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SYNTHESIS, CRYSTAL STRUCTURE, AND CONFORMATION OF 1(*S*)-ACETOXY-3-[6(*R*)-*O*-BENZYL-1,2:3,4-DI-*O*-ISOPROPYLIDENE-α-D-GALACTOPYRANOS-6-YL]-1-(METHYL 2,3,4-TRI-*O*-BENZYL-6-DEOXY-β-D-GALACTOPYRANOSID-6-YL)PROPYNE

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ABSTRACT

Condensation of 6-*O*-benzyl-7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-D-*glycero*-α-D-*galacto*-oct-7-ynopyranose with methyl 2,3,4-tri-*O*-benzyl-6-deoxy-β-D-*galacto*-heptodialdo-1,5-pyranoside afforded a 2:1 mixture of the 1*S* and 1*R* isomers (**1a** and **1b**) of 3-[6(*R*)-*O*-benzyl-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranos-6-yl]-1-hydroxy-1-(methyl 2,3,4-tri-*O*-benzyl-6-deoxy-β-D-galactopyranosid-6-yl)propyne. A single crystal of the 1-*O*-acetyl derivative (**1c**) of **1a** was investigated by X-ray diffraction methods in a four-circle diffractometer. Compound **1c** crystallises in the monoclinic system, space group $P2_1$ ($Z = 2$) with cell dimensions $a = 14.896(2)$, $b = 8.295(1)$, $c = 20.547(3)$ Å, and $\beta = 102.66(1)°$. The structure was solved by direct methods and refined by a full-matrix, least-squares procedure against 3839 unique reflections ($F > 2\sigma_F$), resulting in a final $R = 0.045$ (unit weights). The configuration at the new chiral center (C-1) was established as *S*(D). The galactopyranose rings have conformations $^4C_1$ (tri-*O*-benzylated moiety) and $^oS_5 + {}^oT_2$ (di-*O*-isopropylidenated moiety). The 1,2- and 3,4-*O*-isopropylidene rings have $^3T_2$ and ^2E conformations, respectively.

INTRODUCTION

Such antibiotics as tunicamycin[1,2] or hikizimycin[3] contain, as components, higher sugars consisting of eleven carbon atoms. Few syntheses of sugars consisting of ten or more carbon atoms have been reported[4–8]. There are two routes of synthesis, namely, dimerisation of monosaccharide units[5] or coupling of two sugar molecules[6–8]. The latter route offers the possibility of stereoselective synthesis of partially or fully protected higher sugars.

We now report a different approach to the synthesis of higher sugars, using acetylenic derivatives of monosaccharides. An ethynyl group can be functionalised at both ends and also stereoselectively reduced to either *cis* or *trans* olefins.

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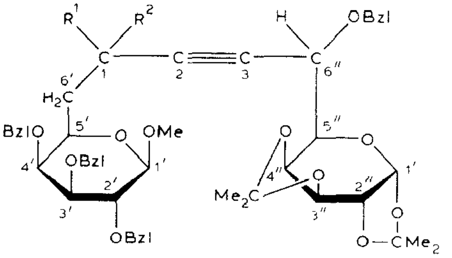
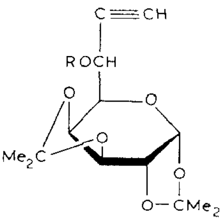
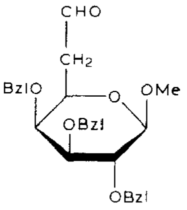
3-(6-*O*-Benzyl-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranos-6-yl)-1-hydroxy-1-(methyl 2,3,4-tri-*O*-benzyl-6-deoxy-β-D-galactopyranosid-6-yl)propyne diastereoisomers (**1a, 1b**) were obtained by condensation of 6-*O*-benzyl-7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-D-*glycero*-α-D-*galacto*-oct-7-ynopyranose (**2b**) and methyl 2,3,4-tri-*O*-benzyl-6-deoxy-β-D-*galacto*-heptodialdo-1,5-pyranoside (**3**). Compounds **1a** and **1b** are potential precursors for stereoselective synthesis of 6-deoxypentadecoses.



1a $R^1 = H, R^2 = OH$ **1c** $R^1 = H, R^2 = OAc$
1b $R^1 = OH, R^2 = H$ **1d** $R^1 = OAc, R^2 = H$



2a $R = H$
2b $R = CH_2Ph$



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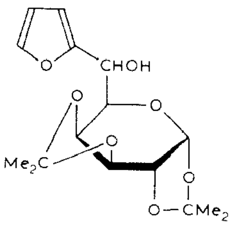

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The X-ray diffraction study was performed on the 1-*O*-acetyl derivative (**1c**) of **1a** in order to investigate, in the 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose system, whether the ring conformations differ from those found recently[9,10], and in order to establish the configuration of the newly created chiral center at C-1, a knowledge of which is essential for further syntheses of higher sugars.

EXPERIMENTAL

General. — Melting points were determined with a Kofler apparatus and are not corrected. Optical rotations were measured with a Perkin–Elmer 141 polarimeter for solutions in ethyl acetate, unless otherwise stated. ^{1}H-N.m.r. spectra were recorded with a JEOL JNM-4H-100 or Bruker 400-MHz spectrometer for solutions in $CDCl_3$ (internal Me_4Si). Column chromatography was performed on silica gel (230–400 mesh, Merck). All reactions of anions were conducted under argon. Tetrahydrofuran was distilled over lithium aluminium hydride prior to each use. Yields were not optimised.

