Carbohydrate Research, 114 (1983) 169–180
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THE CRYSTAL STRUCTURE OF METHYL 3,4-*O*-ISOPROPYLIDENE-2,6-DI-*O*-(2,3,4,6-TETRA-*O*-ACETYL-β-D-GALACTOPYRANOSYL)-α-D-GALACTOPYRANOSIDE AT 97 K

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(Received June 28th, 1982; accepted for publication, August 12th, 1982)

ABSTRACT

The crystal structure of methyl 3,4-*O*-isopropylidene-2,6-di-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-α-D-galactopyranoside (**1**), $C_{38}H_{54}O_{24} \cdot (C_4H_8O_2)_{0.32}$ was determined by X-ray diffraction; **1** crystallises in space group $P2_1$ with a = 12.480(3), b = 8.821(3), c = 21.182(4) Å, β = 98.46(3)°, and Z = 2. The structure was solved by Patterson-search and Fourier-recycling procedures and refined to $R_w(R)$ = 0.048(0.063), using 4348 [3112 with $I > 2\sigma(I)$] independent reflections. The β-D-galactosyl rings are slightly distorted and, due to the isopropylidene group, the α-D-galactoside ring is severely distorted. The conformation near the β-(1→6) and β-(1→2) linkages between the pyranoid rings is not significantly affected by the acetyl groups, but the anomeric C-O-C bridge angles have unusual values. The C-6–O-6 bond in the β-D-galactosyl group (1→2)-linked to the α-D-galactoside residue has an unusual *gauche–trans* conformation with respect to C-4 and O-5. The CH_3-(C=O)-O-C moieties are planar within 0.01 Å, and 32.6% of all unit cells contain a molecule of ethyl acetate.

INTRODUCTION

Although many unsubstituted carbohydrates have been investigated by X-ray diffraction methods, the number of conformational studies of substituted sugars is rather small.

However, in the last four years, substituted, especially acetylated, carbohydrates have been investigated[1–4] in order to assess the influence of the substituents on the geometry as well as the distortions of the anomeric bridge linkages.

Methyl 3,4-*O*-isopropylidene-2,6-di-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-α-D-galactopyranoside (**1**) is an intermediate in the synthesis of oligosaccharides[5]. In the absence of hydroxyl groups (Fig. 1) and, consequently, of hydrogen bonds, it is of interest to study the influence of the acetyl and isopropylidene groups on the conformation and overall shape of the molecule. The numbering of the atoms is indicated in Fig. 1.

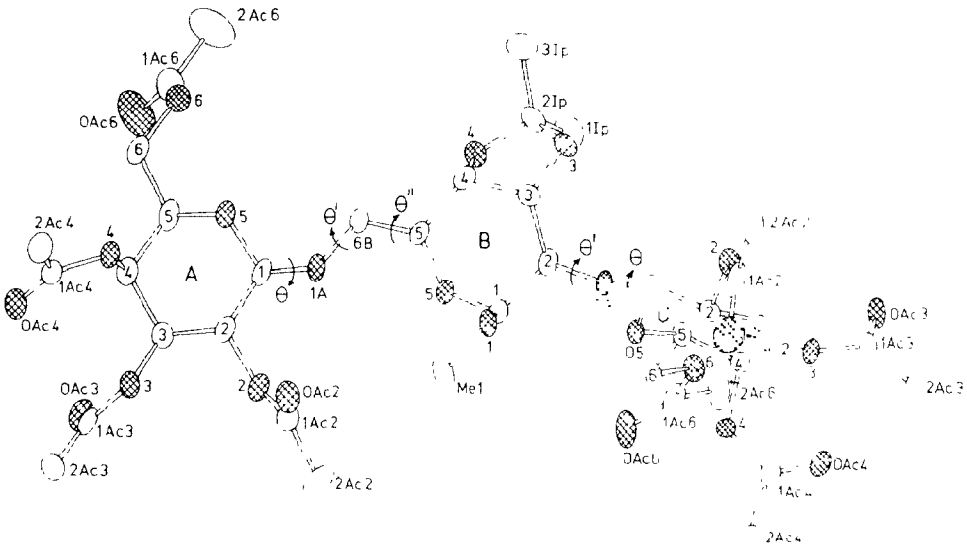

Fig. 1. ORTEP projection of the molecule with omission of the hydrogen atoms. The carbon atoms are open and the oxygen atoms are hatched. The numbering of the atoms is indicated. The contours of the atoms represent 50% probability ellipsoids. The angles θ, θ', and θ'' are defined by θ $\equiv$ φ(O-5A–C-1A–O-1A–C-6B), θ' $\equiv$ φ(C-1A–O-1A–C-6B–C-5B), and θ'' $\equiv$ φ(O-1A–C-6B–C-5B–O-5B) in the β-(1→6) linkage, and by θ $\equiv$ φ(O-5C–C-1C–O-2B–C-2B) and θ' $\equiv$ φ(C-1C–O-2B–C-2B–C-1B) in the β-(1→2) linkage.

