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The Chemistry of the Natural Order Cupressales 47 *

The Structures and Absolute Configurations of Widdrol and Widdrol-α-epoxide **

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Widdrol and widdrol-α-epoxide, first isolated from *Widdringtonia* species, are shown to have the structures (3) and (4), respectively.

In 1958 Erdtman and Thomas [1] investigated the heartwood constituents of the species belonging to the South African genus *Widdringtonia*. These trees were found to contain a number of structurally unknown sesquiterpenes, *i.e.* "widdrene" (= thujopsene), [2,3] "widdrene II" (= cuparene) [4], widdrol, "alcohol, $C_{15}H_{26}O_2$, m.p. 154°", "diol, $C_{15}H_{28}O_2$, m.p. 138°" (= selina-4,7-diol) [5], "widdrenic acid" (= hinokiic acid) [2,3], "acid III" (= cuparenic acid) [4], as well as cedrol and eudesmol. Subsequently the structures of all these compounds with the exception of widdrol and the alcohol $C_{15}H_{26}O_2$ have been determined. The elucidation of their structures is the subject of the present paper.

Erdtman and Thomas [1], on the basis of a preliminary investigation, concluded that widdrol was a dicyclic, tertiary sesquiterpene alcohol containing one double bond. They also obtained the unusual 1,7-dimethyl-4-isopropyl naphthalene (1) from the products of the selenium dehydrogenation of widdrol. Recently Nagahama [6] made the important observation that widdrol was formed on attempted acid isomerisation of thujopsene (2) [2,3] with oxalic acid. During the present investigation an epoxidation product of widdrol, widdrol-α-epoxide, was found to be identical with the above alcohol, $C_{15}H_{26}O_2$, isolated from *Widdringtonia juniperoides* [1].

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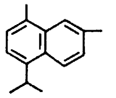
* Part 46, *Acta Chem. Scand.* 16 (1962) 1311.

** This structure of widdrol was first reported by H. Erdtman at the Chemical Society Symposium on Terpene Chemistry in London (23.2.1961) *Proc. Chem. Soc.* **1961** 129. Preliminary communication: Enzell, C. *Acta Chem. Scand.* **15** (1961) 1191. Itô, S., Endo, K., Takeshita, H., Nozoe, T. and Stothers, J. B. *Chem. & Ind. London* **1961** 1618, have also arrived at the correct structure for widdrol. Their conclusions were mainly based on spectral data.

Widdrol and widdrol-α-epoxide are assigned the structures (3) and (4), respectively, on the following evidence.

Ozonolysis of widdrol in methylene chloride followed by reduction of the product with lithium aluminium hydride in ether gave a triol (5) together with minor amounts of widdrol-α-epoxide (4). The triol (5) was oxidised under mild conditions to give a hydroxyketoaldehyde (6). This, on treatment with sodium hydroxide in aqueous methanol, gave an octalone (7) and acetaldehyde which were characterised as the 2,4-dinitrophenylhydrazones. The structure of the octalone (7) was established by comparison with synthetic 8,8,10-trimethyl-$\Delta^{1:9}$-2-octalone, recently described in connection with the total synthesis of (±) widdrol [7].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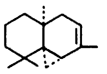
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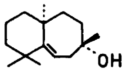

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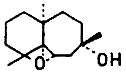

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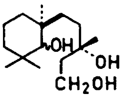

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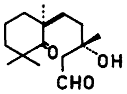

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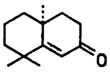

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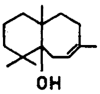

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These results favour structure (3) for widdrol. The alternative structure (8) is excluded by the following reactions. Hydrogenation of widdrol over Adams catalyst in acetic acid gave dihydrowiddrol (9) and a small amount of a hydrocarbon $C_{15}H_{28}$. The latter, probably formed by dehydration and subsequent hydrogenation, is assigned structure (10) of widdrane. Dihydrowiddrol on treatment with acetyl chloride in dimethyl aniline [8], gave the corresponding acetate (11) in good yield. Pyrolysis of the acetate furnished a mixture of unsaturated isomeric hydrocarbons, containing, according to its infrared absorption, minor amounts of the exocyclic isomer. Ozonolysis of the hydrocarbon mixture followed by steam distillation gave a low yield of formaldehyde. The non-volatile material was oxidised with silver oxide to give a ketoacid (12 or 13) as the main product. The ketoacid on oxidation with sodium hypoiodate gave iodoform and the corresponding dicarboxylic acid (14 or 15). These results eliminate structure (8) and widdrol must therefore have structure (3).

The infrared * and mass spectra of widdrol (Figs. 1 and 2) are in good agreement with structure (3). The strongest peak in the mass spectrum of widdrol

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* Widdrol in concentrated bromoform or carbon tetrachloride solutions shows a band at 1635 cm^{-1}, attributable to the double bond. The frequency of this band is close to that found for 1,1,10-trimethyl-$\Delta^{8:9}$-octalin (1640 cm^{-1}) and 4,4-dimethylchlolest-5-en-3β-ol (1635 cm^{-1}) but outside the range (1664—1672 cm^{-1}) reported for Δ^5-unsaturated steroids [9].

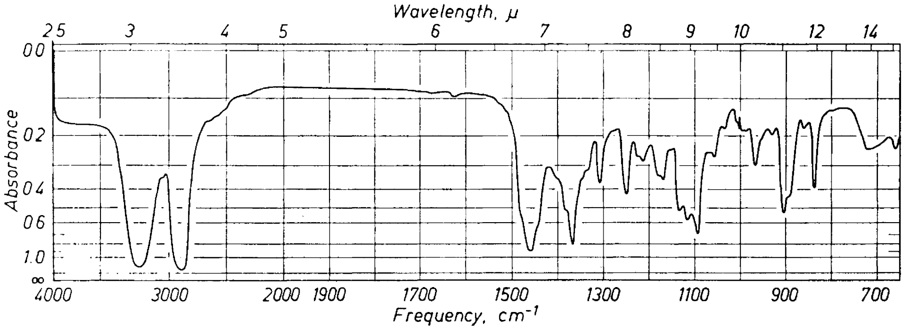


Fig. 1. Infrared spectrum of widdrol (KBr).

occurs at *m/e* 151 and the formation of an ion of this mass number is readily explained since the bonds between C(7) and C(8) and between C(10) and C(11) should be easily cleaved[10]. The resulting ion on uptake of hydrogen would have the required mass number. In agreement with this interpretation the spectrum of dihydrowiddrol exhibits a fairly strong peak at *m/e* 153 corresponding to the cleavage of the same bonds. Similar cleavages have been described in the diterpene series[11]. The proton magnetic resonance spectra of widdrol and many of its derivatives support the structure (3) for widdrol and they will be discussed in a forthcoming publication[12].

