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Structural Features at the Anomeric Center in Aryl Pyranosides: Structure of *p*-Nitrophenyl α-D-Glucopyranoside

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Abstract

$C_{12}H_{15}NO_8$, $M_r = 301{\cdot}26$, is monoclinic, $P2_1$, with $a = 28{\cdot}810\ (10)$, $b = 6{\cdot}747\ (3)$, $c = 6{\cdot}729\ (5)$ Å, $\beta = 103{\cdot}68\ (5)°$, $Z = 4$, $V = 1271$ Å^3, $D_c = 1{\cdot}574$ Mg m^{-3}, μ(Cu $K\alpha$) $= 1{\cdot}173$ mm^{-1}. The structure was refined to an R of 0·039 for 1900 reflections. The valence angles at the bridge oxygen atom O(1′) are significantly different between the two molecules. In both molecules the endocyclic C—O bond lengths are unequal (Δl = 0·044, 0·035 Å) and the glycosidic bond lengths are close to the mean C—O bond length. A comparison of the present axial glucoside structure with the known equatorial aryl pyranosides indicates that the molecular geometry around the anomeric center is not significantly different between the α and β anomers.

Introduction

A detailed analysis of the structural and conformational properties of alkyl glucosides has improved the understanding of the difference in the electronic properties of α- and β-pyranosides and the preferred *gauche* conformation about the glycosidic bonds (Lemieux & Chu, 1958; Berman, Chu & Jeffrey, 1967; Sundaralingam, 1968; Lemieux, Koto & Voisin, 1979; Jeffrey, 1979). In contrast to the large amount of crystal structure data available on the alkyl glucosides, only two crystal structures of aryl glucosides, *viz.* *p*-nitrophenyl *N*-acetyl-β-D-glucosaminide monohydrate (Brehm & Moult, 1975) and 1-naphthyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (Makinen & Isaacs, 1978), have been reported so far. As a general program of research on sugars in these laboratories, the crystal structure of *p*-nitrophenyl α-D-glucopyranoside has been determined. The present structure indicates that the geometrical features around the α anomeric center are similar to those observed in aryl β-D-glucosides.

Needle-shaped crystals of *p*-nitrophenyl α-D-glucopyranoside growing along the *c* axis were obtained by slow evaporation of an aqueous solution of the substance. Zero- and first-layer Weissenberg photographs collected about the *c* axis showed that the reflections with odd *h* indices were systematically weaker than the rest of the reflections. This suggested the presence of a pseudotranslational symmetry in the structure. A crystal of dimensions 0·1 × 0·1 × 0·4 mm mounted along the *c* axis was used for data collection on a four-circle Picker FACS-I automatic diffractometer. Intensities of 2255 reflections were measured

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to a 2θ limit of 128° employing the θ–2θ scan technique with a scan rate of 1° min^{-1} and using Ni-filtered Cu $K\alpha$ radiation. Lorentz and polarization corrections were applied to the intensity data. A total of 1900 reflections were considered observed [$I > 1{\cdot}5\sigma(I)$, where $\sigma(I)$ is given by the expression $\sigma(I) = (I_{scan} + I_{bkg} + 0{\cdot}03I^2_{scan})^{1/2}$].

Since the crystal structure has an inherent pseudosymmetry, the normalized structure amplitudes used for the direct methods were calculated using the molecular scattering factor (Swaminathan, McAlister & Sundaralingam, 1980). The structure was solved by multisolution methods using the program *MULTAN* (Germain, Main & Woolfson, 1971). Three cycles of full-matrix least-squares refinement of the structure with unit weights and individual isotropic temperature factors for the atoms reduced the R index to 0·10. All the H atoms of the molecule were determined from a difference Fourier map. For further refinement individual reflections were given weights ($w = 1/\sigma^2_F$) based on counting statistics. A block-diagonal approximation was used to refine the nonhydrogen atoms with anisotropic temperature factors. The H atoms were refined with isotropic temperature factors. After four cycles of refinement R converged to 0·039. The fractional positional parameters of the nonhydrogen atoms are given in Table 1.* Fig. 1 shows the atom numbering.

