

Structures of Some Aliphatic Monoterpenoids Isolated from the Essential Oil of *Ledum palustre* L.

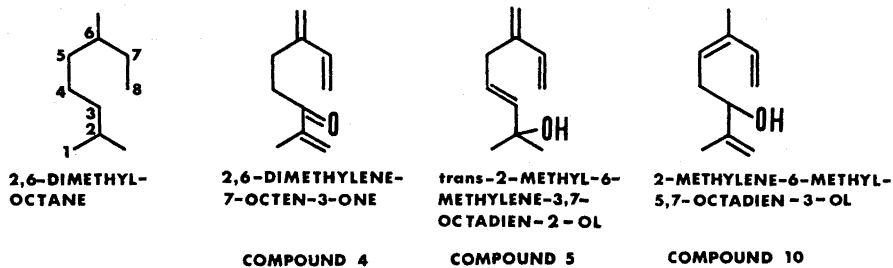
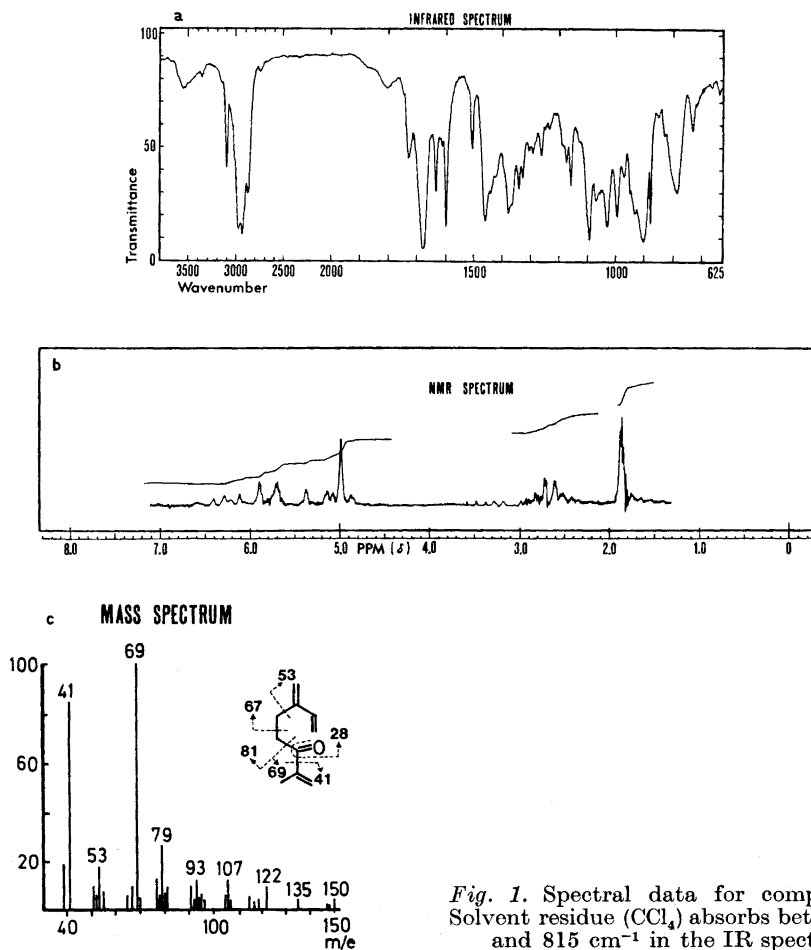
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The elucidation of the structures of 2,6-dimethylene-7-octen-3-one, 2-methylene-6-methyl-5,7-octadien-3-ol, and *trans*-2-methyl-6-methylene-3,7-octadien-2-ol, all three isolated from the essential oil of *Ledum palustre* L., is described.

Two of us¹ reported recently on the composition of the essential oil of *Ledum palustre* L. In this investigation we elucidate and revise the structures of some of the compounds dealt with in the earlier study.