EXPERIMENTAL

Crystals were grown by diffusion of 330 μL of 1-propanol into a solution of 3 mg of **1** in 420 μL of ethyl acetate. A lath-shaped crystal (0.6 × 0.3 × 0.15 mm) was put into a sealed glass-capillary and mounted on a Nonius CAD-4 diffractometer. The lattice constants are a = 12.708(3), b = 8.942(4), c = 21.202(6) Å, β = 99.13(2)°, and V = 2379 Å^3 at 293 K; and a = 12.480(3), b = 8.821(3), c = 21.182(4) Å, β = 98.46(3)°, and V = 2306 Å^3 at 97 K. The space group is $P2_1$. Assuming Z to be 2 and the molecular composition to be $C_{38}H_{54}O_{24} \cdot (C_4H_8O_2)_{0.32}$, the calculated density d_x was 1.330 g.cm^{-3} at 97 K. The linear absorption coefficient μ(MoKα) was 1.2 cm^{-1}. Graphite-monochromated Mo-Kα radiation (λ 0.71073 Å) was used for the collection of diffraction intensities from one crystal at 293 and 97 K in the range $2° < \theta < 25°$ for both sets of data. The number of symmetry-independent reflections collected at 97 K (293 K) was 4348 (4476) and the number of reflections with $I > 2\sigma(I)$ was 3112 (2314). The intensities were corrected for loss of scattering power of the crystal during exposure (14% at 97 K; 10% at 293 K). No absorption correction was applied.

STRUCTURE DETERMINATION

Attempts to solve the structure by direct methods, using room temperature

TABLE I

POSITIONAL PARAMETERS ($\times 10^4$) AND B(eq) ($Å^2 \times 10$) OF THE NON-HYDROGEN ATOMS[a]

Atom	x/a	y/b	z/c	*B(eq)*
*C-1A	2745(3)	1346	5627(1)	23(1)
O-1A	3177(2)	1538(3)	5066(1)	24(1)
C-2A	3385(3)	82(5)	5995(1)	24(1)
O-2A	3149(2)	−1308(3)	5653(1)	31(1)
C-7	3947(6)	−1885(6)	5352(2)	39(1)
O-7	4811(3)	−1293(5)	5354(1)	42(1)
C-8	3588(6)	−3357(6)	5032(2)	64(2)
C-3A	3038(3)	−138(5)	6642(2)	24(1)
O-3A	3771(2)	−1214(3)	6979(1)	27(1)
C-9	3368(4)	−2117(6)	7399(2)	29(1)
O-9	2429(3)	−2100(3)	7467(1)	37(1)
C-10	4217(4)	−3071(6)	7756(2)	36(1)
C-4A	3071(3)	1351(5)	7008(2)	25(1)
O-4A	4183(2)	1871(3)	7183(1)	23(1)
C-11	4689(3)	1502(5)	7778(2)	24(1)
O-11	4298(2)	694(3)	8138(1)	29(1)
C-12	5776(4)	2195(6)	7896(2)	33(1)
C-5A	2486(3)	2584(5)	6581(2)	26(1)
O-5A	2904(2)	2699(3)	5995(1)	25(1)
C-6A	2592(4)	4119(5)	6896(2)	29(1)
O-6A	2002(2)	5269(3)	6492(1)	30(1)
C-13	965(4)	5460(6)	6573(2)	37(1)
O-13	521(3)	4709(5)	6916(2)	58(1)
C-14	458(5)	6744(8)	6142(3)	64(2)
C-1B	3001(4)	542(5)	3174(2)	26(1)
O-1B	4119(2)	425(3)	3277(1)	31(1)
C-15	4497(5)	−734(6)	3747(2)	45(2)
C-2B	2659(3)	1694(5)	2662(1)	21(1)
O-2B	3041(2)	1269(3)	2083(1)	20(1)
C-3B	3041(3)	3286(5)	2863(2)	22(1)
O-3B	2397(2)	4395(3)	2486(1)	25(1)
C-4B	2806(3)	3647(5)	3534(2)	21(1)
O-4B	1688(2)	4060(3)	3419(1)	25(1)
C-17	443(4)	4428(6)	2459(2)	38(1)
C-16	1516(4)	4874(5)	2820(2)	29(1)
C-18	1630(4)	6573(5)	2940(2)	36(1)
C-5B	3021(3)	2347(5)	3999(1)	22(1)
O-5B	2562(2)	952(3)	3733(1)	26(1)
C-6B	2606(3)	2567(5)	4617(1)	24(1)
C-1C	2205(3)	1102(5)	1574(1)	17(1)
C-2C	2668(3)	600(5)	981(1)	18(1)
O-2C	3295(2)	1847(3)	787(1)	20(1)
C-19	4345(3)	1559(6)	716(2)	28(1)
O-19	4743(2)	313(5)	782(1)	37(1)
C-20	4894(4)	2959(7)	546(2)	38(1)
C-3C	1741(3)	287(5)	443(1)	16(1)
O-3C	2207(2)	−354(2)	−73(1)	17(1)
C-21	1577(3)	−300(5)	−658(1)	20(1)
O-21	735(2)	374(3)	−749(1)	24(1)

