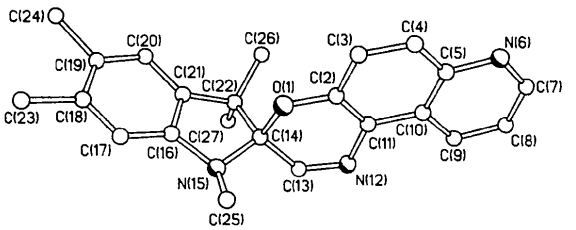

Fig. 1. A view of the molecule showing the atom-numbering scheme adopted. Only one component of the disorder is shown; the other exchanges the role of N(15) and C(22), replacing C(27) by C(27x) attached to N(15). H atoms omitted.

Related literature. The compound is a member of a class of spiroindolinopyridobenzoxazines which exhibit photochromic properties (Kwak & Hurditch, 1984). Additional classes of compounds, namely the spiroindolinobenzopyrans and spiroindolinonaphthoxazines (Chu, 1983) also show similar photochromic properties. This is the first report of structural data for the spiroindolinopyridobenzoxazines although structures have been reported on spiroindolinobenzopyrans (Simkin, Makarov, Furmanova, Karaev & Minkin, 1984). A general discussion of these and other photochromic compounds is available (Bertelson, 1971).

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The Tetrasaccharide Stachyose

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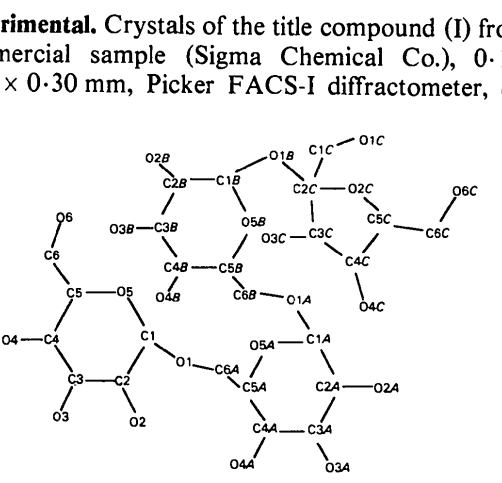
Abstract. *O*-α-D-Galactopyranosyl-(1→6)-*O*-α-D-galactopyranosyl-(1→6)-*O*-α-D-glucopyranosyl (1→2)-α-D-fructofuranoside pentahydrate, $C_{24}H_{42}O_{21}.5H_2O$, M_r = 756·7, orthorhombic, $P2_12_12$, a = 12·801 (6), b = 24·026 (5), c = 10·856 (6) Å, V = 3338·8 (2) Å^3, Z = 4, D_x = 1·505 Mg m^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, μ = 1·159 mm^{-1}, $F(000)$ = 1616, T = 568 K, final R = 0·060 for 3120 unique observed reflections. The three pyranose rings are normal chair forms and the fructofuranosyl ring is puckered with conformation $_3T^4$ according to the nomenclature of Jeffrey & Park [*Acta Cryst.* (1972), B**28**, 257–267]. Several distinct H_2O molecules were found in difference maps. All of the waters refined to partial occupancies; however, none could be omitted without a significant increase in the overall R factor. No single hydrogen-bonding network can involve the full set of solvent molecules which contains several pairs which cannot coexist because they are too close to one another. Several distinct hydrogen-bonding schemes are possible, each involving different sets of three or four solvent molecules.

0108-2701/87/040806-03$01.50

Experimental. Crystals of the title compound (I) from a commercial sample (Sigma Chemical Co.), 0·15 × 0·10 × 0·30 mm, Picker FACS-I diffractometer, $\theta/2\theta$



(I)

data collection, scan width 2°, 2θ scan rate 2° min^{-1}, 10 s background count, $2\theta < 127·3°$, lattice parameters from 12 reflections with $35 < 2\theta < 50°$, corrections for Lorentz and polarization but not

absorption, $h = 0$–14, $k = 0$–27, $l = 0$–12, standard reflections 007, 782, 161 monitored every 100 reflections, intensity variation 2·0%, 3120 unique reflections, all considered observed. Structure solution by direct methods (Karle & Karle, 1966; Karle, 1968). All H_2O disordered; all seven water molecule sites partially occupied; range of occupancies 0·34–0·70, sum of water occupancies 3·57. 1:1 disorder is also proposed for four atoms of stachyose itself; when refined without this disorder, the thermal ellipsoids were extremely elongated and one solvent peak (*W*3) was too close to

