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THE *p*-MENTH-1-ENE-3,6-DIOLS

CORRELATION OF ABSOLUTE CONFIGURATION WITH OPTICAL ROTATION[1]

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Abstract—The large discrepancy between calculated and reported optical rotations for two of four compounds (A–D) described previously as diastereoisomeric *p*-menth-1-ene-3,6-diols (I–IV) has been resolved by reassignment of configuration to diol B, m.p. 112°, and reassignment of *constitution* to diol A, m.p. 54°, a *p*-menth-2-ene-1,6-diol (VI). The set of four diastereoisomeric *p*-menth-1-ene-3,6-diols has been completed by synthesis of a new diol (IV), m.p. 123°. Hydrogenation of each *p*-menth-1-ene-3,6-diol yielded a different pair of *p*-menthane-2,5-diols, identification of which allowed assignment of configuration to diols I–IV.

THE *p*-menth-1-ene-3,6-diols were reviewed by Blumann *et al.*,[2] who sought to account for all four possible diastereoisomers (I–IV) derived from (−)-α-phellandrene (V) with retention of absolute configuration at the isopropyl group. The four reported diols,[2] referred to by m.p., were: A, m.p. 54°, B, m.p. 112°, C, m.p. 148°, and D, m.p. 165°. The molecular rotations reported[2] for diols A and B differed from the values we calculated for their assigned[2] structures by 422° and 585°, respectively. Resolution of so large a discrepancy was deemed important. Clearly, either the calculated rotations or the assigned structures were wrong. At issue was the usefulness in structure elucidation of the correlation of absolute configuration with optical rotation.[3]

With the kind encouragement and cooperation of Dr. Blumann, it has been possible to reappraise the *p*-menth-1-ene-3,6-diols.[2,4] This paper reports new structural assignments for diol A, a *p*-menth-2-ene-1,6-diol (VI), and diol B (I), as well as preparation of a new diol, m.p. 123°, assigned structure IV. The previous assignments[2] of structure II to diol C and structure III to diol D are consistent with all the available data.[5] Absolute configurations and optical rotations for diols I–IV are given in Table 1. A reasonable correlation has been achieved.

Optical rotations for diols I–IV were calculated by adapting Brewster's method for

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[1] This work was supported in part by the National Science Foundation, in part by Public Health Service Research Grant GM-08813 from the National Institutes of Health, and in part by the Research Corporation.

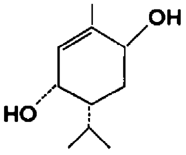
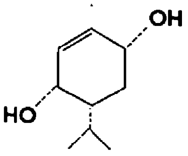
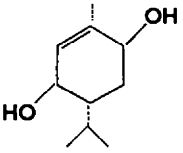
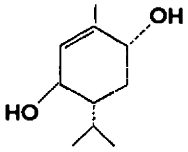
[2] A. Blumann, E. W. Della, C. A. Henrick, J. Hodgkin, and P. R. Jefferies, *Austr. J. Chem.* **15**, 290 (1962).

[3] E. L. Eliel, *Stereochemistry of Carbon Compounds* pp. 398–412. McGraw-Hill, New York (1962).

[4] We are deeply indebted to Dr. A. Blumann for generous samples of diols A, B, and D, as well as crude dextrorotatory fractions of *Eucalyptus dives* oil distillation residues and of oxidized (−)-α-phellandrene.

[5] R. D. Stolow, *J. Amer. Chem. Soc.* **86**, 2170 (1964).

TABLE 1. OPTICAL ROTATIONS AND ABSOLUTE CONFIGURATIONS OF THE *p*-MENTH-1-ENE-3,6-DIOLS

				
Structure	I	II	III	IV
Diol	B[a]	C	D	new
m.p.	112°	149°	168°	123°
$[M]_D$ lit.[b]	−425°	−244°	−19°	—
$[M]_D$ found	−461°	−256°	−18°	+198°
$[M]_D$ calc.	−480°[c]	−260°[d]	−60°[e]	+160°[f]

[a] Formerly assigned structure IV, Ref. 2.

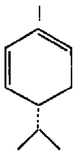
[b] See Ref. 2 and Refs. therein.

[c] −270−(−160)−370.

