34}O_{16} \cdot H_2O \cdot 0.25[C_2H_6O]$
Formula weight	548.00 g mol^{-1}
Crystal system	Monoclinic
Space group	$P2_1$
Unit-cell dimensions	$a = 7.9978(11)$ Å
	$b = 76.38(4)$ Å
	$c = 8.9908(6)$ Å
	$\beta = 116.40(1)°$
Volume	4919(3) $Å^3$
Z	8
Density	1.480 (calcd), 1.50(2) (obsd) g cm^{-3}
$F(000)$	2340
Radiation: Cu $K\alpha$	1.54178 Å
Absorption coefficient	11.42 cm^{-1}
Transmission coefficient	max = 0.9532min = 0.7014
θ range for data collection	$0 \le \theta \le 60°$
Index ranges	$-8 \le h \le 8$, $-56 \le k \le 85$, $-6 \le l \le 10$
Reflections collected	13,303
Independent reflections	7327 [R(int) = 0.1297] [b]
Refinement method	Full-matrix least-squares on F^2
Data [c]/restraints/parameters	6878/1/1454
Goodness-of-fit (S) [d] on F^2	1.167
Final R [e]	$wR_2 = 0.1820$ for 6878 data
	$wR_2 = 0.4593$ for all 7327 data [f]
	$R_1 = 0.0671$ for 6394 data [$I > 2\sigma_I$]
	$R_1 = 0.1062$ for all 7327 data
Extinction coefficient	0.0011(2)
Largest diff. peak and hole	0.366 and −0.352 e $Å^{-3}$

[a] Lists of bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, observed and calculated structure factors have been deposited with the Cambridge Data Centre and may be obtained on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

[b] $R(\text{int}) = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma(F_o^2)$.
R(int) of 0.074 for 3399 reflections with synchrotron data.

[c] 449 negative data have been omitted during the refinement.

[d] $S = [\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)]^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

[e] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.1011 * P)^2 + 4.85 * P]$, $P = (\text{Max}(F_o^2, 0) + 2 * F_c^2)/3$.

[f] Reflections with asymmetric background included.

distance (0.98 Å) and C–O–H angle (110°). The positions of hydrogen atoms of the water and ethanol molecules have not been calculated. The list of the final atomic parameters is given in Table 2. The tables of atomic parameters for hydrogen atoms, anisotropic temperature factors for non-hydrogen atoms, and observed, and calculated structure amplitudes have been deposited with the Cambridge Crystallographic Data Centre.

Table 2
Fractional atomic coordinates ($\times 10^4$) [a] and equivalent isotropic (U_{eq}) [b] displacement parameters ($Å^2 \times 10^3$) for methyl β-cellotrioside

	x	y	z	U_{eq}
C-1(1a)	3110(12)	4656(1)	4609(11)	47(2)
C-2(1a)	4743(11)	4538(1)	5403(10)	42(2)
C-3(1a)	4175(10)	4357(1)	4523(10)	36(2)
C-4(1a)	2408(10)	4299(1)	4596(9)	33(2)
C-5(1a)	868(10)	4432(1)	3850(10)	41(2)
C-6(1a)	−903(10)	4385(1)	3959(12)	46(2)
C-7(1a)	2074(20)	4948(2)	4470(19)	94(4)
O-1(1a)	3506(9)	4822(1)	5386(8)	61(2)
O-2(1a)	6315(8)	4607(1)	5252(8)	53(2)
O-3(1a)	5714(7)	4248(1)	5286(9)	58(2)
O-4(1a)	1716(6)	4136(1)	3669(6)	37(1)
O-5(1a)	1544(7)	4591(1)	4757(7)	45(1)
O-6(1a)	−2321(8)	4506(1)	3092(8)	54(2)
C-1(2a)	2202(9)	3982(1)	4557(9)	37(2)
C-2(2a)	635(9)	3851(1)	3786(9)	32(2)
C-3(2a)	1273(9)	3678(1)	4735(9)	38(2)
C-4(2a)	3082(9)	3621(1)	4695(8)	31(2)
C-5(2a)	4561(10)	3758(1)	5430(9)	33(2)
C-6(2a)	6347(10)	3719(1)	5350(11)	45(2)
O-2(2a)	−951(7)	3912(1)	3956(7)	44(1)
O-3(2a)	−152(8)	3554(1)	4057(10)	64(2)
O-4(2a)	3818(6)	3463(1)	5642(6)	36(1)
O-5(2a)	3846(6)	3918(1)	4498(6)	38(1)
O-6(2a)	7675(7)	3849(1)	6119(7)	48(2)
C-1(3a)	3402(9)	3304(1)	4761(9)	34(2)
C-2(3a)	5040(10)	3179(1)	5543(10)	38(2)
C-3(3a)	4498(10)	3003(1)	4662(11)	48(2)
C-4(3a)	2693(10)	2936(1)	4675(11)	43(2)
C-5(3a)	1163(10)	3071(1)	3997(10)	42(2)
C-6(3a)	−569(11)	3020(1)	4156(11)	50(2)
O-2(3a)	6588(8)	3250(1)	5366(8)	51(2)
O-3(3a)	5969(8)	2884(1)	5327(10)	58(2)
O-4(3a)	2048(8)	2781(1)	3670(9)	63(2)
O-5(3a)	1816(7)	3232(1)	4900(7)	40(1)
O-6(3a)	−2057(9)	3133(1)	3214(9)	63(2)
C-1(1b)	6499(11)	733(1)	4594(11)	45(2)
C-2(1b)	5664(11)	852(1)	5397(10)	41(2)
C-3(1b)	5336(10)	1032(1)	4517(10)	40(2)
C-4(1b)	7187(10)	1096(1)	4595(9)	33(2)
C-5(1b)	7986(11)	959(1)	3862(10)	38(2)
C-6(1b)	9861(12)	1006(1)	3970(12)	50(2)
C-7(1b)	7384(21)	443(2)	4462(19)	88(4)
O-1(1b)	6881(10)	570(1)	5396(9)	65(2)
O-2(1b)	3942(8)	785(1)	5250(8)	54(2)
O-3(1b)	4563(10)	1147(1)	5257(10)	63(2)
O-4(1b)	6951(7)	1255(1)	3670(6)	37(1)
O-5(1b)	8210(7)	799(1)	4757(7)	46(1)
O-6(1b)	10403(8)	884(1)	3090(8)	55(2)
C-1(2b)	7359(10)	1409(1)	4557(9)	38(2)
C-2(2b)	8164(9)	1542(1)	3801(9)	34(2)