Table 1. *Positional parameters and equivalent isotropic temperature factors B_{eq} of the non-hydrogen atoms*

$B_{eq} = \frac{4}{3}\sum_i\sum_j \beta_{ij}\,\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq} (Å^2)
O(41)*A*	−0·0968 (1)	−0·2498 (8)	−0·5000 (6)	6·1 (1)
O(42)*A*	−0·0518 (1)	−0·2533 (8)	−0·7149 (6)	5·8 (1)
N(1)*A*	−0·0575 (1)	−0·2433 (7)	−0·5405 (7)	4·5 (1)
C(1)*A*	0·0620 (2)	−0·1957 (8)	−0·0449 (7)	3·5 (1)
C(2)*A*	0·0166 (2)	−0·1584 (8)	−0·0167 (7)	3·7 (1)
C(3)*A*	−0·0225 (2)	−0·1745 (9)	−0·1785 (7)	3·8 (1)
C(4)*A*	−0·0156 (2)	−0·2234 (8)	−0·3685 (8)	3·8 (1)
C(5)*A*	0·0293 (2)	−0·2562 (9)	−0·4014 (7)	3·9 (1)
C(6)*A*	0·0686 (2)	−0·2413 (9)	−0·2359 (8)	4·0 (1)
C(1′)*A*	0·1446 (2)	−0·2361 (8)	0·1187 (8)	3·6 (1)
C(2′)*A*	0·1752 (2)	−0·2580 (8)	0·3396 (8)	3·8 (1)
C(3′)*A*	0·1855 (1)	−0·0613 (8)	0·4427 (7)	3·0 (1)
C(4′)*A*	0·2033 (1)	0·0833 (8)	0·3077 (7)	3·0 (1)
C(5′)*A*	0·1687 (2)	0·0998 (8)	0·0979 (7)	3·1 (1)
C(6′)*A*	0·1847 (2)	0·2370 (9)	−0·0480 (7)	4·0 (1)
O(1′)*A*	0·0977 (1)	−0·1799 (6)	0·1305 (5)	3·9 (1)
O(2′)*A*	0·1534 (1)	−0·3850 (6)	0·4554 (7)	5·6 (1)
O(3′)*A*	0·2213 (1)	−0·0899 (6)	0·6297 (5)	3·8 (1)
O(4′)*A*	0·2090 (1)	0·2737 (5)	0·4016 (5)	3·8 (1)
O(5′)*A*	0·1642 (1)	−0·0962 (5)	0·0064 (5)	3·5 (1)
O(6′)*A*	0·2316 (1)	0·1938 (6)	−0·0684 (5)	4·1 (1)
O(41)*B*	−0·6020 (1)	−0·2414 (7)	−0·5981 (5)	5·1 (1)
O(42)*B*	−0·5568 (1)	−0·2044 (7)	−0·8047 (5)	4·8 (1)
N(1)*B*	−0·5629 (1)	−0·2180 (6)	−0·6328 (6)	3·3 (1)
C(1)*B*	−0·4438 (1)	−0·1774 (7)	−0·1339 (6)	2·8 (1)
C(2)*B*	−0·4888 (1)	−0·1551 (8)	−0·1035 (6)	3·2 (1)
C(3)*B*	−0·5286 (1)	−0·1728 (8)	−0·2674 (7)	3·3 (1)
C(4)*B*	−0·5209 (1)	−0·2080 (7)	−0·4584 (6)	2·8 (1)
C(5)*B*	−0·4760 (1)	−0·2264 (7)	−0·4937 (6)	3·0 (1)
C(6)*B*	−0·4367 (1)	−0·2145 (7)	−0·3273 (6)	2·9 (1)
C(1′)*B*	−0·3620 (1)	−0·2344 (7)	0·0450 (6)	2·8 (1)
C(2′)*B*	−0·3390 (1)	−0·2772 (7)	0·2683 (7)	3·0 (1)
C(3′)*B*	−0·3316 (1)	−0·0886 (8)	0·3942 (6)	2·7 (1)
C(4′)*B*	−0·3054 (1)	0·0624 (8)	0·2963 (6)	2·7 (1)
C(5′)*B*	−0·3279 (1)	0·0913 (7)	0·0680 (6)	2·8 (1)
C(6′)*B*	−0·2967 (2)	0·2146 (8)	−0·0357 (7)	3·3 (1)
O(1′)*B*	−0·4082 (1)	−0·1596 (5)	0·0390 (4)	3·2 (1)
O(2′)*B*	−0·3675 (1)	−0·4130 (6)	0·3473 (6)	4·3 (1)
O(3′)*B*	−0·3022 (1)	−0·1384 (6)	0·5920 (4)	3·9 (1)
O(4′)*B*	−0·3056 (1)	0·2473 (5)	0·3993 (5)	3·4 (1)
O(5′)*B*	−0·3342 (1)	−0·0979 (5)	−0·0358 (4)	3·1 (1)
O(6′)*B*	−0·2499 (1)	0·1291 (6)	−0·0050 (5)	4·1 (1)

