Synthesis and Crystal Structure of
trans-2,8-Dihydroxy-1(7)-*p*-menthene, a New Terpenoid Diol[*][1]

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The crystal structure of a new terpenoid diol, *trans*-2,8-dihydroxy-1(7)-*p*-menthene, has been determined from three-dimensional X-ray data obtained near the temperature of liquid nitrogen. The structure was solved by application of the symbolic addition method for noncentrosymmetric crystals. It refined to an R index of 0.083. The methylenecyclohexane ring took on the ordinary chair conformation with the ring hydroxyl group axial and the 2-hydroxyisopropyl group equatorial. As indicated by the dihedral angles, 45.5 and 52.6°, the ring is flatter than that of cyclohexane. The molecules are held together in the crystal by a network of hydrogen bonds in which each hydroxyl participates in linkages with two other molecules.

The reaction between lead tetraacetate and β-pinene in glacial acetic acid has been shown to produce a complex mixture of monoacetate and diacetate products.[2-5] In the course of investigating the reaction in this laboratory a white, crystalline material was isolated from the transesterified product mixture. The infrared and nuclear magnetic resonance spectra of the material suggested the presence of a double bond exocyclic to a six-membered ring. Structure I was compatible with

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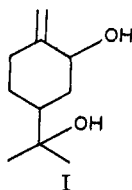
the evidence. No reference to any such compound was found in the literature. A single-crystal X-ray analysis of the material was undertaken in order to establish its correct structure and to provide information on the effect substituents have in distorting the cyclohexane ring from the ideal chair conformation.

Experimental Section

Synthesis of *trans*-2,8-Dihydroxy-1(7)-*p*-menthene.—β-Pinene (75 g, 0.55 mol), glacial acetic acid (707 ml), and acetic anhydride (280 ml) were mixed together in a three-necked, 2-l. flask which was fitted with a condenser and stirrer. Lead tetraacetate (331 g of 85% slurry in acetic acid, 0.65 mol) was added to the stirred mixture (55–65°) over a period of 2 hr, and then the reaction solution was poured into cold water and allowed to remain overnight. After extracting this mixture with three 600-ml portions of ether, the combined extracts were neutralized with saturated sodium bicarbonate, washed with three 1000-ml portions of water, and dried over anhydrous magnesium sulfate. Removal of the ether by distillation left a yellow, sweet-smelling oil, yield 101.8 g.

The oil was distilled using a spinning-band column operating at a pressure of 0.15 mm. The fraction boiling at 77–85° (11.2 g) was collected. This fraction, whose ir spectrum contained bands (906 and 1654 cm⁻¹) indicative of a disubstituted alkene,

was deesterified with sodium methoxide in methanol. The product was isolated in the usual manner, and the light yellow, crystalline solid (3.8 g) was recrystallized from benzene to give 2.8 g of needle-like crystals, mp 129.5–130.0°.

Anal. Calcd as $C_{10}H_{18}O_2$: C, 70.53; H, 10.68; O, 18.79. Found: C, 70.85; H, 10.58; O, 18.57.

The infrared spectrum (Perkin-Elmer 21) showed bands at 3360 (s), 3300 (s), 3060 (w), 2960 (s), 2925 (s), 1820 (w), 1654 (w), 906 (s), 875 (m), 829 (m), 785 (w), 768 (w), 725 (w), and 670 cm⁻¹ (m). Bands from the nmr spectrum (Varian A-60A, CDCl₃) were centered at δ 4.75 (2 H), sextet (ethylenic hydrogens), 4.37 (1 H), triplet (carbinol proton), 2.23–1.75 (7 H), multiplets, 1.58 (2 H), singlet (hydroxyl), and 1.17 (6 H), singlet (methyl groups).

The crystals obtained from benzene were unsuitable for X-ray studies. Water was found to be a more suitable recrystallization solvent, producing prisms having approximately uniform dimensions.