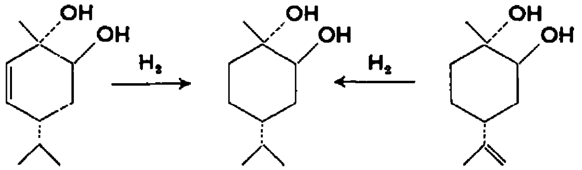
[d] −50−(−160)−370.

[e] −270−(−160)+50.

[f] −50−(−160)+50.



V



VI

diol A[6]
m.p. 54°
$[M]_D$ lit.[2] −58°

VII

VIII

the *p*-menth-1-en-3-ols (IX and X) and the *p*-menth-1-en-6-ols (XI and XII).[7] To calculate the molecular rotations for each of structures I–IV ($[M]_D$ calc. in Table 1), the difference in calculated molecular rotation ($[M]_D$ calc.) between the corresponding *p*-menth-1-en-6-ol (XI or XII) and (−)-*p*-menth-1-ene (XIII) was added to the calculated molecular rotation for the appropriate *p*-menth-1-en-3-ol (IX or X).[7,8]

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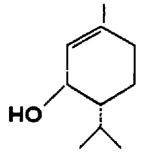
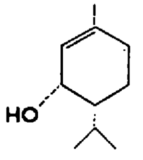
[6] Formerly assigned structure I, on the basis of a degradative study.[2]

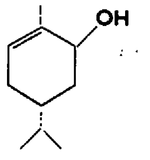
[7] J. H. Brewster, *J. Amer. Chem. Soc.*, **81**, 5493 (1959). See structures XVIIIa, XIXa, XX and XXI, therein.

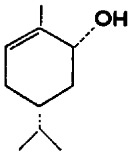
[8] See Ref. 3 and Ref. 4g on p. 398 therein; also pp. 110–114. It is assumed that the contribution of the 6-hydroxyl group to the optical rotation is independent of the presence or absence or configuration of the 3-hydroxyl group in diols I–IV. It is further assumed that the predominant conformation of the ring is the same in IX–XIII as in I–IV; that the average conformation of the isopropyl group is the same in XIII as in XI and XII, the same in IX as in III and IV, and the same in X as in I and II. A calculation similar to that in Table 1, but employing $[M]_D$ lit., rather than $[M]_D$ calc. values for IX–XIII, gives values of $[M]_D$ calc. for diols I–IV of −500°, −305°, −78° and +117°, respectively, values all too negative by 60 ± 20°, not in as good agreement with $[M]_D$ found as those calculated in Table 1, which are all too negative by 23 ± 20°. The $[M]_D$ lit. value for XII appears to be in doubt.[9]

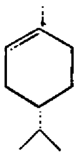
[9] For XI, see Ref. 2. For XII, see: A. S. Hallsworth, H. B. Henbest and T. I. Wrigley, *J. Chem. Soc.* 1969 (1957), and S. Schroeter, Dissertation, Gottingen, 1962. But S. Schroeter *Liebigs Ann.* **674**, 118 (1964) gives $[M]_D$ lit.: for XI, −288°; for XII, −32°. $[M]_D$ calc. for diols II and IV, using this latter value for XII, are in better agreement with $[M]_D$ found: II, −250°; IV, +172°.











	IX	X	XI	XII	XIII
$[M]_D$ lit.[7,9]	+43°	−379°	−282°	−87°	−161°
$[M]_D$ calc.[7]	+50°	−370°	−270°	−50°	−160°

The integrated NMR spectrum of diol A (Table 2) is not consistent with that expected for a *p*-menth-1-ene-3,6-diol such as B, C, D or IV but is reasonably consistent with that expected for a *p*-menth-2-ene-1,6-diol, as shown by comparison with *cis-p*-menth-2-ene-1,4-diol (XIV).[10] Upon hydrogenation of the double bond, each diol I–IV would be expected to give two *p*-menthane-2,5-diols, a pair of diastereoisomers epimeric at C_1. Whereas diols B, C, D and IV each gave two products, hydrogenation of diol A, m.p. 54°, under the same conditions, gave in good yield, a single diol, m.p. 58–59° (hydrate), m.p. 88–89° (anhydrous), identified by direct comparison with an

