

The Structure of α -Longipinene, a Minor Sesquiterpene of the Wood of *Pinus silvestris* L. and of Swedish Sulphate Turpentine^{*, **}

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α -Longipinene, one of the minor sesquiterpenes occurring in the wood of *Pinus silvestris* L. and in Swedish sulphate turpentine has been shown to possess structure (1) on spectroscopic and chemical evidence.

The high-boiling neutral constituents of the wood of *Pinus silvestris* L. and of Swedish sulphate turpentine derived mainly from this species have been investigated. Some of the results from this investigation have already been reported.¹⁻⁴ This paper describes the structure elucidation of one of the minor sesquiterpene hydrocarbons, α -longipinene (1), which was isolated from sulphate turpentine² and has been shown to occur¹ in the wood of *Pinus silvestris*. α -Longipinene has also been isolated from the wood of *Pinus longifolia*.⁵ The hydrocarbons from the two species^{***} were shown to be identical by ozonolysis to the crystalline ketoacid (2), m.p. 92°.²

The formation of the ketoacid (2) showed that α -longipinene contained a trisubstituted double bond.

The IR and NMR spectra of α -longipinene are reproduced in Figs. 1 and 2, and show characteristic similarities to those of α -pinene, which, for comparison, are also included in the figures. As can be seen from Fig. 1, the characteristic double bond absorptions at *ca.* 1660 and *ca.* 785 cm⁻¹ appear at almost the same frequencies for the two hydrocarbons.

The NMR spectrum of α -longipinene (Fig. 2) reveals the presence of three methyl groups attached to saturated carbon atoms bearing no hydrogen atoms, one methyl group linked to a double bond and one olefinic proton. The NMR spectra of α -pinene and α -longipinene show signals due to A₃X systems consist-

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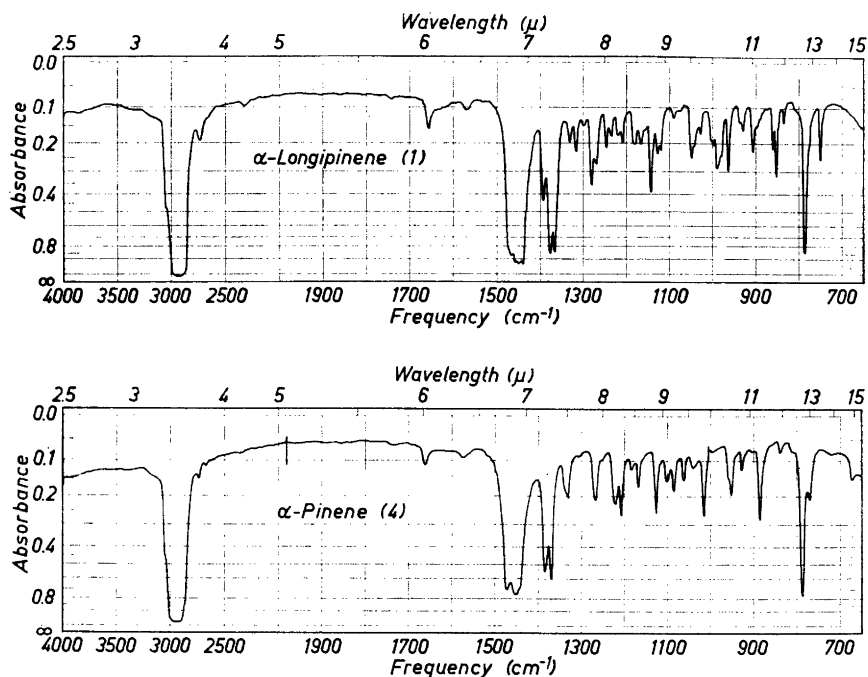


Fig. 1. IR spectra of α -longipinene (1) and α -pinene (4) as liquid films (0.025 mm).

ing of the protons of the methyl groups on the double bonds and the olefinic protons. As can be seen from Fig. 2, the signals assigned to these A_3X systems are very similar with respect to both, the chemical shifts and coupling constants. Consequently, the environments of the protons constituting the A_3X systems of the two hydrocarbons must be similar. Also the bond angles of these systems

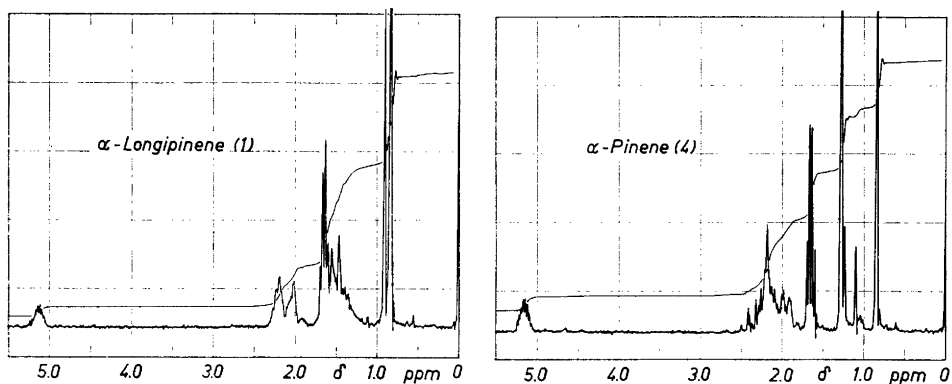
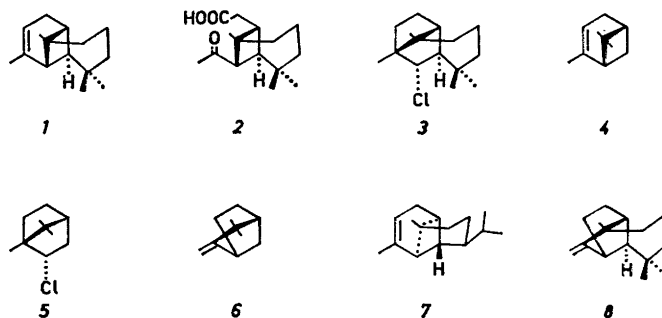


