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Structure of Racemic Perseitol (D,L-*glycero*-D,L-*galacto*-Heptitol)

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Abstract. $C_7H_{16}O_7$, $M_r = 212{\cdot}20$, monoclinic, Cc, $a = 20{\cdot}888\,(1)$, $b = 4{\cdot}858\,(1)$, $c = 9{\cdot}221\,(1)$ Å, $\beta = 99{\cdot}888\,(5)°$, $V = 921{\cdot}8\,(2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}529$ g cm^{-3}, $\lambda(\mathrm{Cu}\,K\alpha_1) = 1{\cdot}54051$ Å, $\mu = 11{\cdot}5$ cm^{-1}, $F(000) = 456$, $T = 293$ K, $R = 0{\cdot}026$ for 963 observed reflexions. The molecules adopt a planar zigzag conformation. They are interchained by a complex pattern of intermolecular hydrogen bonds involving all hydroxyl groups as donors and acceptors. The packing of the molecules is more dense than in the case of the pure enantiomers.

Introduction. Heptitols can occur as ten diastereomers, of which four are *meso* forms and the others are found as six enantiomeric pairs. As yet, the crystal structures of *meso-glycero-gulo*-heptitol (Nimgirawath, James & Mills, 1976), D-*glycero*-L-*allo*-heptitol (Angyal, Saunders, Grainger, Le Fur & Williams, 1986), D-*glycero*-D-*galacto*-heptitol, 'D-perseitol' (Kanters, Schouten, van der Sluis & Duisenberg, 1990), D-*glycero*-L-*galacto*-heptitol (Kopf, Köll & Angyal, 1991) and D-*glycero*-D-*manno*- and D-*glycero*-D-*gluco*-heptitol (Köll, Komander, Angyal, Morf, Zimmer & Kopf, 1991) have been determined. We now report the first structure determination of the racemate of one of the chiral diastereomers, namely of D,L-perseitol.

Experimental. Crystals suitable for X-ray analysis were obtained from a mixture of equal amounts of D- and L-perseitol dissolved in moist ethanol. D-perseitol was a commercial sample (Pfanstiehl Laboratories), while L-perseitol was prepared according to known procedures (Wolfrom & Thompson, 1963) from commercially available D-*glycero*-L-*mannono*-1,4-lacton (Janssen–Chimica) by sodium borohydride reduction at pH 6. The thus obtained racemic crystals of D,L-perseitol melted at 479–480 K. Therefore, a conglomerate of pure D- and L-perseitol crystals could be excluded (Jacques, Collet & Wilen, 1981) because the melting point of pure enantiomers is 20 K lower. A colorless transparent crystal of dimensions 0·6 × 0·2 × 0·1 mm was used for data collection on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Cu $K\alpha$ radiation. From the systematic absences (hkl: $h + k = 2n$ and $h0l$: $l = 2n$) the possible space groups are Cc (No. 9) or $C2/c$ (No. 15). The calculated density with $Z = 4$ gives the expected value of 1·529 g cm^{-3}. Therefore, only the space group Cc is possible, because with $Z = 4$ the molecules in $C2/c$ must possess either a center of inversion ($\bar{1}$) or a twofold rotation axis (2). Both cases are impossible for chiral molecules with a central carbon chain of seven C atoms. The cell parameters were determined by least-squares refinement of the setting angles of 24 reflexions within $39{\cdot}7 \leq 2\theta \leq 50{\cdot}4°$. Intensity data were measured by $\theta/2\theta$ scans ($4{\cdot}5 \leq 2\theta \leq 153°, 0 \leq h \leq 26, 0 \leq k \leq 6, -11 \leq l \leq 11$). There was no significant decay in the intensities for three standards monitored after every 2 h. Initially, the data collection was performed with the primitive Bravais-lattice type and, accordingly, of 2299 measured data, 1240 were rejected as systematically absent. Finally, 981 reflexions were symmetry independent ($R_{\rm int} = 0{\cdot}011$) of which 963 intensities were considered observed [$|F_o| > 3\sigma(F_o)$]. The data were corrected for Lorentz and polarization effects, but not for absorption.

