

active oxygen had disappeared. Isolation of products as well as quantitative determinations were carried out separately for the two phases.

2-Chloro-3-methyl-1,4-naphthoquinone. From the chloroform phase was isolated methylphenylglyoxal-*o*-carboxylic acid, m.p. 65°C (benzene-petrol ether). Quinoxaline derivative with *o*-phenylenediamine, m.p. 182.5° alone and mixed with an authentic sample. Equiv. wt. 279, calc. 282. From the aqueous phase was isolated phthalonic acid, m.p. 146°C (ether), undepressed in mixture with an authentic sample. Equiv. wt. 96, calc. 97. Further was identified acetic acid (S-benzylisothiuronium acetate, m.p. and mixed m.p. 139°C) and chloride ions.

Quantitative determinations. Methylphenylglyoxal-*o*-carboxylic acid occurred almost quantitatively in the chloroform phase, accompanied by 0.5 % or less phthalonic acid. The chloroform was evaporated and the residue dissolved in water. Aliquots were titrated with 0.05 N NaOH (phenolphthalein). Found, as a mean of four ozonolyses, 64.5 % of theoretical. The aqueous phase was distilled with additions of several portions of water until no more volatile acid passed over. Aliquots of the residue, containing phthalonic acid only, were titrated with 0.05 N NaOH (phenolphthalein). Found, as a mean of three ozonolyses, 32.7 % of theoretical.

Total acid in the distillate (acetic and hydrochloric) was titrated with 0.05 N NaOH. Hydrochloric acid was determined separately as AgCl. Found acetic acid, as a mean of three ozonolyses, 34.5 % of theoretical.

The ratio of phthalonic to acetic acid is thus 0.95, and close to the theoretical ratio of 1.00. Recovered carbon is 98 %.

2-Hydroxy-3-methyl-1,4-naphthoquinone. From the chloroform phase was isolated and determined methylphenylglyoxal-*o*-carboxylic acid as above. Found, as a mean of three ozonolyses, 67.1 % of theoretical. The aqueous phase was also treated and analysed as above. Found phthalonic acid, as a mean of three ozonolyses, 32 % of theoretical. Found acetic acid, as a mean of three ozonolyses, 34.2 % of theoretical.

The ratio of phthalonic to acetic acid is 0.93. Recovered carbon is 98 %.

2-Amino-3-chloro-1,4-naphthoquinone. The chloroform phase contained only very small amounts of organic matter. The aqueous phase was concentrated to a small volume and a white substance separated. Recrystallised at low temperature from strong hydrochloric acid, m.p. 134–36°C (decomp.) undepressed in mixture with an authentic sample of phthalonic acid semiamide. Infra-red spectra of the

product and authentic compound coincided completely. The semiamide could be titrated as a monobasic acid in the residue of the aqueous phase after removing the volatile acids. Found, as a mean of three ozonolyses, 95.0 % of theoretical.

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Note on the Crystal Structure of NH_4CuSO_3

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The crystal structure of ammonium copper(I) sulphite has been determined from three-dimensional X-ray data obtained with $\text{CuK}\alpha$ radiation for a single-crystal selected from a sample prepared according to Ramberg.¹ The structure was derived from Patterson and Fourier syntheses. The parameters of the nonhydrogen atoms were refined using least squares techniques with isotropic temperature factors.

The following data were obtained for the trigonal structure:

Unit cell dimensions (from a Guinier powder photograph taken with $\text{CuK}\alpha_1$ radiation): $a = 5.4287 \pm 0.0004 \text{ \AA}$, $c = 23.166 \pm 0.004 \text{ \AA}$.