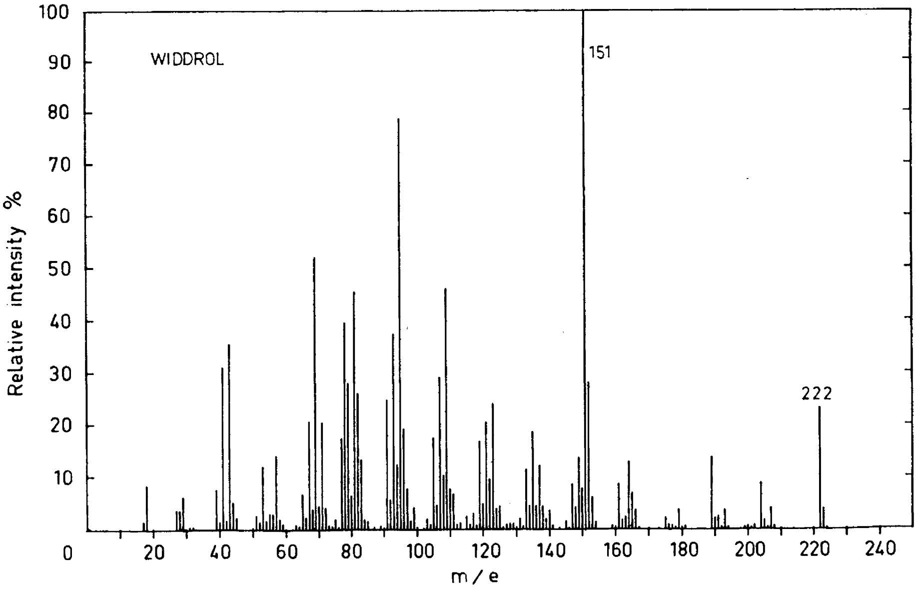
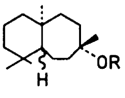
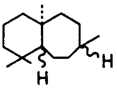


Fig. 2. Mass spectrum of widdrol.



9 (R, H)
11 (R, Ac)



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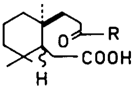
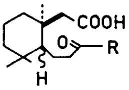


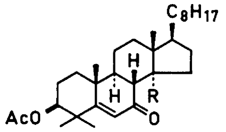
12 (R, CH_3)
14 (R, OH)



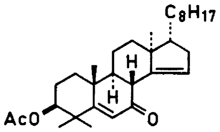
13 (R, CH_3)
15 (R, OH)

The absolute configuration at C(11) in widdrol follows from results obtained by rotatory dispersion measurements, kindly made by Professor W. Klyne. The trimethyl octalone (7) exhibits a positive Cotton effect while 3β-acetoxy-Δ^5-lanosten-7-one (16), 4,4-dimethyl-7-ketocholesteryl acetate (17) and $\Delta^{5,14}$-7-ketoapoeuphadienyl acetate (18), all show negative Cotton effects [13]. Inversions of rotatory dispersion curves of α,β-unsaturated ketones are only known to occur on modification of the adjacent ring to which the α,β-unsaturated carbonyl system is exocyclic [13] whilst modification of the same ring, or of the adjacent ring when the conjugated group is not exocyclic to it, has no major effect [13]. It may therefore be concluded that the octalone (7) has the absolute configuration depicted. Reduction of the octalone (7) with lithium in liquid ammonia gave the decalone (19), which on the basis of the accepted views on the steric course of such reductions is assigned a *trans* ring junction [14]. It exhibits a positive Cotton effect and hence, according to the octant rule [15], the angular methyl group is α-oriented. It therefore follows that the angular methyl group in widdrol is α-oriented.

The conversion [6] of thujopsene (2) into widdrol (3) and the results presented above establish that these compounds have the same configuration at C(11), *i.e.* the angular methyl group in thujopsene is α-oriented. Recent conclusions by Norin [2,16] based on independent evidence confirm this assignment.



16 (R, CH_3)
17 (R, H)



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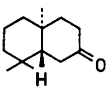

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The orientations assigned to the hydroxyl group in widdrol (3) and to the 1,2-epoxide group in the naturally occurring widdrol-α-epoxide (4) are based on the following evidence.

Widdrol, on treatment with perphthalic acid in ether, gave widdrol-α-epoxide (4) and widdrol-β-epoxide (20) (ratio 1:2.6), which were readily separated on alumina. Only widdrol-β-epoxide (20) shows an infrared band ($\nu_{\max}^{\mathrm{CCl_4}}$ 3620 cm^{-1}, *c* 0.005 M) attributable to a non-hydrogen bonded hydroxyl group. This indicates, in agreement with the results given below, that its oxygen atoms are in a *trans*-relationship to each other.

It is known that allylic hydroxyl groups may alter the normal, sterically determined course of epoxidation and this has been attributed to hydrogen bonding of the hydroxyl group with the reagent[17,18]. It appeared possible that a similar effect was responsible for the production of widdrol-α-epoxide and widdrol acetate was therefore oxidised with perphthalic acid. The oxidation product, on treatment with lithium aluminium hydride followed by chromatography, gave, however, both epoxides (4) and (20) but in a lower ratio (1:5.1) than above. It seems that the hydroxyl group has negligible or no *cis*-directing effect and that the introduction of the acetate group only increases the steric hinderance to attack from the α-side.

As mentioned previously ozonisation of widdrol gave widdrol-α-epoxide (4) and the triol (5) (ratio 1:3.5). This result is readily explained by assuming that an attack of ozone from the sterically more hindered side yields the epoxide (4), whereas an attack from the less hindered side gives the normal ozonide. A direct formation of epoxides from sterically hindered olefins is well known [19].

Reduction of widdrol-α-epoxide (4) with lithium in ethylamine gave the 5α,8α-diol (21) and the 6α,8α-diol (22), which were eluted from alumina in this order. Lithium aluminium hydride in tetrahydrofuran gave one product only, the 5α,8α-diol. The 6α,8α-diol (22) is strongly intermolecularly hydrogen bonded as shown by its infrared absorption ($\nu_{\max}^{\mathrm{CCl_4}}$ 3530 cm^{-1}, *c* 0.0046 M) [20]. This and its chromatographic behaviour show the *cis*-relationship between the two hydroxyl groups in this diol as well as between the two oxygen atoms in the parent compound, widdrol-α-epoxide. Oxidation of the 6α,8α-diol (22) furnished the corresponding hydroxy ketone (23) while the 5α,8α-diol (22) was unaffected.

Widdrol-β-epoxide (20) on reduction with lithium in ethylamine gave the 5β,8α-diol (24) and the 6β,8α-diol (25), which were eluted from alumina in the order mentioned. Attempts to reduce widdrol-β-epoxide with lithium aluminium hydride in tetrahydrofuran gave only starting material. The infrared

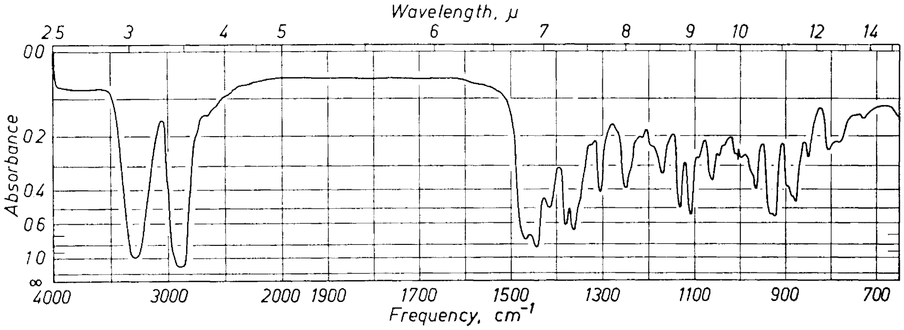
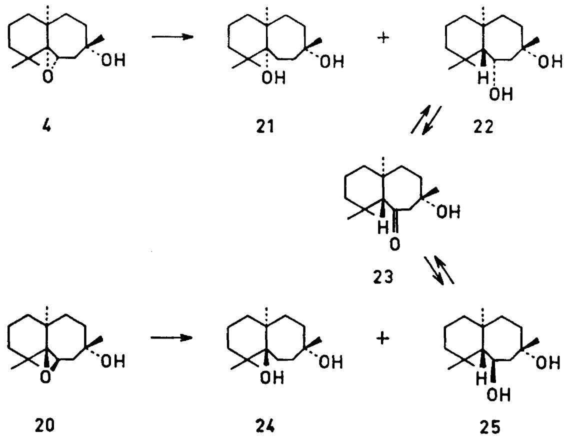


Fig. 3. Infrared spectrum of widdrol-α-epoxide (KBr).

spectrum of the 6β,8α-diol did not exhibit absorption attributable to intramolecular hydrogen bonding. Oxidation of the 6β,8α-diol (25) gave the same hydroxyketone (23) as that obtained from the 6α,8α-diol (22), whereas the 5β,8α-diol (24) was stable to oxidation under similar conditions.