Table 2 (continued)

	x	y	z	U_{eq}
C-3(2b)	8472(10)	1715(1)	4746(10)	36(2)
C-4(2b)	6610(10)	1772(1)	4685(8)	32(2)
C-5(2b)	5878(10)	1633(1)	5425(9)	33(2)
C-6(2b)	3983(11)	1675(1)	5354(11)	42(2)
O-2(2b)	9902(7)	1480(1)	3941(7)	43(1)
O-3(2b)	9213(11)	1838(1)	4042(10)	65(2)
O-4(2b)	6834(7)	1929(1)	5646(6)	38(1)
O-5(2b)	5651(6)	1472(1)	4503(6)	38(1)
O-6(2b)	3450(7)	1539(1)	6125(7)	50(2)
C-1(3b)	6370(10)	2089(1)	4758(9)	35(2)
C-2(3b)	5505(10)	2209(1)	5544(10)	38(2)
C-3(3b)	5180(11)	2389(1)	4676(10)	43(2)
C-4(3b)	6988(11)	2458(1)	4685(11)	44(2)
C-5(3b)	7834(10)	2319(1)	3984(10)	41(2)
C-6(3b)	9742(12)	2372(1)	4163(12)	50(2)
O-2(3b)	3786(7)	2145(1)	5368(8)	51(2)
O-3(3b)	4368(9)	2508(1)	5333(9)	60(2)
O-4(3b)	6628(10)	2610(1)	3678(10)	61(2)
O-5(3b)	8081(7)	2160(1)	4894(7)	41(1)
O-6(3b)	10275(9)	2259(1)	3222(8)	63(2)
C-1(1c)	1999(12)	3256(1)	−567(11)	49(2)
C-2(1c)	673(10)	3386(1)	−424(10)	41(2)
C-3(1c)	1048(10)	3576(1)	−841(10)	41(2)
C-4(1c)	3144(10)	3618(1)	−30(9)	37(2)
C-5(1c)	4245(10)	3476(1)	−275(10)	43(2)
C-6(1c)	6341(11)	3495(2)	678(13)	57(2)
C-7(1c)	2799(26)	2952(2)	−162(21)	110(5)
O-1(1c)	1757(11)	3097(1)	87(9)	66(2)
O-2(1c)	−1181(8)	3342(1)	−1471(7)	56(2)
O-3(1c)	58(9)	3689(1)	−275(9)	59(2)
O-4(1c)	3545(7)	3772(1)	−735(6)	37(1)
O-5(1c)	3850(8)	3313(1)	406(7)	48(1)
O-6(1c)	7306(10)	3347(1)	537(10)	70(2)
C-1(2c)	3416(9)	3933(1)	−69(9)	31(2)
C-2(2c)	4758(9)	4060(1)	−226(9)	37(2)
C-3(2c)	4459(10)	4250(1)	205(9)	38(2)
C-4(2c)	2420(10)	4296(1)	−591(9)	35(2)
C-5(2c)	1247(9)	4159(1)	−358(9)	32(2)
C-6(2c)	−834(10)	4191(1)	−1289(11)	49(2)
O-2(2c)	6617(7)	4003(1)	792(6)	44(1)
O-3(2c)	5531(8)	4359(1)	−293(9)	54(2)
O-4(2c)	2071(7)	4457(1)	85(6)	37(1)
O-5(2c)	1552(6)	3994(1)	−1024(6)	39(1)
O-6(2c)	−1890(7)	4047(1)	−1268(8)	52(2)
C-1(3c)	2251(10)	4615(1)	−617(10)	40(2)
C-2(3c)	872(10)	4746(1)	−557(10)	40(2)
C-3(3c)	1159(12)	4925(1)	−1221(12)	52(2)
C-4(3c)	3199(12)	4983(1)	−377(12)	50(2)
C-5(3c)	4492(11)	4836(1)	−320(12)	47(2)
C-6(3c)	6506(13)	4874(2)	787(16)	63(3)
O-2(3c)	−1004(7)	4688(1)	−1506(8)	54(2)

Table 2 (continued)

	x	y	z	U_{eq}
O-3(3c)	2(10)	5049(1)	−1033(10)	69(2)
O-4(3c)	3398(11)	5125(1)	−1314(10)	74(2)
O-5(3c)	4080(7)	4681(1)	392(7)	45(1)
O-6(3c)	7737(9)	4739(1)	846(10)	73(2)
C-1(1d)	2454(11)	2132(1)	−567(11)	48(2)
C-2(1d)	3891(11)	2003(1)	−436(10)	42(2)
C-3(1d)	3106(10)	1814(1)	−844(9)	42(2)
C-4(1d)	1825(10)	1773(1)	−33(9)	38(2)
C-5(1d)	487(10)	1921(1)	−267(9)	41(2)
C-6(1d)	−641(13)	1896(2)	678(12)	57(2)
C-7(1d)	2041(21)	2437(2)	−159(20)	97(4)
O-1(1d)	3336(10)	2296(1)	81(10)	69(2)
O-2(1d)	4711(9)	2049(1)	−1479(8)	59(2)
O-3(1d)	4666(8)	1703(1)	−273(9)	59(2)
O-4(1d)	719(6)	1620(1)	−737(6)	37(1)
O-5(1d)	1555(8)	2075(1)	411(7)	47(1)
O-6(1d)	−1764(9)	2044(1)	546(10)	70(2)
C-1(2d)	1512(9)	1459(1)	−74(9)	35(2)
C-2(2d)	7(10)	1331(1)	−242(9)	38(2)
C-3(2d)	748(10)	1145(1)	225(9)	39(2)
C-4(2d)	1991(9)	1094(1)	−587(9)	36(2)
C-5(2d)	3404(9)	1237(1)	−363(9)	36(2)
C-6(2d)	4533(11)	1200(1)	−1294(11)	47(2)
O-2(2d)	−834(7)	1389(1)	779(6)	44(1)
O-3(2d)	−821(7)	1032(1)	−290(9)	52(2)
O-4(2d)	3017(7)	936(1)	89(6)	40(1)
O-5(2d)	2425(7)	1395(1)	−1021(6)	40(1)
O-6(2d)	5637(7)	1345(1)	−1251(8)	51(2)
C-1(3d)	2140(10)	776(1)	−612(10)	40(2)
C-2(3d)	3568(10)	645(1)	−572(9)	40(2)
C-3(3d)	2632(12)	470(1)	−1217(11)	52(2)
C-4(3d)	1428(13)	409(1)	−391(12)	54(2)
C-5(3d)	180(12)	558(1)	−325(11)	50(2)
C-6(3d)	−735(15)	518(2)	781(16)	68(3)
O-2(3d)	4501(8)	704(1)	−1504(7)	53(2)
O-3(3d)	3960(10)	339(1)	−1027(10)	67(2)
O-4(3d)	310(11)	267(1)	−1299(10)	72(2)
O-5(3d)	1305(7)	711(1)	382(7)	44(1)
O-6(3d)	−1904(9)	652(1)	839(11)	72(2)
O-1(1e)	3350(25)	47(3)	3694(23)	89(5)
O-1(1e)′	4638(27)	346(3)	6295(23)	91(5)
C-1(1e)	2989(42)	41(5)	5025(36)	94(8)
C-1(1e)′	2999(44)	340(5)	4962(38)	97(8)
C-2(1e)	1797(27)	202(4)	4980(27)	126(5)
O-(1w)	3935(33)	5336(3)	2746(28)	114(7)
O-(1w)′	6208(31)	5059(3)	7294(28)	114(7)
O-(2w)	5768(21)	2459(2)	−1293(18)	149(5)
O-(3w)	7953(21)	2923(2)	−1299(18)	151(5)
O-(4w)	8117(24)	2696(3)	1195(18)	163(5)

[a] Standard deviations are given in parentheses.

[b] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

The set of intensities resulting from the synchrotron collection was corrected by scaling with respect to the CAD4 data. The final coordinates of the structure were then tested against the corrected synchrotron data without further refinement. This test gave a *R*-factor of 0.076 that proved that the two data collections led to the same structure and in particular that the synchrotron data were of the same quality as those of the CAD4, despite the fact that we used a crystal whose volume was close to one hundred times smaller.