X-Ray Data.—Three-dimensional data were obtained at approximately liquid nitrogen temperature using the multiple film equiinclination Weissenberg technique and a previously described gas flow cryostat[6] (Cu Kα radiation). Two crystals were used: one, 0.58 × 0.41 × 0.20 mm ($\mu R \simeq 0.18$) to obtain (hk0) to (hk5) and the other, 0.50 × 0.30 × 0.20 mm ($\mu R \simeq 0.15$), to obtain (0kl) to (4kl). The reflection intensities were measured visually by means of a calibrated intensity scale. The Lorentz and polarization corrections were made. No correction for absorption was made. The data from the two crystal settings were put on the same relative scale by the method of Rollett and Sparks.[7] A total of 999 unique observed reflections were obtained. An additional 190 reflections were either unobserved or too weak to be measured with confidence. The relative intensities were converted to normalized structure factors, $|E_{hkl}|$, by the K-curve method of Karle and Hauptman.[8,9]

The orthorhombic unit cell dimensions are: at low temperature, $a = 6.952 \pm 0.002$ Å, $b = 17.527 \pm 0.005$ Å, $c = 8.016 \pm 0.001$ Å; at room temperature, $a = 7.181 \pm 0.002$ Å, $b = 17.873 \pm 0.005$ Å, $c = 8.053 \pm 0.001$ Å. All the unit cell dimensions were determined by the back-reflection Weissenberg technique. Other crystal data are: $d_c = 1.093$ g/cm³, $Z = 4$, $d_m = 1.130$ g/cm³, $V_{LT} = 994.86$ Å³, $V_{RT} = 1033.50$ Å³, $\mu = 6.11$/cm; systematic absences, h00 when h is odd, 0k0 when k is odd, 00l when l is odd; space group, $P2_12_12_1$.

Structure Determination and Refinement.—The crystal structure was determined by application of the symbolic addition method for noncentrosymmetric crystals.[10-12] The structure was refined by block–diagonal least-squares methods (anisotropic temperature factors, hydrogen atoms held constant with isotropic temperature factors equal to those of the attached atom)

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(1) A portion of a thesis submitted by W. E. Scott in partial fulfillment of the requirements of The Institute of Paper Chemistry for the degree of Doctor of Philosophy from Lawrence University, Appleton, Wis., Jan 1969.

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(3) L. Gruenewald and D. Johnson, *J. Org. Chem.*, **30**, 1673 (1965).

(4) T. Sato, *J. Chem. Soc. Jap., Pure Chem. Sect.*, **86**, (2), 252 (1965).

(5) W. E. Scott, unpublished work.

(6) G. Richards, Ph.D. Dissertation, Iowa City, Iowa, Feb 1964.

(7) J. Rollett and R. Sparks, *Acta Crystallogr.*, **13**, 273 (1960).

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(10) J. Karle and I. Karle, *Acta Crystallogr.*, **21**, 849 (1966).

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(12) Five known phases, $\phi_{320} = -90°$, $\phi_{203} = 90°$, $\phi_{087} = 90°$, $\phi_{246} = 90°$, and $\phi_{043} = 0°$, along with one symbolic phase, $\phi_{066} = a$, were used to assign phases to 112 reflections from the original 135 $|E_{hkl}| \geq 1.5$ (σ-2 formula). The 12 largest peaks in an E map calculated from 181 phased $|E_{hkl}| \geq 1.3$ (tangent formula refined, $a = 180°$) were related in such a manner as to form a reasonable chemical structure ($R = 0.21$).
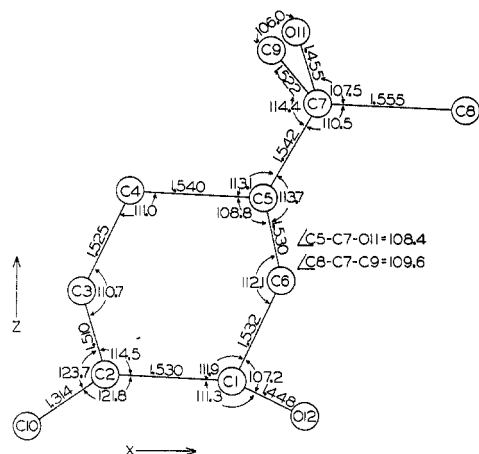
Figure 1.—The most significant atomic distances and bond angles in the molecule of *trans*-DHM given in the orthogonal projection on the plane (010).