*6-O-Benzyl-7,8-dideoxy-1,2:3,4-di-O-isopropylidene-*D-glycero-α-D-galacto-*oct-7-ynopyranose* (**2b**). — A solution of 7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-D-*glycero*-α-D-*galacto*-oct-7-ynopyranose[11] (**2a**; 4.90 g, 17.2 mmol) in tetrahydrofuran (60 mL) was added to a stirred slurry of sodium hydride (50% dispersion in oil; 1.60 g, 33 mmol) and imidazole (~100 mg) in tetrahydrofuran during 30 min. The mixture was then boiled under reflux and stirred for 2 h. Benzyl bromide (2.99 g, 2.09 mL, 17.5 mmol) was added, and the mixture was boiled under reflux for another 30 min and then cooled to room temperature. The excess of hydride was decomposed with water, saturated aqueous ammonium chloride (50 mL) was added, the aqueous layer was extracted with ether (100 mL), and the combined organic phases were dried ($MgSO_4$) and concentrated. Column chromatography (light petroleum–ether, 4:1) of the residue gave **2b** (4.35 g, 67%), m.p. 98.5–100°. Recrystallisation from ether–light petroleum gave material having m.p. 103–103.5°, $[\alpha]_D$ −116.5° (*c* 1.1, chloroform). ^{1}H-N.m.r. data: δ 7.48 (m, 5 H, Ph), 5.63 (d, 1 H, $J_{1,2}$ 5.25 Hz, H-1), and 2.53 (d, 1 H, $J_{6,8}$ 2.0 Hz, H-8).

Anal. Calc. for $C_{21}H_{26}O_6$: C, 67.4; H, 7.0. Found: C, 67.2; H, 6.8.

*Methyl 2,3,4-tri-O-benzyl-6-deoxy-β-*D-galacto-*heptodialdo-1,5-pyranoside* (**3**). — Methyl 2,3,4-tri-*O*-benzyl-β-D-galactopyranoside[12] (4.65 g, 10 mmol) was oxidised with methyl sulfoxide–oxalyl chloride[13]. A solution of the crude product in dry tetrahydrofuran (40 mL) was added dropwise at −78° to methoxymethylenetriphenylphosphorane[14] (generated by the addition of 25 mmol of lithium di-isopropylamide in 40 mL of tetrahydrofuran to a slurry of methoxymethylenetriphenylphosphonium chloride in 100 mL of tetrahydrofuran at −78°). The mixture was stirred for 1 h at −78° and then for 1 h at room temperature. Wet ether (100 mL) was added, followed by saturated aqueous ammonium chloride (50 mL). The organic layer was dried ($MgSO_4$) and concentrated. Column chromatography (light petroleum–ether, 9:1, then 3:1) of the residue gave the crude vinyl ether (2.07 g, 4.22 mmol). ^{1}H-N.m.r. data: δ 6.57 (d, 1 H, $J_{6,7}$ 13.0 Hz, H-7 of *trans* enol ether), 5.82 (d, 1 H, $J_{6,7}$ 6.6 Hz, H-7 of *cis* enol ether), and 3.50 (bs, 6 H, 2 OMe).

A solution of this product in 1,4-dioxane–water (4:1, 50 mL) containing pyridinium *p*-toluenesulfonate[15] was boiled under reflux for 3 h, then cooled to room temperature, and poured into water (200 mL), and the product was extracted with ether (3 × 50 mL). Concentration of the combined extracts gave the crude aldehyde **3** (1.52 g) which was homogeneous by t.l.c. (light petroleum–ether, 1:1; and benzene–ether, 2:1) and had m.p. 48–53°. ^{1}H-N.m.r. data: 9.60 (bs, 1 H, CHO), 3.48 (s, 3 H, OMe), and 2.53 (2 H, CH_2).

Compound **3** was used without further purification in the next reaction.

*Preparation of the 1*S *and 1*R *isomers* (**1a** *and* **1b**) *of 3-(6-O-benzyl-1,2:3,4-di-O-isopropylidene-α-*D-*galactopyranos-6-yl)-1-hydroxy-1-(methyl 2,3,4-tri-O-benzyl-*

6-deoxy-β-D-galactopyranosid-6-yl)propyne (**1b**). — To 2 mmol of lithium di-isopropylamide (generated from 0.28 mL of di-isopropylamine and 1.26 mL of 1.6M butyl-lithium in 2 mL of tetrahydrofuran at 0° for 15 min) was added a solution of **2b** (750 mg, 2 mmol) in tetrahydrofuran (3 mL). After stirring (45 min) at 0°, the mixture became reddish, a solution of **3** (700 mg, 1.49 mmol) in tetrahydrofuran (5 mL) was then added slowly, and the mixture was stirred at 0° for another 15 min. T.l.c. (toluene–acetone, 9:1) then showed the disappearance of **3** and the formation of a more polar product which was isolated by column chromatography (toluene–acetone, 95:5). The product (610 mg, 48%) contained the diastereoisomeric alcohols **1a** and **1b** (~2:1 ratio) that could be differentiated by t.l.c. (light petroleum–ethyl acetate, 2:1, two developments). Column chromatography (light petroleum–ethyl acetate, 85:15) gave, first, **1a** (106 mg), isolated as an oil, $[\alpha]_D$ −36° (*c* 4.3). ^{1}H-N.m.r. data (400 MHz): δ 5.31 (d, 1 H, $J_{1'',2''}$ 5.0 Hz, H-1''), 3.51 (s, 3 H, OMe), 2.36 (m, 1 H, H-6'a), 1.63 (m, 1 H, H-6'b), and 1.49, 1.40, 1.33, and 1.18 (2 CMe_2). Eluted second was **1a** contaminated with **1b** (308 mg). Eluted third was **1b** (150 mg, isolated as an oil), $[\alpha]_D$ −34° (*c* 1.7). ^{1}H-N.m.r. data (400 MHz): δ 5.33 (d, 1 H, $J_{1'',2''}$ 5.0 Hz, H-1''), 3.53 (s, 3 H, OMe), 2.33 and 1.53 (2 m, 2 H, H-6'a,6'b), and 1.48, 1.37, 1.33, and 1.18 (2 CMe_2).