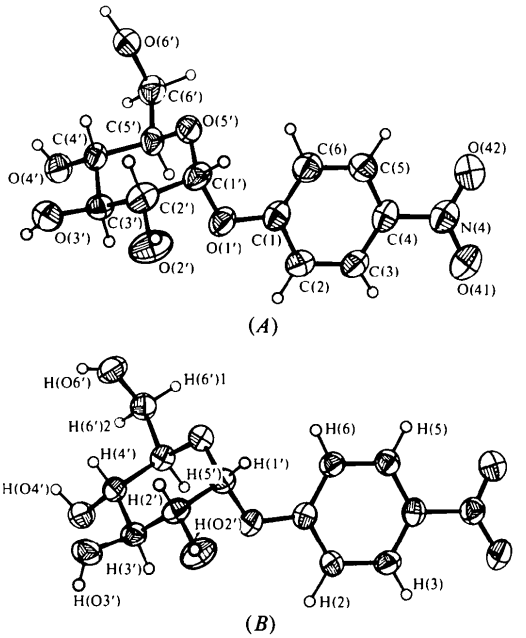

Fig. 1. An *ORTEP* (Johnson, 1965) drawing of the molecules showing the atom numbering and the overall molecular conformation.

Results and discussion

The bond lengths and angles involving the nonhydrogen atoms of both molecules are tabulated in Table 2. The half-normal probability plot analysis (Abrahams & Keve, 1971) indicated no significant difference between the geometries of the two molecules. The C—C bond lengths vary from 1·494 (7) to 1·546 (7) Å with a mean of 1·518 (6) Å. The mean C(5′)—C(6′) bond length of 1·505 (5) Å for the two molecules is shorter by $2{\cdot}5\sigma$ than the mean ring C—C bond length. The C—O bond lengths in both the molecules vary from

* Lists of structure factors, anisotropic thermal parameters, the positional parameters of the H atoms and hydrogen-bond distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36264 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

1·403 (7) to 1·452 (7) Å with a mean of 1·431 (7) Å. The glycosidic bond lengths are 1·424 (7) (molecule *A*) and 1·415 (4) Å (molecule *B*) which are not significantly different from the mean exocyclic C–O bond length. The endocyclic C–O bond lengths are unequal in both the molecules. In molecule *A* the C(1′)–O(5′) and C(5′)–O(5′) bond lengths are 1·408 (7) and 1·452 (7) Å while in molecule *B* these bond lengths are 1·411 (4) and 1·446 (4) Å, respectively. Similar unequal endocyclic C–O bond lengths are observed in other aryl pyranoside structures reported so far (Table 3).

Table 2. *Bond lengths* (Å) *and angles* (°)

The mean standard deviation in C–C bond lengths is 0·006 Å, in C–O bond lengths 0·006 Å, in C–N bond lengths 0·005 Å, in N–O bond lengths 0·005 Å, and in the bond angles 0·3°.