The 6α,8α-diol (22) and the 6β,8α-diol (25) are also obtained on reduction of the hydroxyketone (23) with lithium aluminium hydride and must accordingly have the same configuration at C(5). They are probably the more stable products[14] and are therefore assigned *trans*-fused ring systems by analogy with the more stable isomer of the bicyclo(5,4,0)undecane-2-ones[21]. The difference in reactivity of the two epoxides with lithium aluminium hydride is consistent with the configurations assigned to them, *i.e.* only that epoxide which can be attacked from the sterically less hindered β-side is reduced. Similarly, application of the "benzoate rule"[22] to the difference in molecular rotation ($\Delta[M]_D = +15°$) between the non-hydrogen bonded 6β,8α-diol (25) and its mono-*p*-nitrobenzoate suggests that its secondary hydroxyl group is β-oriented as depicted.



Treatment of widdrol-β-epoxide (20) with aqueous formic acid at room temperature gave the 6β-hydroxyether (26) which may be formed by protonation of the epoxide group and a rear side attack of the hydroxyl group. Oxidation of the hydroxyether gave the corresponding ketoether (27) ($\nu_{\max}^{\mathrm{CCl_4}}$ 1745 cm^{-1}). Attempts to reduce the ketoether by a modified Wolff-Kishner procedure[23] gave only starting material. Refluxing the ketoether with lithium aluminium hydride in ether for 16 h gave starting material and the 6β-hydroxyether (26) as the main products together with a small amount of the 6α-hydroxyether (28). The preferential formation of the 6β-hydroxyether indicates that reduction takes place mainly by attack from the sterically less hindered side of the ketoether.

The difference in molecular rotation ($\Delta[M]_D = +203°$) between the 6β-hydroxyether and its *p*-nitrobenzoate is consistent with the configuration (26) but not with the alternative (29). The same conclusion is reached on the basis of the negative Cotton effect (*a* −72) * exhibited by the ketoether. A com-

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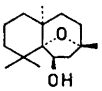
* Amplitudes (*a*) are given as the algebraic difference between [Φ] for peak and through — divided by 100. See Ref.[24]

parison of molecular models (Dreiding) shows that the ether oxygen and C(8) are found in negative octants in structure (27) but in positive octants in the alternative structure (30). Klyne[24] has pointed out that the signs of the Cotton effects shown by cyclopentanones are the same as those of the octants in which are found the atoms of the five-membered ring in the β-position to the carbonyl group, and that this, as well as the large amplitude normally found, is due to "first-order" effects of this ring system. It seems probable that tetrahydrofuranones should exhibit similar effects and that the observed Cotton effect is consistent only with structure (27). Comparison with bicyclo(3,2,1)octan-6-ones gives the same results, *i.e.* the bridge-ring bicyclo(3,2,1)structures of the general type (31), analogous to (27), show negative Cotton effects and those of the enantiomeric type (32), analogous to (30), show positive effects[24].



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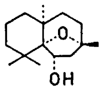

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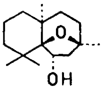

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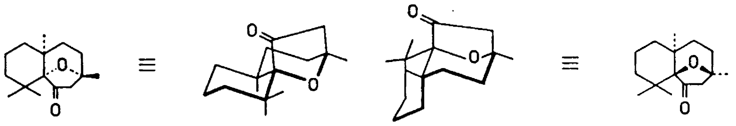

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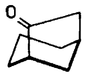

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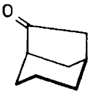

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Widdrol-α-epoxide (4) on treatment with boiling water gave two unsaturated diols, which on the basis of their spectral data may be formulated as (33) and (34). In view of the high ionising power of the solvent it seems probable that they are formed *via* a solvated carbonium ion. Oxidation of these diols furnished the corresponding non-conjugated hydroxyketones (35) and (36).

Widdrol was oxidised with osmium tetroxide to give the 5α,6α,8α-triol (37) and the 5β,6β,8α-triol (38). The former structure is assigned to the minor product and the latter structure to the main product (ratio 1:4.5) since the α-side of widdrol should be less readily attacked. In agreement with this the more hindered 5α,6α,8α-triol is not attacked by lead tetracetate[25] and on oxidation with chromium trioxide-sulphuric acid in acetone gives the dihydroxyketone (39), whereas the less hindered 5β,6β,8α-triol yields the hydroxyketoaldehyde (6) with both these reagents. The dihydroxyketone (39) exhibits a negative Cotton effect (a -43) which supports the *cis*-fusion of the rings *.

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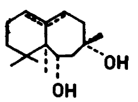
* The corresponding compound with the rings *trans*-fused has the C(5)-hydroxyl group in a positive octant and would, assuming that its conformation is the same as that of the hydroxyketone (23), be expected to exhibit the same positive Cotton effect as (23)[26].

On treatment with N-bromosuccinimide in aqueous *t*-butyl alcohol widdrol gave a bromoether which is probably formed by attack of bromine from the sterically less hindered side. The bromoether, in agreement with its spectral data, is assigned structure (40). It was possible to reduce this compound to the ether (41) but attempts to convert it to the corresponding hydroxyether failed.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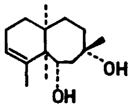
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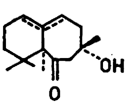
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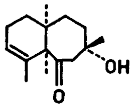
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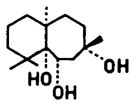
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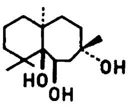
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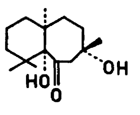
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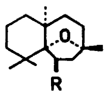
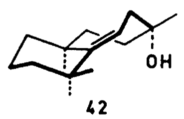

40 (R, Br)
41 (R, H)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The conformations of cycloheptane and cycloheptene systems have recently been discussed by several authors [27,28,29]. In those derivatives of widdrol containing a cycloheptane or cycloheptanone ring *trans*-fused to the cyclohexane ring an "all-chair" conformation may be expected to be energetically favoured and this is supported by the positive Cotton effect exhibited by the hydroxyketone (23). Inspection of molecular models indicates that a conformation of widdrol such as that depicted in (42) should be quite rigid. Such a conformation may explain why widdrol on acetylation [8] gives mainly dehydrated material, whereas dihydrowiddrol * gives the corresponding acetate in 92 % yield and why the double bond becomes noticeably less accessible to attack from the α-side in widdrolacetate in comparison to widdrol and, finally, why the mass spectrum of widdrol (Fig. 2) exhibits a parent peak of high intensity (1.85 % of total ion yield) while there is no parent peak in the spectrum of dihydrowiddrol [30].

Erdtman and Thomas [1] obtained a small amount of 1,7-dimethyl-4-isopropyl naphthalene (1), characterised as the picrate, from the selenium dehydrogenation products of widdrol. This result was confirmed and it was found that dehydrogenation with palladium on charcoal gave similar results. Analysis of the dehydrogenation mixture by vapour phase chromatography showed that it consisted of at least nine compounds. It was possible to isolate the naphthalene (1) and to show that one or several of the other compounds were *p*-disubstituted benzene derivatives, since on oxidation with nitric acid the product gave terephthalic acid in low yield. These results show that extensive rearran-

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* Dihydrowiddrol should consist largely of the *trans* isomer which, in the more probable of the two "all-chair" conformations has the hydroxyl group "equatorially" oriented.

gements take place during the dehydrogenation of widdrol. The naphthalene (1) has also been isolated from the dehydrogenation products of carotol[31] and thujopsene[3].