To a solution of the mixture of **1a** and **1b** in dry pyridine (2 mL) was added acetic anhydride (0.2 mL) followed by a crystal of dimethylaminopyridine. After 15 min, the pyridine was evaporated under reduced pressure and the residue was subjected to column chromatography (light petroleum–ethyl acetate, 9:1).

Eluted first was the acetate **1c** (220 mg), m.p. 107.5–108° (from ether–light petroleum, 1:3), $[\alpha]_D$ −52° (*c* 6.3). ^{1}H-N.m.r. data (400 MHz): δ 5.51 (dd, 1 H, $J_{1,6'b}$ 3.5, $J_{1,6'a}$ 10.0 Hz, H-1), 5.23 (d, 1 H, $J_{1'',2''}$ 5.0 Hz, H-1''), 3.53 (s, 3 H, OMe), 2.36 (m, 1 H, $J_{5',6'}$ 8.7, $J_{6'a,6'b}$ 13.5 Hz, H-6'a), 2.07 (s, 3 H, Ac), 1.71 (m, 1 H, $J_{5',6'b}$ <2.0 Hz, H-6'), and 1.48, 1.38, 1.33, and 1.13 (2 CMe_2).

Anal. Calc. for $C_{52}H_{60}O_{13}$: C, 69.9; H, 6.8. Found: C, 69.7; H, 7.0.

Eluted second was acetate **1d** (80 mg), isolated as an oil, $[\alpha]_D$ −29° (*c* 4.1). ^{1}H-N.m.r. data (400 MHz): δ 5.62 (dd, 1 H, $J_{1,6'a}$ 9.0, $J_{1,6'b}$ ~2.5 Hz, H-1), 5.41 (d, 1 H, $J_{1'',2''}$ 5.0 Hz, H-1''), 3.53 (s, 3 H, OMe), 2.34 (m, 1 H, $J_{5',6'a}$ ~9.0, $J_{6'a,6'b}$ 13.5 Hz, H-6), 2.06 (s, 3 H, Ac), 1.84 (m, 1 H, $J_{5',6'b}$ ~2.0 Hz, H-6'b), and 1.51, 1.40, 1.34, and 1.25 (2 CMe_2).

*X-Ray diffraction investigations**. — A well-shaped crystal of **1c** (0.2 × 0.4 × 0.85 mm) obtained from ether–light petroleum was used in a Syntex $P2_1$ diffractometer with CuKα radiation (λ 1.54178 Å) (Institute of Organic Synthesis, Riga, Latvian SSR). Stability was controlled on two reflections at 50 reflection intervals at room temperature. Lattice parameters were refined against 20 reflec-

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**Supplementary material.* — Tables listing the structure factors and other data have been 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/320/*Carbohydr. Res.*, 144 (1985) 183–195.

tions. Crystal data: $C_{52}H_{60}O_{13}$, M_r 893.00, monoclinic, space group $P2_1$, $Z = 2$, a = 14.896(2), b = 8.295(1), c = 20.547(3) Å, β = 102.66(1)°, V = 2477.1(5) Å^3, F(000) = 952, D_x = 1.20 Mg.m^{-3}, μ(CuKα) = 7.1 cm^{-1}.

Of the 4513 intensities collected with an $\omega/2\theta$ scan technique up to $2\theta_{max}$ = 150°, 3839 had $F > 2\sigma_F$. No absorption correction was applied. The structure was solved by direct methods (MULTAN-80[16]). The refinement of the atomic positional and thermal parameters (initially isotropic, then anisotropic) was performed by the full-matrix, least-squares procedure (X-RAY 70 System, program CRYLSQ[17]) with the atomic scattering factors taken from the International Tables for X-ray Crystallography[18]. The positions of non-aromatic hydrogen atoms were found from a difference Fourier synthesis, and those of phenyl groups were calculated geometrically. The final refinement step involved all atomic parameters except the hydrogen isotropic temperature factors (fixed as B_{eq} of the adjacent atom + 1 Å^2). The final R factor was 0.045 (R_w 0.041, unit weights), at $\Delta/\sigma < 0.1$. The residual electron density on ΔF maps was < 0.4 e Å^{-3}.

RESULTS AND DISCUSSION

Compound **1** was obtained in relatively good yield by the addition of **2b** to **3**, affording two epimers **1a** and **1b** which, after acetylation, gave **1c** and **1d**, respectively. Detailed discussion of the results and aspects of this synthesis will be published elsewhere.

The refined non-H atomic coordinates for **1c**, resulting from the X-ray diffraction studies, are presented in Table I. Tables II and III contain the calculated bond lengths and valence angles, respectively. A steric view (parallel projection) of the molecular structure of **1c** is shown in Fig. 1. Table IV gives the characteristic bond lengths and angles in the *O*-benzyl groups of **1c**.

Configuration at C-1 in **1c**. — In order to elucidate unambiguously the configuration at the new chiral center at C-1, atoms surrounding C-1 were projected onto a plane bisecting the C-1 tetrahedron (Fig. 2). As may be clearly seen, the configuration at C-1, assuming the D configuration for both sugar moieties, is *S*(D) (the preference order of atoms is HC-1<C-6′<C-2<O-1).

Conformations of galactopyranose and dioxolane rings. — The galactopyranose ring A has a slightly deformed $^4C_1$ chair conformation (Tables V and VI). The deformation may be due to substitution by three *O*-benzyl groups (E, F, and G).