TABLE 2. NMR DATA FOR *p*-MENTHENEDIOLS VIII, XIV, A–D, AND IV

Diol[a]	CH_3 at C_1	Olefinic proton(s)		OH + H—C—OH	
	δ, PPM	δ, PPM	No.[b]	δ, PPM	No.[b]
VIII	1·20[d]	4·67	1·94	3·0–3·7	3·06
XIV[c]	1·16[d]	5·51[e]	1·74	3·29,[d] 3·64[d]	1·98
A	1·20[d]	5·52[d]	1·71	3·0–3·9	3·10
B	1·75[f]	5·60[g]	0·94	2·7–4·2	4·03
C	1·74[f]	5·53[g]	0·92	2·7–4·2	3·90
D[h]	1·67[f]	5·32[g]	1·00	3·4–4·7	3·60
IV	1·72[f]	5·35[g]	0·96	3·3–4·3	3·66

[a] Solutions in acetone-d_6. Absorption attributable to the protons of methyls at C_8, PPM: VIII, 1·70 (3 protons); all others, 6 protons, interpretable as pairs of methyl group doublets, occasionally not resolved (A, IV, VII), with J = 7 ± 1 c/s for each doublet, individual peaks given rather than centers of doublets: XIV, 0·79, 0·86, 0·91, 0·97; A, 0·84, 0·95, B; 0·89, 0·94, 0·98, 1·04; C, 0·88, 0·91, 1·00, 1·02; D, 0·69, 0·80, 0·82, 0·93; IV, 0·76, 0·89, 1·00. NMR data for VII and XXI are given in the experimental.

[b] Number of protons determined by integration.

[c] *cis-p*-menth-2-ene-1,4-diol.[10]

[d] Sharp sym. singlet.

[e] Quartet.

[f] Unsym.

[g] Multiplet.

[h] Solution in dimethyl sulphoxide-d_6.

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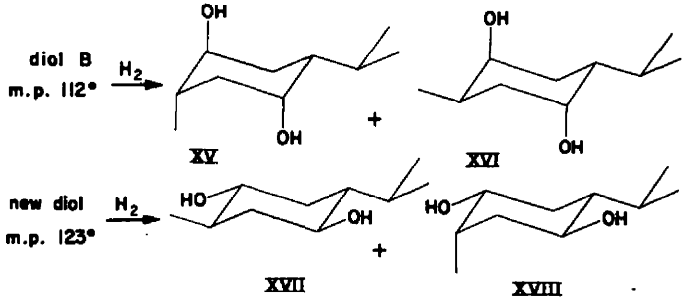
[10] The NMR spectrum of diol A suggests the presence of an isopropyl group, *two* olefinic protons, a tertiary hydroxyl group at C_1, and a secondary hydroxyl group (at C_6 or C_5). Diol XIV, m.p. 80–82°, was prepared from ascaridole by D. Schumacher by the method of M. Matic and D. A. Sutton, *J. Chem. Soc.* 2679 (1952).

authentic sample as (+)-1-hydroxyneocarvomenthol (VII).[11] Of the 5 possible *p*-menth-x-ene-1,2-diols which could give diol VII upon hydrogenation, only two, diols VI and VIII, would be expected to give diol VII exclusively; only two, diols VI and VIII, have *two* olefinic protons. Diol VIII is known[11]; its NMR spectrum (Table 2) is consistent with presence of an isopropenyl group. Therefore, the NMR and hydrogenation results provide evidence adequate for assignment of structure VI to diol A, beyond reasonable doubt.

The structure which had been reported as established[2] for diol A, structure I, gives a calculated molecular rotation in good agreement with that found for diol B (Table 1). Therefore, assignment of structure VI to diol A permits reassignment of structure I to diol B, if one has sufficient confidence in the calculated molecular rotation values (Table 1). Evidence supporting assignment of structure I to diol B was provided by hydrogenation. Diol B gave (+)-*p*-menthane-2,5-diols XV, m.p. 121°, and XVI, m.p. 129°.[12] Additional supporting evidence resulted from hydrogenation of a new (+)-*p*-menth-1-ene-3,6-diol, m.p. 123°, described below, which gave (+)-*p*-menthane-2,5-diols XVII, m.p. 145°, and XVIII, m.p. 169°. Therefore, structure IV, formerly assigned to diol B, should be reassigned to the new diol, m.p. 123°.