TABLE I *(continued)*

Atom	x/a	y/b	z/c	*B(eq)*
C-22	2081(3)	-1146(6)	1143(2)	27(1)
C-4C	918(3)	800(5)	662(1)	16(1)
O-4C	1436(2)	2260(2)	810(1)	17(1)
C-23	1267(3)	3328(5)	346(2)	20(1)
O-23	757(2)	3134(3)	-168(1)	23(1)
C-24	1821(4)	4770(5)	580(2)	31(1)
C-5C	579(3)	214(5)	1271(1)	18(1)
O-5C	1508(2)	53(3)	1746(1)	18(1)
C-6C	174(3)	1253(5)	1564(1)	19(1)
O-6C	- 1193(2)	- 1226(3)	1145(1)	21(1)
C-25	-1983(3)	2034(5)	1347(2)	23(1)
O-25	- 1848(2)	2726(3)	1845(1)	30(1)
C-26	3004(3)	-1951(6)	892(2)	31(1)
C-1Ea	-1152(12)	3688(19)	5571(8)	55(4)
O-1Ea	595(13)	3216(19)	5356(8)	107(5)
C-2Ea	239(14)	3918(24)	5248(11)	111(8)
O-2Ea	- 244(15)	5269(18)	4948(8)	125(6)
C-3Ea	328(15)	5443(19)	4404(7)	59(4)
C-4Ea	623(26)	7144(22)	4414(14)	119(9)

[a]Estimated standard deviations in the least-significant digits are given in parentheses. The x/b parameter of the marked atom was fixed during refinement. B(eq) $\frac{8}{3}\pi^2$ trace ($\bar{U}$).

data and, later, the data collected at 97 K, failed altogether. Although the multiple-solution program MULTAN in its latest version[6] was available and the statistics of the calculation of E values was improved by assuming the presence of six pyranoid rings and sixteen acetyl groups in random position and orientation, the resulting F maps could not be interpreted.

The structure was solved by the Patterson-search method[7]. Using 11 atoms of α-D-glucose as a trial model for the galactose moiety, a rotation and translation search was performed. These calculations did not lead to the correct solution until the rotational and translational increments were reduced to 5° and 0.15 Å, respectively. The failure with larger steps was caused by the extreme sharpness of the minimum corresponding to the correct position. The five most-promising solutions were inspected by refining the atomic positions using an overall temperature factor. The best solution (R = 0.46) was used in a Fourier-recycling procedure[8], taking the 40 highest Fourier peaks in each cycle. After seven cycles, 37 peaks corresponded with a reasonable geometry. Using these positions, the atoms still missing (25) were found in a search for 62 peaks in seven subsequent cycles.

Using individual, isotropic temperature factors and refining the parameters of all atoms, the weighted R-factor, $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{\frac{1}{2}}$, where $w = \bar{\sigma}^2(F_o)$, from 0.29, dropped to 0.134. Difference Fourier maps revealed peaks that could be interpreted as a molecule of ethyl acetate occupying 32.6(5)% of the possible

locations. Since its atomic positions were badly defined (see packing), the geometry of the ethyl acetate molecule was constrained during further refinement. With the exception of the hydrogen atoms H-8‴, H-14‴, and H-26‴, and the hydrogens of the ethyl acetate molecule, all hydrogen atoms were located in difference Fourier maps. During further cycles, the hydrogen atoms were kept at fixed orientations and fixed distances (1.0 Å) with respect to the bonded C atoms, but their isotropic B values were refined.