The structure was solved by direct methods. The solution with the highest figure of merit showed all non-H atoms. All aliphatic H atoms were localized in theoretical positions (sp^3 hybridization) with a C—H distance of 0·96 Å. The hydroxyl group H atoms were all taken from a difference map. Full-matrix least-squares refinement on F of 190 parameters including scale factor, positional and anisotropic thermal parameters for all non-H atoms, and positional and isotropic parameters for all H atoms

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Table 1. *Final fractional coordinates of* C *and* O *atoms with equivalent isotropic thermal parameters* (Å^2) *and of* H *atoms with isotropic thermal parameters* (Å^2); *e.s.d.'s are given in parentheses*

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	U_{eq}
O(1)	0·0467 (1)	0·3342 (4)	0·5828 (2)	0·0450 (5)
O(2)	0·1052 (1)	0·8541 (3)	0·8568 (2)	0·0287 (4)
O(3)	0·1709	0·3336 (3)	0·8951	0·0271 (4)
O(4)	0·2302 (1)	0·8524 (3)	0·6653 (2)	0·0240 (3)
O(5)	0·2954 (1)	0·3312 (3)	0·6787 (1)	0·0278 (4)
O(6)	0·3534 (1)	0·8551 (3)	0·9515 (2)	0·0280 (4)
O(7)	0·4216 (1)	0·3363 (3)	0·9928 (2)	0·0323 (4)
C(1)	0·0457 (1)	0·5045 (5)	0·7067 (3)	0·0298 (5)
C(2)	0·1079 (1)	0·6725 (4)	0·7359 (3)	0·0228 (4)
C(3)	0·1690 (1)	0·4949 (3)	0·7643 (3)	0·0200 (4)
C(4)	0·2312 (1)	0·6667 (3)	0·7860 (3)	0·0196 (3)
C(5)	0·2927 (1)	0·4922 (3)	0·8070 (3)	0·0205 (4)
C(6)	0·3546 (1)	0·6661 (4)	0·8330 (3)	0·0236 (4)
C(7)	0·4163 (1)	0·4958 (5)	0·8607 (3)	0·0307 (5)
H(11)	0·040 (1)	0·396 (1)	0·795 (1)	0·033 (1)
H(12)	0·004 (1)	0·628 (1)	0·690 (1)	0·047 (1)
H(2)	0·110 (1)	0·779 (1)	0·648 (1)	0·031 (1)
H(3)	0·169 (1)	0·377 (1)	0·682 (1)	0·024 (1)
H(4)	0·234 (1)	0·776 (1)	0·877 (1)	0·043 (1)
H(5)	0·292 (1)	0·376 (1)	0·893 (1)	0·024 (1)
H(6)	0·358 (1)	0·770 (1)	0·748 (1)	0·029 (1)
H(71)	0·455 (1)	0·614 (1)	0·872 (1)	0·049 (1)
H(72)	0·421 (1)	0·370 (1)	0·775 (1)	0·052 (1)
H(10)	0·007 (1)	0·277 (1)	0·544 (1)	0·052 (1)
H(20)	0·094 (1)	0·759 (1)	0·933 (1)	0·051 (1)
H(30)	0·147 (1)	0·172 (1)	0·875 (1)	0·050 (1)
H(40)	0·218 (1)	0·755 (1)	0·582 (1)	0·050 (1)
H(50)	0·273 (1)	0·176 (1)	0·679 (1)	0·051 (1)
H(60)	0·340 (1)	0·756 (1)	1·024 (1)	0·052 (1)
H(70)	0·397 (1)	0·181 (1)	0·974 (1)	0·051 (1)

Table 2. *Bond lengths* (Å) *and bond angles* (°) *between* C *and* O *atoms and selected torsion angles* (°)