Table 1. *Atomic coordinates and equivalent isotropic temperature coefficients* (Å²)

$B_{eq} = \frac{1}{3}\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	*y*	*z*	B_{eq}
C1	0·2070 (4)	0·2765 (2)	0·6275 (5)	2·5 (6)
C2	0·1912 (4)	0·3223 (2)	0·5348 (5)	2·7 (6)
C3	0·2856 (4)	0·3275 (2)	0·4526 (5)	2·7 (6)
C4	0·3862 (4)	0·3343 (2)	0·5277 (5)	2·6 (6)
C5	0·3930 (3)	0·2874 (2)	0·6212 (4)	2·4 (6)
C6	0·4824 (4)	0·2910 (2)	0·7124 (5)	3·1 (7)
C1*A*	0·3512 (3)	0·0658 (2)	0·5244 (4)	2·1 (6)
C2*A*	0·2850 (4)	0·0154 (1)	0·5593 (4)	2·3 (6)
C3*A*	0·1712 (4)	0·0268 (2)	0·5301 (4)	2·4 (6)
C4*A*	0·1375 (3)	0·0793 (2)	0·5977 (4)	2·3 (5)
C5*A*	0·2081 (3)	0·1271 (2)	0·5626 (4)	2·2 (5)
C6*A*	0·1842 (4)	0·1790 (2)	0·6368 (5)	2·6 (6)
C1*B*	0·4249 (4)	0·0791 (2)	0·0253 (4)	2·8 (1)
C2*B*	0·3163 (9)	0·0944 (6)	−0·0179 (10)	4·6 (22)
C3*B*	0·2782 (8)	0·1460 (7)	0·0434 (11)	5·1 (24)
C4*B*	0·2919 (4)	0·1431 (2)	0·1839 (5)	3·6 (8)
C5*B*	0·4022 (4)	0·1241 (2)	0·2176 (4)	2·8 (7)
C6*B*	0·4162 (4)	0·1154 (2)	0·3542 (4)	2·9 (7)
C1*C*	0·5628 (5)	0·0835 (3)	−0·2042 (5)	4·2 (9)
C2*C*	0·5875 (4)	0·1039 (2)	−0·0760 (5)	3·5 (8)
C3*C*	0·6638 (5)	0·1528 (3)	−0·0677 (6)	5·2 (10)
C4*C*	0·7128 (4)	0·1422 (2)	0·0577 (5)	3·9 (9)
C5*C*	0·7269 (4)	0·0797 (3)	0·0557 (5)	4·3 (9)
C6*C*	0·7316 (5)	0·0502 (3)	0·1786 (6)	4·9 (9)
O1	0·2124 (2)	0·2260 (1)	0·5637 (3)	2·6 (4)
O2	0·0989 (3)	0·3090 (1)	0·4678 (3)	3·5 (5)
O3	0·2724 (3)	0·3728 (1)	0·3677 (3)	3·6 (5)
O4	0·3854 (3)	0·3863 (1)	0·5911 (3)	3·3 (4)
O5	0·3006 (2)	0·2855 (1)	0·6965 (3)	2·5 (4)
O6	0·5811 (2)	0·2950 (1)	0·6505 (3)	3·7 (5)
O1*A*	0·3456 (2)	0·0720 (1)	0·3957 (3)	2·4 (4)
O2*A*	0·3230 (3)	−0·0350 (1)	0·5050 (3)	3·0 (4)
O3*A*	0·1059 (3)	−0·0193 (1)	0·5660 (4)	3·4 (4)
O4*A*	0·1405 (2)	0·0703 (1)	0·7272 (3)	3·0 (5)
O5*A*	0·3159 (2)	0·1136 (1)	0·5870 (3)	2·1 (4)
O1*B*	0·4954 (2)	0·1209 (1)	−0·0123 (3)	3·0 (5)
O2*B*	0·3232 (6)	0·1013 (5)	−0·1487 (7)	6·1 (19)
O3*B*	0·1670 (6)	0·1416 (4)	0·0130 (9)	5·9 (17)
O4*B*	0·2747 (3)	0·1953 (1)	0·2400 (4)	4·8 (6)
O5*B*	0·4283 (2)	0·0730 (1)	0·1550 (3)	2·7 (4)
O1*C*	0·5153 (3)	0·1260 (1)	−0·2764 (3)	4·0 (6)
O2*C*	0·6372 (3)	0·0587 (1)	−0·0120 (3)	3·9 (6)
O3*C*	0·6173 (4)	0·2053 (2)	−0·0780 (5)	8·2 (7)
O4*C*	0·8101 (3)	0·1700 (2)	0·0702 (4)	5·4 (7)
O6*C*	0·6423 (3)	0·0619 (1)	0·2543 (3)	4·3 (6)
Disorder(1:1)				
C2*BS*	0·3154 (9)	0·0966 (5)	−0·0156 (10)	3·9 (18)
C3*BS*	0·2853 (10)	0·1508 (6)	0·0456 (11)	4·7 (19)
O2*BS*	0·3212 (6)	0·1012 (4)	−0·1456 (7)	5·2 (15)
O3*BS*	0·1826 (6)	0·1731 (3)	0·0143 (9)	4·7 (12)
Solvent*				
*W*1|0·70|	0·4059 (7)	0·2791 (3)	0·1393 (8)	9·3 (14)
*W*2|0·61|	0·4413 (7)	0·3959 (5)	0·2118 (9)	10·0 (24)
*W*3|0·54|	0·0993 (8)	0·2341 (4)	0·9049 (9)	6·6 (15)
*W*4|0·52|	0·0259 (8)	0·0472 (6)	0·2462 (16)	13·7 (26)
*W*5|0·44|	0·0432 (12)	0·0544 (10)	0·0225 (14)	16·9 (48)
*W*6|0·42|	0·4496 (13)	0·4588 (6)	0·1830 (12)	10·6 (23)
*W*7|0·34|	0·4778 (14)	0·3573 (8)	0·0711 (20)	10·5 (32)

