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THE STRUCTURE OF A NEW SESQUITERPENE EPOXYLACTONE FROM *LACTARIUS SCROBICULATUS* SCOP. (RUSSULACEAE) BY SPECTROSCOPIC METHODS

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In the last few years from the *Lactarius* species some hydroazulenic sesquiterpenes with characteristic structures have been isolated[1]. In the pine woods of the Northern regions of Italy in late summer *Lactarius Scrobiculatus* Scop. grows. Its milky juice, the colour of which turns quickly and dramatically from white to yellow upon contact with the air, has an intensely pungent taste and is probably responsible for the high toxicity of this mushroom, which causes serious intestinal diseases. During our study of the metabolites of *L. scrobiculatus* several sesquiterpenes were isolated and some seem to have new structures. We wish to report here on a tetracyclic sesquiterpene epoxylactone which has not been isolated before. We consider this structure quite interesting because of the unusual position of the epoxy-ring expecially in these hydroazulenic structures.

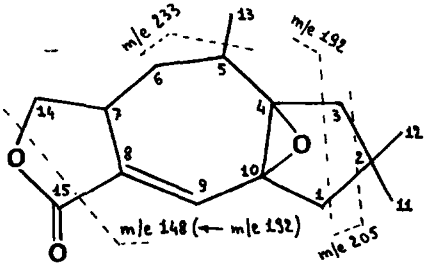
(I) is obtained as a pale yellow oil, α_D +102° (C_6H_6, c 0.021), λ_{max}^{MeOH} 213 nm, log ε 3.86. The M.W.(MS) 248 and the (^{13}C and ^1H)NMR data indicated a formula $C_{15}H_{20}O_3$. In the IR spectrum(film) of (I) strong bands at 1768, 1695 and 840 cm^{-1} can be attributed to an α,β-unsaturated-γ-lactone. The NMR data, attributed by double resonance experiments, have shown that ten protons can be joined in a spin system as indicated in the partial structure (II), where C_a and C_b might be quaternary carbons[2]. The last NMR data suggested the presence of a quaternary geminal dimethyl group bonded to two isolated methylene groups (eight lines of two widely overlapped AB systems centered at δ 1.83 and 1.91 in the ^{1}HNMR).

The unsaturation number deduced from the formula and the spectroscopic data can be explained by the presence of two double bonds (C=C and C=O) and four rings. Besides tha lactone ring, the other three rings can be accounted for by the signals of the quaternary carbons C_a and C_b in the ^{13}CNMR spectrum indicating that both are bonded to an oxygen atom. This means that C_a and C_b must be shared by two fused rings and must belong to an epoxy-ring too. The two fused rings are respectively a seven and a five membered rings as in (I). The absence of hydroxyl groups (IR and ^{1}HNMR spectra) confirmed the presence of the oxirane ring. The frag mentation[3] of the molecular ion (as indicated in the formula) gave further evidence of the assigned structure (I). The NMR data along with the inspection of Dreiding models led to some assumptions about the stereochemistry of (I). If one considers that the vicinal coupling constants mainly depend on the dihedral angles, the $J_{H\underline{g}-H\underline{e}}$ and $J_{H\underline{g}-H\underline{f}}$ values suggest an equatorial-equatorial and axial-equatorial interactions between the protons. This fact and the absence of an appreciable Overhauser effect, when $H_{\underline{d}}$ was irradiated, indicated that the methyl on C_5 should be axial and anti to $H_{\underline{d}}$. Furthermore the low field chemical shift of the methyl can be explained by an 1,3-diaxial interaction with the oxygen atom of the epoxide ring[4]. No appreciable change of the NMR spectrum was observed by lowering the temperature indicating a fixed conformation for (I). In the following NMR data are reported the chemical shifts ($CDCl_3$,ppm), the attributions of the signals and the corresponding J:

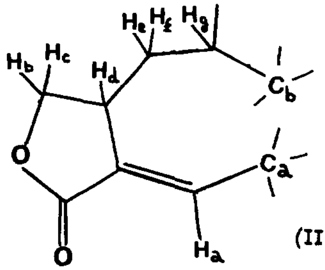
^{1}HNMR (100 MHz): 1.03(s,C_2-$\underline{CH_3}$); 1.09(s,C_2-$\underline{CH_3}$); 1.20(d,C_5-$\underline{CH_3}$); 1.50(m,$H_{\underline{f}}$); 1.83 (m,CH_2); 1.91(m,CH_2); 1.97(m,$H_{\underline{e}}$); 2.52(m,$H_{\underline{g}}$); 3.20(m,$H_{\underline{d}}$); 3.73(t,$H_{\underline{c}}$); 4.41 (t,$H_{\underline{b}}$); 6.91(d,$H_{\underline{a}}$).

J (Hz): $J_{CH_3-H\underline{g}}$=7.2 $J_{H\underline{a}-H\underline{b}}$=0.3 $J_{H\underline{g}-H\underline{f}}$=5.0 $J_{H\underline{e}-H\underline{f}}$=13.5 $J_{H\underline{f}-H\underline{d}}$=3.5 $J_{H\underline{e}-H\underline{g}}$=3.0
$J_{H\underline{b}-H\underline{d}}$=8.5 $J_{H\underline{e}-H\underline{d}}$=11.5 $J_{H\underline{c}-H\underline{d}}$=9.0 $J_{H\underline{b}-H\underline{c}}$=8.5 $J_{H\underline{a}-H\underline{d}}$=3.5

^{13}CNMR (25.2 MHz): 171.20(s,C=0,15); 134.49(s,C=C,8); 134.07(d,C=CH,9); 80.78 (s,C-0,10 or 4); 70.61(t,$CH_2$0,14); 69.00(s,C-0,4 or 10); 47.06(t,CH_2,1 or 3); 45.81(t,CH_2,3 or 1); 3610(d,CH,5 or 7); 34.37(s,-C-,2); 32.34(q,CH_3,11 or 12); 31.83(d,CH,7 or 5); 31.83(t,CH_2,6); 29.81(q,CH_3,12 or 11); 16.25(q,CH_3,13).



(I)



(II)

References and footnotes

1. G. Magnausson et al., Acta Chem.Scand., B 28, 841 (1974) and references cited therein.
2. This partial structure was confirmed by a simulated spectrum of the spin system (CH_3CH and H_a protons decoupled) with very good agreement between the experimental and the theoretical spectra.
3. MS (DIS,70eV) m/e (%): 248(M^+,11), 233(16), 230(25), 215(33), 205(13), 192(19), 177(11), 161(27), 159(19), 148(65), 133(35), 124(35), 119(31), 109(39), 105(46), 91(48), 83(30), 79(30), 77(37), 69(43), 55(48), 41(100).
4. K Tori et al., Tetr.Letters, 559 (1964).