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APPLICATION OF VICINAL CARBON–PROTON COUPLING CONSTANTS TO THE CONFORMATIONAL ANALYSIS OF BENZYLIDENE-TYPE ACETALS OF 1,6-ANHYDRO-β-D-HEXOPYRANOSES

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ABSTRACT

^{13}C-N.m.r. chemical shifts and $^3J_{C,H}$ values have been used to investigate the conformation of dioxolane-type acetals of 1,6-anhydro-β-D-hexopyranoses. The crystal structures of some of these compounds have been determined by X-ray diffraction methods. The conformations in solution accord with those in the solid state.

INTRODUCTION

Dioxolane-type acetals *cis*-fused to dioxolane rings distort the usual chair conformation of the six-membered ring[1,2]. The conformation in solution of pyranoid rings can be investigated by ^{1}H-n.m.r. spectroscopy[3], but this technique is not adequate to study the conformation of dioxolane rings. Carbon–proton vicinal couplings also depend on torsion angles and may give information on the conformation of these rings. Acetal carbons of dioxolane-type acetals *cis*-fused to pyranoid rings show heteronuclear coupling only with axial bridgehead protons, and the values of these couplings and the chemical shifts of the signals of the carbons involved in the dioxolane ring can be correlated with the configuration of the acetal carbon[1]. In order to relate heteronuclear couplings with torsion angles in dioxolane-type acetals of carbohydrate derivatives, it is necessary to study such rigid molecules as the dioxolane-type acetals of 1,6-anhydro-β-D-hexopyranoses[4,5]. We now report on the ^{1}H- and ^{13}C-n.m.r. spectra of 2-*O*-acetyl-1,6-anhydro-3,4-*O*-(*S*)-benzylidene-β-D-galactopyranose (**1**), 2-*O*-acetyl-1,6-anhydro-3,4-*O*-(*R*)-benzylidene-β-D-galactopyranose (**2**), 4-*O*-acetyl-1,6-anhydro-2,3-*O*-(*S*)-benzylidene-β-D-mannopyranose (**3**), 4-*O*-acetyl-1,6-anhydro-2,3-*O*-(*R*)-benzylidene-β-D-mannopyranose (**4**), 1,6-anhydro-4-*O*-benzoyl-2,3-*O*-(*S*)-benzylidene-β-D-gulopyranose (**5**), and 1,6-anhydro-4-*O*-benzoyl-2,3-*O*-(*R*)-benzylidene-β-D-gulopyranose (**6**). The crystal and molecular structures of **1**–**3** have been determined.

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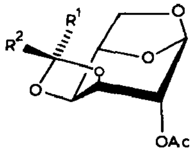
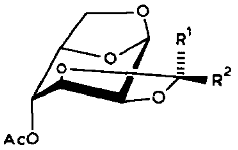
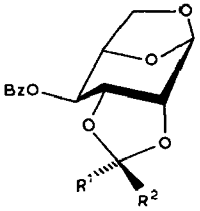


1 $R^1 = Ph, R^2 = H$
2 $R^1 = H, R^2 = Ph$



3 $R^1 = Ph, R^2 = H$
4 $R^1 = H, R^2 = Ph$



5 $R^1 = Ph, R^2 = H$
6 $R^1 = H, R^2 = Ph$

RESULTS AND DISCUSSION

The 300-MHz ^{1}H-n.m.r. spectra of **1–6** have been analysed, and the computed best values of the chemical shifts and coupling constants are given in Table I. Table II shows the vicinal proton torsion angles of the pyranoid ring calculated from the $^3J_{H,H}$ values using the equation of Altona[6]. The conformations of the pyranoid rings of **1–6** can be described as flattened $^1C_4$(D), which is caused by the *cis*-fusion of the dioxolane ring. The values of the torsion angles suggest that the pyranoid ring of the *endo*-phenyl compounds (**1**, **3**, and **5**) is more distorted than that of the *exo*-phenyl (**2**, **4**, and **6**) isomers.