Atom	$x \pm \sigma(x)$	$y \pm \sigma(y)$	$z \pm \sigma(z)$	$b \pm \sigma(B) \text{ \AA}^2$
Cu	0	0	0.1999 ± 0.0002	1.99 ± 0.07
S	0	0	0.1074 ± 0.0003	1.36 ± 0.09
O	0.1472 ± 0.0012	0.2944 ± 0.0012	0.9188 ± 0.0005	1.86 ± 0.19
N	0	0	0.3635 ± 0.0011	2.16 ± 0.44

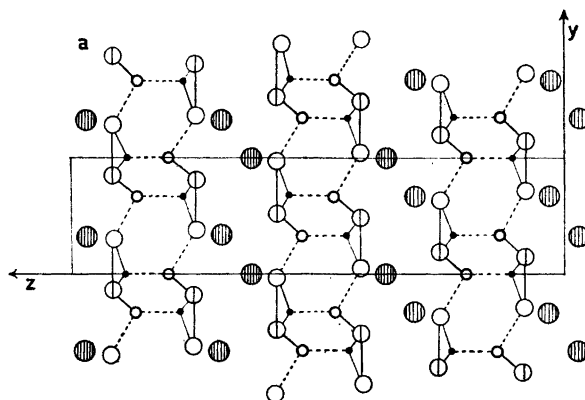
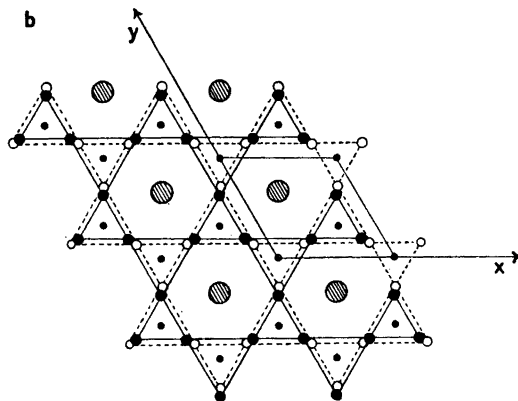


Fig. 1. Schematic drawings showing the structure of NH_4CuSO_3 . a) The structure viewed along $[100]$ showing the double layers formed by CuO_3S tetrahedra and SO_3 groups linked together by sharing corners and also showing the stacking of the double layers and the ammonium ions. Open large circles denote oxygen atoms linked to the sulphur atoms (small filled circles) and the copper atoms (heavy contour circles). Lined open circles denote two overlapping oxygen atoms and hatched large circles denote ammonium ions. The hydrogen atoms are not indicated.



b) The double layers formed by CuO_3S tetrahedra and SO_3 pyramids. Only one double layer is indicated (*i.e.* atoms with z parameters within the limits $0 < z < 0.26$). Open and full circles denote oxygen atoms situated in two planes $c(1/3 + 2z_0) = 3.96 \text{ \AA}$ apart. The small crossmarked circles denote overlapping sulphur and copper atoms 2.14 \AA apart. The large hatched circles denote ammonium ions situated between and linking together the double layers as indicated in Fig. 1a.

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 = $2.143 \pm 0.007\ \text{\AA}$
 Cu—3 O = $2.119 \pm 0.012\ \text{\AA}$
 S—3 O = $1.506 \pm 0.012\ \text{\AA}$
 O—O = $2.397 \pm 0.015\ \text{\AA}$ (within the SO_3 pyramid)
 = $3.031 \pm 0.015\ \text{\AA}$ (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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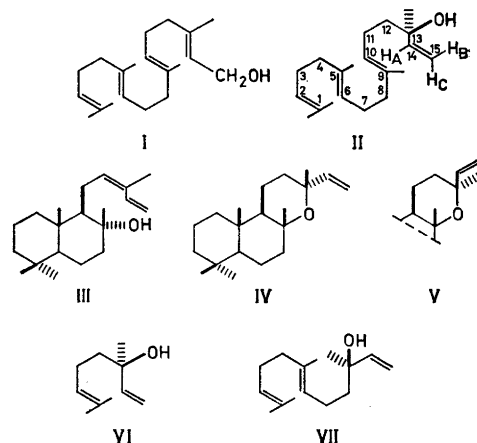
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The Oleoresin of Norwegian Spruce, *Picea abies* (L.) Karst.— Isolation of (-)-Geranyllinalool

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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 jasmine 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