

at this temperature for 4 h. The reaction mixture was then allowed to reach room temperature and the precipitated salt removed before the filtrate was evaporated to dryness. The residue was triturated with ether and recrystallised from a small volume of water; yield 0.9 g (56 %), m.p. > 270°C (decomp.). Anal. $C_{20}H_{32}ClNOS \cdot HBr$: C, H, 1H NMR (60 MHz, TFA): δ 3.9 (CH_2-S), 5.2 (CH_2-N), 7.6 and 8.2 (Pyr., J 6.5 Hz).

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Isoabienol, the Principal Diterpene Alcohol in *Pinus sylvestris* Needles

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The abienols, labdane diterpenoids with conjugated double bonds in the side chain, are widely distributed in the firs. To our knowledge there is only one isolation of isoabienol reported, namely from the oleoresin of *Abies sibirica* Ldb. (Siberian fir).¹ However, it has later been shown, that this natural product was actually impure *trans*-abienol.²

The present paper reports the finding of isoabienol as the principal diterpene alcohol in needles of *Pinus sylvestris* L. (Scots pine). In an earlier paper the major diterpene alcohol from technical foliage of Scots pine has erroneously been characterized as abienol.³

The isolated compound had m.p. 68–68.5°C, $[\alpha]_D^{20}$ –6.4 ($CHCl_3$), λ_{max} (EtOH) 227 nm ($\log \epsilon$ 4.26) ν_{max} (KBr) 3320, 2920, 1600, 1463, 1390, 890 cm^{-1} .

Hydrogenation yielded a product identical with tetrahydroabienol (a quasiracemic compound⁴) obtained from the hydrogenation of *cis*-abienol from the oleoresin of Norway spruce, (^{13}C NMR, MS, GLC), suggesting a normal labdane skeleton.

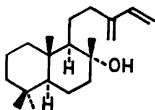
The mass spectrum of compound 1 [IP 70 eV; m/e (rel. int.): 290 (2, M), 275 (3, M– CH_3), 272 (5, M– H_2O), 257 (13, M– H_2O – CH_3), 191 (100, M– H_2O –side chain) indicated the presence of a bis-unsaturated side chain and the λ_{max} value led us to suggest conjugation.

The 1H NMR spectrum showed signals from five vinylic protons. Three of the protons formed an AMX-system at 270 MHz ($CDCl_3$): δ 6.38 (H-14, dd, J 10.6 and 17.6 Hz), 5.34 (H-15, dd, J 17.6 and 0.7 Hz), 5.09 (H-15, dd, J 10.6 and 0.7 Hz). The two vinylic protons at C-16 gave a rather broad singlet at δ 5.05. Three separate methyl singlets were shown, one from the C-18 and C-19 methyls at δ 0.80, one from the C-17 methyl at δ 1.16 and one from the C-20 methyl at δ 0.88. The allylic protons at C-12 gave a symmetrical multiplet centered at δ 2.32.

The low field part of the noise decoupled ^{13}C NMR spectrum ($CDCl_3$) showed four signals due to the olefinic carbons in the side chain. Two of the signals appeared as triplets in the off-resonance decoupled spectrum confirming the presence of two terminal vinylic methylene groups. In analogy to the spectrum of myrcene,⁵ the triplet at δ 113.5 was assigned to C-16 and the other one at δ 115.6 to C-15. In the off-resonance decoupled spectrum the C-14 signal

at δ 138.8 and C-13 at δ 147.5 appeared as a doublet and singlet, respectively.

The above analytical and spectroscopic data for the compound are consistent with the structure 1.



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The melting point and UV and MS data were in close agreement with those reported for isoabienol synthesized from sclareol.^{3,5}

Experimental. The gas chromatographic analysis was performed with a Varian 2400 gas chromatograph equipped with a packed glass column (1 % XE-60, 110–180 °C, 4 °C/min). Mass spectra were recorded with a GLC-MS instrument model LKB-9000 and the same column and conditions as above. IR spectra were obtained with a Perkin-Elmer model 257 spectrometer. ¹H NMR spectra were recorded on a Bruker WH 270 spectrometer operating at 270 MHz and ¹³C NMR spectra on a JEOL FX-60 spectrometer at 15.03 MHz. TLC separations were carried out on precoated plates with silica as adsorbent. Petroleum ether:Et₂O:AcOH (50:50:1, v/v) was used as solvent.

Extraction and isolation. Fresh pine needles were defiberized in liquid N₂ with an Ultra-Turrax atomizer. The ground and freeze-dried material (50 g) was extracted in a Soxhlet apparatus with light petroleum (40–60 °C) for 5 h. The extract was treated with aqueous NaHCO₃ (5 %) to remove free fatty and resin acids. The solvent was evaporated from the neutral fraction at reduced pressure and the residue was dissolved in a minimum amount of Et₂O. The neutrals were quantitatively applicated on TLC silica layers and a main fraction separated at *R_F* 0.53–0.56. The diterpene alcohol was eluted from the silica and recrystallized 3 times from pentane. The yield was 370 mg.

GLC analysis of total neutrals gave an isoabienol content of 0.8 % of the needle dry weight and about 90 % of the diterpene alcohols.

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