Although $^3J_{C,H}$ depends on several factors[7,8], a Karplus-like relationship has been suggested[9]. Table III shows $J_{C\text{-}6,H\text{-}1}$, the coupling between C-7 and the bridge-

TABLE I

^{1}H-N.M.R. SPECTRAL PARAMETERS (δ) AND J (Hz) OF **1–6** IN $CDCl_3$

Parameter	*Compound*					
	1	**2**	**3**	**4**	**5**	**6**
H-1	5.359	5.373	5.534	5.568	5.765	5.691
H-2	4.955	4.987	4.212	4.376	4.273	4.249
H-3	4.158	3.846	4.173	4.165	4.561	4.764
H-4	4.518	4.534	5.119	5.138	5.380	5.432
H-5	4.585	4.590	4.617	4.618	4.862	4.830
H-6*endo*	4.071	4.123	4.075	4.173	4.062	4.035
H-6*exo*	3.446	3.684	3.838	3.824	3.738	3.719
$J_{1,2}$	1.0	1.0	3.1	2.9	1.3	0.7
$J_{1,3}$	0.5	0.5	1.0	0.7	0.0	0.0
$J_{1,5}$	0.2	0.2	0.1	0.7	0.1	0.5
$J_{2,3}$	0.8	0.9	6.9	6.0	7.2	6.3
$J_{3,4}$	7.3	6.7	0.5	0.7	5.2	5.8
$J_{3,5}$	0.5	0.5	1.0	0.5	0.0	0.0
$J_{4,5}$	5.7	6.0	1.0	0.8	5.5	5.5
$J_{4,6exo}$	0.5	0.5	0.0	0.0	0.8	0.5
$J_{5,6endo}$	0.5	0.4	1.4	0.5	1.0	1.0
$J_{5,6exo}$	5.8	5.3	6.2	5.7	5.6	5.5
$J_{6endo,6exo}$	−7.6	−7.7	−7.6	−7.5	−7.9	−8.2

TABLE II

PROTON TORSION ANGLES (DEGREES) FOR **1–6** FROM N.M.R. DATA[6]

Angle	*Compound*					
	1	**2**	**3**	**4**	**5**	**6**
$\phi_{1,2}$	89	89	−58	−60	86	84
$\phi_{2,3}$	−85	−85	24	33	22	31
$\phi_{3,4}$	−18	−23	95	95	−145	−147
$\phi_{4,5}$	48	44	−80	−80	47	47

head protons, and also the coupling between the acetal proton (H-7) and the bridgehead carbon atoms. These last values were determined by selective decoupling of the protons and observation of the fully coupled carbon spectra. The values for $J_{\text{C-6,H-1}}$ are almost the same in all of the compounds and, due to the rigidity of the 1,6-anhydro bridge, could be taken as model values for a torsion angle of ~140° in carbohydrate derivatives. The acetal carbon shows coupling only with an axial bridgehead proton. These values are larger for the *exo*-phenyl (**2**, **4**, and **6**) than for the *endo*-phenyl isomers (**1**, **3**, and **5**). The couplings of H-7 can be only observed in **2** and **4**. An $^{\text{o3}}E$ conformation could be assigned to the benzylidene ring of **1** and **2** on the basis of the small values for $J_{\text{C-7,H-3}}$, $J_{\text{C-7,H-4}}$, and $J_{\text{C-4,H-7}}$ (torsion angles ~120°) and the large value for $J_{\text{C-3,H-7}}$ in **2** (torsion angle ~140°). A similar conformation could be assigned to the benzylidene ring of **3**. The data for **4** indicate a different conformation of the benzylidene ring of this compound. A $^{2}T_{\text{o2}}$ somewhat distorted towards a ^{2}E conformation would account for the large $J_{\text{C-7,H-2}}$ and the small $J_{\text{C-2,H-7}}$ and $J_{\text{C-3,H-7}}$ values. On the same basis, the conformation of the benzylidene ring of **5** could be described as E_{o2} and that of **6** as $^{\text{o3}}E$. Thus, the conformation of the benzylidene ring would be the same for both galactopyranose derivatives (**1** and **2**), but would depend on the configuration at C-7 in the mannopyranose (**3** and **4**) and gulopyranose (**5** and **6**) derivatives.

