

- NISHIKAWA, M., KAMIYA, K., ASAHI, Y. & MATSUMURA, H. (1969). *Chem. Pharm. Bull.* **17**, 932–938.
- SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- SHIN, W. (1988). *Acta Cryst.* **C44**, 1754–1757.
- SHIN, W. & CHOI, J. W. (1989). *Acta Cryst.* **C45**, 1186–1189.
- SHIN, W. & CHUN, K. S. (1987). *Acta Cryst.* **C43**, 2123–2125.
- SHIN, W. & KIM, Y. C. (1986). *Bull. Korean Chem. Soc.* **7**, 331–334.
- SHIN, W. & LAH, M. S. (1987). *Acta Cryst.* **C43**, 125–129.
- TAYLOR, R. & KENNARD, O. (1982). *J. Am. Chem. Soc.* **104**, 5053–5070.

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2,2,6,6-Tetramethylpiperidine-1-oxyl-4-yl α -D-Glucopyranoside*

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Abstract. $C_{15}H_{28}NO_7$, $M_r = 334.39$, monoclinic, $P2_1$, $a = 9.239$ (4), $b = 14.475$ (6), $c = 6.404$ (3) Å, $\beta = 91.19$ (5)°, $V = 856.25$ Å³, $Z = 2$, $D_m = 1.297$, $D_x = 1.303$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 0.766$ mm⁻¹, $F(000) = 362.00$, $T = 293$ K, final $R = 0.040$ for 1395 observed reflections. The sugar moiety adopts a ⁴C₁ conformation. The piperidine moiety has a chair conformation in which four ring atoms are planar. The glycosidic linkage is confirmed to be α . Strong intermolecular three-dimensional hydrogen bonding exists in the crystal structure.

Introduction. The spin-labelled sugar 2,2,6,6-tetramethylpiperidine-1-oxyl-4-yl α -D-glucopyranoside (TEMPOG) has been synthesized as described by Stassinopoulou & Troganis (1990). The saccharide has been used as a probe to study the modes of interaction of the legume lectin concanavalin A (con A) with carbohydrate ligands (Stassinopoulou & Troganis, 1990). We have been performing modelling studies of con A-saccharide complexes combining evidence from ¹H NMR, ESR and fluorescence

* 4-(α -D-Glucopyranosyloxy)-2,2,6,6-tetramethylpiperidine 1-oxide.

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measurements, semi-empirical energy calculations and interactive graphics modelling, which require precise molecular geometries (Hamodrakas, Alexandraki, Troganis & Stassinopoulou, 1989). In this report, we present the molecular geometry of TEMPOG, currently used in similar modelling studies (Hamodrakas, Alexandraki, Troganis & Stassinopoulou, 1992), as determined by X-ray crystallography.

Experimental. Crystals were grown from methanol as pale-orange prisms. Unit-cell parameters and space group were determined from precession photographs and refined by least-squares refinement of the setting angles for 12 high-angle ($40 < 2\theta < 60^\circ$) reflections automatically centered on a Picker Facs-1 diffractometer. D_m by flotation. Intensity data were collected at room temperature from a crystal of dimensions $0.4 \times 0.6 \times 0.4$ mm using Ni-filtered Cu $K\alpha$ radiation and θ - 2θ scan mode. A total of 1529 unique reflections (after merging equivalents, merging $R_{\text{int}} = 0.05$) were recorded, of which 1395 were considered observed at the 3σ level [$I > 3\sigma(I)$]. 2θ range was $3 < 2\theta < 130^\circ$. Index range: -10 to 10 (h), 0 to 17 (k), 0 to 7 (l). Intensities were corrected for Lorentz and polarization effects but not for absorption. The structure was solved in $P2_1$ by direct

Table 1. Fractional atomic coordinates ($\times 10^4$) for non-H atoms and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^4$) with *e.s.d.*'s in parentheses