* Occupancies for solvent molecules given in square brackets.

Table 2. *Stachyose bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Disordered values are given in square brackets.

C1–C2	1·505 (8)	C1*A*–C2*A*	1·526 (7)	
C1–O1	1·399 (6)	C1*A*–O1*A*	1·407 (6)	
C1–O5	1·430 (6)	C1*A*–O5*A*	1·410 (6)	
C2–C3	1·508 (8)	C2*A*–C3*A*	1·514 (8)	
C2–O2	1·424 (7)	C2*A*–O2*A*	1·433 (6)	
C3–O3	1·436 (6)	C3*A*–O3*A*	1·441 (6)	
C3–C4	1·534 (8)	C3*A*–C4*A*	1·523 (7)	
C4–O4	1·427 (6)	C4*A*–O4*A*	1·425 (6)	
C4–C5	1·521 (7)	C4*A*–C5*A*	1·508 (7)	
C5–C6	1·515 (8)	C5*A*–C6*A*	1·515 (7)	
C5–O5	1·439 (6)	C5*A*–O5*A*	1·443 (6)	
C6–O6	1·434 (7)	C6*A*–O1	1·428 (6)	
C1*C*–O1*C*	1·424 (8)	C1*B*–C2*B*	1·513 (13)	[1·530 (13)]
C2*C*–C1*C*	1·509 (8)	C1*B*–O1*B*	1·411 (7)	
C2*C*–O1*B*	1·426 (7)	C1*B*–O5*B*	1·416 (6)	
C2*C*–O2*C*	1·438 (8)	C2*B*–C3*B*	1·488 (22)	[1·565 (21)]
C2*C*–C3*C*	1·531 (9)	C2*B*–O2*B*	1·432 (14)	[1·398 (14)]
C3*C*–O3*C*	1·398 (9)	C3*B*–O3*B*	1·466 (14)	[1·423 (16)]
C3*C*–C4*C*	1·521 (9)	C3*B*–C4*B*	1·537 (14)	[1·517 (14)]
C4*C*–O4*C*	1·421 (8)	C4*B*–O4*B*	1·412 (8)	
C4*C*–C5*C*	1·513 (10)	C4*B*–C5*B*	1·528 (8)	
C5*C*–C6*C*	1·511 (9)	C5*B*–C6*B*	1·508 (7)	
C5*C*–O2*C*	1·454 (8)	C5*B*–O5*B*	1·443 (7)	
C6*C*–O6*C*	1·434 (8)	C6*B*–O1*A*	1·451 (7)	

