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THE STRUCTURE OF A TETRACYCLIC SESQUITERPENIC ALCOHOL[+] FROM LIVERWORT MYLIA TAYLORII (HOOK.) GRAY

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In our earlier papers[1-4] we described the isolation and the structure of some new compounds from liverworts (Hepaticae). This paper is devoted to the major component from the liverwort Mylia taylorii (Hook.) Gray, to which we gave the name myliol.

According to its elemental analysis and m/e value in the mass spectrum this crystalline compound (m.p. 111°C), which is very unstable in air, has the composition $C_{15}H_{22}O$. Its NMR spectrum[5] contains characteristic signals of three tertiary methyl groups at 0.93 and 1.06 (6H) ppm, a multiplet of a proton of the CH-OH type (corroborated by an exchange experiment in d_6-DMSO) at 4.73 ppm, two doublets at 5.04 ($J = 2.8$ Hz) and 5.14 ppm ($J = 2.4$ Hz) which in agreement with the IR spectrum were attributed to the protons of the exomethylene group, a complex three-proton multiplet in the region of 0.2-0.6 ppm which may be assigned to cyclopropane protons. As the CH-OH proton is coupled to both olefinic protons (confirmed by tickling experiment), the hydroxy group is probably bound in the allylic position.

Hydrogenation of myliol on Pt catalyst in ethanol and in acetic acid gives rise to two dihydro derivatives IIa,b of the composition $C_{15}H_{24}O$ (m/e 220). In the IR spectrum of both dihydro derivatives the absorption of the hydroxy group remains preserved (OH 3 620 cm^{-1}) and the absorption of the cyclopropane ring is quite distinct, without substitution on the methylene group (3 040 cm^{-1})[6]. In the IR spectrum the presence of methyl groups is also accentuated (1 377, 1 386, and 1 390 cm^{-1}), the doublet

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[+] Part CCXI of the series On Terpenes.

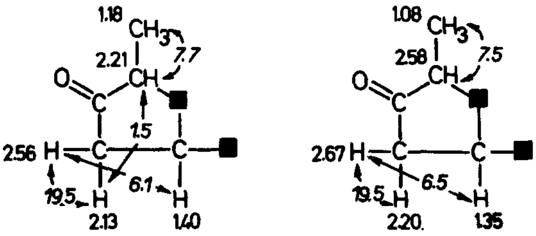
splitting of which suggests the possibility of geminal arrangement of the two methyls.

The NMR spectrum[5] of the less polar dihydromyliol IIa contains three singlets of methyls at 0.99 and 1.25 ppm, a doublet (J = 7.5 Hz) of a secondary methyl at 1.04 ppm, a system of three coupled protons between 0.25 and 0.90 ppm; the CH-OH proton is reflected by a doublet of triplets at 4.47 ppm (splitting 9 and 2.4 Hz). The multiplets of protons in the region 0.25-0.9 ppm do not change their shape on irradiation of the signals of the remaining protons; from this it can be concluded that either no hydrogen atom is present in its neighbourhood, or only one with a small or zero vicinal interaction. Both 9 Hz couplings of the methine proton of the CH-OH type concern protons in the 2.3-2.7 ppm region the multiplets of which are superimposed; the coupling constant 2.4 Hz is due to the proton at 1.61 ppm. One of the protons in the mentioned multiplet (localised by the INDOR experiment) is responsible for the doublet splitting of the secondary methyl, and the second for the 16 Hz interaction with the proton at 1.61 ppm. As follows from the NMR spectra of ketones IIIa,b, described below, this interaction is geminal, which substantiates the formulation of the partial structure $CH_3CHCH(OH)CH_2$. The formation of the secondary methyl group, the upfield shift of the resonance of the CH-OH proton and its interaction with the corresponding methine proton of this methyl group are in agreement with the hydrogenation course of the exomethylene double bond and corroborate the allylic character of the starting alcohol.

Oxidation of both dihydroderivatives IIa,b with chromium oxide-pyridine mixture gives two isomeric ketones $C_{15}H_{22}O$ (m/e 220); IIIa,b. Their infrared spectra contain bands characteristic of five-membered cyclic ketone (CO 1 741 cm^{-1}), of the methylene group in the α-position to the carbonyl group (1 413 cm^{-1}), and of the cyclopropane ring (3 055 cm^{-1}).

The NMR spectrum[5] of ketone IIIb, formed from the more polar dihydromyliol IIb, contains three methyl singlets at 0.89, 1.02 and 1.05 ppm, a doublet of the secondary methyl at 1.18 ppm (J = 7.7 Hz), the methine proton of which, located at 2.21 ppm, gives a doublet of a quartet (further splitting 1.5 Hz), and a system of three strongly coupled protons at 2.56, 2.13, and 1.4 ppm. The first two protons of this trio have mutual coupling 19.5 Hz (J_{gem} in the CH_2CO group), while the coupling of the lower proton with the methine proton of the secondary methyl is 6.1 Hz (through carbonyl coupling). The doublet structure of the signal at 1.40 ppm indicates that the remaining carbon atoms in the vicinity are quaternary, which is in agreement with the observed multiplicity of the methine proton of the secondary methyl group (Scheme 1-A). The spectrum of the second ketone IIIa (Scheme 1-B) is analogous.

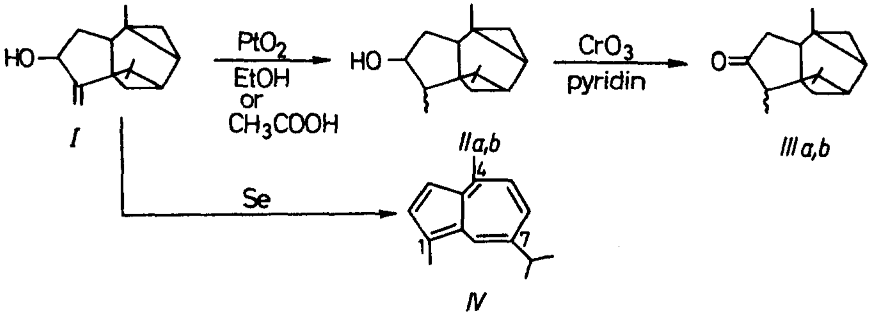
Scheme 1



1A 1B

Three carbon and three hydrogen atoms remain unassigned which may represent three methine groups or the groups CH, CH_2, and a quaternary carbon. In the first case the molecule of myliol should contain either an additional double bond or another cyclopropane ring. However, the NMR spectra of myliol or its derivatives do not contain signals for unassigned olefinic or cyclopropane protons. In the case of the second alternative, the more plausible one (CH, CH_2 and a quaternary carbon atom) it must be decided whether the CH and CH_2 groups are coupled or isolated. The NMR spectra demonstrate a coupling between these two groups. On dehydrogenation with selenium myliol smoothly gave S-guaiazulene IV. Its formation determines the position of the exomethylene group at C_1 and the methyl group at C_4. The presence of an isopropyl group at C_7, which is not present in native myliol, may be explained only by the opening of another ring containing the geminal dimethyl group. On the basis of all the above mentioned facts we propose structure I for myliol (Scheme 2). The results in extenso together with other data will be published in Coll. Czech. Chem. Commun.

Scheme 2



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