The matrix of normal equations was split into four blocks, three of which contained the atomic parameters of each sugar ring while the fourth contained those of the ethyl acetate molecule. Using the same blocks, anisotropic refinement of the heavy atoms resulted in $R_w = 0.048$ and $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.063$. The scattering factors of C, H, and O were taken from ref. 9.

The refinement using room temperature data did not result in an acceptable structure. The resulting $R_w(R)$ factors were unsatisfactory: 0.086 (0.133). Lack of significant data and possible rotational disorder about the ester linkage of the acetyl groups may have been responsible.

The positional parameters of the heavy atoms, their standard deviations, and the B(eq) values are given in Table I. The hydrogen positions, the anisotropic vibrational parameters, and a list of observed and calculated structure factors have been deposited*.

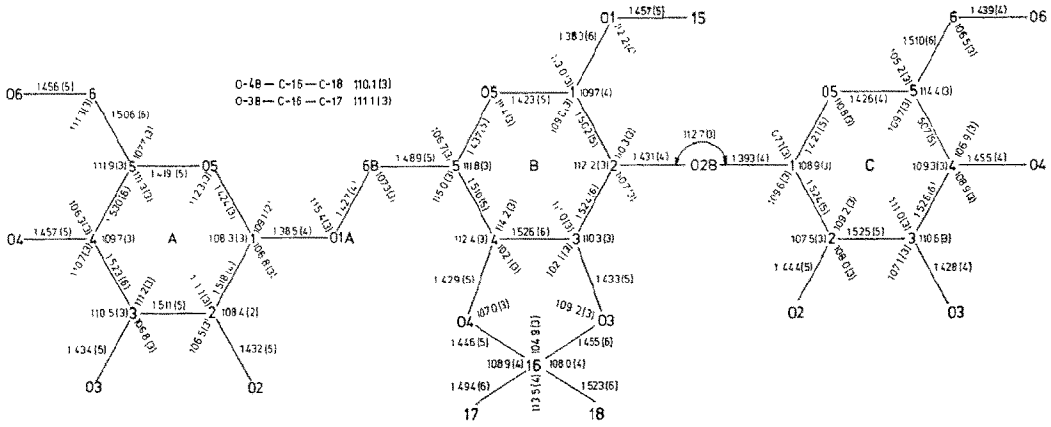

Fig. 2. Bond distances (Å) and bond angles (°). Estimated standard deviations in the least-significant digit are given in parentheses.

*The vibrational parameters U_{ij} of the heavy atoms, the co-ordinates and B values of the H atoms, and a list of structure factors F_o and F_c are deposited with, and can be obtained from: Elsevier Scientific Publishing Company, BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/240/*Carbohydr. Res.*, 114 (1983) 169–180.

TABLE II

AVERAGE VALUES (Av), RANGE (δ), STANDARD DEVIATION (σ) (CALCULATED FROM INDIVIDUAL E.S.D. VALUES), AND ESTIMATOR S $[n^{-1}(n-1)^{-1}\Sigma_i(p_i - p_{Av})^2]^{\frac{1}{2}}$ OF BOND DISTANCES (Å) AND BOND ANGLES (°) OF ACETYL GROUPS

Compound[a]		*C-O*	*C=O*	*C-C*	*O-C=O*	*C-C-O*	*C-C=O*	*n*
1								
	δ	0.031	0.029	0.059	2.5	2.1	0.6	8
	Av	1.356	1.197	1.489	123.1	110.7	126.1	
	σ	0.0017	0.0019	0.0023	0.13	0.12	0.14	
	S	0.0041	0.0033	0.0068	0.31	0.29	0.07	
2								
	δ	0.011	0.006	0.013	1.8	1.7	1.0	4
	Av	1.353	1.195	1.491	123.1	111.1	125.8	
	σ	0.0032	0.0032	0.0036	0.20	0.20	0.20	
	S	0.0023	0.0014	0.0029	0.43	0.35	0.28	
3								
	δ	0.031	0.026	0.049	1.6	2.3	2.1	8
	Av	1.348	1.190	1.486	122.3	110.9	126.8	
	σ	0.0026	0.0032	0.0044	0.22	0.22	0.27	
	S	0.0035	0.0032	0.0061	0.19	0.25	0.27	
Total average of **1**, **2**, *and* **3**								
	δ	0.037	0.035	0.067	2.9	2.5	2.5	20
	Av	1.354	1.195	1.489	122.9	110.8	126.1	
	σ	0.0013	0.0015	0.0017	0.10	0.09	0.11	
	S	0.0022	0.0020	0.0036	0.20	0.16	0.15	
Acetic anhydride[37]								
	Av	1.405	1.183	1.493	121.7	114.5	123.8	1
	σ	0.001	0.001	0.002	0.2	0.2	0.2	
Acetic acid[38]								
	Av	1.319	1.229	1.478	121.1	113.8	125.1	1
	σ	0.006	0.005	0.006	0.5	0.3	0.5	

[a] **2**, 2,4-Dinitrophenyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside[1]. **3**, 1,2,4,6-Tetra-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl-D-galactopyranosyl)-α-D-galactopyranose[11].