O1–C1–O5	110·3 (4)	O1*A*–C1*A*–O5*A*	112·1 (4)	
O1–C1–C2	108·0 (4)	O1*A*–C1*A*–C2*A*	107·6 (4)	
O5–C1–C2	110·7 (4)	O5*A*–C1*A*–C2*A*	110·4 (4)	
C1–C2–C3	110·5 (4)	C1*A*–C2*A*–C3*A*	109·8 (4)	
C1–C2–O2	106·8 (4)	C1*A*–C2*A*–O2*A*	112·3 (4)	
O2–C2–C3	112·4 (5)	O2*A*–C2*A*–C3*A*	113·1 (4)	
C2–C3–C4	111·5 (5)	C2*A*–C3*A*–C4*A*	108·8 (4)	
C2–C3–O3	110·3 (4)	C2*A*–C3*A*–O3*A*	111·3 (4)	
O3–C3–C4	111·1 (4)	O3*A*–C3*A*–C4*A*	110·0 (4)	
C3–C4–C5	108·9 (4)	C3*A*–C4*A*–C5*A*	109·8 (4)	
C3–C4–O4	110·1 (4)	C3*A*–C4*A*–O4*A*	109·9 (4)	
O4–C4–C5	109·1 (4)	O4*A*–C4*A*–C5*A*	110·5 (4)	
C4–C5–O5	110·8 (4)	C4*A*–C5*A*–O5*A*	110·8 (4)	
C4–C5–C6	115·9 (4)	C4*A*–C5*A*–C6*A*	111·8 (4)	
O5–C5–C6	104·6 (4)	O5*A*–C5*A*–C6*A*	106·2 (4)	
C5–O5–C1	113·3 (4)	C5*A*–O5*A*–C1*A*	113·6 (4)	
C5–C6–O6	111·4 (5)	C5*A*–C6*A*–O1	107·8 (4)	
C1–O1–C6*A*	113·5 (4)	C1*A*–O1*A*–C6*B*	110·7 (4)	
O1*C*–C1*C*–C2*C*	111·4 (6)	O1*B*–C1*B*–O5*B*	110·0 (4)	
O2*C*–C2*C*–O1*B*	110·4 (4)	O1*B*–C1*B*–C2*B*	108·9 (7)	[107·9 (6)]
O2*C*–C2*C*–C3*C*	105·7 (5)	O5*B*–C1*B*–C2*B*	111·1 (6)	[110·2 (6)]
O2*C*–C2*C*–C1*C*	107·0 (5)	C1*B*–C2*B*–C3*B*	111·5 (9)	[110·0 (9)]
C1*C*–C2*C*–C3*C*	116·0 (5)	C1*B*–C2*B*–O2*B*	106·3 (8)	[105·2 (8)]
C1*C*–C2*C*–O1*B*	111·5 (5)	O2*B*–C2*B*–C3*B*	111·4 (12)	[112·5 (11)]
O1*B*–C2*C*–C3*C*	106·1 (5)	C2*B*–C3*B*–C4*B*	111·6 (11)	[108·6 (10)]
C2*C*–O2*C*–C5*C*	109·4 (5)	C2*B*–C3*B*–O3*B*	99·3 (11)	[116·7 (11)]
O3*C*–C3*C*–C4*C*	113·6 (6)	O3*B*–C3*B*–C4*B*	109·3 (9)	[109·0 (9)]
C2*C*–C3*C*–O3*C*	114·6 (5)	C3*B*–C4*B*–C5*B*	110·8 (6)	[109·0 (7)]
C4*C*–C3*C*–C2*C*	100·6 (5)	C3*B*–C4*B*–O4*B*	111·7 (8)	[108·2 (7)]
C3*C*–C4*C*–C5*C*	101·9 (5)	O4*B*–C4*B*–C5*B*	107·8 (5)	
C3*C*–C4*C*–O4*C*	111·5 (5)	C4*B*–C5*B*–O5*B*	110·8 (4)	
C5*C*–C4*C*–O4*C*	111·2 (5)	C4*B*–C5*B*–C6*B*	112·7 (4)	
O2*C*–C5*C*–C4*C*	104·8 (5)	O5*B*–C5*B*–C6*B*	108·5 (4)	
O2*C*–C5*C*–C6*C*	108·4 (5)	C5*B*–O5*B*–C1*B*	111·9 (4)	
C4*C*–C5*C*–C6*C*	117·1 (6)	C5*B*–C6*B*–O1*A*	109·3 (4)	
C5*C*–C6*C*–O6*C*	112·5 (6)	C1*B*–O1*B*–C2*B*	117·7 (4)	