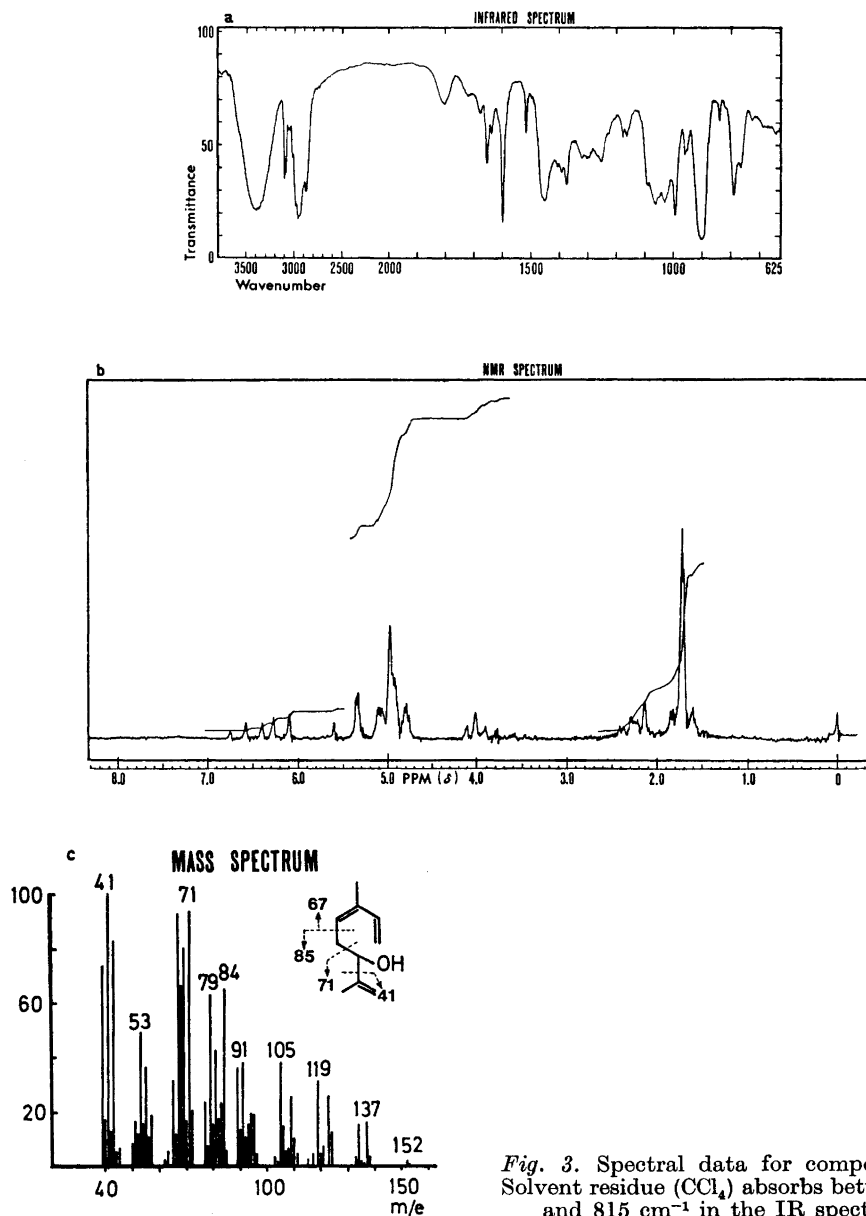
Spectral data for compound 4 (numbering as in the paper of v. Schantz and Hiltunen¹) are presented in Fig. 1. According to the parent peak in the mass spectrum of the compound, its molecular weight is 150. On carbon skeleton chromatography² in combination with mass spectrometry, three different hydrocarbons were produced, namely 2,6-dimethyloctane (90 %), 2,6-dimethylheptane, and 2-methyloctane (the last two together amounting to about 10 %). It is thus very likely that compound 4 has the normal aliphatic head-to-tail monoterpene skeleton [2,6-dimethyloctane or hexahydromyrcene (Fig. 2)]. As its molecular weight is 150, the molecule must have the formula $C_{10}H_{14}O$ and contain four double bonds. The IR spectrum has a strong absorption based at 1679 cm^{-1} which reveals a carbonyl group and hence one double bond. The NMR spectrum contains only one signal of three methyl protons (δ 1.85 ppm). The other three double bonds must hence be vinylidene or vinyl ones. The corresponding six methylene protons give signals at δ 4.99 (4H) and 5.82 ppm (2H) in the NMR spectrum, while the methine proton absorption is centered at δ 6.35 ppm as two pairs of doublets. The position of the keto group is then to be settled. According to the IR spectrum, the compound is α,β -unsaturated (absorption at 1679 cm^{-1}). The UV spectrum corresponds to a monosubstituted butadiene or a ketone with the carbonyl group conjugated with one olefinic double bond [λ_{max} (ethanol) 224 nm]. So C-3 seems a very likely position for the carbonyl group. Hence, the structure of compound 4 is 2,6-dimethylene-7-octen-3-one (Fig. 2).

*Fig. 2.*

Further support for this structure is found in the fragmentation pattern of the mass spectrum (Fig. 1). The fragment with $m/e = 79$ probably corresponds to a hexatrienyl ion formed by fission of the bond between C-3 and C-4 and subsequent elimination of hydrogen (*cf.* Ohloff *et al.*³). Also the IR spectrum speaks in favour of the structure proposed for compound 4. The absorption based at 991 cm^{-1} can be attributed to the vinyl double bond, which together with the vinylidene double bonds absorbs also at 3089 and 897 cm^{-1} (broad absorptions). The last mentioned double bonds give absorption bands at 1649 and 1800 cm^{-1} . Finally, the strong band at 1597 cm^{-1} can be attributed to conjugated double bonds.