The conformation of ring B (fused with C and D), similar to that in 6-*C*-(2-furyl)-1,2:3,4-di-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-hexopyranose[9] (**4**), deviates markedly from a chair. However, the hybrid conformation $^{\circ}T_2 + B_{2,5}$ found in **4** differs significantly from that observed in **1c**, regarding the endocyclic torsion angles (Table V), particularly for bonds involving C-1″. The placing of puckering parameters on the Cremer and Pople diagram[20] allows the assignment to ring B in **1c** of a hybrid conformation (1,3-diplanar) skew-boat (*S*) + twist (*T*). Two four-

TABLE I

FRACTIONAL CO-ORDINATES ($\times 10^4$)[a] AND EQUIVALENT TEMPERATURE FACTORS ($Å^2$)[b]

Atom	*x/a*	*y/b*	*z/c*	B_{eq}
C-1	−1729(2)	5(5)	4253(2)	3.6(1)
C-2	−1131(2)	284(5)	3776(2)	3.5(1)
C-3	−690(3)	443(5)	3376(2)	3.7(1)
C-4	−800(3)	747(7)	5300(2)	4.8(1)
C-5	−669(4)	1985(8)	5833(3)	6.6(2)
O-1	−1520(2)	1134(4)	4798(1)	4.0(1)
O-2	−357(2)	−437(5)	5299(2)	6.5(1)
C-1′	−2888(2)	−3736(5)	3152(2)	3.6(1)
C-2′	−3888(3)	−3870(5)	2779(2)	3.7(1)
C-3′	−4257(2)	−2247(5)	2509(2)	3.7(1)
C-4′	−4063(2)	−928(5)	3040(2)	3.4(1)
C-5′	−3040(2)	−971(5)	3371(2)	3.5(1)
C-6′	−2751(2)	211(5)	3937(2)	3.7(1)
O-1′	−2612(2)	−5200(4)	3451(1)	4.3(1)
O-2′	−3956(2)	−4898(4)	2210(1)	4.3(1)
O-3′	−5219(2)	−2440(4)	2246(1)	4.6(1)
O-4′	−4581(2)	−1146(4)	3536(1)	4.0(1)
O-5′	−2822(2)	−2540(4)	3657(1)	3.5(1)
C-7′	−1663(3)	−5217(6)	3809(2)	5.2(1)
C-1″	−1692(3)	−1102(6)	1498(2)	4.2(1)
C-2″	−1072(3)	−1807(6)	1058(2)	4.2(1)
C-3″	−127(3)	−1039(6)	1136(2)	4.2(1)
C-4″	289(3)	−319(6)	1831(2)	3.9(1)
C-5″	−344(2)	−464(5)	2309(2)	3.6(1)
C-6″	−73(3)	659(5)	2909(2)	4.0(1)
O-5″	−1260(2)	0(4)	1979(1)	3.9(1)
O-1″	−1985(2)	−2466(4)	1806(1)	4.8(1)
O-2″	−931(2)	−3439(4)	1270(1)	4.8(1)
C-7″	−1725(3)	−3902(6)	1509(2)	4.4(2)
C-8″	−1452(4)	−5178(7)	2039(3)	6.4(2)
C-9″	−2510(4)	−4436(8)	945(3)	6.9(2)
O-3″	−234(2)	312(4)	694(1)	4.7(1)
O-4″	416(2)	1337(4)	1694(1)	4.5(1)
C-10″	394(3)	1505(6)	1001(2)	4.6(2)
C-11″	1348(3)	1195(8)	864(3)	6.3(2)
C-12″	7(4)	3143(6)	777(2)	5.7(2)
O-6″	850(2)	266(5)	3208(1)	5.2(1)
C-10	1270(4)	1292(9)	3741(2)	6.8(2)
C-11	2012(3)	2322(7)	3580(2)	5.6(2)
C-12	2546(4)	3150(8)	4108(3)	7.3(2)
C-13	3281(5)	4092(10)	4004(5)	9.6(3)
C-14	3448(5)	4182(10)	3371(5)	8.9(3)
C-15	2933(5)	3381(11)	2859(4)	8.7(3)
C-16	2214(4)	2430(10)	2971(3)	7.3(2)
C-20	−4183(5)	−6517(7)	2306(3)	6.8(2)
C-21	−4501(4)	−7281(7)	1623(2)	5.3(2)
C-22	−3951(4)	−8316(8)	1384(3)	6.7(2)
C-23	−4241(5)	−8978(9)	771(3)	7.7(2)
C-24	−5087(5)	−8632(9)	383(3)	7.3(2)
C-25	−5647(5)	−7619(10)	619(3)	8.5(3)
C-26	−5353(5)	−6909(7)	1249(3)	7.6(2)

TABLE I *(continued)*

Atom	*x/a*	*y/b*	*z/c*	B_{eq}
C-30	−5564(4)	−1698(8)	1648(3)	7.1(3)
C-31	−6484(3)	−2402(7)	1333(2)	5.1(2)
C-32	−6740(3)	−2449(8)	650(2)	6.0(2)
C-33	−7574(4)	−3117(7)	345(2)	6.2(2)
C-34	−8154(3)	−3720(7)	711(3)	5.9(2)
C-35	−7906(3)	−3657(8)	1396(3)	6.3(2)
C-36	−7072(3)	−2980(8)	1709(2)	6.2(2)
C-40	−5293(4)	−35(9)	3510(3)	6.7(4)
C-41	−5693(3)	−225(6)	4109(2)	4.6(2)
C-42	−6342(4)	−1373(7)	4129(3)	6.6(2)
C-43	−6700(4)	−1549(9)	4690(4)	7.3(3)
C-44	−6418(5)	−552(12)	5219(4)	7.9(4)
C-45	−5800(6)	555(10)	5199(3)	8.4(3)
C-46	−5416(4)	728(8)	4657(3)	7.0(2)

[a]Estimated standard deviations in parentheses. [b]$B_{eq} = 8\pi^2 \cdot D_u^{1/3}$, where D_u is the determinant of the U matrix.