Nagahama[6] obtained widdrol on treatment of thujopsene with oxalic acid in aqueous ethanol. In view of the present results it appears probable that this is due to a *trans* diaxial addition of the elements of water to the double bond followed by opening of the three membered ring. Tanka and Yamashita[32] on hydration of thujopsene under mild Bertram-Wahlbaum conditions obtained an alcohol $C_{15}H_{26}O$, m.p. 120—122°, $[\alpha]_D + 115°$, which may possibly be an intermediate in the isomerisation of thujopsene to widdrol.

In the conifers, widdrol has almost always been found to occur[33] together with cedrene[34,35] cedrol[34], cuparene[4] and thujopsene[2,3]. The corresponding acids, *i.e.* cedrolic acid[36], cuparenic acid[4] and hinokiic acid[2,3] have also been isolated from the same sources.Their co-occurrence and absolute configurations obviously suggest that they arise from a common, properly oriented 2,3-*cis*-farnesyl precursor[37,38]. This will be discussed elsewhere[39].

EXPERIMENTAL

Melting points were determined on a Kofler micro hot stage and are corrected. Infrared spectra were recorded on a Perkin Elmer No 21 instrument (NaCl prism), ultraviolet spectra on a Beckman DK 2 recording spectro-photometer and mass spectra on an instrument[40] with an all glass, heated inlet system (energy of electrons 70 eV). Microanalysis by Dr. A. Bernhardt, Mülheim.

Ozonisation of widdrol (3). Widdrol (1.0 g) in methylene chloride (15 ml) was treated with ozone at —70° until excess ozone was present. Nitrogen was passed through the solution and the solvent removed under reduced pressure at 5—10°. The residue, dissolved in dry ether (20 ml), was added to a stirred suspension of lithium aluminium hydride (0.6 g) in dry ether (100 ml). The reaction mixture was boiled under reflux for one hour, cooled and the excess lithium aluminium hydride destroyed with ethyl acetate. The resulting suspension was acidified and extracted repeatedly with ether. The ether phase gave a residue (1.1 g), which crystallised on treatment with isopropyl ether. Repeated recrystallisation from isopropyl ether gave the triol (5), (0.63 g), m.p. 97—98°, $[\alpha]_D -1°$ ($CHCl_3$, *c* 2.2), (Found C 70.0; H 11.8; O 18.9. $C_{15}H_{30}O_3$ requires C 69.7; H 11.7; O 18.6 %). ν_{max}^{KBr} 3360, 1147, 1062, 1022, 1008 cm^{-1}. Its mass spectrum includes major peaks at *m/e*: 240 (2, *M*-18) *, 225 (10, *M*-18-15), 222 (17, *M*-2 × 18), 207 (14, *M*-2 × 18—15), 204 (7, *M*-3 × 18), 195 (26), 177 (49), 168 (35), 140 (52), 137 (49), 123 (56), 109 (61), 94 (44), 88 (53), 81 (53), 81 (100), 69 (71), 55 (44), 43 (93).

The mother liquors were combined and chromatographed on alumina (neutral, activity III, 30 g). Elution with light petroleum (b.p. 35—60°)-ether (3:1) gave a crystalline material, which on recrystallisation from isopropyl ether gave widdrol-*α*-epoxide (4), (0.19 g), m.p. and mixed m.p. 156—157°. Infrared spectrum identical with that of widdrol-*α*-epoxide obtained from perphthalic acid oxidation of widdrol. Elution with ether-ethanol (20:1) gave a further amount (0.04 g) of the triol (5).

Very similar results were obtained when widdrol in methanol was treated with ozone and the solution of the ozonide was added to an aqueous methanolic solution of potassium borohydride.

Trimethyl octalone (7). A solution of chromium trioxide (1.06 g) in water (12 ml) and conc. sulphuric acid (1.8 ml) was added all at once to a stirred solution of the triol (5), (2.0 g) in acetone, which was kept at *ca.* —30°. The reaction mixture was stirred until it reached room temperature (*ca.* 15 min) and then diluted with water (300 ml) and extracted with ether. Work up gave the liquid hydroxyketoaldehyde (6), (1.38 g)

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* The figures within brackets give peak intensities as percentages of the strongest peak in the spectrum.

(Found C 70.8; H 9.9. $C_{15}H_{26}O_3$ requires C 70.8; H 10.3). λ_{max}^{EtOH} 301 mμ (e 31), $\nu_{max}^{CCl_4}$ 3610; 2720, 1717; 1690 cm^{-1}. Attempts to obtained crystalline derivatives of this compound were unsuccessful.

The hydroxyketoaldehyde (1.2 g) in methanol (p.a., 50 ml) was added to aqueous sodium hydroxide (5 %, 50 ml). This mixture was boiled gently for 3 h under a slow stream of oxygen-free nitrogen and a small amount (*ca.* 10 ml) was removed over a short Vigreux column. The distillate was added to a saturated ethanol solution of 2,4-dinitrophenylhydrazine, which was left for a day and then diluted with water. The resulting crystals were dissolved in benzene and filtered through silica gel. Recrystallisation from ethanol gave acetaldehyde 2,4-dinitrophenylhydrazone (80 mg), m.p. and mixed m.p. 165–167° (decomp.). Infrared spectrum identical with that of authentic material.

The reaction mixture was cooled and steam distilled after addition of water. The distillate (500 ml) was extracted with ether to give an oil (0.66 g), which was chromatographed on alumina (neutral, activity I, 20 g). Elution with light petroleum (b.p. 35–60°)-benzene (5:1) followed by a quick distillation at low pressure gave the trimethyl octalone (7), (0.34 g), n_D^{25} 1.5142, (Found: C 81.1; H 10.4. $C_{13}H_{20}O$ requires C 81.2; H 10.5), λ_{max}^{EtOH} 240 mμ (ε 13 000), $\nu_{max}^{CCl_4}$ 1670, 1597, 1420; 1390, 1380, 1368 cm^{-1}. Rotatory dispersion curve (MeOH): $[\Phi]_{500}$ + 400°, $[\Phi]_{356}$ + 3500°, $[\Phi]_{303}$ −4500°, $[\Phi]_{300}$ −4300°. The mass spectrum includes major peaks at *m/e*: 192, (100, *M*), 177 (17, *M*-15), 164 (49, *M*-28), 149 (69, *M*-28-15), 136 (71), 123 (62), 107 (33), 93 (35), 79 (29), 69 (14), 55 (21), 41 (31), 27 (14), 15 (2). The infrared, ultraviolet and mass spectra were identical with corresponding spectra of 8,8,10-trimethyl-$\Delta^{1:9}$-octalone [7].

The trimethyl octalone (7) 2,4-dinitrophenylhydrazone, m.p. 204–205°, $[\alpha]_D$ + 3° (benzene, *c* 1.0), (Found: C 61.4; H 6.4; N 14.8. $C_{19}H_{24}N_4O_4$ requires C 61.3; H 6.5; N 15.1), λ_{max}^{EtOH} 213 mμ (ε 22 000), 254 mμ (ε 19 000), 298 mμ (ε 12 000), 383 mμ (ε 28 000). Its mass spectrum includes major peaks at m/e: 372 (100, *M*), 357 (29, *M*-15), 302 (17), 287 (14), 267 (12), 183 (7), 175 (9), 159 (22), 147 (10), 131 (14), 119 (18), 105 (33), 91 (46), 79 (29), 69 (20), 55 (25), 41 (30), 18 (16). The infrared, ultraviolet and mass spectra were identical with corresponding spectra of the 2,4-dinitrophenylhydrazone of 8,8,10-trimethyl-$\Delta^{1:9}$-octalone [7].