Nomenclature.—The recommendations and symbols proposed by the Joint Commission on Biochemical Nomenclature (JCBN) are used throughout this paper [17]. When referring to the trisaccharide, the sugar residues are numbered 1, 2 and 3 from the reducing end. The atoms of the sugar molecules are labelled [atom–name(*ij*)] as shown

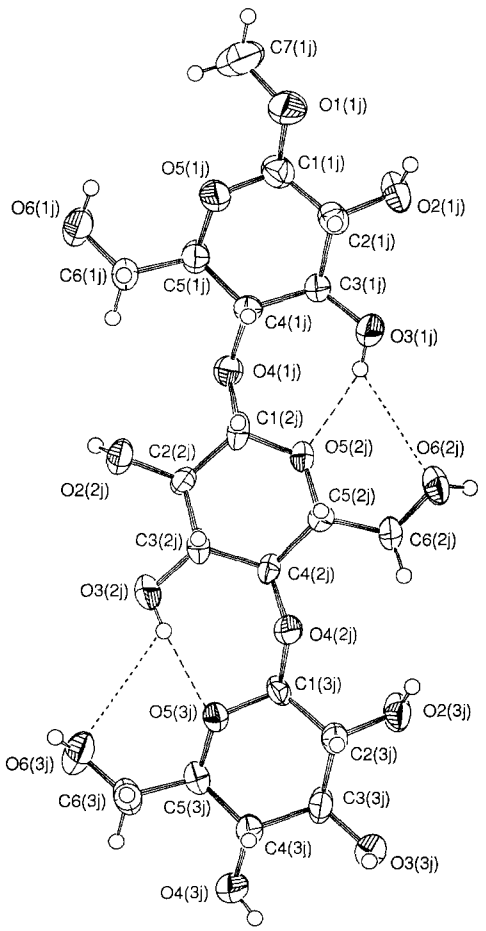

Fig. 1. The atomic notation and thermal ellipsoids (50% probability) for the methyl β-cellotrioside molecule (**a**) at room temperature. The dashed lines represent intramolecular hydrogen bonds.

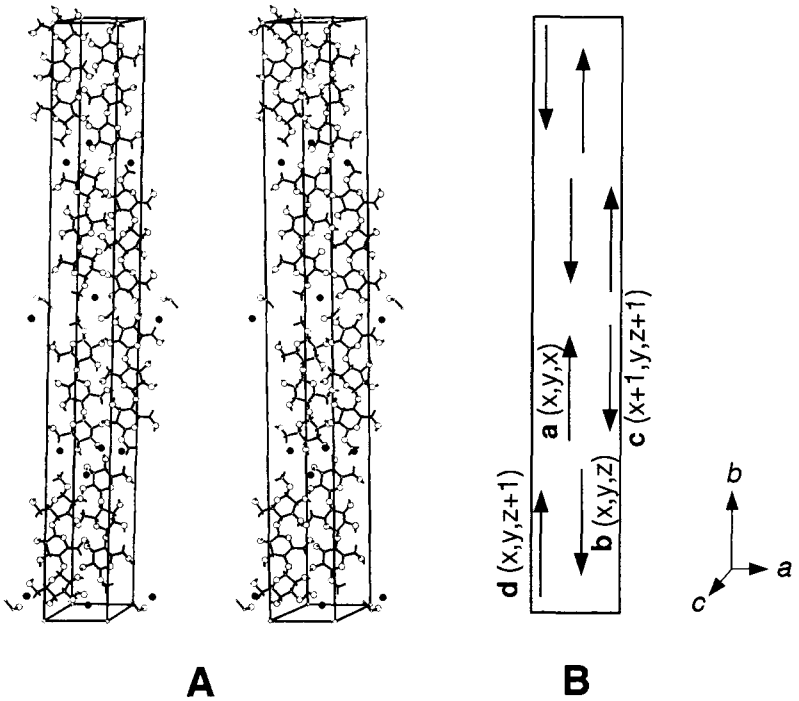

Fig. 2. A, Molecular packing (stereoviews) of the four methyl β-cellotrioside molecules, the water molecules (as black dots) and ethanol molecules. B, Schematic view of the organization of molecules **a**, **b**, **c** and **d** in the unit cell.

in Fig. 1. In this labelling scheme, the letter i in parentheses refers to the sugar residue number and the letter j to one of the four independent molecules **a**, **b**, **c** or **d**. The ethanol molecules are labelled **e** and the water molecules **w**. The relative orientation of a pair of contiguous sugar residues is described by the glycosidic angle τ and the torsion angles ϕ and ψ. Thus, in general, for residues i and $(i\text{-}1)$ these angles are given by: $\tau(i)$ = C-1(i)–O-4(i-1)–C-4(i-1), $\phi(i)$ = O-5(i)–C-1(i)–O-4(i-1)–C-4(i-1), $\psi(i)$ = C-1(i)–O-4(i-1)–C-4(i-1)–C-3(i-1). The conformation of the primary hydroxyl group at C-6 is referred to as either *gauche–trans* (*gt*), *gauche–gauche* (*gg*) or *trans–gauche* (*tg*) [18]. In this terminology, the torsion angle $\chi(i)$ = O-5(i)–C-5(i)–C-6(i)–O-6(i) is stated first and the torsion angle $\chi'(i)$ = C-4(i)–C-5(i)–C-6(i)–O-6(i) second.

3. Results and discussion

The packing of the molecules in the unit cell is shown in Fig. 2A. All four independent methyl β-cellotrioside molecules (**a**, **b**, **c** and **d**) are extended and organized as two pairs of antiparallel molecules facing each other: **a** facing **c**, and **b** facing **d**. Within each pair, the two molecules are shifted along the b axis with respect to one

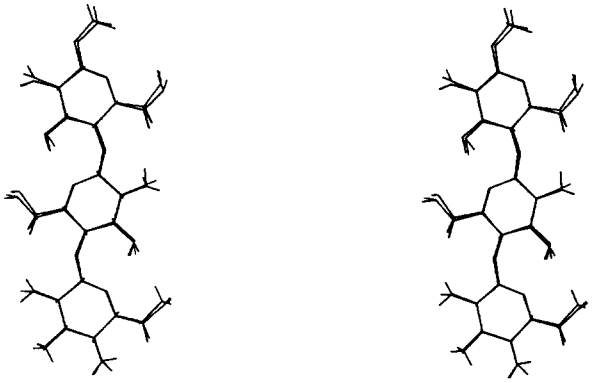

Fig. 3. Superimposition (stereoviews) of the four independent methyl β-cellotrioside molecules.

another by roughly 2.5 Å, i.e. half a glucose residue. In addition, there are some water and ethanol molecules located at the extremities of the methyl β-cellotrioside entities. These solvent molecules act as linkages between the successive trisaccharides along the *b* axis.

Molecular geometry.—The four independent methyl β-cellotrioside molecules have almost the same geometry and conformation. Stereoscopic pairs of the superimposition of the four independent molecules are shown in Fig. 3 (root mean square = 0.09 Å for a match of all endocyclic atoms). In these molecules, the mean endocyclic C–C bond length is 1.519 Å, ranging from, 1.472 to 1.559 Å. The mean exocyclic C-5–C-6 bond length is 1.507 Å, ranging from 1.491 to 1.522 Å. The mean exocyclic C–O bond length, excluding the anomeric oxygen atoms [O-4(2*j*) and O-4(1*j*)], is 1.410 Å, ranging from 1.390 to 1.437 Å. The mean C-1–O-5 bond length is 1.424 Å, ranging from 1.403 to 1.436 Å. It is, on average, shorter than the C-5–O-5 bond which has a mean length of 1.442 Å, ranging from 1.416 to 1.479 Å. The equatorial glycosidic bonds C-1(*i*, *j*)–O-4(*i*-1, *j*) are the shortest of all C–O bonds: their mean value is 1.401 Å ranging from 1.377 to 1.428 Å. These values, as well as other geometric parameters around the anomeric carbons, are in agreement with those observed with other β-pyranosides [19,20].