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j \quad (\text{Hamilton, 1959}).$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
O(1)	785 (3)	3230	1332 (3)	333 (13)
O(2)	346 (3)	5126 (3)	-2427 (5)	377 (14)
O(3)	2628 (3)	2393 (3)	-177 (3)	411 (14)
O(4)	6740 (3)	245 (3)	3625 (5)	493 (16)
C(5)	388 (3)	2524 (3)	-2071 (6)	328 (18)
O(6)	895 (3)	1882 (3)	-3546 (5)	519 (18)
C(7)	208 (3)	4232 (3)	-1541 (6)	288 (17)
C(8)	529 (3)	3476 (3)	-3070 (6)	279 (17)
O(9)	-474 (3)	3549 (3)	-4779 (3)	368 (13)
O(10)	-377 (3)	5056 (3)	2558 (5)	471 (17)
C(11)	3404 (5)	890 (3)	913 (6)	386 (21)
N(12)	5738 (3)	751 (3)	2813 (5)	346 (16)
C(13)	1174 (3)	4095 (3)	392 (6)	313 (18)
C(14)	1133 (3)	2451 (3)	66 (6)	336 (18)
C(15)	4887 (5)	2278 (3)	1569 (6)	405 (22)
C(16)	3382 (3)	1906 (3)	1484 (6)	339 (18)
C(17)	5928 (3)	1772 (3)	3063 (6)	383 (21)
C(18)	4314 (3)	292 (3)	2417 (6)	357 (19)
C(19)	1064 (5)	4869 (3)	1979 (6)	426 (23)
C(20)	3573 (6)	125 (5)	4487 (7)	563 (27)
C(21)	4620 (6)	-627 (3)	1348 (9)	563 (28)
C(22)	7473 (5)	2008 (3)	2506 (9)	564 (29)
C(23)	5669 (6)	2030 (5)	5345 (7)	660 (33)

methods using *SHELXS86* (Sheldrick, 1985). H atoms were located from difference Fourier maps or calculated from geometrical considerations. Refinement of 262 parameters was by least squares on *F*; space group *P2*₁. In the final cycles, non-H atoms had anisotropic temperature factors. All H atoms, except those of the methyl groups, were given a fixed isotropic temperature factor of 0.05 \AA^2 and their positional parameters were refined. The methyl groups were set up as staggered methyl groups and then refined as rigid bodies. The methyl H atoms were given a common temperature factor of 0.05 \AA^2 , which refined to a higher value of 0.083 \AA^2 . Unit weights were used. Final *R* = 0.04, *S* = 2.35, (Δ/σ)_{max} = 0.06. Maximum and minimum heights in the final difference Fourier synthesis map were 0.22 and -0.20 $e \text{\AA}^{-3}$, respectively. Refinement calculations used *SHELX76* (Sheldrick, 1976) with atomic scattering factors as supplied by the program.

Discussion. Positional and isotropic thermal parameters of non-H atoms are listed in Table 1.* Bond lengths, bond angles and selected torsion angles are given in Table 2. A perspective view of the molecule showing the atomic numbering scheme is given in Fig. 1 and the unit-cell packing is depicted stereoscopically in Fig. 2.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55558 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR1005]

Table 2. Bond lengths (\AA), bond angles ($^\circ$), selected torsion angles ($^\circ$) and hydrogen-bonding geometry (\AA , $^\circ$) with *e.s.d.*'s in parentheses