O(1)—C(1)	1·413 (3)	O(2) C(2)	1·431 (3)
O(3)—C(3)	1·433 (3)	O(4)—C(4)	1·430 (3)
O(5)—C(5)	1·427 (3)	O(6)—C(6)	1·431 (3)
O(7)—C(7)	1·432 (3)	C(1)—C(2)	1·519 (4)
C(2)—C(3)	1·525 (4)	C(3)—C(4)	1·527 (4)
C(4)—C(5)	1·523 (4)	C(5)—C(6)	1·529 (4)
C(6)—C(7)	1·515 (4)		
O(1)—C(1)—C(2)	109·1 (2)	O(2)—C(2)—C(1)	108·8 (2)
O(2)—C(2)—C(3)	111·1 (2)	C(1)—C(2)—C(3)	113·1 (1)
O(3)—C(3)—C(2)	110·8 (2)	O(3)—C(3)—C(4)	106·8 (2)
C(2)—C(3)—C(4)	112·4 (1)	O(4)—C(4)—C(3)	110·1 (2)
O(4)—C(4)—C(5)	110·5 (2)	C(3)—C(4)—C(5)	113·1 (1)
O(5)—C(5)—C(4)	110·6 (2)	O(5)—C(5)—C(6)	106·2 (2)
C(4)—C(5)—C(6)	112·6 (1)	O(6)—C(6)—C(5)	110·4 (2)
O(6)—C(6)—C(7)	110·3 (2)	C(5)—C(6)—C(7)	113·4 (1)
O(7)—C(7)—C(6)	112·2 (2)		
Angles in the chain			
O(1)—C(1)—C(2)—C(3)	−59·0 (3)	C(3)—C(4)—C(5)—C(6)	−178·3 (2)
C(1)—C(2)—C(3)—C(4)	177·2 (2)	C(4)—C(5)—C(6)—C(7)	177·6 (2)
C(2)—C(3)—C(4)—C(5)	−177·2 (2)	C(5)—C(6)—C(7)—O(7)	−63·8 (3)
Angles between vicinal O atoms			
O(1)—C(1)—C(2)—O(2)	177·2 (2)	O(4)—C(4)—C(5)—O(5)	−61.0 (2)
O(2)—C(2)—C(3)—O(3)	59·1 (2)	O(5)—C(5)—C(6)—O(6)	174·4 (2)
O(3)—C(3)—C([4)—O(4)	−174·8 (2)	O(6)—C(6)—C(7)—O(7)	60·7 (3)
Angles between vicinal H atoms			
H(11)—C(1)—C(2)—H(2)	−178 (1)	H(4)—C(4)—C(5)—H(5)	61 (1)
H(12)—C(1)—C(2)—H(2)	−64 (1)	H(5)—C(5)—C(6)—H(6)	176 (1)
H(2)—C(2)—C(3)—H(3)	−61 (1)	H(6)—C(6)—C(7)—H(71)	58 (1)
H(3)—C(3)—C(4)—H(4)	−174 (1)	H(6)—C(6)—C(7)—H(72)	−60 (1)

resulted in $R = 0{\cdot}026$ and $wR = 0{\cdot}032$. The ratio of observations to number of variables is 5·1. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with weights $w = 1/\sigma^2(|F_o|)$. Max. shift/e.s.d. was 0·44 in the final cycle; max. and min. heights in the final $\Delta\rho$ map were 0·22 and $-0{\cdot}25$ e Å^{-3}, respectively. Complex neutral-atom scattering factors were taken from *SHELX76* (Sheldrick, 1976). Programs used were *SHELXS90* (Sheldrick, 1990), *SHELX76* (Sheldrick 1976), *PLATON88* (Spek, 1982) and *SCHAKAL88* (Keller, 1986) on MicroVAX II and VAX 3200 computers.

Discussion. The final fractional coordinates and isotropic or equivalent isotropic thermal parameters of C, O and H atoms are listed in Table 1.* Bond distances and angles between C and O atoms and some selected torsion angles of the title compound are given in Table 2. A perspective view of the D enantiomer including the numbering scheme is presented in Fig. 1. The asymmetric unit is defined by the L enantiomer.

As expected, the molecules adopt a planar zigzag conformation. No unusual features are observed. The orientations of the C and O atoms resemble those found in enantiomerically pure D-perseitol (Kanters, Schouten, van der Sluis & Duisenberg, 1990). Although the dimensions of the unit cells of both heptitols are strikingly similar, the space groups

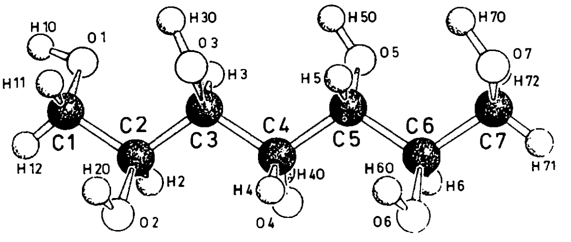

Fig. 1. *SCHAKAL88* drawing (Keller, 1986) of the title compound (only the D enantiomer is shown).