The internal endocyclic C–C–C ring angles are close to tetrahedral with a mean value of 110.5°, ranging from 107.5 to 113.3°. However, the exocyclic C-4–C-5–C-6 angles exhibit a significant opening with a mean value of 113.9°, ranging from 112.2 to 115.5°. The endocyclic angles C-1–O-5–C-5 vary little and their mean value is 112.2°, ranging from 111.0 to 113.7°. The mean endocyclic C–C–O bond angle is 109.5°, ranging from 107.1 to 111.8°. The mean exocyclic C–C–O angle is 110.2°, but presents a wide range of variation from 106.0 to 116.3°. The average valence angle at the glycosidic oxygen atom with the methyl glycosidic group is 112.3°, ranging from 110.3 to 113.7°. This mean value agrees with the corresponding angle found in the crystal structure of methyl β-cellobioside (113.1°) [21]. The mean valence bond angle (τ) for all glycosidic oxygen atoms between two glucopyranose rings is 117.2°, ranging from 116.6 to 117.5°. This mean value is larger than those found for methyl β-cellobioside

Table 3
Cremer and Pople puckering parameters for methyl β-cellotrioside [a]

Ring(ij)	Q (Å)	θ (°)
1a	0.595(9)	2.6(9)
2a	0.593(8)	0.0(8)
3a	0.579(9)	3.2(9)
1b	0.599(9)	0.9(9)
2b	0.594(8)	2.5(8)
3b	0.579(9)	3.5(9)
1c	0.572(9)	13.2(9)
2c	0.562(8)	11.8(8)
3c	0.580(9)	9.8(10)
1d	0.568(9)	13.6(9)
2d	0.568(8)	10.0(8)
3d	0.569(9)	10.0(10)

[a] Estimated standard deviation values are given in parentheses and refer to the least significant digit.

(115.8°) [21] and cellobiose (116.1°) [22]. The mean ϕ torsion angle is −94.4°, ranging from −91.6 to −96.8°. The mean ψ torsion angle is 91.7°, ranging from 85.8 to 97.9°. All primary hydroxymethyl groups (O-6) have the *gt* conformation. The mean χ torsion angle is 61.9°, ranging from 51.0 to 72.2°, whereas the mean χ' takes the value of 179°, ranging from −168.1 to 169.9°.

The 12 independent (1 → 4)-linked β-D-glucopyranose residues have the $^4C_1$ conformation. Their Cremer–Pople puckering parameters [23] (Q and θ) are given in Table 3. The puckering amplitude (Q) of the pyranose rings describes the distortion from a planar structure. In the present work, the average puckering amplitude is 0.580 Å. It is slightly less than the Q value of an ideal cyclohexane chair that displays a value of 0.63 Å for C–C bond lengths of 1.54 Å and C–C–C angles of 109.4°. Remarkably, the magnitude of distortion from the ideal chair, given by θ in degrees, shows two distinct average values: one of 2.1° for molecules **a** and **b**, and another of 11.4° for molecules **c** and **d**. Thus, the molecules **c** and **d** appear more distorted from the standard $^4C_1$ conformation than **a** and **b**. This is of interest because the antiparallel molecules facing each other are **a**/**c** and **b**/**d**.

In order to evaluate whether the distortion of the pyranose rings had an effect on the τ, ϕ, ψ, χ or χ' values, we have averaged separately these values for the molecules **a** and **b** and for **c** and **d**. These mean values [mean(**ab**) and mean(**cd**)] together with the individual values are presented in Table 4. For the τ angles, the mean(**ab**) and mean(**cd**) are almost the same. For the torsion angles ϕ, all the averages are almost equivalent and this can be attributed to the stabilizing influence of the anomeric effect [20,24]: we observe a small difference (of ca. 3.8°) between $\phi(2)$ and $\phi(3)$. In comparison, the mean $\psi(2)$ and $\psi(3)$ values are very close for (**ab**), and they are the same for (**cd**). However, a substantial difference of 11° is observed between the mean(**ab**) ψ and the corresponding value for the mean (**cd**). This difference is ca. 14 times the average estimated standard deviation for these torsion angles. The $\phi(1)$ angle differs by almost 25° from the values listed for $\phi(2)$ and $\phi(3)$. Regarding this value, it is interesting to

Table 4
Selected geometrical parameters for molecules of methyl β-cellotrioside [a]

j =	a	b	c	d	mean (ab)	mean (cd)	delta [b]
Linkage bond angles (°)							
C-1(2j)–O-4(1j)–C-4(1j): τ(2)	117.3(5)	116.8(5)	117.4(5)	117.1(5)	117.0	117.1	−0.1
C-1(3j)–O-4(2j)–C-4(2j): τ(3)	117.4(5)	116.6(5)	117.5(6)	117.5(6)	117.0	117.5	−0.5
Linkage torsion angles (°)							
O-5(2j)–C-1(2j)–O-4(1j)–C-4(1j): ϕ(2)	−93.7(7)	−93.3(7)	−91.6(7)	−91.7(7)	−93.5	−91.6	1.9
C-1(2j)–O-4(1j)–C-4(1j)–C-3(1j): ψ(2)	96.0(7)	97.6(7)	86.0(8)	86.1(8)	96.8	86.0	10.8
O-5(3j)–C-1(3j)–O-4(2j)–C-4(2j): ϕ(3)	−96.6(7)	−96.8(7)	−96.3(7)	−95.5(7)	−96.7	−95.9	0.8
C-1(3j)–O-4(2j)–C-4(2j)–C-3(2j): ψ(3)	96.9(7)	97.9(7)	85.8(8)	87.1(8)	97.4	86.4	11.0
Primary alcohol groups torsion angles (°)							
O-5(1j)–C-5(1j)–C-6(1j)–O-6(1j): χ(1)	67.6(9)	67.1(9)	56.1(9)	57.3(9)	67.4	56.7	10.7
C-4(1j)–C-5(1j)–C-6(1j)–O-6(1j): χ'(1)	−173.8(7)	−172.8(7)	173.5(8)	174.9(7)	−173.3	174.2	12.5
O-5(2j)–C-5(2j)–C-6(2j)–O-6(2j): χ(2)	63.4(8)	61.7(8)	51.0(8)	52.9(8)	62.6	52.0	10.6
C-4(2j)–C-5(2j)–C-6(2j)–O-6(2j): χ'(2)	−177.5(6)	−178.2(6)	169.9(6)	171.8(6)	−177.8	170.8	11.4
O-5(3j)–C-5(3j)–C-6(3j)–O-6(3j): χ(3)	71.3(9)	72.2(9)	61.2(11)	61.5(11)	71.8	61.4	10.4
C-4(3j)–C-5(3j)–C-6(3j)–O-6(3j): χ'(3)	−168.1(8)	−168.4(7)	−179.5(8)	−179.2(9)	−168.2	−179.4	11.2

[a] Estimated standard deviation values are given in parentheses and refer to the least significant digit.
[b] Delta = mean (**ab**) − mean (**cd**).