Diols C and D gave the *p*-menthane-2,5-diols reported previously.[5] The two (+)-*p*-menthane-2,5-diones and the eight diastereoisomeric *p*-menthane-2,5-diols related to the *p*-menth-1-ene-3,6-diols (I–IV) provide the subject for a subsequent publication in which absolute configurations are assigned.[12]

Preparation

Samples of diols A and B used in this work were supplied by Dr. Blumann.[2,4] Diols C and D were prepared from (−)-α-phellandrene (V) by photosensitized

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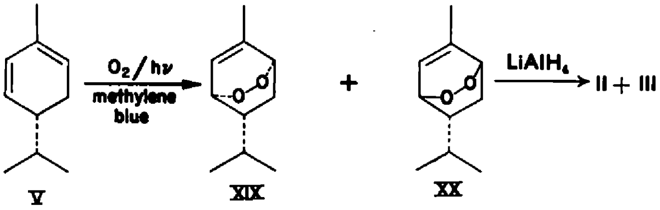
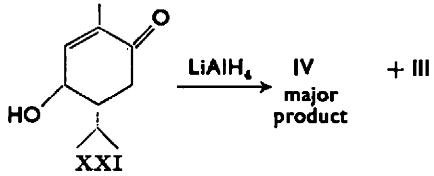
[11] The authors are grateful to Dr. William F. Newhall for a sample of diol VII prepared from diol VIII. See W. F. Newhall, *J. Org. Chem.* **29**, 185 (1964), and Refs. cited; H. Kuczynski and M. Walkowicz, *Rocz. Chem.* **37**, 955 (1963); J. C. Leffingwell, Ph.D. dissertation, Emory University, 1963; S. A. Kozhin and G. G. Kainova, *Zh. Obshch. Khim.* **34**, 1680 (1964). Samples of VII prepared from diol A and from VIII gave identical m.p., mixed m.p., optical rotation, IR and NMR spectra. It is interesting to note that in Ref. 2, the identity of VII and the hydrogenation product of diol A was not recognized, although each was carried through an identical sequence of reactions leading to (−)-*trans*-carvotanacetol (XI). However, we are at a loss to explain the degradation of VII to (+)-neoisomenthol reported in Ref. 2; we doubt its reproducibility.

[12] R. D. Stolow and K. Sachdev, unpublished work.

oxidation followed by LAH reduction of the resulting mixture containing both *exo*- and *endo*-3,6-epidioxy-*p*-menth-1-ene (XIX and XX).[13]



Since diol IV had not been accounted for previously, its isolation from oxidized (—)-α-phellandrene was attempted.[4] Dextrorotatory product fractions were selected for study because a positive rotation had been calculated for structure IV (Table 1). A liquid fraction, $[\alpha]_D$ +42°, was shown by gas chromatography to contain several minor components, two with the retention times of diols A and B, plus a major component of unique retention time. By chromatography on alumina, a dextrorotatory oil greatly enriched in the latter component was isolated. This oil gave a hydrogenation product containing two major components corresponding in retention time to *p*-menthane-2,5-diols XVII and XVIII, the products to be expected (and later found) upon hydrogenation of pure diol IV. However, the major component of the oil, purified further by preparative gas chromatography, gave IR, UV and NMR spectra which were *not* consistent with a diol of structure IV, but which were consistent with a structure such as XXI, an α,β-unsaturated hydroxyketone. Reduction with LAH gave as



the major product, the new diol, m.p. 123°, assigned structure IV, above. Since diol III also was formed as a minor reduction product, tentative assignment of structure XXI to the ketone seemed reasonable.[14]

EXPERIMENTAL

Routine spectral data were recorded by use of Perkin–Elmer Model 21 and Beckman DK-2 spectrophotometers, and a Varian A-60 NMR spectrometer with TMS as internal standard. The diols were analyzed by gas chromatography at 105° by use of a flame ionization detector and a 240-cm, 0·188 in. o.d. Cu column packed with 1·5% GEXE-60 (General Electric Co., cyanoethylated silicon polymer) and 0·10% polyethylene glycol 1500 (Matheson, Coleman and Bell, 9135) on 60/80 mesh HMDS-treated Chromosorb W, (Fisher Scientific Co.) conditioned by heating in an oven at 213° for 1 hr without gas flow, and at 139° for 4·5 hr with 30 ml/min dried N_2 gas flow through the column. The authors are grateful to Arthur E. Clements who developed and prepared this and

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[13] G. O. Schenck, K. G. Kinkel, and H. J. Mertens, *Liebigs Ann.* **584**, 125 (1953).