	Molecules			Molecules			Molecules	
	A	*B*		*A*	*B*		*A*	*B*
Glucose								
O(1′)–C(1)	1·374	1·362	C(1′)–O(1′)–C(1)	117·3	120·4	C(4′)–C(5′)–O(5′)	107·4	110·3
O(1′)–C(1′)	1·424	1·415	O(1′)–C(1′)–C(2′)	107·8	106·5	C(4′)–C(5′)–C(6′)	114·6	112·1
C(1′)–C(2′)	1·546	1·520	C(2′)–C(1′)–O(5′)	111·7	110·5	C(6′)–C(5′)–O(5′)	107·2	106·5
C(1′)–O(5′)	1·408	1·411	O(1′)–C(1′)–O(5′)	111·0	111·8	C(5′)–C(6′)–O(6′)	112·6	110·7
C(2′)–C(3′)	1·494	1·516	C(1′)–C(2′)–C(3′)	111·5	111·3	C(5′)–O(5′)–C(1′)	113·0	114·1
C(2′)–O(2′)	1·403	1·415	C(1′)–C(2′)–O(2′)	111·4	109·8			
C(3′)–C(4′)	1·503	1·509	O(2′)–C(2′)–C(3′)	110·5	110·6			
C(3′)–O(3′)	1·439	1·438	C(2′)–C(3′)–C(4′)	110·8	110·0			
C(4′)–C(5′)	1·528	1·532	C(2′)–C(3′)–O(3′)	108·0	107·2			
C(4′)–O(4′)	1·424	1·428	O(3′)–C(3′)–C(4′)	109·8	108·4			
C(5′)–O(5′)	1·452	1·446	C(3′)–C(4′)–C(5′)	111·4	112·8			
C(5′)–C(6′)	1·499	1·511	C(3′)–C(4′)–O(4′)	109·7	108·6			
C(6′)–O(6′)	1·420	1·436	O(4′)–C(4′)–C(5′)	109·0	109·0			
Nitrophenyl								
C(1)–C(2)	1·388	1·368	C(2)–C(1)–O(1′)	114·0	114·3	C(3)–C(4)–N(4)	118·7	117·9
C(2)–C(3)	1·373	1·395	C(6)–C(1)–O(1′)	125·3	124·7	O(42)–N(4)–C(4)	119·3	118·6
C(3)–C(4)	1·380	1·376	C(2)–C(1)–C(6)	120·7	121·0	O(41)–N(4)–C(4)	117·3	118·5
C(4)–C(5)	1·381	1·375	C(1)–C(2)–C(3)	120·0	120·2	O(41)–N(4)–O(42)	123·4	122·9
C(5)–C(6)	1·391	1·394	C(2)–C(3)–C(4)	118·9	118·0			
C(6)–C(1)	1·378	1·387	C(5)–C(6)–C(1)	119·8	119·5			
N(4)–C(4)	1·468	1·475	C(3)–C(4)–C(5)	122·2	122·9			
N(4)–O(42)	1·225	1·214	C(4)–C(5)–C(6)	118·4	118·3			
N(4)–O(41)	1·226	1·214	C(5)–C(4)–N(4)	119·1	119·1			

Table 3. *Acetal geometry in the aryl pyranoside structures*

Compound	C(5′)–O(5′) (Å)	O(5′)–C(1′) (Å)	C(1′)–O(1′) (Å)	Mean[b] C–O (Å)	Mean σ(Å)	Angle[d] δ(°)	Torsion angles[a] θ_1(°)	θ_2(°)	θ_3(°)	Reference
PNPG										
Mol. *A*	1·452	1·408	1·424	1·425	0·006	117·3 (3)	61·1	71·8	−7·3	This study
Mol. *B*	1·446	1·411	1·415	1·426	0·005	120·4 (3)	58·5	84·4	−18·7	
NGTA[c]	1·440	1·403	1·410	1·446	0·007	119·7 (5)	−174·1	−79·4	11·1	Makinen & Isaacs (1978)
p-Nitrophenyl *N*-acetyl-β-D-glucosaminide[c]	1·442	1·409	1·399	1·432	0·008	120·0 (5)	−176·8	−80·9	18·3	Brehm & Moult (1975)
Axial 2-phenoxy-*trans*-1-oxadecalin[c]	1·448	1·405	1·433	1·428	0·003	118·9 (2)	64·6	66·9	−3·4	Jones, Kennard, Chandrasekhar & Kirby (1978*a*)
Equatorial 2-phenoxy-*trans*-1-oxadecalin[c]	1·437	1·411	1·415	1·428	0·003	117·4 (2)	−177·4	76·8	−7·2	Jones *et al.* (1978*b*)
Equatorial 2-(4-nitrophenoxy)-*trans*-1-oxadecalin[c]	1·448	1·412	1·424	1·428	0·004	118·2 (3)	176·8	−66·9	6·2	Jones *et al.* (1979)