MOLECULAR GEOMETRY

Omitting the acetyl groups, the bond distances and valence angles are shown in Fig. 2. The average geometry of the acetyl groups is given in Table II. The endocyclic and a number of salient exocyclic torsion angles are given in Table III.

Fig. 1 clearly shows that A and C are β-D-galactopyranosyl groups, whereas B is the corresponding α anomer. The linkage between A and B is β-(1→6), whereas C and B are β-(1→2)-linked (see Figs. 1 and 3); the β-(1→2) linkage in **1** is the first example of such connection between two galactopyranose residues.

Disregarding the acetyl groups and the isopropylidene group, the C-C bond distances vary between 1.489(5) and 1.530(6) Å. The mean value [1.515(11) Å] is in close agreement with the corresponding average [1.520(11) Å] of five galactopyranose

TABLE III

TORSION ANGLES (°, ESTIMATED STANDARD DEVIATIONS IN THE LEAST-SIGNIFICANT DIGIT ARE GIVEN IN PARENTHESES)

(a) Endocyclic torsion angles			
	Ring A	*Ring B*	*Ring C*
C-1–C-2–C-3–C-4	−52.5(4)	−46.6(5)	−52.3(4)
C-2–C-3–C-4–C-5	49.1(4)	40.7(4)	52.0(4)
C-3–C-4–C-5–O-5	−53.6(4)	−47.1(5)	−57.8(4)
C-4–C-5–O-5–C-1	62.8(4)	60.0(4)	66.4(4)
C-5–O-5–C-1–C-2	−63.8(4)	−65.9(4)	−66.2(4)
O-5–C-1–C-2–C-3	58.1(4)	59.3(5)	58.2(4)
Puckering parameters (Cremers and Pople[39])			
	Ring A	*Ring B*	*Ring C*
Q(Å)	0.564(4)	0.539(4)	0.593(4)
θ(°)	5.9(1)	13.9(1)	5.9(1)
ϕ(°)	27.9(3)	35.1(1)	5.4(1)
(b) Exocyclic torsion angles			
	Ring A	*Ring B*	*Ring C*
O-1–C-1–C-2–O-2	−67.8(4)	58.9(4)	−68.0(4)
O-2–C-2–C-3–O-3	69.0(4)	77.4(4)	70.3(4)
O-3–C-3–C-4–O-4	50.6(4)	36.6(4)	54.2(3)
O-4–C-4–C-5–C-6	−54.5(4)	−53.3(4)	−58.0(4)
C-4–C-5–C-6–O-6	−178.2(4)	−160.4(3)	−69.4(4)
O-5–C-5–C-6–O-6	59.2(4)	75.0(4)	170.1(3)
C-3–C-4–O-4–C-16		−36.6(4)	
C-4–O-4–C-16–O-3		22.3(4)	
O-4–C-16–O-3–C-3		2.4(4)	
C-16–O-3–C-3–C-4		−23.9(4)	
(c) Linkages between the rings			
β-(1→6) between A and B			
θ	O-5A–C-1A–O-1A–C-6B	−69.9(4)	
	C-2A–C-1A–O-1A–C-6B	173.3(4)	
θ'	C-1A–O-1A–C-6B–C-5B	−166.8(3)	
θ''	O-1A–C-6B–C-5B–O-5B	75.0(4)	
β-(1→2) between C and B			
θ'	C-1B–C-2B–O-2B–C-1C	121.7(4)	
	C-3B–C-2B–O-2B–C-1C	−113.6(3)	
θ	C-2B–O-2B–C-1C–O-5C	−60.2(4)	
	C-2B–O-2B–C-1C–C-2C	−178.2(3)	

compounds[10] and the value [1.515(6) Å] reported by Foces-Foces *et al.*[11]. The C–O bonds can be divided into two groups: (*a*) the anomeric bonds C-1–O-1 [3X, 1.383–1.393 Å, mean value 1.387(5) Å] and (*b*) all other C–O bonds [21X, 1.419–1.457 Å, mean value 1.437(13) Å]. Comparison with Sheldrick's data[10] shows that the average values of (*a*) and (*b*) agree with the corresponding values 1.401(10) and 1.430(10) Å of the compounds reported.