to an R index of 0.083.[13] Weights were assigned during the final refinement cycles according to the equation

$$w = \left(1 + \frac{(|F_o| - b)^2}{a^2}\right)^{-1}$$

where the constants $a = 8.9$ and $b = 6.9$ were evaluated by the method suggested by Cruickshank.[19] Table I shows the final atomic parameters and their estimated standard deviations as determined by the least-squares refinement. The numbering system corresponds to that followed in Figure 1. The anisotropic temperature factors are normal for a structure determined near liquid nitrogen temperature.[20] Standard deviations in the bond lengths are 0.005 Å for carbon–oxygen bonds and 0.006 Å for carbon–carbon bonds. The standard deviations for the bond angles are 0.3° (Figure 1).

Results and Discussion

Figure 1 illustrates the general molecular features of the compound (abbreviated name, *trans*-DHM). The six-carbon ring takes on the ordinary chair conformation

(13) The hydrogen atom positions were determined from a three-dimensional Fourier difference calculation after refinement to an R index of 0.11 (anisotropic temperature factors). The atomic scattering factors for carbon and oxygen were taken from Hanson, *et al.*,[14] and the hydrogen scattering factors were those of Stewart, *et al.*[15] Calculations were made on an IBM 1620 computer. Scaling programs (P. T. Beurskens[16]) and intensity correction and three-dimensional Fourier synthesis programs (R. Shiono, D. Hall, and S. C. Chu[17]) were provided by The Crystallography Laboratory, University of Pittsburgh. The refinement programs (F. R. Ahmed and G. Mair[18]) were provided by F. R. Ahmed. Programs for the application of the symbolic addition method were written locally by J. T. Ham and W. E. Scott.

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(15) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(16) Technical Report No. 45, The Crystallography Laboratory, The University of Pittsburgh, Pittsburgh, Pa., 1963.

(17) Technical Report No. 43, The Crystallography Laboratory, The University of Pittsburgh, Pittsburgh, Pa., 1963.

(18) Programs written by F. R. Adhmed and G. Mair of the Divisions of Pure Physics and Pure Chemistry, National Research Council, Ottawa, Canada, 1963.

(19) D. W. J. Cruickshank, *et al.*, in "Computing Methods and the Phase Problem in X-ray Crystal Analysis," R. Pepinsky, J. M. Robertson, and J. C. Speakman, Ed., Pergamon Press, New York, N. Y., 1961, p 44.

(20) The tables and figures listed in this footnote will appear following these pages in the microfilm edition of this journal: tables containing anisotropic temperature factors, thermal ellipsoid volumes, observed and calculated structure factors, least-squares planes, bond lengths and bond angles, nearest neighbor distances, and interatomic distances and angles involved in hydrogen bonding; figures illustrating crystal packing and intermolecular hydrogen bonding.[21]

(21) Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth Street, N.W., Washington D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.
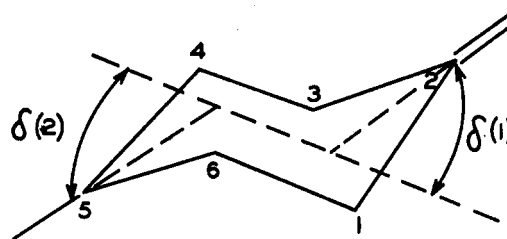
Figure 2.—Dihedral angles, $\delta(1)$ and $\delta(2)$, formed by the chair conformation of a six-membered ring.

