

either (0, 1/4, 1/4) or (1/4, 0, 0). The Patterson syntheses show that there are layers of molecules  $c/2$  apart approximately parallel to the  $ab$ -plane. Correspondingly, the 002 reflexion is extremely strong. It is interesting that the corresponding hexose sugar, methyl  $\alpha$ -mannofuranoside, has the same space group and very similar unit cell dimensions, namely 4.64 Å, 11.73 Å and 15.87 Å. These two sugars have the same furanose configuration, the mannoside being derived by substituting a hydrogen at C<sub>5</sub> in the lyxoside with  $-\text{CH}_2\text{OH}$ . This increases the length of the  $a$  axis from 10.34 Å to 11.73 Å, whereas the other axes remain nearly unchanged. This indicates, as is seen from models, that the methyl lyxoside molecule is most extended in the direction of  $b$ .

Further attempts to solve the structure are being carried out.

1. McDonald, T. R. R. and Beevers, C. A. *Acta Cryst.* **5** (1952) 654.
2. Hordvik, A. *Acta Chem. Scand.* **15** (1961) 16.
3. Augestad, I. and Berner, E. *Acta Chem. Scand.* **8** (1954) 251.
4. Augestad, I. and Berner, E. *Acta Chem. Scand.* **10** (1956) 911.
5. Cox, E. G., Goodwin, T. H. and Wagstaff, A. I. *J. Chem. Soc.* **1935** 1495.
6. Cox, E. G. and Goodwin, T. H. *J. Chem. Soc.* **1932** 1844.

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## The Structures of Widdrol\* and the Alcohol, C<sub>15</sub>H<sub>26</sub>O<sub>2</sub>, Isolated from *Widdringtonia juniperoides* (L.) Endl.

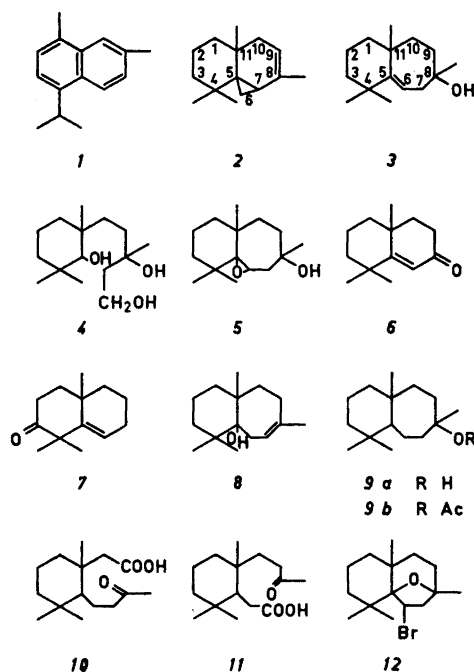
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Erdtman and Thomas<sup>1</sup> isolated the sesquiterpene alcohol widdrol, C<sub>15</sub>H<sub>26</sub>O, (m.p. 98°) and a further alcohol, C<sub>15</sub>H<sub>26</sub>O<sub>2</sub>, (m.p. 154°;  $[\alpha]_D -9^\circ$ ) from the heartwood of

\* Presented by H. Erdtman at the Chemical Society symposium on terpene chemistry in London (23.2.1961). *Proc. Chem. Soc.* **1961** 129.

*Widdringtonia* species. These authors suggested that widdrol was a dicyclic, tertiary alcohol containing one double bond and they obtained 1,7-dimethyl-4-isopropyl-naphthalene (1) on selenium dehydrogenation. Recently Nagahama<sup>2</sup> has shown that widdrol is formed on hydration of thujosene<sup>3</sup> (2) with oxalic acid. The following experimental evidence shows that widdrol has structure (3).



Widdrol [I.R.:  $\nu_{\text{max}}^{\text{CHBr}_3}$  839, 1635  $\text{cm}^{-1}$ ; PMR:  $\tau$  4.50 ( $\text{CR}_2 = \text{CRH}$ )] on ozonolysis, followed by reduction with lithium aluminium hydride, gave a triol (4) (m.p. 97–98°) together with minor amounts of an epoxyalcohol (5) (m.p. 153–154°).