Spectral data for compound 10 are given in Fig. 3. According to the mass spectrum, the molecular weight is 152. On carbon skeleton chromatography, about 95 % hexahydromyrcene was produced, which fact suggests the same skeleton. The formula $\text{C}_{10}\text{H}_{16}\text{O}$, which implies three double bonds, evolves for compound 10. IR bands at 3400 and 1054 cm^{-1} indicate an alcohol. The NMR spectrum contains a triplet centered at $\delta 4.03\text{ ppm}$ (1H) which is attributable to a proton attached to the same carbon as the oxygen. The alcohol must hence be a secondary one. On oxidation with chromic acid, a ketone (mol. wt. 150) was obtained whose mass spectrum was practically identical with that of compound 4. As the keto group directs the fragmentation very much, the position of the oxygen atom can now be fixed at C-3 as in compound 4, and one double bond can tentatively be placed in the isopropyl group, while the other two must be on the other side of C-3. The UV absorption [λ_{max} (ethanol) 224 nm] corresponds to that of a butadiene. The existence of conjugated double bonds is confirmed also by the strong IR absorption band at 1596 cm^{-1} . A band attributable to a vinyl double bond is found in the IR spectrum at 990 cm^{-1} . The NMR spectrum reveals six methyl protons and hence two methyl groups which are attached to double-bonded carbon atoms (signals at $\delta 1.70$ and 1.75 ppm). Taking into consideration the position of the oxygen atom and the spectral data for the double bonds, we must place the two conjugated double bonds in positions five and seven. Probably the trisubstituted double bond absorbs at 834 cm^{-1} in the IR spectrum. One of the two methyl groups revealed by the NMR information has thus been located. The third double bond and the other methyl group must then both be in the isopropyl group. The aliphatic vinylidene double bond gives infrared absorption bands at 1654 and 1800 and, together with the vinyl double bond, also at 3100 and 900 cm^{-1} (broad bands). The structure of compound 10 is then 2-methylene-6-methyl-5,7-octadien-3-ol (Fig. 2). Additional confirmation of this structure is provided by its mass spectrometric fragmentation (Fig. 3). The question whether compound 10 is the *cis* or *trans* isomer in respect of the trisubstituted double bond, we have not been able to decide.

In a similar way as the structures of the above two compounds, the structure *trans*-2-methyl-6-methylene-3,7-octadiene-2-ol could be deduced for compound 5 by analysis of its spectra. However, this compound has been isolated earlier from *Pinus ponderosa* Laws. by Silverstein *et al.*,⁴ who also elucidated its structure mainly by spectral methods. As we came to the same conclusion about the structure, we refer to the paper of these authors for spectral details and their interpretation.



All three compounds discussed above differ from other known naturally occurring acyclic, oxygenated monoterpenoids in having three olefinic double bonds instead of two.

EXPERIMENTAL

Details about the isolation of the compounds have been reported by v. Schantz and Hiltunen.¹ About 10 mg of each compound was available. They were all greenish liquids.

IR spectra were run on a Pye Unicam SP 1000 instrument (sample as liquid film) and NMR spectra on a Varian A 60 spectrometer operating at 60 Mc/s (with carbon tetrachloride as solvent and tetramethylsilane as internal standard). Mass spectra were recorded on a Perkin-Elmer 270 GC-MS instrument (ion source 190°C, manifold 200°C, electron energy 70 eV, ion source and analyzer pressures about 10^{-6} and 10^{-7} torr, respectively). The UV spectrophotometer used was a Beckman DB-G instrument.

Carbon skeleton chromatography was carried out on-line with the Perkin Elmer 270 GC-MS instrument using 3 % platinum on Chromosorb W as catalyst at 200°C, a 50 m, 0.25 mm i.d., OV-17 WCOT column, and hydrogen as carrier gas (Widén⁵). The reaction products were identified with the aid of the mass spectra.

Oxidation of compound 10 with chromic acid was carried out in the following way. A solution of the compound (10 mg) in ether (2 ml) was stirred with a solution of sodium dichromate dihydrate in sulphuric acid (20 mg) and water (0.3 ml) at room temperature overnight. After addition of water, the product was taken up in ether, washed with 10% sodium bicarbonate solution and dried with sodium sulphate. After evaporation of the solvent, the product was studied by GC-MS and found to be a ketone (amounting to about 90 % of the reaction mixture) with a mass spectrum practically identical with that of compound 4.

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