

Cell content: 6 NH_4CuSO_3 (observed density 2.73, calculated density 2.72).

Space group $R\bar{3}m$ (No. 166). Arrangement of atoms:

(000; $\frac{1}{3}\frac{1}{3}\frac{1}{3}$; $\frac{2}{3}\frac{2}{3}\frac{2}{3}$) + 6 Cu, 6 S and 6 N in 6(c); $\pm(0\ 0\ z)$ 18 O in 18(h): $\pm(x\ \bar{x}\ z)$; $\pm(x\ 2x\ z)$; $\pm(2\bar{x}\ \bar{x}\ z)$

Corresponding value of discrepancy factor $R = 0.090$

Interatomic distances:

Cu—S = 2.143 ± 0.007 Å
 Cu—3 O = 2.119 ± 0.012 Å
 S—3 O = 1.506 ± 0.012 Å
 O—O = 2.397 ± 0.015 Å (within the SO_3 pyramid)
 = 3.031 ± 0.015 Å (within the Cu(I) tetrahedron)

The structure may be described in terms of SO_3 trigonal pyramids and CuO_3S tetrahedra. The tetrahedral coordination around copper is provided by three oxygen atoms and one sulphur atom of four SO_3 groups. The CuO_3S tetrahedra and SO_3 pyramids form double layers extending parallel to the ab plane. These are held together by the ammonium ions. Schematic drawings showing the linking of the CuO_3S tetrahedra and the SO_3 pyramids are given in Fig. 1.

Full details of this investigation and a discussion of the structure will be given elsewhere.

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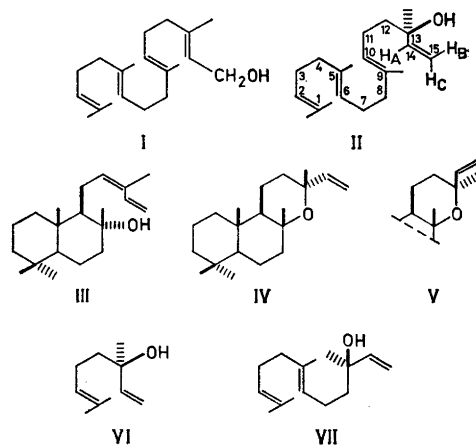
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The Oleoresin of Norwegian Spruce, *Picea abies* (L.) Karst.— Isolation of (-)-Geranyllinalool

BJARNE KIMLAND and
TORBJÖRN NORIN

Wood Chemistry Department, Swedish Forest Products Research Laboratory, Stockholm Ö, Sweden

Although diterpenoids are widely distributed in Nature there are only a few reports of the occurrence of geranylgeraniol (I) and closely related compounds such as geranyllinalool (II) which are commonly accepted as close biogenetic precursors of diterpenoids. Small amounts of geranyllinalool have been isolated from jasmin oil of Egyptian origin¹ and geranylgeraniol is a constituent of linseed oil.² Very recently the latter alcohol was found to be one of the major wood extractives of *Cedrela toona* Roxb.³



In this communication we wish to report the isolation of (-)-geranyllinalool (II) from the oleoresin of Norwegian spruce, *Picea abies* (L.) Karst., in which it occurs together with a number of other diterpenoids such as abienol (III), manoyl oxide (IV), 13-epimanoyl oxide (V), common resin acids of pimaric and abietic acid types and related compounds.⁴

Consecutive chromatography of the neutral light petroleum soluble part of the

Table 1. Characteristic signals in the NMR-spectrum of (-)-geranyllinalool (II).*

Chemical shifts ppm	Number of protons	Signal pattern	Assignment**
5.88	1	Quartet; J 18.5 and 10.5 cps	C(14)-H _A
5.19	1	Quartet; J 18.5 and 2.0 cps	C(15)-H _B
5.00	1	Quartet; J 10.5 and 2.0 cps	C(15)-H _C
5.12	3	Broad signal	C(2)-H; C(6)-H; C(10)-H
1.66	3	Slightly broadened signal	C(1)-CH ₃
1.60	9	Overlapping, slightly broadened signals	C(1)-CH ₃ ; C(5)-CH ₃ ; C(9)-CH ₃
1.22	3	Singlet	C(13)-CH ₃

* The NMR-spectrum was recorded on a Varian A-60 instrument (60 Mc/s) using a CCl₄-solution. Chemical shifts are given in δ ppm from TMS (internal standard).

** For numbering of protons and carbon atoms see structure II.

fresh oleoresin on alumina and silver nitrate impregnated silica yielded (-)-geranyllinalool (II) (C₂₀H₃₄O; MW 290, determined by mass spectrometry; $[\alpha]_D - 10.1^\circ$, c 1.2 in chloroform), which was shown to be pure by thin layer (AgNO₃-SiO₂) and gas liquid chromatography. The alcohol constitutes about 2 % of the crude oleoresin.

The alcohol was easily identified by its characteristic NMR-spectrum (Table 1) which showed close similarities to those of linalool (VI) and nerolidol (VII). Signals due to methyl groups on *trans* substituted double bonds in acyclic isoprenoids are shown to appear at 1.60 ppm whereas those of *cis* substituted double bonds appear at 1.66 ppm.^{5,6} The alcohol from *P. abies* exhibits a signal pattern which clearly demonstrates the all-*trans* nature of the compound as indicated in structure (II).

The identity of the alcohol was further confirmed by a direct comparison of its IR-spectrum with a previously published spectrum of a synthetic material.¹

The absolute configurations of (-)(*R*)-linalool (VI) and (-)(*R*)-nerolidol (VII) are established.⁷⁻⁹ On catalytic hydrogenations both compounds form the saturated derivatives which possess low rotations of the same signs as those of the parent alcohols ($[\Delta[M]_D - 32^\circ$ and -33° , respectively). (-)-Geranyllinalool from *P. abies*

on catalytic hydrogenation similarly forms a saturated product with low rotation ($[\Delta[M]_D - 29^\circ$). The characteristic differences in molecular rotations for the three pairs of compounds strongly suggest a 13(*R*)-configuration in (-)-geranyllinalool as shown in structure (II). The corresponding dextrorotatory alcohol ($[\alpha]_D + 14^\circ$) from jasmine oil should therefore be of the opposite (*S*)-configuration.

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