TABLE III

$J_{\text{C,H}}$ VALUES FOR SOLUTIONS OF **1–6** IN $CDCl_3$

$J_{C,H}$	*Compound*					
	1	**2**	**3**	**4**	**5**	**6**
$J_{\text{C-2,H-7}}$	—	—	0.0	1.2	0.0	0.0
$J_{\text{C-3,H-7}}$	0.0	4.5	0.0	2.1	0.0	0.0
$J_{\text{C-4,H-7}}$	0.0	0.5	—	—	—	—
$J_{\text{C-7,H-2}}$	—	—	2.8	5.7	0.0	0.0
$J_{\text{C-7,H-3}}$	0.0	0.0	0.0	0.0	3.2	6.0
$J_{\text{C-7,H-4}}$	2.1	3.2	—	—	—	—
$J_{\text{C-6,H-1}}$	5.2	5.3	6.0	5.8	5.6	5.6

TABLE IV

^{13}C-N.M.R. CHEMICAL SHIFT DATA FOR SOLUTIONS OF **1–6** IN CDCl$_3$

Atom	*Compound*					
	1	**2**	**3**	**4**	**5**	**6**
C-1	99.0	98.8	98.9	99.6	98.6	99.5
C-2	70.9	70.6	71.3	73.1	77.0	75.6
C-3	75.3	73.0	75.7	73.5	74.6	75.7
C-4	69.5	70.0	70.9	70.8	73.1	71.5
C-5	72.3	72.4	73.2	73.0	71.8	70.0
C-6	63.6	63.9	64.5	65.1	63.3	63.4
C-7	103.0	103.6	104.4	104.8	105.7	104.0

TABLE V

EXPERIMENTAL TORSION ANGLES (DEGREES) FOR THE PYRANOID, 1,6-ANHYDRO, AND DIOXOLANE RINGS IN **1–3**

Angles	*Compound*		
	1	**2**	**3**
Pyranoid ring			
O-5–C-1–C-2–C-3	−50.4(4)	−51.9(4)	−52.6(3)
C-1–C-2–C-3–C-4	23.5(4)	27.1(4)	24.3(3)
C-2–C-3–C-4–C-5	−24.1(4)	−28.9(4)	−22.8(3)
C-3–C-4–C-5–O-5	51.8(4)	53.6(3)	49.2(3)
C-4–C-5–O-5–C-1	−77.0(3)	−77.1(3)	−77.8(2)
C-5–O-5–C-1–C-2	77.1(3)	77.3(3)	78.6(2)
1,6-Anhydro ring			
O-5–C-1–O-1–C-6	20.2(4)	20.1(3)	24.5(3)
C-1–O-1–C-6–C-5	7.7(4)	7.4(3)	2.1(3)
O-1–C-6–C-5–O-5	−32.6(4)	−31.3(3)	−27.1(3)
C-6–C-5–O-5–C-1	43.6(3)	43.7(3)	41.4(2)
C-5–O-5–C-1–O-1	−42.1(4)	−40.6(3)	−41.9(2)
Dioxolane ring			
C-2–O-2–C-7–O-3	—	—	−23.7(2)
O-2–C-7–O-3–C-3	—	—	40.1(2)
C-7–O-3–C-3–C-2	—	—	−39.7(2)
O-3–C-3–C-2–O-2	—	—	25.1(2)
C-3–C-2–O-2–C-7	—	—	−1.2(2)
C-3–O-3–C-7–O-4	−39.5(3)	−32.1(3)	—
O-3–C-7–O-4–C-4	24.6(3)	13.0(3)	—
C-7–O-4–C-4–C-3	0.3(3)	9.9(3)	—
O-4–C-4–C-3–O-3	−24.4(3)	−28.7(3)	—
C-4–C-3–O-3–C-7	39.4(3)	37.2(3)	—