[14] Further support for assignment of structure XXI to the hydroxy-ketone may be provided by its NMR spectrum, a striking feature of which is a peak at 6·7 ppm, tentatively assigned to the olefinic proton of XXI. A *p*-menth-1-en-6-ol-3-one, like *p*-menth-1-en-3-one (piperitone), would be expected to show its olefinic proton absorption at ca. 5·9 ppm. A *p*-menth-1-en-3-ol-6-one (XXI) would resemble carvone, olefinic proton, 6·8 ppm. See the *NMR Spectra Catalog* Vol. I, Varian Associates, Palo Alto, California (1962).

related columns (two described previously[5]) for gas chromatographic analyses of the *p*-menthane-2,5-diols. In a typical case, peaks with the following retention times were recorded for diols VI, I, II, III, and IV, and ketone XXI, respectively: 7·2, 11·6, 13·6, 15·1, 16·7 and 17·6 min. Microanalyses were determined by Dr. S. M. Nagy.

Photosensitized oxidation of (−)-*α-phellandrene* (V). A solution of V, (Matheson, Coleman and Bell, redistilled, 13·0 ml, 0·0735 moles), and Methylene Blue (0·25 g) in 95% EtOH (190 ml) and benzene (640 ml, redistilled) was irradiated for 110 min.[15] Removal of the solvent at 35–40° (red. press.) gave a blue liquid. The combined product of ten runs was distilled through a 10 cm Vigreux column. The fraction, b.p. 40–80° (1 mm), was not studied further. The fraction, b.p. 57–64° (0·004 mm), collected as a yellowish liquid, was presumed to be a crude mixture containing both XIX and XX (55 g, 34%), reported[13] b.p. 59–62° (0·01 mm).

Diols C *and* D. *Lithium aluminium hydride reduction of* 3,6-*epidioxy*-p-*menth*-1-*enes* (XIX *and* XX). To a stirred suspension of LAH (8·5 g, 0·22 mole) in anhydrous ether (700 ml) in a dry N_2 atm., was added during 2 hr a solution of crude mixed XIX and XX (35 g, 0·21 mole) in anhydrous ether (170 ml). After adding anhydrous ether (500 ml), the reaction mixture was heated under reflux for 3 hr more. Sat. Na_2SO_4 aq (50 ml) was added to the ice-cooled reaction mixture to hydrolyze excess hydride. After the mixture was stirred at room temp for 2 hr, the salt was separated by filtration and was washed with several portions of ether. Removal of solvent from the combined filtrates left a colourless semisolid (30 g). Since the wt. of semisolid was less than the expected amount of product, the salt cake was extracted with absolute EtOH (200 ml). Evaporation of the EtOH gave a white solid residue which was digested in boiling benzene (250 ml). The hot suspension was filtered, and the benzene filtrate, upon cooling, gave white crystals, m.p. 167° (3·0 g), essentially identical with diol D (III).[2,4,5]

The semisolid (30 g), the major fraction of the reduction product, was triturated with ether (150 ml), the suspension was filtered, the white solid was washed with ether and was dried to give a mixture, m.p. 127–145° (15·5 g). The filtrate, after evaporation of the ether, gave a viscous, colourless oil (14·5 g). The solid fraction, recrystallized twice from benzene, gave m.p. 132–145°. Part of this solid (3·0 g), after 3 recrystallizations from water, gave white needle-like crystals, m.p. 147–149° (1·0 g), dried under vacuum, $[\alpha]_D^{26}$ −150° (c = 1·69, EtOH), identified as diol C (II), reported[16] m.p. 148°, $[\alpha]_D^{20}$ −143°. The IR spectrum (KBr) was essentially identical to that recorded in Prof. Schenck's laboratory.[16] (Found: C, 70·47; H, 10·41. Calc. for $C_{10}H_{18}O_2$: C, 70·55; H, 10·66%.)