Trimethyl decalone (19). The trimethyl octalone (7) (350 mg) was dissolved in tetrahydrofuran (7 ml) and added dropwise over 20 min. to a stirred solution of lithium (60 mg) in ammonia (100 ml, distilled over sodium). The solution was stirred for 30 min. Ammonium chloride was added and the ammonia evaporated. The residue was extracted with light petroleum (b.p. 35–60°) and chromatographed on alumina (neutral, activity I, 12 g). Elution with benzene followed by distillation at reduced pressure gave the trimethyl decalone (19) (150 mg), $\nu_{max}^{CCl_4}$ 1707 cm^{-1}. Rotatory dispersion curve (MeOH): $[\Phi]_{500}$ + 550°, $[\Phi]_{313}$ + 1650°, $[\Phi]_{275}$ −1600°, $[\Phi]_{273}$ −1300°. 2,4-Dinitrophenylhydrazone, m.p. 169–184° (slight decomp.), $[\alpha]_D$ + 80° ($CHCl_3$, *c* 0.9), (Found: C 60.7; H 7.1; N 15.1. $C_{19}H_{26}N_4O_4$ requires C 60.9; H 7.0; N 15.0). λ_{max}^{EtOH} 230 mμ (e 15 000), 363 mμ (e 20 000). Further elution with benzene-ether (20:1) gave starting material (95 mg).

Dihydrowiddrol (9). Widdrol (2.0 g) was hydrogenated at room temperature and atmospheric pressure over Adam's catalyst (180 mg) in acetic acid (20 ml). Hydrogenation ceased after 15 h when 240 ml of hydrogen had been consumed. The catalyst was removed by filtration and the filtrate diluted with water (100 ml), made alkaline and extracted with ether. Removal of the solvent gave a residue (2.0 g), which was chromatographed on alumina (neutral, activity II, 100 g). Elution with light petroleum (b.p. 35–60°) gave the hydrocarbon (10) (0.22 g), n_D^{25} 1.4833, $[\alpha]_D$ + 24° ($CHCl_3$, *c* 5.0), (Found: C 86.6; H 13.3. $C_{15}H_{28}$ requires C 86.5; H 13.5 %). Elution with ether followed by recrystallisation from methanol and sublimation gave dihydrowiddrol (1.6 g), m.p. 54–61°, $[\alpha]_D$ + 51° ($CHCl_3$, *c* 1.1), (Found: C 80.1; H 12.5. $C_{15}H_{28}O$ requires C 80.3; H 12.6 %). The mass spectrum of dihydrowiddrol includes major peaks at *m/e*: 209 (4, *M*-15), 206 (31, *M*-18), 191 (40, *M*-15-18), 178 (20), 163 (22), 153 (33), 137 (33), 123 (90), 109 (92), 95 (100), 83 (55), 69 (69), 55 (57), 41 (62), 29 (18), 18 (13).

Dihydrowiddrol acetate (11). Dihydrowiddrol (1.5 g) was dissolved in dry N-dimethyl aniline (redist.) and acetyl chloride (1.5 ml) was added slowly to the stirred solution. The solution was stirred for 20 h at 40° and the resulting blue solution was diluted with ether and acidified with ice cold dilute sulphuric acid (5 %). The ether solution was washed with ice-cold dilute sulphuric acid (20 %) and water until neutral, dried and concentrated. The residue (1.77 g) was chromatographed on alumina (neutral, activity I, 100 g) and elution with light petroleum (b.p. 35—60°) gave a small amount (5 mg) of a dehydrated product. Benzene eluted dihydrowiddrol acetate (11), (1.63 g), n_D^{25} 1.4867, $[\alpha]_D$ + 32° ($CHCl_3$, *c* 2.4), (Found: C 76.4; H 11.3. $C_{17}H_{30}O_2$ requires C 76.6; H 11.4), $\nu_{\max}^{\text{pure oil}}$ 1727 cm^{-1}.

Ketoacid (12 or 13). Dihydrowiddrol acetate (0.58 g) was distilled (bath temp. 320°) through a short column (200°) at atmospheric pressure. The distillate, in light petroleum (b.p. 35—60°), was filtered through alumina (neutral, activity I, 50 g) and the filtrate redistilled to give a mixture of hydrocarbons (0.43 g), $\nu_{\max}^{\text{pure oil}}$ 1675, 844; 1643, 885 cm^{-1}. The hydrocarbon mixture in methylene chloride (10 ml) was treated with ozone at —70° until a blue colour persisted and excess ozone was removed by passing through nitrogen. The solution together with the water in the water trap was steam distilled and the distillate collected in an almost saturated aqueous solution of dimedone at 0°. Evaporation of the methylene chloride gave a precipitate, which on recrystallisation from aqueous ethanol gave formaldehyde-dimethon (17 mg), m.p. and mixed m.p. 189—190°. (Negative blank.) The non-volatile part was extracted with ether. The product (0.38 g) was added to a solution of silver nitrate (0.66 g) in water (1 ml). A solution of sodium hydroxide (0.24 g) in water (1 ml) was added and the mixture was stirred for 3 h at 90°, cooled, filtered and washed with ether. The aqueous phase was acidified with dilute sulphuric acid (10 %) and extracted with ether to give a mixture of acids (0.26 g). This was chromatographed on thick, dimethylsulphoxide impregnated paper [41] (2 sheets of Whatman 3 MM, 24 × 36 cm) with ether, saturated with dimethylsulphoxide, as the mobile phase. Ether extraction of the strips gave as the main product the liquid ketoacid (12 or 13) (0.16 g, R_F 0.7), $[\alpha]_D$ —6° ($CHCl_3$, *c* 2.0), (Found: C 71.2; H 10.1. $C_{15}H_{26}O_3$ requires C 70.8; H 10.3), $\nu_{\max}^{CCl}$ 1700—1715 (broad) cm^{-1}. "Anhydrous 2,4-dinitrophenylhydrazone", m.p. 232—236°, (Found: N 13.5. $C_{21}H_{28}N_4O_5$ requires N 13.5).

Diacid (14 or 15). The ketoacid (140 mg) was dissolved in dilute sodium hydroxide (10 %, 5 ml) and a 10 % solution of iodine in aqueous potassium iodide (20 %) was added dropwise until a slight excess of iodine was present. The reaction mixture was kept at 60° until the iodine colour persisted for 2 min, whereafter it was decolourised by addition of dilute sodium hydroxide (10 %). Addition of water followed by filtration gave iodoform (50 mg), m.p. and mixed m.p. 119—120°. The filtrate, after extraction with ether, was acidified with dilute sulphuric acid (10 %) and extracted with ether. The product (116 mg) was chromatographed on silica gel (20 ml) impregnated with dimethylsulphoxide. Elution with ether, which was almost saturated with dimethylsulphoxide, gave several fractions. Those fractions, which according to paper chromatography contained the diacid, were combined, washed with water and dried. Evaporation of the ether gave the liquid diacid (14 or 15), (95 mg), (Found: C 65.6; H 9.2. $C_{14}H_{24}O_4$ requires C 65.6; H 9.4) $\nu_{\max}^{CCl_4}$ 1707 cm^{-1}. Dimethyl ester n_D^{25} 1.4782, $[\alpha]_D$ —2° ($CHCl_3$, *c* 0.9), $\nu_{\max}^{CCl_4}$ 1732 cm^{-1}.