Table 5
Distances (Å) between oxygen atoms of water and ethanol molecules [a]

O-1(1e)···O-1(1a)	$-x+1, y-1/2, -z+1$	2.850(30)
O-1(1e)···O-3(3c)	$-x, y-1/2, -z$	2.680(20)
O-1(1e)′···O-1(1b)	x, y, z	2.850(30)
O-1(1e)′···O-3(3d)	$x, y, z+1$	2.690(20)
O-(1w)···O-1(1b)	x, y, z	2.710(30)
O-(1w)···O-3(3d)	$x, y, z+1$	2.750(30)
O-(1w)···O-4(3d)	$x+1, y, z+1$	3.090(30)
O-(1w)′···O-1(1a)	$-x+1, y-1/2, -z+1$	2.750(30)
O-(1w)′···O-3(3c)	$-x, y-1/2, -z$	2.720(30)
O-(1w)′···O-4(3c)	$-x+1, y-1/2, -z$	3.070(30)
O-(2w)···O-3(3b)	x, y, z	2.752(16)
O-(2w)···O-1(1d)	$x, y, z+1$	3.000(19)
O-(2w)···O-1(2d)	$x, y, z+1$	3.231(19)
O-(2w)···O-(4w)	$x, y, z+1$	2.840(20)
O-(3w)···O-3(3a)	x, y, z	2.744(17)
O-(3w)···O-1(1c)	$x+1, y, z+1$	3.037(19)
O-(3w)···O-(4w)	$x, y, z+1$	2.790(20)
O-(4w)···O-4(3a)	$x+1, y, z$	3.004(18)
O-(4w)···O-4(3b)	x, y, z	3.035(19)
O-(4w)···O-(2w)	$x, y, z-1$	2.840(20)
O-(4w)···O-(3w)	$x, y, z-1$	2.790(20)

[a] Estimated standard deviation values are given in parentheses and refer to the least significant digit.

note that the bond length C-1–O-7 is larger than those of C-1(i)–O-4(i-1) by 0.1 Å. This variation in length must be connected with the variation in the angle ϕ and can be well explained by the anomeric effect [20,24]. Finally, the χ and χ' torsion angles of each glucose moiety in the molecules **a** and **b** [mean (**ab**)] are systematically different by ca. 11° from those of molecules **c** and **d** [mean (**cd**)]

Organization of water and ethanol molecules.—At the extremities of each pair of methyl β-cellotrioside molecules, there are some water and ethanol molecules. The list of the distances between the oxygen atoms of water, those of ethanol and methyl β-cellotrioside are listed in Table 5. There are three water molecules [O(2w), O(3w) and O(4w)] in the plane (040). These water molecules are in close contact with respect to one another and to the methyl β-cellotrioside molecules. There are two solvent molecules in the plane (020): one of water and one of ethanol. These two solvent molecules are disordered along two positions with an occupancy factor of 1/2. Fig. 4 presents a schematic view of this disorder where the C-2(1e) atom of ethanol is common to both orientations.

Hydrogen bonding.—As described in the Experimental, the coordinates of the hydrogen atoms were not precisely refined along x, y and z. These atoms were positioned after each refinement cycle within the maximum of electron density around their respective oxygen atoms (while keeping a fixed geometry, a C–O–H angle of 110° and a distance for O–H of 0.98 Å). A list of the geometric parameters describing the hydrogen bonds is given in Table 6. In this list, hydrogen bonds are considered when the O···O distance is between 2.5 and 3.54 Å and when the corresponding angle OH···O is within the range 100–180°.

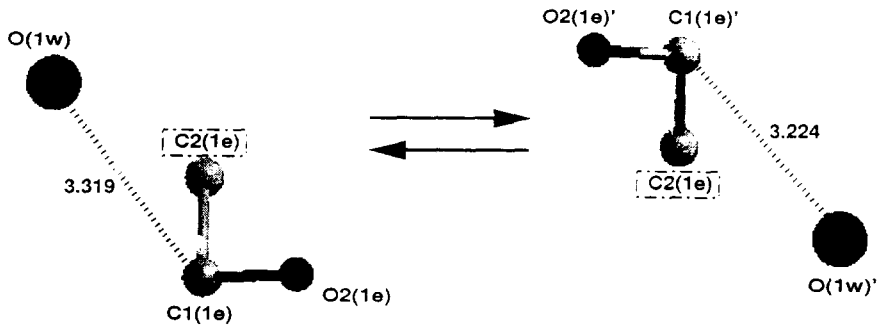

Fig. 4. Schematic drawing of ethanol–water 50:50 flip-flop disorder with C-2(1e) atom common to both orientations.

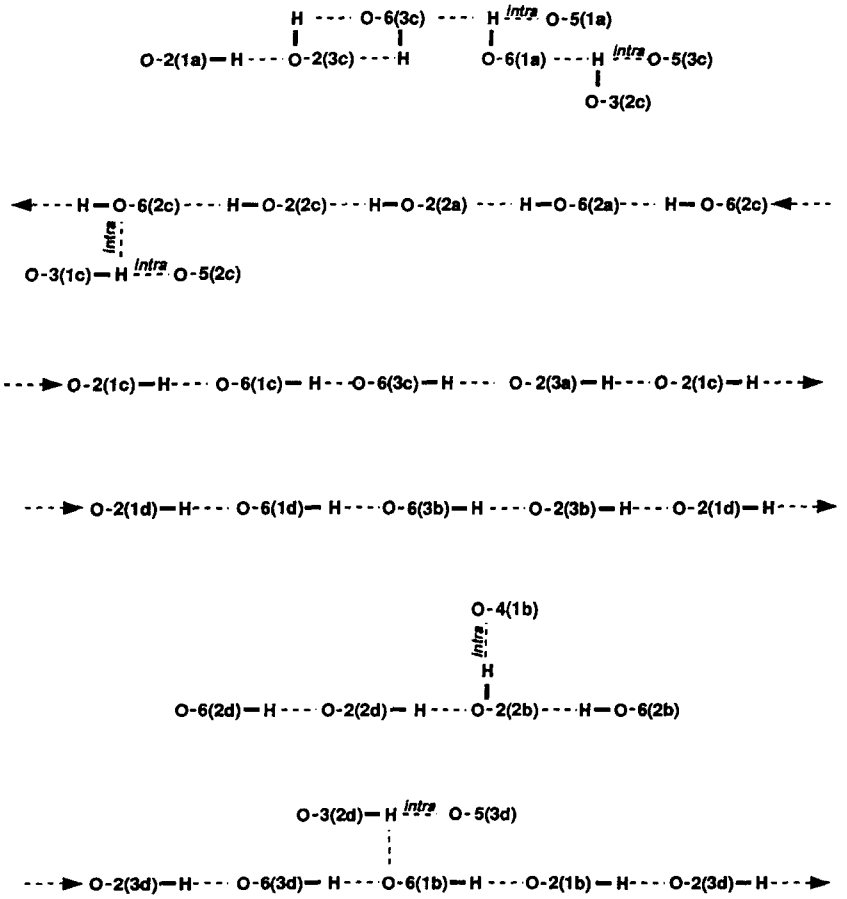

Fig. 5. Schematic drawing of intermolecular distances between O-2 and O-6 atoms for methyl β-cellotrioside.

