

The Constituents of Conifer Needles. VII.* The Configuration of Dehydropinifolic Acid, a Diterpene Acid from the Needles of *Pinus silvestris* L.

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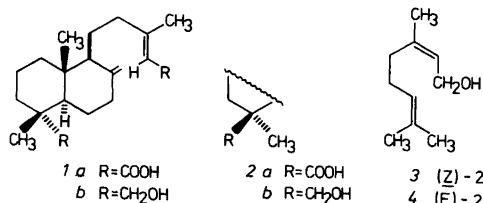
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Dehydropinifolic acid (*1a*) is a constituent of the needles of Scots pine, *Pinus silvestris* L. The isolation and structure elucidation of this acid (*1a*) have been reported.¹ The *E* configuration of the C(13)=C(14) double bond was tentatively assigned from consideration of allylic NMR coupling data. Lanthanide induced shift (LIS) studies offer an opportunity to settle this assignment.

LIS data** of the C(15) and C(16) protons of the diol *1b* obtained from dehydropinifolic acid (*1a*) as well as those of agathadiol (*2b*) and some other model compounds are given in Table 1. LIS data of nerol (*3*) and geraniol (*4*) have previously been reported² and are also included. The configuration of the C(13)=C(14) double bond in agathadiol (*2b*) and agathic acid (*2a*) has been settled to be *E* by chemical studies.³

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** Paramagnetic shift reagent, Eu(dpm)₃, tris(dipivalo-methanato)europium.



The LIS data are presented as κ values which are linearly correlated to Δ_{Eu} values.⁴ The κ value is more convenient to handle since it is a concentration independent parameter. It is defined as the least-squares derived plot of the $\delta_{Eu(dpm)_3}^{n=x}$ values of a proton for arbitrary molar ratios ($n=x$) against the corresponding $\delta_{Eu(dpm)_3}^{n=x}$ values for the reference signal. The signal due to the methylene group of the hydroxymethyl group ($-\text{CH}_2\text{OH}$) has been used as reference.

As can be seen from Table 1 compounds possessing the methyl group ($-\text{CH}_3$) and the hydroxymethyl group ($-\text{CH}_2\text{OH}$) in a cisoid arrangement, exhibit significantly higher κ values for the methyl protons (0.25–0.29) than those possessing transoid arrangements (0.15). The corresponding κ value of the diol derived from dehydropinifolic acid is 0.28, which is very similar to that of agathadiol ($\kappa=0.27$). This clearly demonstrates the *E* configuration of the C(13)=C(14) double bond of dehydropinifolic acid (*1a*).

Experimental. NMR spectra were recorded on a Perkin Elmer R12 instrument operating at 60 MHz (solvent, CDCl_3). Chemical shifts are expressed in δ units, ppm relative to tetramethylsilane (TMS). LIS data were obtained by the method described by Norin *et al.*⁴

The diol *1b* was obtained from dehydropinifolic acid as previously described¹ and had m.p. 107.5–109 °C, $[\alpha]_D +41.5^\circ$ (CHCl_3 , c 0.9).

Table 1. NMR-LIS data of dehydropinifolic acid and some related compounds.

Compound	κ -Value ^a	$ \Delta_{Eu} $ of reference signals, ppm
Dehydropinifolic acid diol (<i>1b</i>)	C(16)-H ₃ 0.28	C(15)-H ₂ OH 28.0
Agathadiol (<i>2</i>)	C(16)-H ₃ 0.27	C(15)-H ₂ OH 27.5
Nerol (<i>3</i>)	C(10)-H ₃ 0.15	C(1)-H ₂ OH 28.4 (CCl_4) ²
Geraniol (<i>4</i>)	C(10)-H ₃ 0.25	C(1)-H ₂ OH 28.2 (CCl_4) ²
3-Methyl-2-butene-1-ol	C(4)-H ₃ 0.26	C(1)-H ₂ OH 23.8
	C(5)-H ₃ 0.15	
<i>o</i> -Methylbenzyl alcohol ⁶	C(8)-H ₃ 0.30	C(1)-H ₂ OH 28.4

^a $\kappa \times \Delta_{Eu}/\Delta_{Eu}$. Reference proton = slope from the plot of the chemical shift of the proton under inspection *vs.* the shift of the reference proton signal.

Agathadiol (2b) was obtained from agathic acid (2a) in a similar way⁵ and had m.p. 107–108 °C, $[\alpha]_D + 31^\circ$ (CHCl₃, c 2.0).

3-Methyl-2-butene-1-ol was prepared by lithium aluminium hydride reduction of β -methylcrotonic acid in diethyl ether. Distillation in vacuum gave the pure alcohol as an oil (purity checked by GLC).

1. Norin, T., Sundin, S. and Theander, O. *Acta Chem. Scand.* 25 (1971) 607.
2. de Haan, J. W. and van de Ven, L. J. M. *Tetrahedron Lett.* (1971) 2703.
3. Bory, S., Fétizon, M. and Lazlo, P. *Bull. Soc. Chim. Fr.* (1963) 2310.
4. Norin, T., Strömberg, S. and Weber, M. *Acta Chem. Scand.* 27 (1973) 1579.
5. Enzell, C. *Acta Chem. Scand.* 15 (1961) 1303.
6. Mill, P. and Short, W. F. *J. Chem. Soc.* (1935) 1123.

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