TABLE II

BOND DISTANCES (Å)[a] (*O*-BENZYL GROUPS NOT INCLUDED)

C-1′–C-2′	1.522(5)	C-6″–O-6″	1.416(4)
C-2′–C-3′	1.513(6)	C-6″–C-5″	1.528(5)
C-3′–C-4′	1.527(6)	C-5″–C-4″	1.508(6)
C-4′–C-5′	1.527(5)	C-4″–C-3″	1.547(5)
C-5′–O-5′	1.436(5)	C-3″–C-2″	1.521(6)
O-5′–C-1′	1.424(5)	C-2″–C-1″	1.542(6)
C-1′–O-1′	1.382(5)	C-1″–O-5″	1.396(5)
C-1′–C-7′	1.444(5)	C-5″–O-5″	1.437(4)
C-2′–O-2′	1.433(5)	C-4″–O-4″	1.423(6)
C-3′–O-3′	1.425(4)	C-4″–C-10″	1.423(5)
C-4′–O-4′	1.418(5)	C-3″–O-3″	1.429(5)
C-5′–C-6′	1.510(5)	O-3″–C-10″	1.413(5)
C-6′–C-1	1.528(5)	C-10″–C-11″	1.530(7)
C-1–O-1	1.440(5)	C-10″–C-12″	1.508(7)
O-1–C-4	1.354(5)	C-2″–O-2″	1.423(6)
C-4–O-2	1.184(7)	O-2″–C-7″	1.428(6)
C-4–C-5	1.482(8)	C-1″–O-1″	1.412(6)
C-1–C-2	1.481(6)	O-1″–C-7″	1.431(6)
C-2–C-3	1.166(6)	C-7″–C-8″	1.510(7)
C-3–C-6″	1.478(6)	C-7″–C-9″	1.520(7)

[a]Estimated standard deviations in parentheses.

atom sets (O-5″, C-1″, C-2″, and C-3″, and C-2″, C-3″, C-4″, and C-5″) are approximately coplanar forming two planes with a dihedral angle of 23.2(2)°, a characteristic feature for (*S*). Fig. 3 shows a schematic view of the ring B along a least-squares plane of the ring. The deviations of ring atoms from this plane are given in Table VI in comparison to those of ring A, and to those found in **4**. Thus, the final conformation assignment for ring B is $^{O}S_{5} + {}^{O}T_{2}$.

TABLE III

BOND ANGLES (DEGREES)[a] (*O*-BENZYL GROUPS NOT INCLUDED)

C-1′–O-1′–C-7′	113.5(3)	O-6″–C-6″–C-5″	105.6(3)
O-1′–C-1′–O-5′	108.7(3)	C-3–C-6″–C-5″	111.0(3)
O-1′–C-1′–C-2′	108.8(3)	C-6″–C-5″–O-5″	105.8(3)
O-5′–C-1′–C-2′	108.8(3)	C-6″–C-5″–C-4″	112.7(3)
C-1′–C-2′–C-3′	110.9(3)	O-5″–C-5″–C-4″	109.7(3)
C-2′–C-3′–C-4′	112.3(3)	C-5″–C-4″–C-3″	112.9(3)
C-3′–C-4′–C-5′	108.3(3)	C-4″–C-3″–C-2″	115.7(4)
C-4′–C-5′–O-5′	108.6(3)	C-3″–C-2″–C-1″	116.0(4)
C-5′–O-5′–C-1′	111.0(3)	C-2″–C-1″–O-5″	114.9(3)
C-1′–C-2′–O-2′	109.9(3)	C-1″–O-5″–C-5″	113.7(3)
C-3′–C-2′–O-2′	106.0(3)	C-3″–C-4″–O-4″	103.5(3)
C-2′–O-2′–C-20	115.4(4)	C-4″–C-3″–O-3″	104.5(4)
C-2′–C-3′–O-3′	107.0(3)	C-4″–O-4″–C-10″	108.5(3)
C-4′–C-3′–O-3′	111.6(3)	C-3″–O-3″–C-10″	107.1(3)
C-3′–O-3′–C-30	116.0(4)	O-4″–C-10″–O-3″	104.2(4)
C-3′–C-4′–O-4′	112.0(3)	O-4″–C-10″–C-11″	110.5(3)
C-5′–C-4′–O-4′	108.9(3)	O-4″–C-10″–C-12″	108.5(4)
C-4′–O-4′–C-40	114.7(4)	O-3″–C-10″–C-11″	110.6(4)
C-4′–C-5′–C-6′	114.6(3)	O-3″–C-10″–C-12″	108.8(3)
O-5′–C-5′–C-6′	105.8(3)	C-11″–C-10″–C-12″	113.8(5)
C-5′–C-6′–C-1	110.1(3)	C-1″–C-2″–O-2″	104.4(4)
C-6′–C-1–O-1	106.5(3)	C-2″–C-1″–O-1″	104.1(4)
C-2–C-1–O-1	110.7(3)	C-2″–O-2″–C-7″	106.5(3)
C-1–O-1–C-4	116.0(3)	C-1″–O-1″–C-7″	109.6(4)
C-1–C-4–O-2	122.9(4)	O-2″–C-7″–O-1″	104.2(4)
O-1–C-4–C-5	110.7(4)	O-2″–C-7″–C-8″	108.9(4)
O-2–C-4–C-5	126.4(4)	O-2″–C-7″–C-9″	111.9(4)
C-1–C-2–C-3	176.2(4)	O-1″–C-7″–C-8″	109.3(4)
C-2–C-3–C-6″	175.9(4)	O-1″–C-7″–C-9″	109.4(4)
C-3–C-6″–O-6″	112.0(3)	C-8″–C-7″–C-9″	112.7(3)
C-6″–O-6″–C-10	114.7(4)		

[a]Estimated standard deviations in parentheses.