O(3)—C(14)	1.396 (5)	O(3)—C(16)	1.445 (4)
C(14)—C(5)	1.523 (5)	C(16)—C(15)	1.491 (6)
C(5)—C(8)	1.525 (5)	C(15)—C(17)	1.529 (6)
C(8)—C(7)	1.503 (5)	C(17)—N(12)	1.495 (5)
C(7)—C(13)	1.525 (5)	N(12)—C(18)	1.491 (5)
C(13)—O(1)	1.440 (5)	C(18)—C(11)	1.533 (6)
O(1)—C(14)	1.428 (5)	C(11)—C(16)	1.516 (6)
C(5)—O(6)	1.413 (5)	C(17)—C(23)	1.532 (6)
C(8)—O(9)	1.423 (5)	C(17)—C(22)	1.517 (6)
C(7)—O(2)	1.418 (5)	C(18)—C(20)	1.524 (6)
C(13)—C(19)	1.516 (6)	C(18)—C(21)	1.526 (6)
C(19)—O(10)	1.417 (6)	N(12)—O(4)	1.282 (4)
O(3)—C(14)—C(5)	109.4 (3)	O(3)—C(14)—O(1)	110.2 (3)
O(1)—C(14)—C(5)	110.6 (3)	C(14)—C(5)—O(6)	113.9 (3)
C(14)—C(5)—C(8)	113.6 (3)	O(6)—C(5)—C(8)	106.3 (3)
C(5)—C(8)—O(9)	109.2 (3)	C(5)—C(8)—C(7)	108.3 (3)
O(9)—C(8)—C(7)	108.3 (3)	C(8)—C(7)—O(2)	112.5 (3)
C(8)—C(7)—C(13)	108.3 (3)	O(2)—C(7)—C(13)	112.8 (3)
C(7)—C(13)—C(19)	113.7 (3)	C(7)—C(13)—O(1)	107.7 (3)
C(19)—C(13)—O(1)	110.0 (6)	C(13)—C(19)—O(10)	113.2 (4)
C(13)—O(1)—C(14)	112.9 (3)	C(14)—O(3)—C(16)	114.2 (3)
O(3)—C(16)—C(11)	107.7 (3)	O(3)—C(16)—C(15)	106.6 (3)
C(11)—C(16)—C(15)	110.0 (3)	C(16)—C(11)—C(18)	113.9 (3)
C(11)—C(18)—C(20)	112.7 (4)	C(11)—C(18)—C(21)	106.3 (4)
C(11)—C(18)—N(12)	109.0 (3)	C(20)—C(18)—C(21)	110.0 (4)
C(20)—C(18)—N(12)	109.5 (4)	C(21)—C(18)—N(12)	107.2 (3)
C(18)—N(12)—O(4)	116.1 (3)	C(18)—N(12)—C(17)	124.1 (3)
O(4)—N(12)—C(17)	116.1 (3)	N(12)—C(17)—C(22)	107.8 (3)
N(12)—C(17)—C(23)	108.8 (4)	N(12)—C(17)—C(15)	109.6 (3)
C(22)—C(17)—C(23)	109.6 (3)	C(23)—C(17)—C(15)	111.8 (4)
C(17)—C(15)—C(16)	115.0 (4)		
C(5)—C(14)—O(3)—C(16)	-152.4 (3)		
O(1)—C(14)—O(3)—C(16)	85.7 (3)		
C(14)—O(3)—C(16)—C(11)	88.5 (3)		
C(14)—O(3)—C(16)—C(15)	-153.4 (3)		
O(2)...O(4 ^a)	2.820 (5)	O(2)—H...O(4 ^a)	172.6
O(9)...O(1 ^b)	2.808 (5)	O(9)—H...O(1 ^b)	149.6
O(6)...O(10 ^m)	2.761 (5)	O(6)—H...O(10 ^m)	180
O(10)...O(9 ⁿ)	2.773 (5)	O(10)—H...O(9 ⁿ)	180

Symmetry code: (i) *x* + 1, 0.5 + *y*, *z*; (ii) *x*, *y*, *z* - 1; (iii) *x*, *y* - 0.5, *z*; (iv) *x*, *y*, *z* + 1.

The saccharide unit of the molecule adopts the ⁴C₁ chair conformation (Stoddart, 1971). The mean C—C and C—O (hydroxy) bond lengths of 1.519 (5) and 1.418 (5) \AA of the saccharide moiety compare well with similar averages observed in pyranose sugars (Berman, Chu & Jeffrey, 1967). The shortness of the C(14)—O(3) bond, 1.396 (5) \AA , relative to the other C—O bonds in the saccharide, reflects its glycosidic bond character (Berman, Chu & Jeffrey, 1967). The bond lengths and angles in the tetramethylpiperidine oxide group are in good agreement with the values reported for the molecular structures of similar compounds (Lajzerowicz-Bonnetau, 1976, and references therein). The piperidine ring adopts a chair conformation in which four atoms, C(11), C(15), C(17) and C(18), constitute an almost ideal plane (deviations not more than 0.012 \AA). The distances of the N(12) and O(4) atoms from this plane are 0.41 and 0.74 \AA , respectively, and for the C(16) and O(3) atoms the distances are -0.66 and -0.43 \AA , respectively. The *N*-oxide grouping