TABLE VI

PROTON–PROTON AND CARBON–PROTON TORSION ANGLES (DEGREES) FROM X-RAY ANALYSES FOR **1–3**

Angles	*Compound*		
	1	**2**	**3**
H-1–C-1–C-2–H-2	65(4)	60(3)	−53(3)
H-2–C-2–C-3–H-3	−91(3)	−83(3)	28(3)
H-3–C-3–C-4–H-4	−21(3)	−29(3)	90(3)
H-4–C-4–C-5–H-5	42(4)	39(3)	−68(3)
C-2–O-2–C-7–H-7	—	—	94(4)
C-3–O-3–C-7–H-7	75(3)	127(3)	−73(3)
C-4–O-4–C-7–H-7	−93(4)	−144(3)	—
C-7–O-2–C-2–H-2	—	—	−117(2)
C-7–O-7–C-3–H-3	−76(2)	−81(2)	76(2)
C-7–O-7–C-4–H-4	119(2)	131(3)	—
C-6–O-1–C-1–H-1	136(3)	137(2)	145(2)

The ^{13}C-n.m.r. chemical shifts of **1–6** are shown in Table IV. It has been reported[1] that the value for the signal of the carbon atom bearing the axial-oxygen is 2–3 p.p.m. higher and that of the signal of the carbon atom bearing the equatorial-oxygen is 1–2 p.p.m. lower, in the *endo*-phenyl (**1**, **3**, and **5**) than in the *exo*-phenyl (**2**, **4**, and **6**) derivatives. Our data accord with these results, except for C-4 of **1** and **2** for which a chemical shift difference of only 0.5 p.p.m. was found.

Tables V and VI show the main geometrical features of the molecular structures of **1–3** in the solid state, following the numbering scheme presented in Figs. 1–3. Bond lengths are similar to those found in other carbohydrate derivatives[10–13], although **2** displays systematically lower values. The differences in bond angles reflect the arrangement of the substituents in the pyranoid rings. The conformation of the pyranoid rings can be described as $^{1}C_{4}$, flattened at C-3. The 1,6-anhydro bridges show an ^{O5}E conformation, and the other dioxolane moieties present

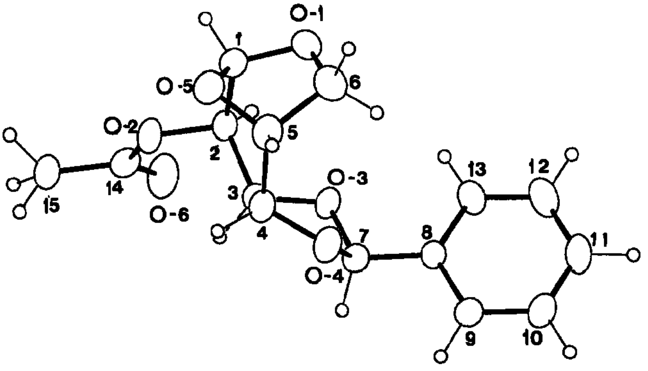


Fig. 1. ORTEP[18] view of the structure of **1**, showing the atomic numbering.

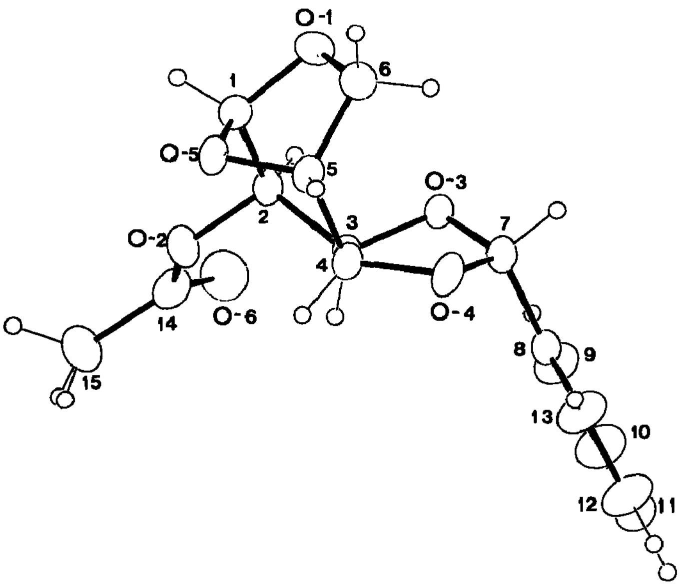


Fig. 2. ORTEP[18] view of the structure of **2**, showing the atomic numbering.