Selected torsion angles

Six-membered rings	C1–O5	C1*A*–O5*A*	C1*B*–O5*B*
C1–C2–C3–C4	−53·4	−56·7	−49·8
C2–C3–C4–C5	52·9	56·3	48·4
C3–C4–C5–O5	−55·0	−56·1	−52·7
C4–C5–O5–C1	60·1	58·4	60·3
C5–O5–C1–C2	−59·7	−58·6	−61·8
O5–C1–C2–C3	55·4	57·7	56·4

Five-membered rings		Others	
C2*C*–C3*C*–C4*C*–C5*C*	41·1	C1–O1–C6*A*–C5*A*	−172·2
C3*C*–C4*C*–C5*C*–O2*C*	−35·3	C1*A*–O1*A*–C6*B*–C5*B*	−175·6
C4*C*–C5*C*–O2*C*–C2*C*	14·8	C1*B*–O1*B*–C2*C*–C3*C*	−161·9
C5*C*–O2*C*–C2*C*–C3*C*	11·7	C1*B*–O1*B*–C2*C*–O2*C*	−47·9
O2*C*–C2*C*–C3*C*–C4*C*	−33·1	C4–C5–C6–O6	−55·7
		O5–C5–C6–O6	−178·1
		O2*C*–C2*C*–C1*C*–O1*C*	−178·6
		O2*C*–C5*C*–C6*C*–O6*C*	−63·4

the stachyose molecule. This suggests that this particular ring moves away when $W3$ is included in the crystal and moves back when it is absent. Refinement by restrained least-squares methods using program *RESLSQ* (Flippen-Anderson, Gilardi & Konnert, 1983). H atoms from difference map. 624 parameters refined: coordinates and anisotropic thermal parameters for all non-H atoms, coordinates for H atoms (thermal parameters set equal to those of covalently bonded atoms). Function minimized $\sum w(|F_o| - |F_c|)^2$ where the weights w were calculated based on counting statistics with a term included for random error (0·02 in this case) (Gilardi, 1973). Scattering factors from *International Tables for X-ray Crystallography* (1962). $R = 0{\cdot}060$, $wR = 0{\cdot}070$ for 3120 reflections, maximum least-squares shift/e.s.d. 0·69 for a H_2O molecule, final difference Fourier $\Delta\rho$ excursions 0·30 and $-0{\cdot}20$ e Å^{-3}. No correction for secondary extinction. Atomic coordinates and equivalent isotropic temperature coefficients are given in Table 1, and bond lengths, bond angles and torsion angles in Table 2.* Fig. 1 shows an *ORTEP* (Johnson, 1965) drawing of the structure.

Related literature. A preliminary note describing the conformation of this structure and its relation to other sugars has been published (Gilardi & Flippen, 1975). Related sugar structures have also been published (Berman, 1970; Rohrer, 1972).

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and torsion angle values have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43586 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

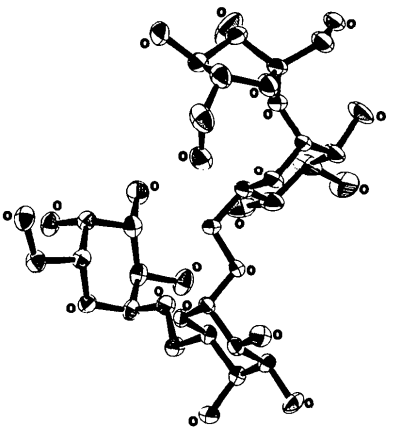


Fig. 1. *ORTEP* (Johnson, 1965) drawing of stachyose.

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