Monoperphthalic acid oxidation of widdrol. Widdrol (1.11 g) in dry ether (20 ml) was added to an ethereal solution of monoperphthalic acid (0.2 M, 75 ml) and left for a week at room temperature in a dark place. The solution was washed with aqueous sodium hydroxide (5 %) and water. Evaporation of the solvent gave a crystalline residue (1.21 g), which was chromatographed on alumina (neutral, activity III, 100 g). Elution with benzene gave widdrol-β-epoxide (20), (796 mg, m.p. 95—114°), which after recrystallisation from isopropyl ether had m.p. 120—121°, $[\alpha]_D$ + 36° ($CHCl_3$, *c* 1.0), (Found: C 75.7; H 11.1. $C_{14}H_{24}O_4$ requires C 75.6; H 11.0 %), $\nu_{\max}^{KBr}$ 1110, 3340, 985, 1258, 1428 cm^{-1}, $\nu_{\max}^{CCl_4}$ 3180—3580 (flat), 3620 cm^{-1} (*c* 0.0046 M). Further elution with benzene gave widdrol-α-epoxide (4), (312 mg, m.p. 148—152°), which on recrystallisation from isopropyl ether had m.p. 156—157°, $[\alpha]_D$ —6°, ($CHCl_3$, *c* 1.5), $\nu_{\max}^{CCl_4}$ 3180—3600 (flat) cm^{-1} (*c* 0.0050 M).

Widdrol-α-epoxide was identical with the alcohol, $C_{15}H_{26}O$, m.p. 154°, $[\alpha]_D$ —9°, previously obtained from *Widdringtonia dracomontana* [1]. The two compounds had undepressed mixed m.p. 154—155° and identical infrared spectra (Fig. 3).

Both widdrolepoxides (50 mg of each) were recovered unchanged in quantitative yields after treatment overnight at room temperature with chromium trioxide (100 mg) in pyridine (5 ml).

Widdrol acetate. Widdrol (300 mg) was added to a mixture of acetic anhydride (5 ml) and pyridine (5 ml) and the solution left at 20° for three weeks. The reaction mixture was diluted with water (100 ml) and extracted with ether. The product (290 mg) was adsorbed on alumina (neutral, activity II, 12 g). Elution with light petroleum gave a small amount of dehydrated material (14 mg). Elution with light petroleum (b.p. 35—60°)-ether (20:1) gave widdrol acetate (137 mg), n_D^{25} 1.490, $[\alpha]_D$ + 20° ($CHCl_3$, *c* 0.9), $\nu_{max}^{CCl_4}$ 1727 cm^{-1}, (Found: C 77.4; H 10.4; O 12.3. $C_{17}H_{28}O_2$ requires C 77.2; H 10.7; O 12.1). Ether eluted widdrol (114 mg).

Monoperphthalic acid oxidation of widdrol acetate. Widdrol acetate (80 mg) in ether (2 ml) was added to an ethereal solution of monoperphthalic acid (0.6 M, 10 ml) and left for a week at 20° in a dark place. The solution was extracted with aqueous sodium hydroxide (5 %) and water, dried and concentrated to 15 ml. The concentrated solution was stirred with lithium aluminium hydride (200 mg) for 3 h at 20°. The crystalline product (71 mg) was chromatographed on alumina (neutral, activity II, 5 g) to give widdrol-β-epoxide (20), (51 mg) and widdrol-α-epoxide (4), (10 mg) which were identical with authentic material in all respects (mixed m.p. and I.R.).

Reduction of widdrol-α-epoxide (4) with lithium in ethylamine. Lithium (200 mg) and boiling ethylamine (25 ml) were stirred for 10 min. Widdrol-α-epoxide (700 mg) was added and the reaction mixture was stirred for 15 min. Ethanol was added (0.2 ml) and after stirring for an hour excess lithium was destroyed by addition of ammonium chloride. Evaporation of the ethylamine, dilution with water (100 ml) and extraction with ether gave on removal of the solvent a residue (704 mg), which was chromatographed on alumina (neutral, activity II, 50 g). Elution with benzene gave the diol (22), (125 mg), which on recrystallisation from isopropyl ether had m.p. 143—144°, $[\alpha]_D$ + 7° ($CHCl_3$, *c* 0.6), (Found: C 74.8, H 11.4. $C_{15}H_{28}O_2$ requires C 75.0; H 11.7), ν_{max}^{KBr} 896, 1088, 1113, 1160, 3375 cm^{-1}, $\nu_{max}^{CCl_4}$ 3530 cm^{-1} (*c* 0.0045 M). Elution with ether furnished the diol (21), (515 mg), which after recrystallisation from isopropyl ether had m.p. 107—108°, $[\alpha]_D$ + 40° ($CHCl_3$, *c* 0.8), (Found: C 75.1; H 11.9. $C_{15}H_{28}O_2$ requires C 75.0; H 11.7), ν_{max}^{KBr} 917, 1028, 1076, 1110, 1212, 3410, 3475 cm^{-1}.

Reduction of widdrol-β-epoxide (20) with lithium in ethylamine. Lithium (700 mg) and boiling ethylamine (40 ml) were stirred for 20 min. Widdrol-β-epoxide (1.00 g) was added and the mixture stirred for 35 min. After addition of abs. ethanol (0.2 ml) the mixture was stirred for an additional 30 min. before the excess lithium was destroyed with ammonium chloride. The product was worked up according to the above procedure and gave a mixture of diols (960 mg), which was chromatographed on alumina (neutral, activity II, 80 g). Elution with light petroleum (b.p. 35—60°)-ether (10:1) gave the diol (24), (560 mg), which on recrystallisation from isopropyl ether had m.p. 91—92°, $[\alpha]_D$ —33° ($CHCl_3$, *c* 0.9), (Found: C 75.1; H 11.7. $C_{15}H_{28}O_2$ requires C 74.9; H 11.7). ν_{max}^{KBr} 928, 1040, 1136, 3450 cm^{-1}. Elution with ether-ethanol (5:1) gave the diol (25) as a glass (390 mg), $[\alpha]_D$ —2° ($CHCl_3$, *c* 0.9), (Found: C 74.5; H 11.4. $C_{15}H_{28}O_2$ requires C 74.9; H 11.7). $\nu_{max}^{CCl_4}$ 3620 cm^{-1} (*c* 0.005 M). Treatment of this diol with excess *p*-nitrobenzoyl chloride in pyridine for 24 h at room temperature followed by chromatography on alumina and recrystallisation gave a mono *p*-nitrobenzoate, m.p. 135—136°, $[\alpha]_D$ —5° ($CHCl_3$, *c* 0.8), (Found: C 68.2; H 8.2. $C_{22}H_{31}O_5N$ requires C 67.8; H 8.0) and the di *p*-nitrobenzoate, m.p. 195—196°, $[\alpha]_D$ + 112° ($CHCl_3$, *c* 0.9), (Found: N 5.6. $C_{29}H_{34}O_8N_2$ requires N 5.2).

Treatment of the widdrolepoxides with lithium aluminiumhydride. Widdrol-α-epoxide (4), (205 mg) in tetrahydrofuran (15 ml) was refluxed with lithium aluminium hydride (300 mg) for 18 h. The crystalline product (202 mg, m.p. 102—107°), was recrystallised from isopropyl ether to give the diol (21), m.p. and mixed m.p. 107—108°. Identical infrared spectra.

Widdrol-β-epoxide (20) was recovered unchanged after the same treatment.

Both epoxides were recovered unchanged after treatment with lithium aluminium hydride in ether for 12 h at 20°.

