

SELIN-11-EN-4 α -OL FROM THE ESSENTIAL OIL
OF PODOCARPUS DACRYDIOIDES

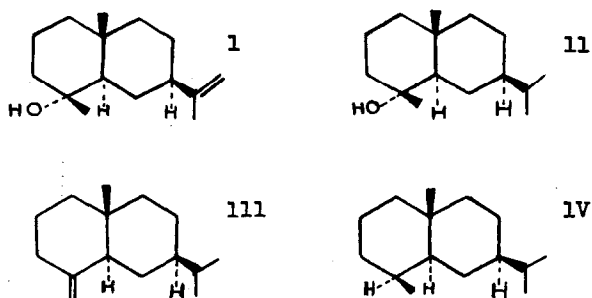
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In this Communication we report the isolation and structural elucidation of a crystalline sesquiterpene alcohol from the essential oil, steam distilled from the leaves of Podocarpus dacrydioides. The alcohol was contained in the fraction of the oil which had b.p. 85-90°/3 mm. and was purified by chromatography on alumina, then on silver nitrate impregnated alumina and finally by preparative scale thin layer chromatography on silver nitrate impregnated silica gel.

The alcohol (1), C₁₅H₂₆O, had m.p. 94-96°, $[\alpha]_D^{20}$ -18°. The infrared spectrum showed bands characteristic of hydroxyl (3300 cm.⁻¹) and acyclic methylene (3080,

Satisfactory analyses were obtained for all compounds reported.



1630, 890 cm.^{-1}) groups, while the nuclear magnetic resonance (n.m.r.) spectrum contained three 3-proton methyl singlets (0.90, 1.07, 1.75 δ) and a 2-proton methylene multiplet (4.65 δ).

Hydrogenation of (I) with Adams catalyst in ethyl acetate resulted in the consumption of 1 mole of hydrogen and gave a saturated (negative tetranitromethane test, and absence of u.v. end absorption) derivative (II), $\text{C}_{15}\text{H}_{28}\text{O}$, m.p. 75°, $[\alpha]_{\text{D}}^{20} +30^\circ$, $\nu_{\text{max.}} 3300 \text{ cm.}^{-1}$ (OH). The n.m.r. spectrum of (II) showed two 3-proton methyl singlets (0.82, 1.03 δ) and two 3-proton methyl doublets (0.89, 0.90 δ ; J 7.0 c/s). The n.m.r. data is diagnostic of an isopropenyl group in (I), hydrogenated to an isopropyl group in (II).

Dehydration of (II) with phosphorus oxychloride in pyridine gave a mixture of hydrocarbons of which the major component was (III) (40% actually isolated, 70% by gas

chromatography), $C_{15}H_{26}$, $[\alpha]_D^{20} +70^\circ$, ν_{max} . 3080, 1640, 884 cm^{-1} ($=CH_2$); proton resonance, 3-proton methyl singlet (0.66 δ), 6-proton methyl doublet (0.88 δ ; J 6.0 c/sec.), 2-proton methylene doublet (4.33, 4.58 δ). Hydrogenation of (111) gave (+)-selinane (1V), $C_{15}H_{28}$, $[\alpha]_D^{20} +9^\circ$, of identical infrared spectrum and refractive index with an authentic specimen. The n.m.r. spectrum showed a 3-proton methyl singlet (0.85 δ), a 6-proton methyl doublet (0.86 δ , J 6.0 c/sec.), and a 3-proton methyl doublet (0.85 δ , J 6.5 c/sec.).

The only structural feature remaining to be defined in (1) is the stereochemistry at C-4. The equatorial conformation (4 α -) of the hydroxyl group was deduced from the dehydration of (11) to (111), and from the n.m.r. spectrum of (11), which shows only one methyl signal at low field. An hydroxyl group at C-4 would cause the 4-methyl signal to appear at low field and if it was axial (4 β -) the 10 β -methyl signal would also be at low field due to 1,3 diaxial interaction with the hydroxyl group. Furthermore, irradiation (Hg lamp) or a solution of (11), lead tetraacetate and iodine in benzene did not give a 1,4 ether. If the 4-hydroxyl group was axial an oxido compound should form relatively readily.¹ Alcohol (1) is therefore selin-11-en-4 α -ol.

Intermedeol has been reported to be the enantiomer of structure (1).² Comparison of the physical constants and infrared and n.m.r. spectra of (1) and (11) with those of intermedeol and dihydrointermedeol show that they are not enantiomeric. The structure assigned to intermedeol is now under review.³ The dihydro-alcohol (11) has been shown to be (+)-dihydrojuniper camphor by direct comparison with (±)-dihydrojuniper camphor (mixed m.p., g.l.c., t.l.c., infrared spectrum), which was assigned structure (11) by Sorm *et al.*⁴, but which was considered to be the C-4 epimer of this structure by Zalkow *et al.*² This epimer has now been isolated and named dihydroneointermedeol.⁵ It is different from dihydrojuniper camphor.

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