Table 6
Geometry of hydrogen bonding for methyl β-cellotrioside [a]

O–H · · · O	sym [b]	d_{O-O} (Å)	d_{H-O} (Å)	∠O–H · · · O (°)
O-2(1a)–HO-2(1a) · · · O-2(3c)	$x+1, y, z+1$	2.813(9)	2.14(7)	139(6)
O-2(2a)–HO-2(2a) · · · O-2(2c)	$x-1, y, z$	2.727(8)	1.91(2)	170(3)
O-2(3a)–HO-2(3a) · · · O-2(1c)	$x+1, y, z+1$	2.694(9)	1.98(7)	145(8)
O-2(1b)–HO-2(1b) · · · O-2(3d)	$x, y, z+1$	2.818(9)	2.00(4)	176(6)
O-2(2b)–HO-2(2b) · · · O-4(1b)	x, y, z	2.845(9)	2.45(7)	111(6)
O-2(3b)–HO-2(3b) · · · O-2(1d)	$x, y, z+1$	2.694(9)	1.98(7)	145(8)
O-2(1c)–HO-2(1c) · · · O-6(1c)	$x-1, y, z$	2.582(11)	1.87(5)	145(8)
O-2(2c)–HO-2(2c) · · · O-6(2c)	$x+1, y, z$	2.634(9)	1.85(6)	161(7)
O-2(3c)–HO-2(3c) · · · O-6(3c)	$x-1, y, z$	2.745(11)	2.26(8)	119(7)
O-2(3c)–HO-2(3c) · · · O-3(3c)	x, y, z	2.854(11)	2.56(6)	103(4)
O-2(1d)–HO-2(1d) · · · O-6(1d)	$x+1, y, z$	2.588(11)	1.85(6)	150(10)
O-2(2d)–HO-2(2d) · · · O-2(2b)	$x-1, y, z$	2.725(8)	2.14(6)	128(5)
O-2(3d)–HO-2(3d) · · · O-6(3d)	$x+1, y, z$	2.734(11)	1.94(4)	163(8)
O-6(1a)–HO-6(1a) · · · O-5(1a)	x, y, z	2.848(9)	2.49(7)	108(4)
O-6(1a)–HO-6(1a) · · · O-6(3c)	$x-1, y, z$	2.710(11)	2.41(8)	103(7)
O-6(2a)–HO-6(2a) · · · O-2(2a)	$x+1, y, z$	2.669(9)	1.98(5)	143(4)
O-6(3a)–HO-6(3a) · · · O-2(3a)	$x-1, y, z$	2.753(11)	1.93(9)	174(9)
O-6(1b)–HO-6(1b) · · · O-2(1b)	$x+1, y, z$	2.733(10)	2.00(6)	147(6)
O-6(2b)–HO-6(2b) · · · O-2(2b)	$x-1, y, z$	2.674(9)	1.88(4)	163(4)
O-6(3b)–HO-6(3b) · · · O-2(3b)	$x+1, y, z$	2.749(10)	1.94(8)	167(10)
O-6(1c)–HO-6(1c) · · · O-6(3a)	$x+1, y, z$	2.766(12)	1.98(7)	159(8)
O-6(2c)–HO-6(2c) · · · O-2(2c)	$x-1, y, z$	2.634(9)	1.86(10)	156(8)
O-6(3c)–HO-6(3c) · · · O-2(3c)	$x+1, y, z$	2.745(11)	1.98(10)	156(8)
O-6(1d)–HO-6(1d) · · · O-6(3b)	$x-1, y, z$	2.768(11)	1.95(9)	170(8)
O-6(2d)–HO-6(2d) · · · O-2(2d)	$x+1, y, z$	2.613(9)	1.85(6)	154(7)
O-6(3d)–HO-6(3d) · · · O-6(1b)	$x-1, y, z$	2.706(11)	2.10(10)	131(10)
O-6(3d)–HO-6(3d) · · · O-5(3d)	x, y, z	2.810(11)	2.43(10)	109(7)
O-6(3d)–HO-6(3d) · · · O-3(2d)	x, y, z	3.315(11)	2.57(10)	151(10)
O-3(1a)–HO-3(1a) · · · O-5(2a)	x, y, z	2.851(10)	2.07(20)	158(3)
O-3(2a)–HO-3(2a) · · · O-5(3a)	x, y, z	2.836(10)	2.03(6)	170(10)
O-3(2a)–HO-3(2a) · · · O-4(3a)	x, y, z	2.929(9)	2.52(10)	112(7)
O-3(3a)–HO-3(3a) · · · O-(3w)	x, y, z	2.744(17)	2.08(6)	138(9)
O-3(1b)–HO-3(1b) · · · O-6(2d)	$x, y, z+1$	3.239(11)	2.58(5)	138(3)
O-3(2b)–HO-3(2b) · · · O-5(3b)	x, y, z	2.842(10)	2.07(9)	156(10)
O-3(2b)–HO-3(2b) · · · O-4(3b)	x, y, z	2.936(11)	2.58(10)	108(10)

In the present structure, all the primary hydroxyl groups are in the *gt* conformation. This implies that only one type of intramolecular hydrogen bond exists, namely O-3–HO-3 · · · O-5. All the other hydrogen bonds occur as an infinite cooperative network of intermolecular three-center bonds linking O-2 and O-6. The hydrogen bonding system is presented in Fig. 5. Fig. 6 shows two projections along the *b* axis and perpendicular to the **ac** pair (Fig. 6A) and the **bd** pair (Fig. 6B). In Fig. 6A, the system of hydrogen bonds between the molecules **a** and **c** extends parallel to the cell axis *c*. In Fig. 6B, the system of hydrogen bonds between the molecules **b** and **d** extends along the (101) direction.

Table 6 (continued)

O–H · · · O	sym [b]	d_{O-O} (Å)	d_{H-O} (Å)	∠O–H · · · O (°)
O-3(3b)–HO-3(3b) · · · O-(2w)	x, y, z	2.752(16)	1.93(2)	177(6)
O-3(1c)–HO-3(1c) · · · O-5(2c)	x, y, z	2.837(10)	2.06(9)	157(10)
O-3(1c)–HO-3(1c) · · · O-6(2c)	x, y, z	3.078(10)	2.48(8)	130(10)
O-3(2c)–HO-3(2c) · · · O-5(3c)	x, y, z	2.898(7)	2.51(9)	110(7)
O-3(2c)–HO-3(2c) · · · O-6(1a)	$x+1, y, z$	2.971(10)	2.21(5)	154(7)
O-3(3c)–HO-3(3c) · · · O-4(2d)	$-x, y+1/2, -z$	2.774(12)	2.43(9)	107(7)
O-3(3c)–HO-3(3c) · · · O-4(3c)	x, y, z	2.986(13)	2.54(7)	108(5)
O-3(1d)–HO-3(1d) · · · O-5(2d)	x, y, z	2.850(10)	2.40(9)	116(9)
O-3(2d)–HO-3(2d) · · · O-5(3d)	x, y, z	2.889(9)	2.33(9)	126(8)
O-3(2d)–HO-3(2d) · · · O-6(1b)	$x-1, y, z$	2.970(10)	2.29(10)	141(9)
O-3(3d)–HO-3(3d) · · · O-(1w)′	$x, y, z-1$	2.690(20)	1.87(6)	179(6)
O-3(3d)–HO-3(3d) · · · O-(1w)	$x, y, z-1$	2.750(30)	2.02(8)	149(6)
O-4(3a)–HO-4(3a) · · · O-3(3b)	x, y, z	2.749(10)	1.93(9)	177(5)
O-4(3b)–HO-4(3b) · · · O-3(3a)	x, y, z	2.748(11)	1.93(9)	174(10)
O-4(3c)–HO-4(3c) · · · O-3(3d)	$-x+1, y+1/2, -z$	2.759(12)	1.95(7)	170(9)
O-4(3d)–HO-4(3d) · · · O-(1w)	$x-1, y, z-1$	3.090(3)	2.29(9)	166(10)

[a] $d_{O\cdots O}$ is the distance between the two oxygen atoms. $d_{H\cdots O}$ is the distance between the atoms H and O. ∠O–H · · · O is the angle between atoms O, H and O. Estimated standard deviation values are given in parentheses and refer to the least significant digit.

[b] Symmetry transformation for the oxygen atoms.