TABLE I
ATOMIC PARAMETERS

Atom	Fractional coordinates		
	X^a	Y	Z
C-1	0.0597 (5)	0.1362 (4)	0.8786 (4)
C-2	0.3496 (5)	0.3889 (4)	0.1345 (4)
C-3	0.3098 (5)	0.4452 (5)	0.2728 (5)
C-4	0.3899 (5)	0.4162 (4)	0.4382 (5)
C-5	0.1073 (4)	0.0992 (4)	0.5744 (4)
C-6	0.1419 (5)	0.1600 (4)	0.7092 (5)
C-7	0.2005 (4)	0.1184 (4)	0.4050 (4)
C-8	0.4229 (5)	0.1240 (5)	0.4227 (5)
C-9	0.1236 (6)	0.1907 (5)	0.3234 (5)
C-10	0.2162 (5)	0.3613 (6)	0.0355 (5)
O-11	0.1591 (3)	0.0567 (3)	0.2892 (3)
O-12	0.1803 (4)	0.0752 (3)	0.9416 (3)
H-1 (C-1)^b	0.060	0.180	0.945
H-1 (C-3)	0.338	0.486	0.216
H-2 (C-3)	0.195	0.460	0.280
H-1 (C-4)	0.338	0.370	0.500
H-2 (C-4)	0.365	0.455	0.500
H-1 (C-5)	0.160	0.055	0.620
H-1 (C-6)	0.080	0.200	0.670
H-2 (C-6)	0.270	0.165	0.715
H-1 (C-8)	0.318	0.120	0.405
H-2 (C-8)	0.475	0.075	0.485
H-3 (C-8)	0.500	0.138	0.318
H-1 (C-9)	0.000	0.190	0.313
H-2 (C-9)	0.195	0.210	0.233
H-3 (C-9)	0.150	0.230	0.388
H-1 (C-10)	0.235	0.325	0.970
H-2 (C-10)	0.085	0.365	0.030
H-1 (O-11)	0.205	0.015	0.370
H-1 (O-12)	0.110	0.068	0.050

^{a} Estimated standard deviation times 10^3 Å in parentheses. ^{b} H-j (n-k) refers to the jth hydrogen atom bonded to the ith atom of kind n.

with an axial hydroxyl at C-1 and an equatorial 2-hydroxyisopropyl group at C-5.

The deviations from the mean plane calculated through the four carbon atoms associated with the ethylene bond, C-1, C-2, C-3, and C-10 are 0.003, −0.011, 0.003, and 0.004 Å, respectively. A similar analysis of ring carbons C-1, C-3, C-4, and C-6 revealed that the ring is slightly puckered, each atom being about 0.02 Å away from the mean plane.

The six-membered ring in *trans*-DHM is somewhat flatter than an ideal cyclohexane ring. The extent of flattening can be measured by its effect on the two dihedral angles formed by the chair conformation, as shown in Figure 2. This distortion from ideality has been discussed by Wohl.[22] Table II summarizes some dihedral angles associated with cyclohexane compounds. The contents of Table II indicate that the extent of ring

(22) R. Wohl, *Chimia*, **18**, 219 (1964).

TABLE II
DIHEDRAL ANGLES IN CYCLOHEXANE COMPOUNDS

Compd	Trigonal angle, deg	Other angles, deg	$\delta(1)$, deg	$\delta(2)$, deg	Ref
Cyclohexane[a]		109.5	60.0	60.2	22
Cyclohexane[b]		111.5	54.6	54.6	22
Methylenecyclohexane[c]	120.0	109.5	40.0[e]	59.5[e]	...[f]
Cyclohexanone[c]	116.0	109.5	51.2[e]	54.4[e]	...[g]
Bicyclohexylidene[d]	110.6	111.2	49.4	51.1	24
trans-DHM	114.5	110.9	45.5	52.6	

[a] Ideal model. [b] Electron diffraction. [c] Vector analysis calculations. [d] X-Ray diffraction. [e] Calculated from data given by authors. [f] E. Corey and R. Sneen, *J. Amer. Chem. Soc.*, **77**, 2505 (1955). [g] W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne, and C. Djerassi, *ibid.*, **83**, 4013 (1961).

flattening reflects two kinds of variations in the structures of methylenecyclohexane compounds: namely, an increase or decrease in the ring angle at the trigonal carbon, and an increase or decrease in the average bond angle in the ring. The dihedral angles found for *trans*-DHM indicate that these effects can be quite substantial.