The endocyclic valence angles vary between 108.3(3) and 114.2(3)°. These

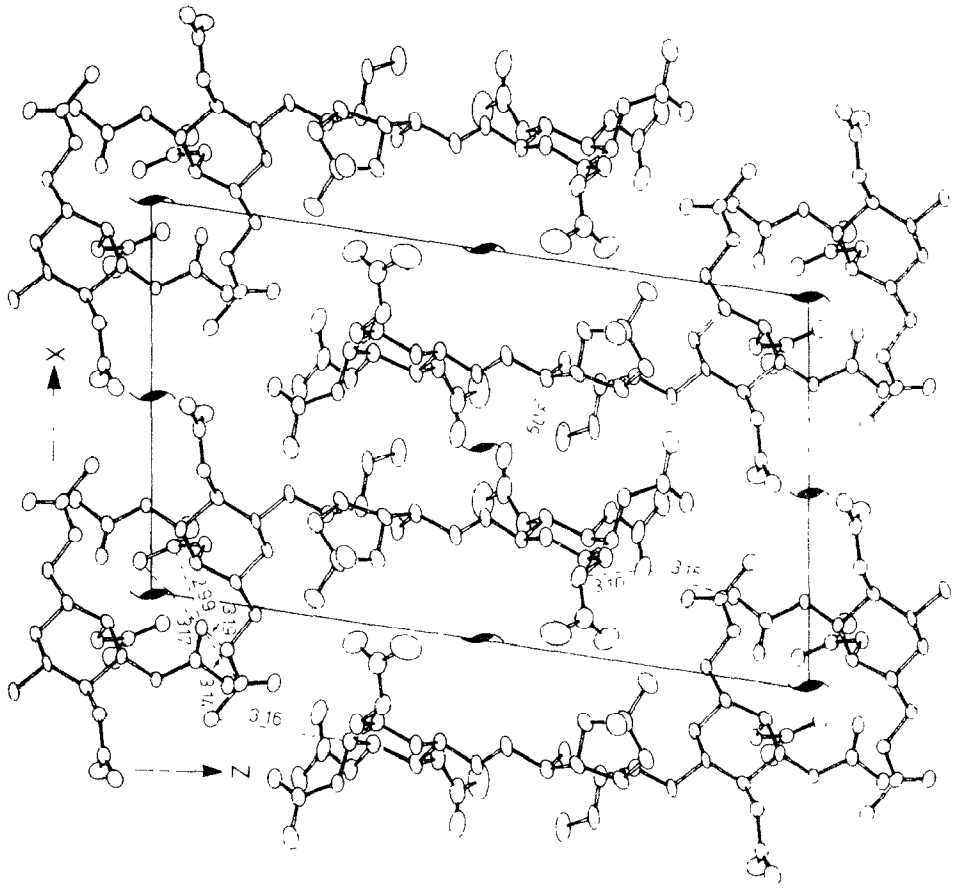

Fig. 3. An ORTEP projection along [010], illustrating the packing of the molecule. A few short C---O and O---O distances are indicated, as well as the contours of the unit cell.

variations more or less reflect variations in the endocyclic torsion angles[12] and are indicative of distortions of the pyranoid rings. Table IIIa shows that the puckering of all rings is largest at atoms O-5 and C-1, and smallest at C-3 and C-4. This phenomenon is observed in most pyranoid compounds[13]. Rings A, B, and C have distorted $^4C_1$ conformations. Due to the presence of the isopropylidene group, the distortion is largest for ring B, but not as large as was observed in similar compounds, *i.e.*, methyl 3,4-*O*-ethylidene-*β*-D-galactopyranoside[14] and methyl 3,4-*O*-isopropylidene-*β*-L-*erythro*-pentopyranosid-3-ulose[15]. In comparison with our value of 40.7(4)°, the torsion angle φ(C-2–C-3–C-4–C-5) is reduced to 34.5 and 34.1°, respectively, in the latter compounds. Following the method of Jeffrey and Yates[16], rings A and B are slightly twisted towards the half-chair $^0H_1$, whereas ring C is distorted towards the half-boat ^0E (see Table III).