TABLE IV

BOND DISTANCES (Å)[a] AND ANGLES (DEGREES)[a] IN *O*-BENZYL GROUPS

				Phenyl rings	
O-Benzyl	*-O-CH$_2$-*	*-CH$_2$-C(Ph)*	*-O-CH$_2$-C(Ph)*	*(C–C)$_{av}$*	*(C–C–C)$_{av}$*
E	1.409(7)	1.518(7)	107.7(4)	1.365(9)	120.0(6)
F	1.370(7)	1.500(7)	109.9(5)	1.374(7)	120.0(6)
G	1.398(7)	1.488(8)	109.7(5)	1.356(10)	120.0(6)
H	1.420(7)	1.491(8)	113.3(4)	1.372(10)	120.0(6)

[a]Estimated standard deviations in parentheses.

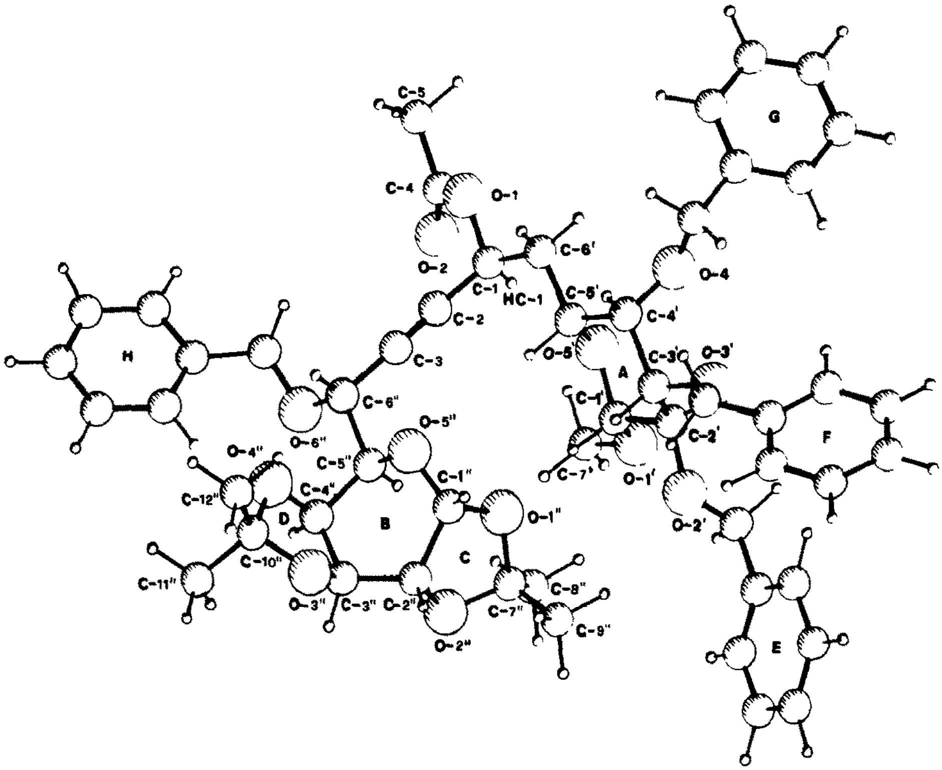

Fig. 1. Parallel projection of **1c** oriented optimally.

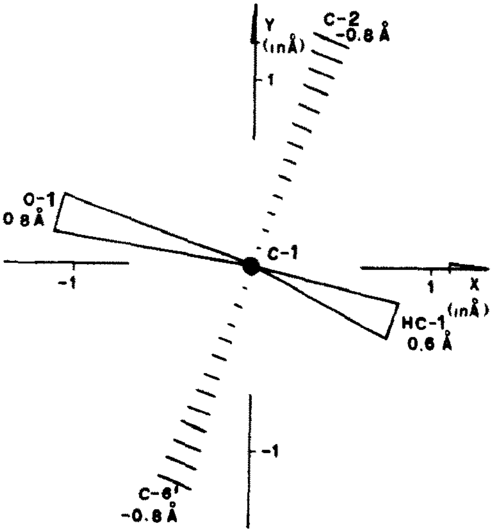

Fig. 2. The projection of the C-1 tetrahedron in **1c**, showing the configuration at the newly created chiral center.

TABLE V

SOME TORSIONAL ANGLES (DEGREES)[a]

O-5′–C-1′–C-2′–C-3′	55.1(4)	C-5″–O-5″–C-1″–C-2″	−41.4(5)
C-1′–C-2′–C-3′–C-4′	−49.8(4)	C-4″–C-5″–C-6″–C-3	−178.1(3)
C-2′–C-3′–C-4′–C-5′	51.2(4)	O-5″–C-5″–C-6″–C-3	62.1(4)
C-3′–C-4′–C-5′–O-5′	−58.8(4)	C-3″–C-4″–C-5″–C-6″	−162.9(3)
C-4′–C-5′–O-5′–C-1′	68.4(4)	C-1″–O-5″–C-5″–C-6″	−167.7(3)
C-5′–O-5′–C-1′–C-2′	−65.6(4)	C-2″–C-1″–O-1″–C-7″	−9.6(4)
C-4′–C-5′–C-6′–C-1	177.1(3)	C-1″–O-1″–C-7″–O-2″	27.2(4)
O-5′–C-5′–C-6′–C-1	57.5(4)	O-1″–C-7″–O-2″–C-2″	−34.5(4)
C-3′–C-4′–C-5′–C-6′	−176.8(3)	C-7″–O-2″–C-2″–C-1″	28.4(4)
C-1′–O-5′–C-5′–C-6′	−168.2(3)	O-2″–C-2″–C-1″–O-1″	−11.6(4)
O-5″–C-1″–C-2″–C-3″	−8.6(5)	C-4″–C-3″–O-3″–C-10″	23.4(4)
C-1″–C-2″–C-3″–C-4″	29.2(5)	C-3″–O-3″–C-10″–O-4″	−34.9(4)
C-2″–C-3″–C-4″–C-5″	−2.0(5)	O-3″–C-10″–O-4″–C-4″	33.2(4)
C-3″–C-4″–C-5″–O-5″	−45.3(5)	C-10″–O-4″–C-4″–C-3″	−18.2(4)
C-4″–C-5″–O-5″–C-1″	70.6(4)	O-4″–C-4″–C-3″–O-3″	−3.1(4)

[a] Estimated standard deviations in parentheses.