Notes: (*a*) Torsion-angle definitions are: θ_1 = C(5′)–O(5′)–C(1′)–O(1′); θ_2 = O(5′)–C(1′)–O(1′)–C(1); θ_3 = C(1′)–O(1′)–C(1)–C(6). (*b*) Mean bond length $\bar{l}$ is calculated by the expression $\bar{l} = (\sum_i l_i/\sigma_i^2)/(\sum_i 1/\sigma_i^2)$ where σ_i is the standard deviation in the observation. (*c*) Equatorially oriented glycosidic bonds. (*d*) δ is the valence angle C(1′)–O(1′)–C(1) at the bridge O atom.

The bond angles C(1′)–O(1′)–C(1), 117·3 (3)° (in molecule *A*) and 120·4 (3)° (in molecule *B*), are significantly (7σ) different from each other. This difference could be attributed to the difference in the torsion angle C(1′)–O(1′)–C(1)–C(6) observed in molecule *A* (−7·3°) and molecule *B* (−18·7°). In general this angle takes values between 117 and 120° in the aryl pyranoside structures reported so far (Table 3), greater than the mean value of 116° reported for alkyl glucosides and disaccharides (Jeffrey, 1979).

In Table 3 are listed the acetal geometry and the important torsion angles for the known aryl pyranosides. It is seen that the two endocyclic C–O bond lengths are significantly different in all the structures (in some cases as large as 14σ) irrespective of the orientation (*a*/*e*) of the glycosidic C–O bond. Similarly, the glycosidic C–O bond lengths are not significantly different from the mean C–O bond lengths. Thus, the molecular geometry around the anomeric center appears to be similar for both α and β aryl pyranosides. This is in contrast to the observation in the case of alkyl glucosides where the bond lengths, valence angles and torsion angles show marked differences in the molecular geometry between the α and β anomers (Jeffrey, 1979; Jeffrey, Pople, Binkley & Vishveshwara, 1978).

A comparison of the values of the torsion angle O(5′)–C(1′)–O(1′)–C(1) observed in different aryl pyranosides indicates (Table 3) that they fall within the range ±65–85° (positive for the axial anomer and negative for the equatorial anomer). Similarly the torsion angle C(1′)–O(1′)–C(1)–C(6) assumes values in the range 0 ± 20°, very much different from the values observed in di- and polysaccharides. Thus the phenyl ring is restricted to be nearly coplanar with the anomeric carbon atom C(1′) in both the α and β anomers of the aryl pyranosides. In this orientation, the delocalization of the electrons from the lone-pair orbitals of the glycosidic O atom to the $p\pi$ orbitals of the phenyl ring is maximized. Hence the preferred orientations of the lone-pair orbitals of O(1′) for both the axial and equatorial anomers of the aryl glycosides (Fig. 2) are different from those observed in alkyl glucosides. This may explain the occurrence of unequal endocyclic C–O bond lengths in aryl pyranosides for both α and β configurations, and a valence angle at the bridge O atom greater than the usual value of 116°.

The packing of the molecules viewed down the *b* axis is shown in Fig. 3. The two independent molecules are related by a pseudo half translation along the *a* axis. The nitrophenyl groups of molecules *A* and *B* are stacked over their symmetry-related equivalents. The pseudosymmetry in the structure is also reflected in the mutually complementary hydrogen-bonding pattern between the two molecules. Both O(3′) and O(4′) hydroxyl O atoms are donors and acceptors. It is interesting that the O(2′) hydroxyl O atoms of both molecules act only as hydrogen-bond donors and not acceptors. In molecule *B*, both the lone-pair orbitals of the ring oxygen are involved in hydrogen bonds while in molecule *A* there is only one hydrogen bond involving the axially oriented lone-pair orbital of the ring O atom.