The five-membered ring containing the isopropylidene group has the shape of an envelope with C-4 as the flap (see Table IIIb and Fig. 1). This conformation is

dictated by the axial and equatorial connections of O-4B and O-3B to the pyranoid ring. The geometry of the five-membered ring requires a small value of the exocyclic torsion angle $\varphi_0 = \varphi$(O-3B–C-3B–C-4B–O-4B) = 36.6(4)°, compared to the values of 50.6(4)° and 54.2(3)° of the equivalent torsion angles in rings A and C, respectively (see Table IIIb). We believe this is the main reason for the greater distortion of the inner galactose ring. Defining the dihedral angle $\varphi_1 = \varphi$(C-3B–C-4B–O-4B–C-16), *etc.*, a pseudo-rotation phase angle $\Delta = -15.8(7)°$ and $\varphi_{max} = 38.7(2)°$ are calculated[17]. The corresponding pseudorotation parameters deduced from the structures of Lindberg[14] and Palmer and Palmer[15] are $\Delta = -31.7°$, $\varphi_{max} = 40.6°$, and $\Delta = -25.6°$, $\varphi_{max} = 40.8°$, respectively. The earlier reported φ_{max} values[18,19] of four dioxolane rings (27.0, 29.5, 37.6, and 30.3°) are much smaller, because these rings are spiro-connected with steroid molecules; for this reason, the torsion angles of those compounds are less dictated by the demands of the central ring system.

The acetal parts of rings A and C have an (*ap*, *-sc*) conformation[20]. According to calculations by Jeffrey *et al.*[21], this conformation has the lowest energy. The acetal part of ring B has a (*+sc*, *+sc*) conformation, a form predicted for α-pyranoses.

The linkage between the pyranoid rings can be described by the torsion angles of the bonds connecting the rings. Adopting the nomenclature of Jeffrey and French[13] (see also Fig. 1), the torsion angle θ' [−166.8(3)°] slightly deviates from the ideal *trans* orientation. This *trans* connection is approximately the same as observed[13] in α-(1→6)-linked sugars, but results for **1** in a roughly parallel orientation of rings A and B, in contrast with the more perpendicular orientation in the α-(1→6) linkages. It follows from the value of θ'' [75.0(4)°] that the conformation about the bond

TABLE IV

LINKAGES BETWEEN RINGS IN SOME β-(1→3)- AND β-(1→4)-LINKED PYRANOSIDES, DESCRIBED BY MEANS OF DIHEDRAL ANGLES θ AND θ' GIVEN IN DECIMAL DEGREES

Compound	θ	θ'	*Ring types*	*Ref.*
β-(1→3)-Linked rings				
β-Laminarabiose	−94	78	Glc–Glc	34
Methyl β-laminarabioside hepta-acetate	−84	128	Glc–Glc	35
Digalactose α-octa-acetate	−71	145	Gal–Gal	11
β-(1→4)-Linked rings				
β-Cellobiose	−76	106	Glc–Glc	28
β-Cellobiose octa-acetate	−77	134	Glc–Glc	29
Methyl β-cellobioside	−91	80	Glc–Glc	30
β-Cellotriose	−98	102	Glc–Glc	2
	−75	134	Glc–Glc	31
α-Lactose	−93	95	Gal–Glc	32
Lactose · $CaCl_2$	−76	108	Gal–Glc	33
Lactose · $CaBr_2$	−77	107	Gal–Glc	36

C-5B–C-6B is $+sc$. This conformation has been observed in planteose · H_2O[22] and in stachyose · $5H_2O$[23], but the $-sc$ conformation frequently occurs[13] in α-(1→6)-linked glucose or fructose residues. Due to steric hindrance between O-1A and O-4B, this conformation is, however, very unfavourable for galactose compounds. The absolute values of θ'' in $+sc$ conformations are somewhat larger (+64 to +87°) than the corresponding values in $-sc$ conformations (−62 to −65°). The torsion angle θ [−69.9(4)°] is almost identical to the value given by Foces-Foces *et al.*[11] [−71.2(4)°] and does not appear to be influenced by the packing.

The torsion angle θ in the β-(1→2) linkage [−60.2(4)°] has nearly the ideal value predicted by Jeffrey *et al.*[21], but differs markedly from the usual values in β-(1→3)- and β-(1→4)-linked pyranosides. The values occurring in β-(1→3)- and β-(1→4)-linked pyranosides (see Table IV) fall within the range of −71 to −98°. The *ab initio* calculations[21] suggest that a shift of θ from these observed values to −60° corresponds to a decrease of 3 kcal/mol in potential energy. Apparently, crystal packing and, particularly, the presence in some structures of the hydrogen bond O-5···H—O-3 may explain the larger values of θ observed.