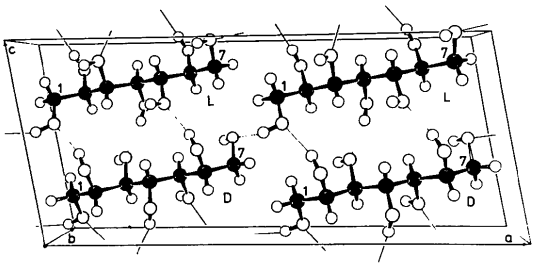

Fig. 2. Perspective view of the contents of the unit cell along **b**, showing only the intermolecular hydrogen bonds in directions **a** and **c**.

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* Lists of structure amplitudes, anisotropic thermal parameters and bond distances and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54118 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Geometry of the hydrogen bonds* (Å,°); *e.s.d.'s are given in parentheses*

D—H···*A*	*D*—H	*D*···*A*	H···*A*	*D*—H···*A*
O(1)—H(10)···O(7^{i})	0·90 (3)	2·731 (3)	1·84 (2)	171 (1)
O(2)—H(20)···O(1^{ii})	0·90 (1)	2·747 (3)	1·89 (2)	158 (2)
O(3)—H(30)···O(2^{iii})	0·93 (1)	2·696 (2)	1·77 (1)	174 (1)
O(4)—H(40)···O(3^{iv})	0·90 (1)	2·738 (2)	1·88 (1)	158 (1)
O(5)—H(50)···O(4^{iii})	0·89 (1)	2·688 (2)	1·80 (1)	175 (2)
O(6)—H(60)···O(5^{v})	0·90 (1)	2·747 (3)	1·89 (2)	159 (1)
O(7)—H(70)···O(6^{iii})	0·91 (1)	2·730 (2)	1·82 (1)	175 (1)

Symmetry operations: (i) $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$; (ii) $x, 1-y, \frac{1}{2}+z$; (iii) $x, y-1, z$; (iv) $x, 1-y, -\frac{1}{2}+z$; (v) $x, 1-y, \frac{1}{2}+z$.

and the orientations of molecules within the cell show substantial differences. In the racemate the molecular planes through the C atoms of each molecule are aligned parallel to each other, whereas the molecular planes of the two sets of crystallographically independent molecules in the pure enantiomer include an angle of approximately 90°. Furthermore, in the pure enantiomer the molecules are orientated head to head, while the D and L enantiomers, respectively, in the racemate are found in a head-to-tail relationship. The unit cell displayed in Fig. 2 demonstrates this orientation. In accordance with the Wallach 'rule', the density D_x of the racemate (1·529 g cm^{-3}) is slightly higher than that of the pure enantiomer (1·510 g cm^{-3}).

All seven hydroxyl group H atoms are involved in intermolecular hydrogen bonds (Table 3). In contrast to the pure enantiomer, no bifurcated hydrogen bonds are observed in the title compound. The pattern of these bonds can partially be discerned in Fig. 2. It is totally different from the hydrogen-bond network found in the pure enantiomer.

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Structure of 4,7-Didehydroneophysalin B, Acid-Induced Rearrangement Product of Physalin A

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Abstract. $C_{28}H_{28}O_9$, $M_r = 508·5$, orthorhombic, $P2_12_12_1$, $a = 14·333\,(2)$, $b = 13·120\,(2)$, $c = 12·445\,(2)$ Å, $V = 2340·3\,(1)$ Å^3, $Z = 4$, $D_x = 1·443$ g cm^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 8·57$ cm^{-1}, $F(000) = 1072$, $T = 295$ K, $R = 0·042$ for 1910 reflections. The rigid molecule consists of eight fused rings involving three lactone rings. An intramolecular hydrogen bond is formed between the ketone and hydroxyl groups. The spiro-fused γ-lactone rings in an envelope conformation are fused to a cyclohexane ring in a half-chair conformation flattened at the distorted spiro junction. The δ-lactone ring fused to the cyclohexane ring also adopts a half-chair conformation.

Introduction. Physalin A (I), isolated as a bitter principle of *Physalis alkekengi var. francheti*, is the first member of a novel class of steroids, physalins,

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