Fig. 2. NMR spectra of α -longipinene (1) and α -pinene (4).

should be almost the same for both hydrocarbons. The α -longipinene structure (1) for the sesquiterpene fulfils these requirements.

When the sesquiterpene was treated with dry hydrogen chloride in ether at -18° , (+)-longibornyl chloride (3) was formed. This confirmed that the hydrocarbon was related to α -pinene (4) [cf. the conversion of α -pinene (4) to bornyl chloride (5)^{6a}].



It is interesting to compare the products obtained on hydrochlorination of the monoterpenes α -pinene (4) and camphene (6) with those obtained from the sesquiterpenes α -longipinene (1), copaene (7), and longifolene (8). α -Pinene^{6a} and α -longipinene both yield *endo* chlorides, (5) and (3), respectively, *via* Wagner-Meerwein rearrangement. Camphene and longifolene do not yield analogous chlorides, the *exo* product, isobornyl chloride, being formed^{6b} from the former compound and the *endo* product, longibornyl chloride, from the latter.⁷

Possibly, the C_4 -bridge in longifolene effectively prevents approach of chloride ion from the *exo* side of the bicyclo[2.2.1]heptane part of the molecule, resulting in preferential formation of *endo*-chloride.⁸ Furthermore, the additional C_4 -bridge of longifolene provides conditions for the intervention of non-classical ions not analogous to the non-classical bornyl cation.⁸

The reaction of hydrogen chloride with copaene follows a quite different pathway in that, instead of proceeding *via* a Wagner-Meerwein rearrangement, the reaction results in cleavage of the four-membered ring with formation of tertiary chlorides. The main product is cadinene dihydrochloride, muurolene dihydrochloride being one of the minor products.⁴ As the mechanism of such hydrochlorination reactions is not known in detail, the reason for the different behaviour of copaene and α -longipinene against hydrogen chloride is not clear. Probably, the difference in ring strain should play an important role.

EXPERIMENTAL

Melting points were taken on a Kofler micro hot stage. IR spectra were recorded on a Perkin-Elmer No. 21 instrument (NaCl prism, sample as liquid film, or, for solids, in KBr) and NMR spectra on a Varian A 60 instrument operating at 60 Mc/s (solvent carbon tetrachloride, internal standard tetramethylsilane). For gas-liquid chromatography

(GLC) a PYE argon chromatograph (column length 1.2 m, inner diameter 4 mm) was used.

Rotations were taken in chloroform. Light petroleum refers to the fraction, b.p. 40–60°.

The isolation of α -longipinene from Swedish sulphate turpentine has been described previously.² The physical constants and the results of ozonolysis of α -longipinene were also reported.²

Hydrogenation of α -longipinene. The compound (0.130 g) was hydrogenated (platinum oxide, glacial acetic acid) and the product was worked up in the usual manner.³ The product (0.110 g) had $[\alpha]_D^{22} + 39.2^\circ$ (*c* 2.0). (Found: C 87.1; H 12.7. $C_{15}H_{26}$ requires C 87.3; H 12.7). It did not colourize a solution of tetranitromethane (5 %) in chloroform.

Longibornyl chloride. α -Longipinene (0.370 g) in dry ether (3 ml) was saturated with dry hydrogen chloride at -18° . The solution was kept in the refrigerator for about 24 h. The ether and excess hydrogen chloride were removed under reduced pressure and the product was induced to crystallize by cooling to *ca.* -30° , addition of one drop of light petroleum, and scratching. The mother liquor was removed in the cold. According to GLC (1 % E 301 column,¹ 120°) the crude crystalline product consisted of a single hydrochloride with sesquiterpene hydrocarbons as the only impurities. It was recrystallized once from light petroleum and twice from methanol to give (+)-longibornyl chloride, m.p. and mixed m.p. $57-59^\circ$, $[\alpha]_D + 12.0^\circ$ (*c* 1.0), IR spectrum identical with that of a sample obtained from longifolene.²

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REFERENCES

1. Westfelt, L. *Acta Chem. Scand.* **20** (1966) 2829.
2. Westfelt, L. *Acta Chem. Scand.* **20** (1966) 2841.
3. Westfelt, L. *Acta Chem. Scand.* **20** (1966) 2852.
4. Westfelt, L. *Acta Chem. Scand.* **21** (1967) 152.
5. Sukh Dev. *Private communication.*
6. Simonsen, J. and Owen, L. N. *The Terpenes* (2nd Ed.), Vol. II, Cambridge 1949 *a* p. 170, *b* p. 346.
7. Simonsen, J. and de Mayo, P. *The Terpenes* (2nd Ed.), Vol. V (Adden. Vol. III), p. 539.
8. Ourisson, G. *Proc. Chem. Soc.* **1964** 274.

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