The eclipse of bond O-2B–C-1C with respect to C-2B–H-2B is illustrated by the large value [121.7(4)°] of θ'. Most values of θ' in β-(1→3) and β-(1→4) structures range from 90 to 140° (Table IV). Apparently, the actual value of θ' mainly results from steric interactions, in our case in the neighbourhood of the screw axis 0,y,0 (see packing). Fig. 1 shows that ring C is viewed obliquely in comparison with the on-top view of rings A and B. According to the convention of Sundararajan and Rao[24], the linkage between B and C can be described with the torsion angles $\omega = \varphi$(C-1C-O-1C–C-2B–H-2B) = 3.9(4)° and $\varphi = \varphi$(H-1C–C-1C–O-1C–C-2B) = 61.5(4)°.

According to Kanters *et al.*[25], the C-O-C angle in the (1→6) linkage should be smaller than the corresponding angle in the (1→2) linkage. In this structure, the respective values [115.4(3) and 112.7(3)°] clearly indicate that this rule does not apply for the title compound.

The eight acetyl groups are virtually identical. A statistical analysis (Table II) resulted in the following values: l(C-O) = 1.356(2), l(C=O) = 1.197(2), l(C-C) = 1.489(2) Å, α(O-C=O) = 123.1(1), α(C-C-O) = 110.7(1), and α(C-C=O) = 126.1(1)°. These numbers differ at most by 2% from the corresponding average values, taken from 20 observations concerning three acetylated sugar compounds (see Table II). According to Lide[26], the C–C bond length adjacent to a carbonyl bond should be 1.501 ±0.004 Å, which agrees fairly well with the experimental value.

Some relevant geometrical parameters of the acetyl groups are tabulated in Table V. The C-(C=O)-O moieties are planar to within 0.015 Å. The carbon atoms in the ester linkages are at most 0.15 Å from the acetyl least-squares planes. This peculiarity of acetyl groups linked to ring systems was first observed by Mathieson[27]. Mathieson also pointed out that the dihedral angle between the carbonyl bond and the exocyclic C–H bond, *e.g.*, (O=C···O···C-H) (see Table V, column 4), should be approximately zero if the carbon atom is tertiary (a ring carbon) and *gauche–gauche* if the carbon atom is secondary (C-6A or C-6C). Table V indicates that Mathieson's

TABLE V

PLANES THROUGH THE ACETYL GROUPS, AND THE ORIENTATION WITH RESPECT TO THE RINGS

Position	*Maximum deviation (Å) from plane*[a]	*Distance (Å) of C(n) with respect to plane*[a]	*Orientation*[b] (°)
2A	0.004(4)	0.031(6)	−14.4(4)
3A	0.005(4)	0.114(6)	−9.9(4)
4A	0.010(3)	0.094(7)	28.7(4)
6A	0.010(4)	0.062(7)	−32.4(4)[c]
			−157.3(6)[d]
2C	0.002(3)	0.064(5)	9.9(3)
3C	0.004(3)	0.149(6)	−36.1(4)
4C	0.002(6)	0.047(11)	30.4(4)
6C	0.015(4)	0.000(7)	55.1(4)[c]
			−54.2(4)[d]

[a]The acetyl groups are described with respect to the best planes through atoms of the C-(C=O)-O moieties, 2A, 3A, *etc.*, being the atomic numbering of the galactose oxygen atom to which the acetyl group is linked. [b]The orientation of the acetyl group is defined as the dihedral angle φ(O=C---O---C-H). [c]Dihedral angle with respect to H-6′A or H-6′C. [d]Dihedral angle with respect to H-6″A or H-6″C.

rule is valid for the tertiary ring atoms within 36°, with an average of 22°. The rule also applies for the secondary atom C-6C, the dihedral angles being 55.1 and −54.2°, but is non-valid for the secondary atom C-6A, the relevant angles being −32.4° and −157.3°.

PACKING

Fig. 3 is a projection of the structure viewed along [010]. The rings A are clustered around the twofold screws at 0,y,0, giving 8 H---H contacts within 2.8 Å. The structure is less dense about the screws $\frac{1}{2}$,y,0 and $\frac{1}{2}$,y,$\frac{1}{2}$, and even empty about 0,y,$\frac{1}{2}$. This "channel" is occupied by ethyl acetate solvent molecules (see refinement). Since ethyl acetate has to be accommodated with its largest dimension (~4.8 Å > half the repeating unit *b*) parallel to *b*, at most one molecule per unit cell can be present. A few short O---O and C---O contacts are indicated in the Figure. Taking an upper limit of 3.5 Å and disregarding all H---H contacts, the molecule x,y,z is surrounded by 12 neighbours at positions ± 1 + x,y,z; x,± 1 + y,z; − x,$\pm\frac{1}{2}$ + y, − z; − x,$\pm\frac{1}{2}$y,1 − z; x,y,± 1 + z; and 1 − x,$\pm\frac{1}{2}$ + y,1 − z.

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