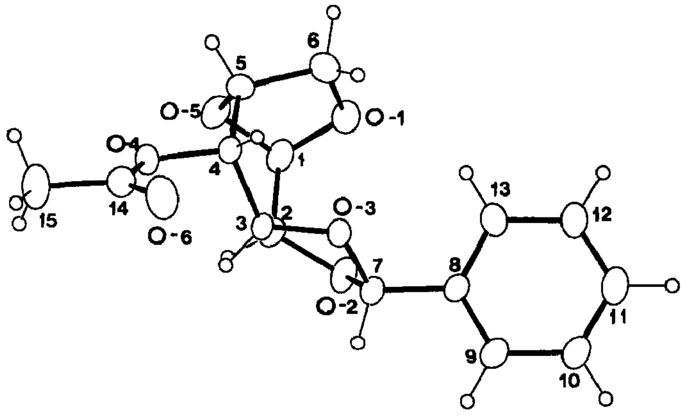


Fig. 3. ORTEP[18] view of the structure of **3**, showing the atomic numbering.

envelopes at O-3 although distorted towards a half-chair for **2**. There exists a reasonable agreement with the proposed conformations in solution for **1**–**3**.

EXPERIMENTAL

General methods. — Melting points were determined in capillary tubes and are uncorrected. T.l.c. was performed on Silica gel GF_{254} (Merck) with detection by charring with sulfuric acid. Flash column chromatography was performed on Macherey Nagel (230–400 mesh) silica gel. Optical rotations were determined with a Perkin–Elmer 141 polarimeter.

TABLE VII

CRYSTAL STRUCTURE PARAMETERS AT ROOM TEMPERATURE FOR **1–3**

Crystal data	**1**	**2**	**3**
Formulae	$C_{15}H_{16}O_6$	$C_{15}H_{16}O_6$	$C_{15}H_{16}O_6$
Crystal habit	Prismatic, transparent, colourless		
Crystal size	0.43 × 0.33 × 0.07 mm	0.17 × 0.23 × 0.43 mm	0.13 × 0.30 × 0.43 mm
Symmetry	$P2_12_12_1$, orthorhombic	Monoclinic, $P2_1$	$P2_12_12_1$, orthorhombic
Unit-cell determination	Least-squares fit, from 86	from 80	from 92
Unit-cell dimensions [a, b, c (Å)] β (°)	19.0795(4), 11.7456(2), 5.9621(1), 90	13.0997(8), 5.5143(2), 9.8036(4), 105.842(4)	17.6301(7), 10.7603(3), 7.3755(1), 90
Packing: V (Å^3), Z	1395.95(3), 4	681.27(6), 2	1399.0(1), 4
D_c (g.cm^{-3}), M	1388, 616	1454, 616	1425, 308
Experimental data			
Technique	Four-circle, PW-1100, bisecting geometry, $\omega/2\theta$, CuK$_\alpha$, θ_{max} = 65°, 1 min/ref.		
Independent reflexions	1371	1289	1398
Observed	1282 [$3\sigma(I)$ criterion]	1237, same	1335, same
Standard	2 reflexions every 90 min; no variation		
Solution and refinement			
Solution, refinement	Multan[19], least squares on F's with one block		
Variables, degrees of freedom	254, 1081	254, 1028	253, 984
Final shift/error	0.06	0.09	0.05
Ratio of freedom	5.1	4.9	5.3
ω-scheme	Empirical to give no trends in Δ^2F *vs.* $\lvert F_{obs}\rvert$ and sin θ/λ		
Max. thermal value (A^2)	U_{33} (C-15) = 0.104(3)	U_{22} (C-15) = 0.099(3)	U_{33} (C-15) = 0.090(3)
Final ΔF peaks (eA^{-3})	0.14	0.17	0.12
Final R and R_w	0.042, 0.051	0.039, 0.043	0.032, 0.037
Computing	X-Ray 76 on a Vax 11/750[20]		
Scattering factors	International Tables for X-Ray crystallography[21]		