The crystal structure of *p*-nitrophenyl α-D-gluco-pyranoside taken in conjunction with the known equatorial pyranosides reveals that both anomers show significant differences in endocyclic C–O bond lengths and similar glycosidic C–O bond lengths in contrast to the alkyl glucosides where the axial glucosides exhibit unequal endocyclic C–O bond lengths while the equatorial glucosides do not. The presence of an aromatic ring at the anomeric hydroxyl O atom appears to be responsible for the observed bonding properties of the aryl glucosides and also explains the differences in their conformation around the glycosidic bonds compared to the alkyl counterpart.

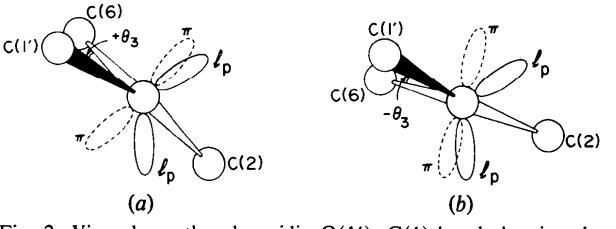

Fig. 2. View down the glycosidic O(1′)–C(1) bond showing the conformation of the C(1′)–O(1′)–C(1)–C(6) system for (*a*) the equatorial and (*b*) the axial orientations. (Note the difference between the two orientations is very small.)

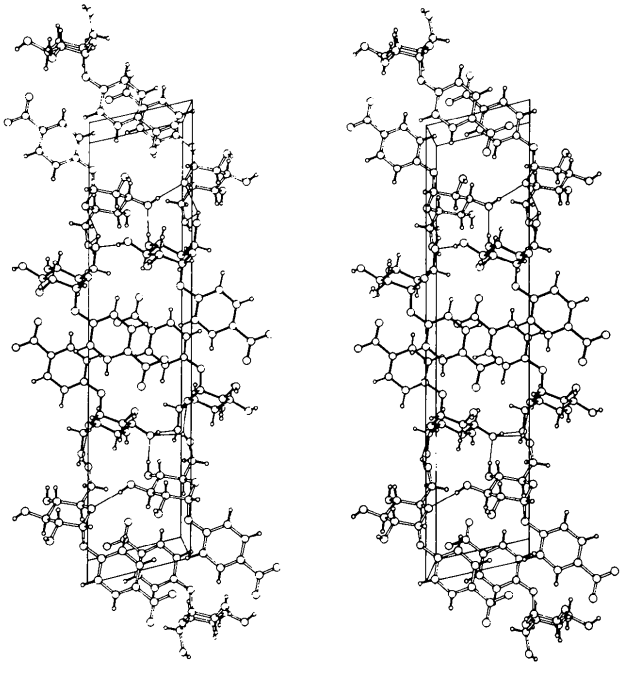

Fig. 3. Stereoview of the packing of the molecules. Molecule *A* is shown by solid bonds and molecule *B* by open bonds.

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Structure and Absolute Configuration of Ajugareptansone A

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Abstract

$C_{29}H_{40}O_{10}$, $M_r = 548{\cdot}6$, is orthorhombic, $P2_12_12_1$, with $a = 16{\cdot}225\,(3)$, $b = 11{\cdot}007\,(3)$, $c = 16{\cdot}401\,(3)$ Å, $Z = 4$, $V = 2929\,(1)$ Å^3, $D_c = 1{\cdot}24$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å. Ajugareptansone A was isolated from *Ajuga reptans*. The structure was solved by the *MULTAN* method and refined to an R of 0·057 for 3497 reflections. The absolute configuration was determined by the Bijvoet-difference method. The *A*,*B* rings adopt a *trans*-fused, chair–chair conformation. The absolute configuration of the title compound is the same as that of other clerodane compounds.

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Introduction

The title compound, ajugareptansone A, is isolated from *Ajuga reptans* (Camps, Coll & Cortel, 1981) and has insect antifeedant activity. It is a diterpenoid with a clerodane skeleton (I). It may be compared with its congener ajugareptansin (Camps, Coll, Cortel & Messeguer, 1979; Solans, Miravitlles, Declercq & Germain, 1979) which differs in having an (*S*)-(+)-2-methylbutyryloxy group β at C(1) and a hydroxy group β at C(3) and a hexahydroxyfurfuran group β at C(9). In order to determine unambiguously the structure and absolute configuration of the title compound, we have undertaken this X-ray study.