TABLE VI

CONFORMATIONS OF GALACTOPYRANOSE RINGS IN **1** AND **4**

Atom deviations (Å)[a] from least-squares planes					
Atom	**1**[b]		**1**[c]		**4**
C-1′	−0.712(4)	C-1″	−0.136(5)[d]	C-1	−0.127(6)[d]
C-2′	0.064(4)[d]	C-2″	−0.244(5)[d]	C-2	−0.310(6)[d]
C-3′	−0.056(4)[d]	C-3″	0.242(5)[d]	C-3	0.271(6)[d]
C-4′	0.687(4)	C-4″	0.116(5)[d]	C-4	0.103(6)[d]
C-5′	0.062(4)[d]	C-5″	−0.434(4)[d]	C-5	−0.481(6)[d]
O-5′	−0.030(3)[d]	O-5″	0.220(3)[d]	O-5	0.175(3)[d]
Asymmetry parameters (°)[19]					
ΔC_2	5.6(4)		5.4(5)		11.2(6)
ΔC_s	13.1(4)		—		—
Puckering parameters[20]					
Q (Å)	0.590		0.592		0.632
Φ (°)	100.4		84.3		81.4
θ (°)	171.4		106.4		100.9
q_2 (Å)[e]	0.088		0.568		0.635
Conformation	$^{4}C_{1}$		$^{O}S_{5} + {}^{O}T_{2}$		$^{O}T_{2} + B_{2,5}$
Conformation of 1,3-dioxolane rings					
1,2-*O*-Isopropylidene			$^{3}T_{2}$		^{3}E
3,4-*O*-Isopropylidene			^{2}E		$^{O}T_{1} + {}^{2}E$

[a] Estimated standard deviations in parentheses. [b] Ring A of **1**. [c] Ring B of **1**. [d] Atoms defining the planes [e] $q_2 = Q\sin\theta$.

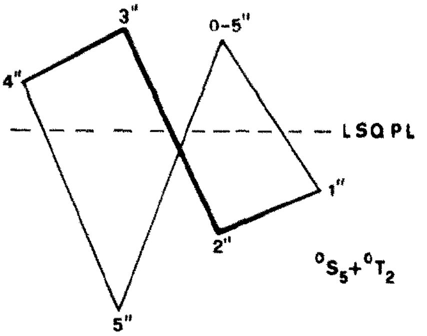

Fig. 3. Schematic projection of ring B in **1c** along the ring least-squares plane (LSQPL). The vertical–horizontal scale ratio is 10:1.

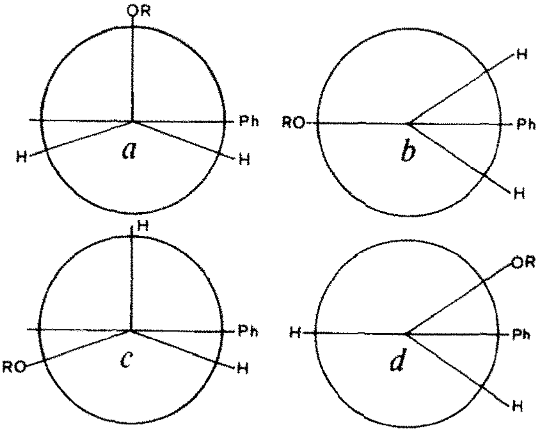

Fig. 4. Projections of possible *O*-benzyl group conformations[21].

The conformations of the 1,2- and 3,4-*O*-isopropylidene rings in **1c** (C and D, respectively) are found easily from calculations of puckering parameters (Table VI). They are defined as $^{3}T_2$ for C, and ^{2}E for D.

Conformations of O-*benzyl groups in* **1c**. — The conformations of the four *O*-benzyl groups in **1c** (E, F, G, and H, Fig. 1) were investigated in comparison with the known conformations of benzyl alcohol and its ethers. Based on ^{1}H-n.m.r. data, Ito and Hirota[21] stated that there are four conformational variants (Fig. 4). Fig. 5 shows the Newman projections of the *O*-benzyl groups E, F, G, and H. It may be seen that groups E and G correspond to variant *a* (both hydrogen atoms placed on the same side of a phenyl plane), whereas groups F and H are close to variant *b* (hydrogen atoms placed on two sides of a phenyl plane).