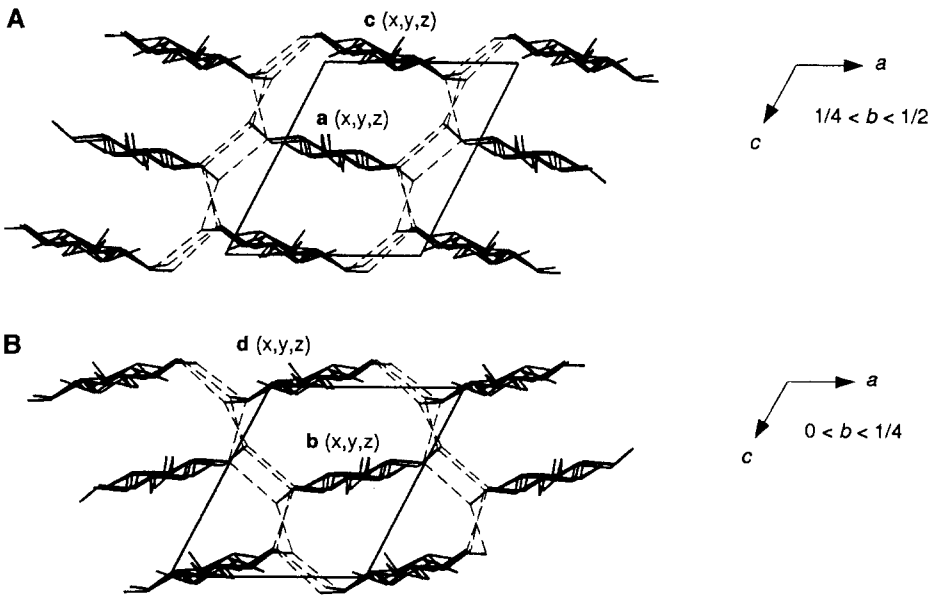

Fig. 6. Two cross sections of the unit cell showing the hydrogen-bonding system between the methyl β-cellotrioside molecules. The dashed lines are the intermolecular hydrogen bonds.

The organization of the hydrogen bonds in various projections parallel to the *b* axis is shown in Fig. 7. In Fig. 7A, the two molecules **c** and **d** located in the (001) plane are represented, whereas in Fig. 7B the two molecules **a** and **b** located at the center of the

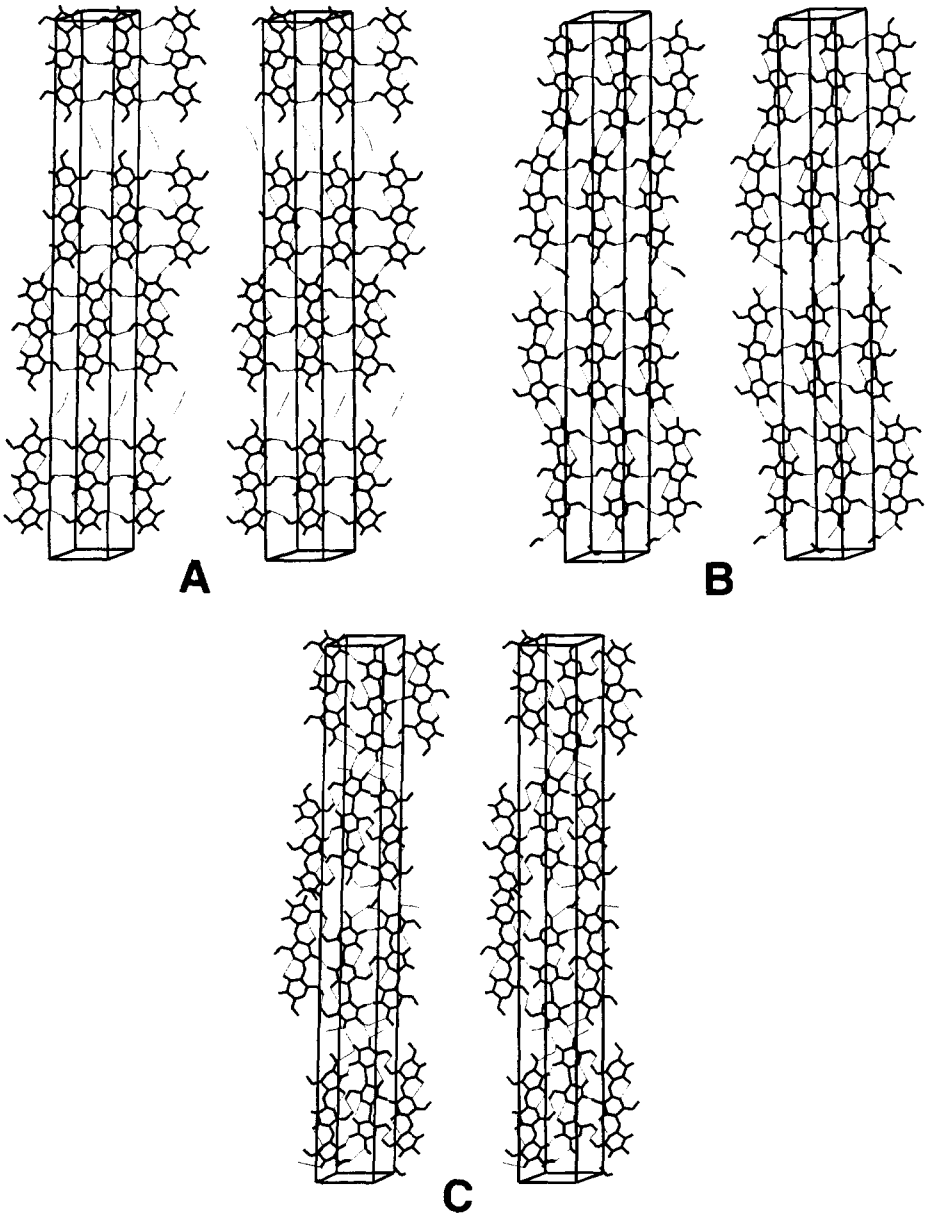

Fig. 7. Stereoviews of the packing and hydrogen bonds (thin line) between methyl β-cellotrioside molecules, ethanol, and water. A, Molecules **c** and **d** in the (001) plane. B, Molecules **a** and **b** located in the (002) plane. C, Combination of the molecules **a** and **b** (in the center) and the molecules **c** and **d** (in the corner).

unit cell in the (002) plane are shown. Finally, in Fig. 7C taken along a diagonal, there is a combination of intermolecular hydrogen bonds between the molecules in the center (**a** and **b**) with those of the corner (**c** and **d**). Fig. 7 also describes the environment of the oxygens (O-3) and (O-4) located at the extremities of methyl β-cellotrioside. Both atoms are not only linked to their neighbours by hydrogen bonds, but also to the water molecules through other hydrogen bonds.

Comparison to the structures of cellotetraose and cellulose II.—The crystalline structure of methyl β-cellotrioside presents a strong similarity with that of cellotetraose [9,10]. Both structures have almost identical cell parameters perpendicular to the long axis of their respective unit cells. In both structures, the molecules are not only organized in antiparallel pairs that are aligned along the long direction of the unit cell, but within the pairs the molecules are shifted with respect to one another by roughly half a glucose residue. In the crystal of cellotetraose, as well as that of methyl β-cellotrioside, the conformation of all the hydroxymethyl groups of the individual glucose moieties is persistently found as *gt*. As there are eight independent glucose residues in the structure of cellotetraose and 12 in methyl β-cellotrioside, this feature appears to be general for this type of cellodextrin. Finally, the similarity between cellotetraose and methyl β-cellotrioside also extends to the difference that exists between the puckering parameters of the sugar residues constituting the "up" molecules as opposed to the "down" ones. For cellotetraose, the Cremer–Pople parameter θ ranges from 2.2 to 4.8° for the "down" molecule as opposed to 6.7 to 18.9° for the "up" one. These values are quite consistent with those presented in Table 3 where the θ values range from 0 to 3.5° for the "down" molecules **a** and **b** and 9.8 to 13.6 for the "up" molecules **c** and **d**.