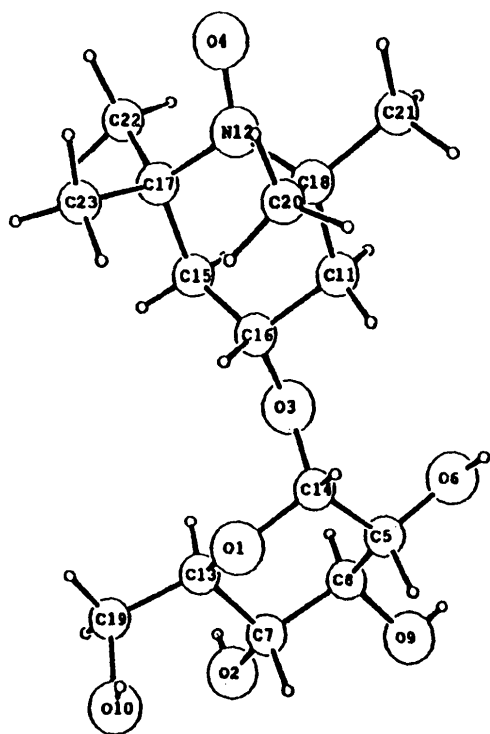


Fig. 1. ORTEP (Johnson, 1976) drawing of the molecule showing the atomic numbering scheme.

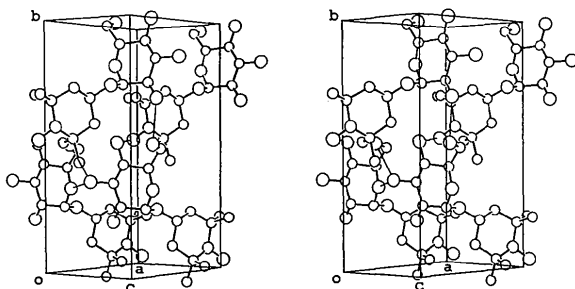


Fig. 2. ORTEP stereoscopic projection of the crystal packing.

approaches planarity, the N atom lying 0.16 Å out of the plane of its three bonded neighbors.

The sugar and piperidine rings are rotated about 30° with respect to each other. This mutual orientation is best illustrated by considering the angles between perpendiculars to the 'best' plane through the sugar ring and the glycosidic link plane and between the 'best' plane through the piperidine ring and glycosidic plane; these values are 92 and 60°, respectively. The glycosidic linkage is confirmed to be α .

As shown in Fig. 2, the molecules are held together by a strong intermolecular three-dimensional hydrogen-bond network in which all hydroxyl H atoms are involved as donors. Acting as acceptors are the sugar ring O(1) atom, the *N*-oxide O(4) atom and hydroxyl O(9) and O(10) atoms. The hydrogen-bonding details are given in Table 2.

References

- BERMAN, H. M., CHU, S. S. C. & JEFFREY, G. A. (1967). *Science*, **157**, 1576–1577.
- HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.
- HAMODRAKAS, S. J., ALEXANDRAKI, E., TROGANIS, A. & STASSINOPOULOU, C. I. (1989). *Int. J. Biol. Macromol.* **11**, 17–22.
- HAMODRAKAS, S. J., ALEXANDRAKI, E., TROGANIS, A. & STASSINOPOULOU, C. I. (1992). In preparation.
- JOHNSON, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- LAJZEROWICZ-BONNETAU, J. (1976). In *Spin Labelling: Theory and Applications*, edited by R. J. BERLINER. London: Academic Press.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- SHELDRIK, G. M. (1985). *SHELX86*. In *Crystallographic Computing 3*, edited by G. M. SHELDRIK, C. KRÜGER & R. GODDARD, pp. 175–189. Oxford Univ. Press.
- STASSINOPOULOU, C. I. & TROGANIS, A. (1990). *Lectins – Biology, Biochemistry, Clinical Biochemistry*, Vol. VII, pp. 161–168. St. Louis, MO: Sigma Chemical Company.
- STODDART, J. F. (1971). *Stereochemistry of Carbohydrates*. New York: Wiley-Interscience.

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Structure of Debrisoquinium Sulfate

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Abstract. 3,4-Dihydro-2(1*H*)-isoquinolinecarboxamidinium sulfate, $2C_{10}H_{14}N_3^+ \cdot SO_4^{2-}$, $M_r = 448.5$, monoclinic, $C2/c$, $a = 27.214$ (10), $b = 6.552$ (1), $c =$

13.241 (1) Å, $\beta = 113.35$ (2)°, $V = 2168$ (1) Å³, $Z = 4$, $D_x = 1.375$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 1.81$ cm⁻¹, $F(000) = 952$, room temperature, final R