Hydrogenation of diol A, *m.p.* 54°, *to give* (+)-1-*hydroxyneocarvomenthol* (VII). The procedure of Blumann *et al.*, was used.[2] To a solution of diol A[4] (1·00 g, 5·88 mmoles) in 95% EtOH (50 ml) was added neutral Raney Ni catalyst moist with EtOH (2 g, No. 28 Raney Ni catalyst in water, Raney Ni Catalyst Co., Chatanooga, Tenn., washed repeatedly with distilled water until the washings were neutral, then washed with 95% EtOH). At 30° and ca. 3 atm. H_2 press. with a Parr apparatus (Model 3911), the reaction, ca. 90% complete within 1 hr, was stopped after 8 hr. The total syrupy product, upon gas chromatography, gave a single peak, clearly different in retention time from diol A and all eight diastereoisomeric *p*-menthane-2,5-diols, but identical in retention time to an authentic sample of diol VII.[11] Residual water and ethanol were partially removed from the product by azeotropic distillation with benzene. Upon crystallization from 10:1:1 hexane–ether–benzene, a crystalline solid was isolated, m.p. 59–60° (0·77 g, 76%), reported[2] m.p. 58–59° (for the trihydrate). Further azeotropic distillation with benzene, as reported,[2] converted the hydrate to the anhydrous form, m.p. 86–87°. Three recrystallizations from anhydrous benzene–hexane gave white crystals, m.p. 86–88°; reported,[2] m.p. 88–89°. $[\alpha]_D$ +51° (c = 1·36, EtOH).

(+)-trans-$\Delta^{8(9)}$-p-*Menthene*-1,2-*diol*, *m.p.* 70–72°, VIII. Newhall's procedure[11] was used to prepare VIII from a mixture of *cis*- and *trans*-limonene monoxide (3·0 g, Aldrich Chemical Co.). Two recrystallizations of the solid product from 1:1 benzene–hexane gave large colourless plates, m.p. 70–72° (0·65 g, 20%), reported,[11] m.p. 70–71·6°.

(+)-1-*Hydroxyneocarvomenthol* VII. The total product of hydrogenation of VIII (2·20 g, 0·0129 moles) in 95% EtOH (110 ml) with neutral Raney Ni catalyst (3 g, moist with EtOH) at 25° and 2–3 atm. H_2 press., as above for diol A, gave a single peak in gas chromatography identical in retention

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[15] The procedure and apparatus used were as described by G. R. Evanega, W. Bergmann and J. English, Jr., *J. Org. Chem.* 27, 13 (1962), first experiment.

[16] G. O. Schenck, *Angew. Chem.* 69, 592 (1957). S. Schroeter, private communication, June 25, 1963.

time with that of both the authentic sample[11] of VII and the hydrogenation product from diol A, above. The product, treated as above, and finally recrystallized twice from 1:1 hexane–benzene, gave large crystals of VII, m.p. 87–88° (1·63 g, 73%), undepressed upon admixture with the authentic sample[11] of VII, as well as with the hydrogenation product from diol A, above. The three samples gave identical IR (KBr) and NMR spectra; NMR, solution in acetone-d_6, ppm (rel, no. of protons): 3·53 (1); 3·24 (2 rapidly exchanging hydroxyl protons); 1·0–2·0 (8); 1·17 (3); 0·81, 0·91 (6). A 0·0040 M solution of diol VII in CCl_4 in a 1 cm cell showed no evidence of intramolecular hydrogen bonding (IR recorded as in Ref. 5); a barely resolved doublet was observed: 3623 cm^{-1} (0·35); 3636 cm^{-1} (0·31); reported maximum,[17] 3624 cm^{-1}.