Oxidation of diol (22). The diol (50 mg) was oxidised as described for the triol (5). The crystalline product (46 mg, m.p. 80—90°), on recrystallisation from isopropyl ether, gave the hydroketone (23), m.p. 91—92°, $[a]_D$ + 30° ($CHCl_3$, *c* 0.6), (Found: C 75.6; H 10.9. $C_{15}H_{26}O_2$ requires C 75.6; H 11.0). λ_{max}^{EtOH} 309 mμ (36). ν_{max}^{KBr} 1107, 3365: 1700 cm^{-1}, $\nu_{max}^{CCl_4}$ 1106, 3430, 3580; 1700 cm^{-1}. Rotatory dispersion curve (MeOH) $[\Phi]_{596}$ —100°, $[\Phi]_{324}$ + 1230°, $[\Phi]_{310}$ + 50°, $[\Phi]_{279}$ + 1300°, $[\Phi]_{271}$ + 1150°.

The diol (21) was recovered unchanged after the same treatment.

Oxidation of diol (25). The diol (150 mg) was oxidised in the same way as described for the triol (5) except that it was stirred for an additional 30 min at room temperature. The crystalline product (131 mg) was recrystallised to give the hydroxyketone (23), m.p. and mixed m.p. 91—92°. Infrared spectrum identical with that of the hydroxyketone obtained from the diol (22).

The diol (24) was recovered unchanged after the same treatment.

Reduction of hydroxy ketone (23) with lithium aluminium hydride. The hydroxy ketone (185 mg) in ether was added to a suspension of lithium aluminium hydride in ether and refluxed for 3 h. The product (186 mg), was chromatographed on alumina (neutral, activity II, 8 g). Elution with light petroleum (b.p. 35—60°)-ether (5:1) gave the diol (22), (108 mg), m.p. and mixed m.p. 143—144°. Elution with ether gave the diol (25) (73 mg). Infrared spectrum identical with that of authentic material. Di-*p*-nitrobenzoate, m.p. and mixed m.p. 195—196°.

Hydroxyether (26). Widdrol-β-epoxide (20) (100 mg) was added to a solution of formic acid (9 ml) and water (1 ml) and left overnight at room temperature. The solvents were removed by distillation at water pump pressure and the residue was refluxed with a mixture of aqueous potassium hydroxide (40 %, 5 ml) and ethanol (10 ml) for 1 h. Dilution with water (100 ml) followed by extraction with ether gave the hydroxyether (26), (87 mg), which on recrystallisation from light petroleum (b.p. 35—60°) and sublimation had m.p. 99—100°, $[a]_D$ + 7° ($CHCl_3$, *c* 0.9), (Found: 75.5; H 10.8. $C_{15}H_{26}O_2$ requires C 75.6; H 11.0). ν_{max}^{KBr} 1008, 1032, 1084, 1096, 1158, 1267, 3590 cm^{-1}. Its mass spectrum includes major peaks at *m/e*: 238 (9, *M*), 220 (1, *M*-18), 194 (8), 179 (7), 167 (6), 149 (2), 140 (100), 125 (19), 109 (12), 95 (9), 81 (12), 69 (28), 55 (24), 41 (37), 29 (14), 18 (1). *p*-Nitrobenzoate, m.p. 148—149° $[a]_D$ —48° ($CHCl_3$, *c* 1.0), (Found: C 68.4; H 7.6. $C_{22}H_{24}O_5N$ requires C 68.2; H 7.5).

Ketoether (27). The hydroxyether (26), (100 mg) was oxidised as described for the triol (5), and gave the ketoether (27), (94 mg), m.p. 39—40°, $[a]_D$ —71° ($CHCl_3$, *c* 0.9), (Found: C 76.2; H 10.2. $C_{15}H_{26}O_2$ requires C 76.2; H 10.4), ν_{max}^{KBr} 1070, 1125, 1189, 1408, 1745 cm^{-1}, λ_{max}^{EtOH} 219 mμ (ε 402), 305 mμ (ε 34), 315 mμ (ε 42). Rotatory dispersion curve (MeOH) $[\Phi]_{596}$ —100°, $[\Phi]_{323}$ —4000°, $[\Phi]_{292}$ + 3200°, $[\Phi]_{260}$ + 1350°.

Reduction of the ketoether (27) with lithium aluminium hydride. The ketoether (500 mg) and lithium aluminium hydride (750 mg) in dry ether (20 ml) were boiled under reflux for 16 h. The product (455 mg), was chromatographed on alumina (neutral, activity II, 25 g). Elution with light petroleum (b.p. 35—60°) gave starting material (201 mg) and elution with light petroleum-ether (1:1) gave the hydroxyether (26), (124 mg). These compounds were identical in all respects (mixed m.p. and I.R.) with corresponding authentic material. Elution with benzene gave a partly crystalline material (32 mg). Repeated recrystallisation from light petroleum (b.p. 35—60°) followed by sublimation gave a small amount (3 mg) of the hydroxyether (28), m.p. 119—121°. The mass spectrum of this compound was practically identical with that of the hydroxyether (26). The main differences, as expected, were the intensities of certain peaks: *m/e* 238 (1), 194 (2), 179 (4), 169 (1), 125 (43), 95 (55), 18 (31).

Diols (33) and (34). Widdrol-a-epoxide (4), (2.0 g) in distilled water (500 ml) was refluxed for 24 h. Extraction with ether gave a product (2.0 g), which was chromatographed on alumina (neutral, activity III, 60 g). Elution with light petroleum (b.p. 35—60°)-ether (1:1) gave a crystalline product (970 mg) which was recrystallised from isopropyl ether to give the diol (33) m.p. 145—146°, $[a]_D$ + 40° ($CHCl_3$, *c* 0.8) (Found: C 75.4; H 10.9. $C_{15}H_{26}O_2$ requires C 75.6; H 11.0). ν_{max}^{KBr} 870, 1415, 1655; 994, 1095, 1187, 1288, 3250 cm^{-1}, $\nu_{max}^{CCl_4}$ 3490, 3550, 3620 cm^{-1} (*c* 0.0050 M). Elution with ether gave further crystalline material (940 mg), which on recrystallisation from isopropyl ether gave the diol (34), m.p.

124 – 125°, $[\alpha]_D$ + 31° ($CHCl_3$, *c* 0.9), (Found: C 76.0; H 10.9. $C_{15}H_{26}O_2$ requires C 75.6; H 11.0). $\nu_{\max}^{\mathrm{KBr}}$ 824; 987, 1024, 1120, 1164, 1223, 3340 cm^{-1}, $\nu_{\max}^{\mathrm{CCl_4}}$ 3530, 3610 cm^{-1} (0.0050 M). The PMR spectra (in $CDCl_3$) of the diol (33) τ 9.13 + 8.87 /2 *s* (6 + 3) $CH_3-C(4)$ and $-C(5)$; 8.80 /*s* (3) $CH_3-C(8)$; 5.89 /2 *d*/ J_{AX} 2.3, J_{BX} 5.8 (1) $H_X-C(6)$; 4.64 /*t* or *m*/ not quite resolved (1) $HC{=}C(11)$, and of the diol (34) τ 9.17 + 9.00 /2 *s* (3 + 3) $CH_3-C(11)$ and $-C(5)$; 8.81 /*s* (3) $CH_3-C(8)$; 8.34 /*s* (3) $CH_3-C(4)$; 6.21 /2 *d*/ J_{AX} 5.3, J_{BX} 10.3 (1) $H_X-C(6)$; 4.28 /*q*/ J 1.5, not quite resolved (1) $H-C(3)$, were determined on a Varian A 60 instrument. Nomenclature, compare Ref.[42]

Hydroxyketones (35) and (36). Oxidation of the diol (33) (35 mg) as described for triol (5), gave the corresponding hydroxyketone (35), (28 mg), m.p. 100 – 101°, $[\alpha]_D$ + 212° ($CHCl_3$, *c* 0.3), (Found: C 76.2; H 10.2. $C_{15}H_{24}O_2$ requires C 76.2; H 10.2), $\lambda_{\max}^{\mathrm{EtOH}}$ 294 mμ (ε 38), $\nu_{\max}^{\mathrm{CCl_4}}$ 1655, 1686, 3450, 3590 cm^{-1}.