Relative steric situation of rings A and B in **1c**. — The relative positioning of rings A and B can hardly be seen from Fig. 1. In order to visualise this steric relativity, a quasi-Newman projection was calculated (Fig. 6) along the least-

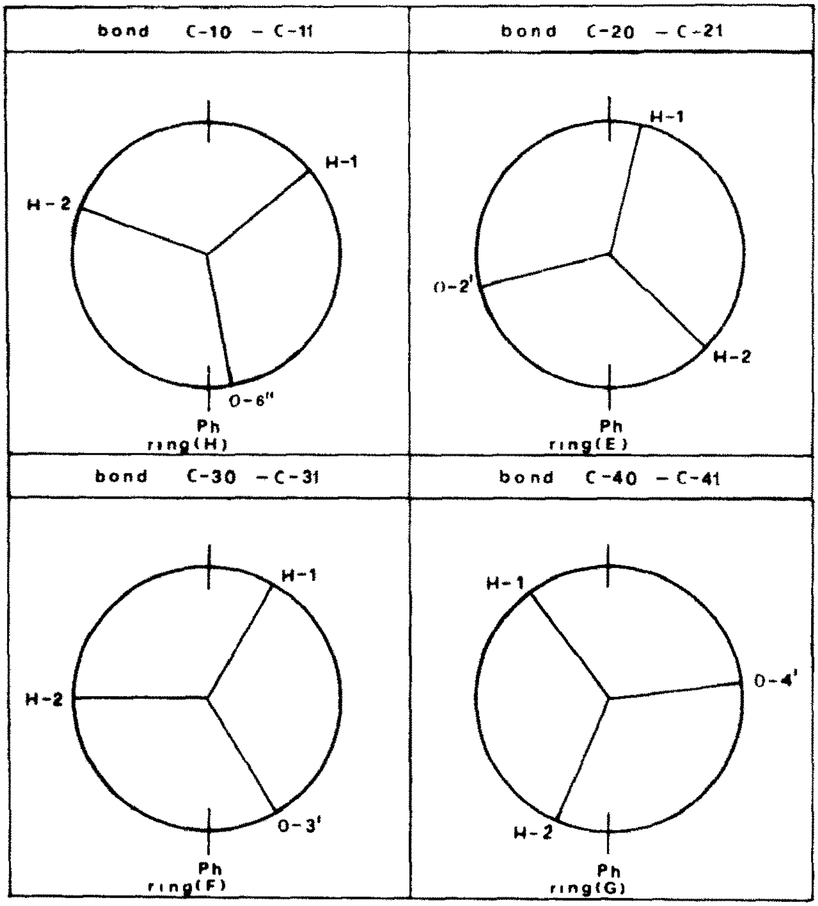

Fig. 5. The calculated Newman projections for *O*-benzyl groups E–H in **1c**.

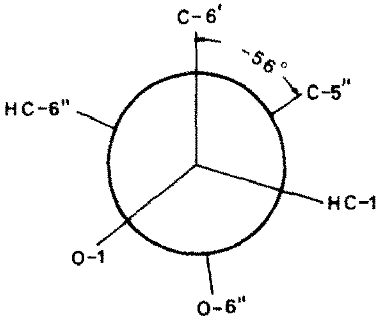

Fig. 6. Calculated Newman-like projection of the acetylene link in **1c**, showing the steric relativity of C-6' and C-5''.

squares line through four atoms forming the acetylene chain (C-1, C-2, C-3, and C-6″). Atoms C-5″ and O-1 are found to be in s-*trans* relative positions.

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REFERENCES

1 A. Takatsuki, K. Arima, and G. Tamura, *J. Antibiot.*, 24 (1971) 215–223.
2 T. Suami, H. Sasai, K. Matsuno, N. Suzuki, Y. Fukuda, and O. Sakanaka, *Tetrahedron Lett.*, 25 (1984) 4533–4536.
3 K. Uchida, T. Ichikawa, Y. Schimauchi, T. Ishikura, and A. Ozaki, *J. Antibiot.*, 24 (1971) 259–262.
4 M. L. Wolfrom, W. W. Binkley, and C. C. Spencer, *J. Am. Chem. Soc.*, 73 (1951) 3357–3358.
5 D. Horton and J.-H. Tsai, *Carbohydr. Res.*, 75 (1979) 151–174.
6 J. A. Secrist, III, and S.-R. Wu, *J. Org. Chem.*, 44 (1979) 1434–1438; J. A. Secrist, III, and K. D. Barnes, *ibid.*, 45 (1980) 4526–4528.
7 H. Paulsen, K. Roden, V. Sinvell, and W. Koebernick, *Angew. Chem.*, 88 (1976) 477.
8 T. Suami, H. Sasai, and K. Matsuno, *Chem. Lett.*, (1983) 819–822.
9 J. W. Krajewski, P. Gluziński, Z. Urbańczyk-Lipkowska, A. Zamojski, and P. Luger, *Carbohydr. Res.*, 139 (1985) 55–63.
10 S. Jarosz, J. W. Krajewski, A. Zamojski, H. Duddeck, and M. Kaiser, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, 33 (1985) in press.
11 R. Hems, D. Horton, and M. Nakadate, *Carbohydr. Res.*, 25 (1972) 201–212.
12 P. J. Garegg and C. G. Swann, *Acta Chem. Scand.*, 26 (1972) 3895–3901.
13 A. J. Mancuso, Sh.-L. Huang, and D. Swern, *J. Org. Chem.*, 43 (1978) 2480–2482.
14 S. G. Levine, *J. Am. Chem. Soc.*, 80 (1958) 6150–6151; L. F. Fieser and M. Fieser, *Reagents for Organic Synthesis*, Vol. I, Wiley, New York, 1967, p. 671.
15 M. Miyashita, A. Yoshikoshi, and P. A. Grieco, *J. Org. Chem.*, 42 (1977) 3772–3774.
16 P. Main, *MULTAN-80, Program for Crystal Structure Determination*, University of York, Great Britain, 1980.
17 J. M. Stewart, F. A. Kundell, and J. C. Baldwin, *The X-Ray 70 System*, Computer Science Center, University of Maryland, U.S.A.
18 *International Tables for X-Ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, 1973.
19 W. L. Duax, C. M. Weeks, and D. C. Rohrer, *Top. Stereochem.*, 9 (1976) 271–383.
20 D. Cremer and J. A. Pople, *J. Am. Chem. Soc.*, 97 (1975) 1354–1358.
21 M. Ito and M. Hirota, *Bull. Chem. Soc. Jpn.*, 54 (1981) 2093–2098.