Isolation of (+)-trans-p-*menth*-1-*en*-3-*ol*-6-*one* XXI. A liquid fraction of the product of oxidation of (−)-α-phellandrene, $[\alpha]_D$ +42°, supplied by Dr. Blumann,[4,18] was analysed by gas chromatography. The major component gave a retention time different from those of diols A–D. Chromatography of the crude liquid (10·0 g) on alumina (450 g, Fisher Scientific Co., A-540), eluting first with dry benzene (2300 ml), then 1:3 ether–benzene (2600 ml), gave fractions which were analyzed by gas chromatography. Those fractions enriched in the major component were combined, the solvent was removed, and the pale yellow residual oil (2·5 g) was purified further by preparative gas chromatography (Wilkens Autoprep Model 700) at 150° with a 60 cm, 0·375″ o.d. copper column packed with 9% GEXE-60 on Gas-Chrom P, 100/120 mesh (Applied Science Laboratories). The colourless liquid obtained (1·3 g) gave a single peak upon gas chromatography; IR, 5·9μ (strong); λ_{max}^{EtOH} 232 mμ (ε 8000); NMR, solution in acetone-d_6, ppm (rel. no. of protons): 6·7 (1); 4·0–4·6 (1); 4·2 (1); 1·8–2·4 (4); 1·70 (3); 0·99, 0·94, 0·88, 0·83 (6). $[\alpha]_D^{25}$ +128° (*c* = 1·57, EtOH).

trans-p-*Menth*-1-*en*-3-*ol*-6-*one* 2,4-*dinitrophenylhydrazone*. To a warm solution of 2,4-dinitrophenylhydrazine (102 mg, 0·51 mmole) in absolute EtOH (6 ml) with conc. HCl (0·2 ml) was added a solution of ketone (80·3 mg, 0·48 mmole) in EtOH (3 ml). The bright orange precipitate (128 mg), after one recrystallization from EtOH (30 ml) plus ethyl acetate (a few drops), gave orange, shiny flakes (105 mg), m.p. 235–237° (dec). Two more recrystallizations gave m.p. 238–239° (dec, uncor.), λ_{max}^{EtOH} 375 mμ (ε 28,730); 260 mμ (ε 16,620); 247 mμ (ε 15,800). (Found: C, 55·26; H, 5·96; N, 15·77. $C_{16}H_{20}N_4O_5$ requires: C, 55·17; H, 5·79; N, 16·08%.)

(+)-p-*Menth*-1-*ene*-3,6-*diol*, *m.p.* 123°, (IV). To a suspension of LAH (0·40 g, 10·5 mmoles) in anhydrous ether (50 ml) was added dropwise with stirring a solution of ketone (XXI; 0·70 g; 4·2 mmoles) during 10 min. The mixture was heated under reflux for 2 hr. Hydrolysis and extraction, as above, gave a colourless oil (0·61 g, 86%) which solidified on standing. The total product showed no detectable absorption near 1700 cm^{-1} (no carbonyl group). Gas chromatography indicated the presence of at least four minor components, including one with the same retention time as diol III, in addition to the major component. One crystallization from hexane–ether (1:3) gave white, shiny, needle-like crystals, m.p. 118–120° (0·3 g). After two more recrystallizations, the crystals gave m.p. 123–123·5°; $[\alpha]_D^{25}$ +115·7 (*c* = 1·063, EtOH); IR, ν_{max}^{KBr} 1005 (*s*), 978 (*s*), 900 (*vs*), 845 (*vw*), 817 (*m*), 775 (*w*) cm^{-1} (uncor.). (Found: C, 70·55; H, 10·91. $C_{10}H_{18}O_2$ requires: C, 70·55; H 10·66%.)

Hydrogenation of diol IV. A solution of diol IV, m.p. 123–123·5° (100 mg, 0·588 mmoles) in 95% EtOH (15 ml) containing Raney Ni (0·2 g) was shaken at 25° under 2 atm. H_2 press. After 2 hr the reaction was complete. The total white solid reaction product (90 mg, 90%) gave two nearly equal peaks upon gas chromatography, with retention times corresponding exactly to XVII and XVIII, as shown by direct comparison. The six other *p*-menthane-2,5-diols, which were shown to give different retention times from diols XVII and XVIII, were not detected. The IR spectrum (KBr) of the total product was consistent with a mixture of diols XVII and XVIII.

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[17] A. R. H. Cole and P. R. Jefferies, *J. Chem. Soc.* 4391 (1956).

[18] (−)-α-Phellandrene was oxidized "by spraying it through a jet into an atmosphere of moist oxygen" at 70°, recycling for several hours. Diol III was isolated from the product by crystallization. The remainder of the product, upon distillation, gave dextrorotatory fractions which had not crystallized during four years storage at room temp. A. Blumann, private communication, September 15, 1964.