Oxidation of the diol (34) (90 mg), as described for the triol (5), gave the corresponding hydroxyketone (36) (74 mg), m.p. 136 – 138°, $[\alpha]_D$ + 79° ($CHCl_3$, *c* 1.0), (Found C 76.4; H 10.1. $C_{15}H_{24}O_2$ requires C 76.2; H 10.2). $\lambda_{\max}^{\mathrm{EtOH}}$ 294 mμ (ε 45) $\nu_{\max}^{\mathrm{CCl_4}}$ 1691, 3440, 3580 cm^{-1}.

Triols (37) and (38). Widdrol (2.22 g) and osmium tetroxide (2.54 g) in dry pyridine (25 ml) were left in a dark place for 20 days at 25°. Most of the pyridine was removed *in vacuo* and a mixture of ethanol (30 ml) and benzene (30 ml) was added to the residue followed by mannitol (12 g) and potassium hydroxide (12 g) dissolved in water (30 ml) and ethanol (60 ml). The reaction mixture was boiled under reflux for 7 h, concentrated to 30 ml, and extracted with ether. The highly viscous product (2.48 g), gave, on treatment with a small amount of ether, some crystalline material. This was recrystallised from isopropyl ether to give the triol (37), (0.26 g), m.p. 178 – 180°, $[\alpha]_D$ + 4° ($CHCl_3$, *c* 1.0), (Found: C 70.3; H 10.9. $C_{15}H_{28}O_3$ requires C 70.3; H 11.0), $\nu_{\max}^{\mathrm{KBr}}$ 973, 1032, 1106, 1177, 1255, 3370 cm^{-1}.

A part (1.65 g) of the combined, concentrated mother liquors was chromatographed on silica gel (300 g). Elution with ether gave the liquid triol (38), (1.43 g), n_D^{25} 1.5179, $[\alpha]_D$ – 66° ($CHCl_3$, *c* 1.4), $\nu_{\max}^{\mathrm{CCl_4}}$ 1048, 1085, 1150, 3440, 3595 cm^{-1}. Further elution with ether gave a small amount (0.13 g) of the crystalline triol (37).

The liquid triol (38), (0.40 g) and *p*-nitrobenzoyl chloride (1.5 g) in dry pyridine (20 ml) were left for 45 h at 20 . The product (0.78 g) was chromatographed on silica gel (50 g). Elution with benzene-ether (4:1) followed by recrystallisation from benzene and ethanol gave the di-*p*-nitrobenzoate (0.38 g), m.p. 176 – 177°, $[\alpha]_D$ + 48° ($CHCl_3$, *c* 1.1). (Found: C 62.6; H 5.9. $C_{29}H_{34}O_9N_2$ requires C 62.8; H 6.2). Elution with ether followed by recrystallisation from ethanol and isopropyl ether-acetone gave the mono-*p*-nitrobenzoate (0.22 g), m.p. 144 – 145°, $[\alpha]_D$ + 26° ($CHCl_3$, *c* 0.9). (Found: C 65.2; H 7.8. $C_{22}H_{31}O_6N$ requires C 65.2; H 7.7 %).

Treatment of triols (37) and (38) with lead tetraacetate. Lead tetraacetate (880 mg) was added to the liquid triol (38) (463 mg) in glacial acetic acid (20 ml). After 15 h at 20° glycerine (1 ml) and water (1 ml) were added and the mixture was left for an additional hour. It was diluted with water and extracted with ether to give the hydroxyketoaldehyde (6) (350 mg), exhibiting an infrared spectrum identical with that of the hydroxyketoaldehyde obtained on oxidation of the triol (5).

The crystalline triol (37), on treatment with lead tetraacetate in glacial acid at 20° for 40 h, was recovered unchanged in nearly quantitative yield.

Chromium oxidation of triols (37) and (38). The crystalline triol (37), (100 mg), on oxidation as described for the triol (5), gave a crystalline residue (98 mg), which was recrystallised from isopropyl ether and light petroleum (b.p. 35 – 60°) to give the dihydroxyketone (39), m.p. 82 – 83° and 119 – 120°, $[\alpha]_D$ – 47° ($CHCl_3$, *c* 1.0). (Found: C 70.6; H 10.1. $C_{15}H_{26}O_3$ requires C 70.8; H 10.3). $\lambda_{\max}^{\mathrm{EtOH}}$ 302 mμ (ε 33), $\nu_{\max}^{\mathrm{CCl_4}}$ 1048, 1139, 1186, 1280, 1700, 3635 cm^{-1}. Rotatory dispersion curve (MeOH): $[\Phi]_{600}$ – 550°, $[\Phi]_{333}$ – 2400°, $[\Phi]_{291}$ + 1900°, $[\Phi]_{271}$ + 1300°.

The liquid diol (38) gave, under the same conditions, the hydroxyketoaldehyde (6), exhibiting an infrared spectrum identical with that of the hydroxyketoaldehyde obtained on oxidation of the triol (5).

Bromoether (40). Widdrol (1.54 g) in t-butyl alcohol (20 ml) and water (2 ml) was stirred with N-bromosuccinimide (2.8 g) for 18 h at 20°. The reaction mixture was diluted with water (400 ml) and extracted with light petroleum (b.p. 35—60°). Filtration of the partly crystalline product (2.20 g), gave crystalline material (1.49 g). This was recrystallised from methanol to give the bromoether (40), m.p. 128—129°, $[\alpha]_D$ $-26°$ ($CHCl_3$, *c* 0.8) $\nu_{\max}^{KBr}$ 1072 cm^{-1}. (Found: C 59.8; H 8.5; Br 26.7. $C_{15}H_{25}OBr$ requires C 59.8; H 8.4, Br 26.5). The same product was also obtained, but in lower yield, on treatment of widdrol in acetic acid with bromine.

Ether (41). Sodium (*ca.* 2 g) was added in pieces to a boiling solution of the bromoether (40), (295 mg) in absolute ethanol (20 ml) over a period of 30 min. The reaction mixture was diluted with water (400 ml) and extracted with light petroleum (b.p. 35—60°). The extract after drying was concentrated and adsorbed on alumina, (neutral, activity I, 13 g). Light petroleum (b.p. 35—60°) eluted the ether (170 mg), which after a quick distillation at low pressure (0.1 mm) had n_D^{25} 1.486, $[\alpha]_D$ $+ 12°$ ($CHCl_3$, *c* 0.8), $\nu_{\max}^{CCl_4}$ 1045, 1058, 1090 cm^{-1}. (Found: C 80.6; H 11.7. $C_{15}H_{26}O$ requires C 81.0; H 11.8).

Dehydrogenation of widdrol. Widdrol (1 g) was heated at 250—280° for 5 h with palladium on charcoal (10 %, 1 g) in an atmosphere of carbon dioxide. After filtration through alumina the product was distilled to give an oil (0.67 g). This had an ultraviolet spectrum corresponding to the presence of about 30 % of a naphthalene hydrocarbon. Analysis by vapour phase chromatography indicated the presence of 9 compounds. The oil (90 mg) and an ethanolic solution of picric acid gave a crystalline product, which on repeated recrystallisation from ethanol and propanol gave a small amount (12 mg) of the picrate of 1,7-dimethyl-4-isopropylnaphthalene, m.p. and mixed m.p. 90—92°. Oxidation of the oil (230 mg) with aqueous nitric acid (30 %, 24 ml) in a sealed tube overnight at 170° gave a small amount of crystalline material (10 mg). This was esterified with an ethereal solution of diazomethane to give the dimethyl ester of terephthalic acid, m.p. and mixed m.p. 138—140°.

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