The triol (4) on oxidation (chromium trioxide-sulphuric acid-acetone) furnished a hydroxyketoaldehyde ( $\nu_{\text{max}}^{\text{CCl}_4}$  2720, 1717, 1690  $\text{cm}^{-1}$ ), which on treatment with alkali yielded an  $\alpha,\beta$ -unsaturated ketone (6) [ $\lambda_{\text{max}}^{\text{EtOH}}$  240  $\text{m}\mu$  ( $\epsilon$  13 000); 2,4-dinitrophenylhydrazone m.p. 204–205°] and acetaldehyde. The DL-octalone (6) was synthesised from the ketone (7)<sup>4</sup> by Huang-

Minlon reduction followed by oxidation with sodium dichromate in acetic acid. It furnished a 2,4-dinitrophenylhydrazone (m.p. 204–205°), which gave ultra-violet, infra-red and mass spectra identical with those of the corresponding derivative of widdrol.

The epoxyalcohol (5), also obtained from widdrol on oxidation with perphthalic acid, was recovered unchanged after treatment with chromium trioxide-sulphuric acid in acetone. Its formation on ozonisation was taken as an indication of the presence of a sterically hindered double bond<sup>5</sup> in widdrol.

The above results favour structure (3) for widdrol. The alternative structure (8) is excluded by the following reactions. Hydrogenation of widdrol with Adams catalyst in acetic acid gave dihydrowiddrol (9a) and a small amount of a saturated hydrocarbon, C<sub>15</sub>H<sub>28</sub>. On pyrolysis dihydrowiddrol acetate (9b) gave a mixture of unsaturated hydrocarbons, containing, according to its infra-red absorption, minor amounts of the exocyclic isomer. This hydrocarbon mixture on ozonolysis and subsequent steam distillation gave a low yield of formaldehyde and a non-volatile product which, on oxidation with silver oxide, furnished a keto acid (10 or 11), (2,4-dinitrophenylhydrazone m.p. 232–236°) as the main product. This keto acid gave iodoform on treatment with sodium hypoiodite.

Structure (3) for widdrol is also in good agreement with the mass spectrometric and PMR results. The strongest peak in the mass spectrum of widdrol is found at *m/e* 151 and corresponds to an ion formed by rupture of the C(7)–C(8) and C(10)–C(11) bonds<sup>6</sup>. The PMR spectrum of dihydrowiddrol shows the presence of the angular methyl group ( $\tau$  9.01), the geminal dimethyl group ( $\tau$  8.90 and 8.96) and the methyl group at C(8) ( $\tau$  8.83); the latter is found at somewhat lower field ( $\tau$  8.53) in the spectrum of dihydrowiddrol acetate.

The configuration at C(11) in widdrol remains unclear. Comparison of the positive R.D. curve of ketone (6) with the negative curve for 3 $\beta$ -acetoxy-4 $\delta^5$ -lanosten-7-one<sup>7</sup> indicates that the angular methyl

group is  $\alpha$ -oriented. This is unexpected since on similar grounds it has been suggested that the angular methyl group in thujopsene is  $\beta$ -oriented. This problem is being further investigated and additional evidence of the  $\alpha$ -orientation will be communicated in the full paper.

The low yield of the exocyclic isomer obtained on pyrolysis of dihydrowiddrol acetate and the formation of a bromoether, probably (12), on bromination of widdrol indicates that the hydroxyl group is quasi-axial.

The alcohol, C<sub>15</sub>H<sub>26</sub>O<sub>2</sub> (m.p. 154°), was found to be identical with widdrol epoxide (5). This compound has been encountered in two conifers of the natural order Cupressales, while widdrol has been found in many.

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1. Erdtman, H. and Thomas, B. R. *Acta Chem. Scand.* **12** (1958) 267.
2. Nagahama, S. *Bull. Chem. Soc. Japan.* **33** (1960) 1467.
3. Norin, T. *Acta Chem. Scand.* **15** (1961). *In press.*
4. Mukherjee, S. L. and Dutta, P. C. *J. Chem. Soc.* **1960** 67.
5. Bailey, P. S. *Chem. Revs.* **58** (1958) 925.
6. Enzell, C. *Acta Chem. Scand.* **15** (1961). *In press.*
7. Djerassi, C., Halpern, O., Halpern, V. and Riniker, B. *J. Am. Chem. Soc.* **80** (1958) 4001.

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