TABLE VIII

FINAL ATOMIC CO-ORDINATES FOR COMPOUND **1**

Atom	*x/a*	*y/b*	*z/c*
O-1	0.3351(1)	0.4037(2)	0.6850(6)
O-2	0.4715(1)	0.2169(2)	0.5329(4)
O-3	0.3018(1)	0.1469(2)	0.7019(4)
O-4	0.2495(1)	0.1675(2)	0.3680(4)
O-5	0.3843(1)	0.3772(2)	0.3451(5)
O-6	0.4925(1)	0.0857(3)	0.7917(6)
C-1	0.3948(2)	0.3665(3)	0.5788(7)
C-2	0.4076(2)	0.2436(3)	0.6363(6)
C-3	0.3545(1)	0.1641(3)	0.5416(6)
C-4	0.3165(2)	0.2091(3)	0.3369(5)
C-5	0.3157(2)	0.3385(3)	0.3224(7)
C-6	0.2821(2)	0.3974(4)	0.5175(9)
C-7	0.2482(2)	0.1040(3)	0.5734(5)
C-8	0.1822(1)	0.1178(3)	0.6874(5)
C-9	0.1261(2)	0.0648(3)	0.5963(6)
C-10	0.0643(2)	0.0748(3)	0.7004(7)
C-11	0.0583(2)	0.1351(4)	0.8954(7)
C-12	0.1134(2)	0.1860(4)	0.9883(7)
C-13	0.1756(2)	0.1780(3)	0.8861(6)
C-14	0.5091(2)	0.1349(3)	0.6271(7)
C-15	0.5716(2)	0.1148(4)	0.4955(10)

Materials. — Compounds **1** and **2** were prepared as reported in the literature[14].

*2-*O*-Acetyl-1,6-anhydro-2,3-*O*-[(*R*) and (*S*)]-benzylidene-β-*D*-mannopyranose* (**3** *and* **4**). — Conventional treatment with acetic anhydride and pyridine of 1,6-anhydro-2,3-*O*-[*(R)* and *(S)*]-benzylidene-β-D-mannopyranose[15], followed by flash chromatography (hexane–ethyl acetate, 4:1) of the product, gave **3**, m.p. 190–192°, $[\alpha]^{20}_{D}$ −92° (*c* 0.7, chloroform).

Anal. Calc. for $C_{15}H_{16}O_6$: C, 61.64; H, 5.52. Found: C, 61.42; H, 5.60.

Compound **4** was isolated as a syrup, $[\alpha]^{20}_{D}$ −42° (*c* 0.5, chloroform).

Anal. Calc. for $C_{15}H_{16}O_6$: C, 61.64; H, 5.52. Found: C, 61.50; H, 5.63.

*1,6-Anhydro-4-*O*-benzoyl-2,3-*O*-[(*R*) and (*S*)]-benzylidene-β-*D*-gulopyranose* (**5** *and* **6**). — Flash chromatography (hexane–ethyl acetate, 4:1) of the mixture of diastereoisomers, prepared as reported in the literature[15], gave **5**, m.p. 102–103°, $[\alpha]^{20}_{D}$ +146° (*c* 0.4, chloroform).

Anal. Calc. for $C_{20}H_{18}O_6$: C, 67.79; H, 5.12. Found: C, 68.00; H, 5.31.

Compound **6** was isolated as a foam, $[\alpha]^{20}_{D}$ +73° (*c* 0.6, chloroform).

Anal. Calc. for $C_{20}H_{18}O_6$: C, 67.79; H, 5.12. Found: C, 68.06; H, 5.29.