The mean sp^3–sp^3 carbon–carbon bond distance in the ring of 1.533 Å agrees within 1 σ with that reported for cyclohexane[23] and within 1.5 σ with the average in bicyclohexylidene.[24] The difference between the mean sp^3–sp^2 carbon–carbon bond length (C-1–C-2, C-2–C-3) and the mean sp^3–sp^3 carbon–carbon bond length is significant at the 99% confidence level. Taken individually, however, bond C-1–C-2 is approximately equal to the mean sp^3–sp^3 bond length.

The two carbon–oxygen bond in *trans*-DHM are slightly longer than the value of 1.430 Å generally accepted for a carbon–oxygen single bond.[25]

The C-2–C-10 double bond (1.314 Å) is shorter than those reported in ethylene (1.334 Å)[26] and bicyclohexylidene (1.332 Å).[24]

The 2-hydroxyisopropyl group assumes an approximately staggered conformation relative to ring atoms C-4 and C-6, with C-9 anti to the hydrogen on C-5. There is considerable crowding, as is shown by the very short C-4–C-9 (3.13 Å) and C-6–C-8 (3.08 Å) distances. This arrangement probably allows O-11 to participate more effectively in hydrogen bonding and improves the molecular packing.

The longest dimension of the molecule is 6.562 Å (C-10–C-8). Comparison of distances C-1–C-3 (2.557 Å) and C-4–C-6 (2.501 Å) illustrates the effect of the large trigonal angle on the ring dimensions.

The average angle in the ring, excluding the trigonal angle, is 110.9°, with a range of 108.8–112.1°. This average compares favorably with the average angle of

111.1° reported for bicyclohexylidene (range, 110.4–111.9°),[24] and the 111.55 ± 0.15° determined for cyclohexane by electron diffraction.[23] The bond angles in the 2-hydroxyisopropyl group exhibit a range of 106.0–114.1°. These angles are probably influenced by the hydrogen bonding in which O-11 participates.

The molecules are held together in the crystal by a network of hydrogen bonds in which each hydroxyl participates in linkages with two other molecules. The individual molecules are bonded "heads-to-tails," forming polymerlike chains which extend through the unit cell approximately parallel to the *c* axis. A secondary chain pairing occurs through the association of two chains by lateral hydrogen bonds. Each unit cell contains one complete chain pair and shares two others with cells located on both sides along the *b* axis. The average distance between chain pairs is approximately 4.3 Å. The distances between each atom in the molecule and its nearest neighbor in another molecule appear to be normal. These distances all lie within a single chain pair. Figures and tables illustrating the molecular packing and hydrogen bonding can be obtained from the microfilm edition of this journal.[20]

As judged by their respective thermal ellipsoid volumes (range, 0.0018–0.0099 Å³), the terminal methylene carbon C-10 exhibits the largest amount of thermal vibration. The two methyl carbons in the 2-hydroxyisopropyl group also show relatively large thermal motion. The smallest volumes are found in the ring, with C-4 and C-5 appearing to be the most restricted. In general, the results of the thermal analysis agreed with what would be expected.

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(24) K. Sasvari and M. Low, *Acta Crystallogr.*, **19**, 840 (1965).
(25) A. Hordvik, *Acta Chem. Scand.*, **20**, 1943 (1966).
(26) L. Bartell and R. Bonham, *J. Chem. Phys.*, **27**, 1414 (1957).