One of the main interests of the crystalline structure of methyl β-cellotrioside is that it presents many common features with the crystalline structure of cellulose II. Indeed, the cell parameters of the base plane of cellulose II are given after conversion to the same convention as $a = 7.96$, $b = 9.09$ Å and $\gamma = 117.3°$ [7] or $a = 8.01$, $b = 9.04$ Å and $\gamma = 117.1°$ [8]. These values compare quite closely with the parameters $a = 7.99$, $c = 8.99$ Å and $\beta = 116.4°$ obtained in this study. Both structures are monoclinic and the cellulose chain axes, as well as the molecular axes of the methyl β-cellotrioside molecules, are parallel to the respective large dimension of their unit cells, namely the chain axis for cellulose and the *b* parameter for methyl β-cellotrioside. Finally, both structures result from the packing of antiparallel molecules. Thus, it is likely that the molecular geometry, the packing as well as the hydrogen bond system of methyl β-cellotrioside, can be directly transposed to the structure of cellulose II. In fact, an excellent fit is observed when an antiparallel pair of methyl β-cellotrioside is superimposed on the structure of cellulose II given by Stipanovic and Sarko [7], or that reported by Kolpak and Blackwell [8]. The superposition achieved by displacement minimization is shown in Fig. 8A–C, where the methyl β-cellotrioside molecules are positioned on the 2_1 screw axes of cellulose. In Fig. 8A, perpendicular to the chain direction, seven molecules of cellulose and seven molecules of methyl β-cellotrioside are so well superimposed that they are indistinguishable. When the molecules labelled 1 and 2 are observed along the chain direction (Fig. 8B), the backbone of cellulose and that of methyl β-cellotrioside match almost perfectly. On the other hand the orientation of O-6 is different: *tg* for cellulose and *gt* for methyl β-cellotrioside. This difference is

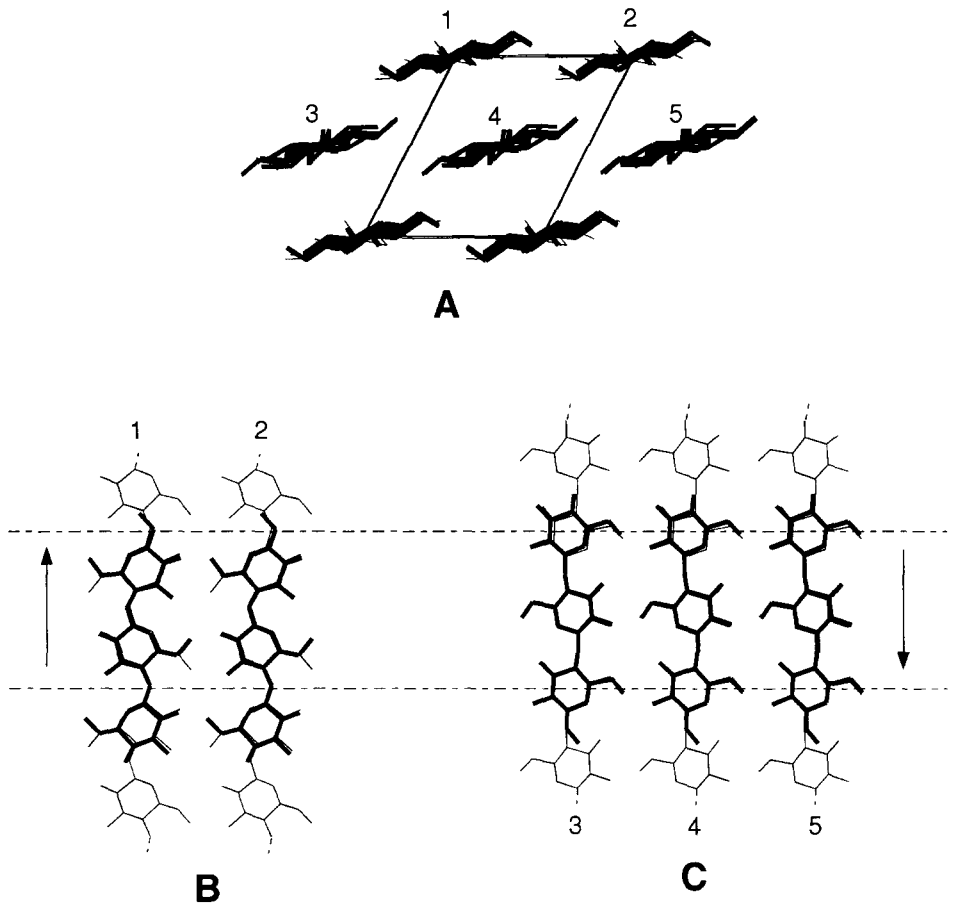

Fig. 8. Superimposition of the antiparallel methyl β-cellotrioside packing over that of cellulose II. A, Projection perpendicular to the long direction of the molecules. B, Molecules **1** and **2** projected parallel to the long direction of the molecules. C, Molecules **3**, **4**, and **5** projected parallel to the long direction of the molecules.

no longer present for molecules **3**, **4**, and **5** (Fig. 8C) since both cellulose and trisaccharide are nearly perfectly matched, both for the backbone and for the O-6 conformation, i.e. *gt* for cellulose II as well as for methyl β-cellotrioside.

The strong similarity between cellulose II and methyl β-cellotrioside indicates in particular that the packing of the cellulose molecules in cellulose II can be achieved even with all the hydroxymethyl groups in the *gt* conformation. Thus, the current model for cellulose [7,8], where only half of the chains are in *gt*, the other half being in the *tg* conformation, needs to be re-evaluated in the light of the present results. Indeed, the occurrence of a *tg* conformation at O-6 implies the presence of an intramolecular hydrogen bond between O-6 and O-2 of the next glucose moiety. Such hydrogen bonding is not observed in methyl β-cellotrioside and disagrees with at least one

analysis of polarized IR data of cellulose II [25]. Also, the ^{13}C CP/MAS NMR resonance line for C-6 in cellulose II occurs as a singlet at 64 ppm [26,27]. It is also a singlet in methyl β-cellotrioside at 64.2 ppm [6]. If cellulose II had one half of its C-6 in *tg* and the other half in *gt*, one would expect a doublet for C-6 with one line around 64 ppm and one around 66 ppm [28]. All these counter arguments are in favor of a revision of the crystalline structure of cellulose II where all the hydroxymethyl groups would be in the *gt* conformation, with a consequential modification of the hydrogen-bonding network.

Finally, our results show that there is a slight difference between the geometry of the glucose rings in the methyl β-cellotrioside molecules that are "up" versus those that are "down". It is important to see whether this situation also occurs in cellulose II. So far, the crystalline structure of cellulose II has been refined with glucose rings of fixed geometry. Our results show that some modifications in the glucose ring conformation may be expected with differences between the rings of the center chain (0.5, 0.5, 0) versus those in the corner chain (0, 0, 0). Such a difference in ring conformation is presently being tested on the refinement of the crystal structure of cellulose II. We are also making some attempts to solve the crystal structure of higher cellodextrins, namely cellopentaose and methyl β-cellotetraoside. Both molecules crystallize in packing systems that are closely related to the present one and both structures result from an antiparallel arrangement. In addition, both compounds yield micron-sized crystals that are suitable for synchrotron experiments. It would be interesting to see whether in these two oligosaccharides all the conformations at O-6 are also in *gt* and whether the conformation of the glucose residues in the molecules that are "up" are also different from those that are "down".

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