N.m.r. data. — The ^{1}H-n.m.r. spectra ($CDCl_3$, internal Me_4Si) were recorded on a Varian XL-300 spectrometer and analysed using a PANIC program. The experimental and calculated spectra from the resulting best values matched satisfactorily. The ^{13}C-n.m.r. spectra (75 MHz) were assigned by selective proton irradiation[16]. The carbon–proton coupling constants were measured through

TABLE IX

FINAL ATOMIC CO-ORDINATES FOR COMPOUND **2**

Atom	*x/a*	*y/b*	*z/c*
O-1	0.3519(2)	0.0000(–)	0.6623(2)
O-2	0.3996(1)	0.1096(7)	0.3215(2)
O-3	0.1637(1)	−0.0997(6)	0.4113(6)
O-4	0.0955(1)	0.2747(7)	0.4306(2)
O-5	0.3825(1)	0.3525(6)	0.5608(2)
O-6	0.3768(2)	−0.2238(8)	0.1863(3)
C-1	0.3997(2)	0.1006(8)	0.5602(3)
C-2	0.3454(2)	−0.0027(8)	0.4151(3)
C-3	0.2289(2)	0.0702(7)	0.3636(3)
C-4	0.2021(2)	0.3101(8)	0.4240(3)
C-5	0.2751(2)	0.3669(8)	0.5713(3)
C-6	0.2766(2)	0.1769(9)	0.6831(3)
C-7	0.0678(2)	0.0257(8)	0.4029(3)
C-8	−0.0141(2)	−0.0037(8)	0.2607(3)
C-9	−0.0126(3)	−0.2007(9)	0.1755(4)
C-10	−0.0910(3)	−0.2271(10)	0.0471(4)
C-11	−0.1703(3)	−0.0575(10)	0.0069(3)
C-12	−0.1725(3)	0.1351(10)	0.0922(4)
C-13	−0.0939(3)	0.1618(10)	0.2191(4)
C-14	0.4092(2)	−0.0218(9)	0.2093(3)
C-15	0.4645(3)	0.1250(12)	0.1220(4)

TABLE X

FINAL ATOMIC CO-ORDINATES FOR COMPOUND **3**

Atom	*x/a*	*y/b*	*z/c*
O-1	0.4130(1)	0.5433(2)	0.2761(3)
O-2	0.3418(1)	0.6900(2)	0.5390(2)
O-3	0.3842(1)	0.8230(1)	0.3236(2)
O-4	0.2519(1)	0.7550(2)	−0.0375(2)
O-5	0.3035(1)	0.5281(2)	0.1176(3)
O-6	0.2728(1)	0.9568(2)	−0.0912(4)
C-1	0.3335(2)	0.5401(2)	0.2950(4)
C-2	0.3021(1)	0.6597(2)	0.3753(3)
C-3	0.3150(1)	0.7725(2)	0.2534(3)
C-4	0.3249(1)	0.7442(2)	0.0515(3)
C-5	0.3508(2)	0.6128(3)	0.0170(3)
C-6	0.4289(2)	0.5866(3)	0.0967(4)
C-7	0.3764(1)	0.8095(2)	0.5130(3)
C-8	0.4514(1)	0.8161(2)	0.6076(3)
C-9	0.4617(2)	0.9005(3)	0.7463(4)
C-10	0.5307(2)	0.9078(3)	0.8357(4)
C-11	0.5894(2)	0.8311(3)	0.7869(4)
C-12	0.5795(2)	0.7463(3)	0.6493(5)
C-13	0.5109(2)	0.7383(3)	0.5584(4)
C-14	0.2331(2)	0.8666(3)	−0.1055(4)
C-15	0.1585(2)	0.8628(4)	−0.1981(7)

selective decoupling[17] and first-order analysis of the partially coupled carbon spectrum.

X-Ray data. — Crystal and experimental data, and refinement parameters, are given in Table VII. Tables VIII–X present the final atomic co-ordinates for **1**–**3**, respectively.

Supplementary material. — Bond distances bond angles, thermal parameters, and a list of observed and calculated structure factors are deposited with, and can be obtained from, Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/345, *Carbohydr. Res.*, 155 (1986) 1–10.

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