Fungal Extractives

V.* The Stereostructure of two Sesquiterpene Lactones from *Lactarius*

GÖRAN MAGNUSSON and SVANTE THORÉN

*Organic Chemistry 2, Chemical Center, The Lund Institute of Technology, Box 740, S-220 07 Lund 7, Sweden*

The stereostructures of two sesquiterpene lactones from *Lactarius vellereus* and *L. pergamenus* have been determined by interrelation with the dialdehyde “velleral” of known relative configuration.

In a previous publication 2 we have reported the structure of two sesquiterpene lactones from the basidiomycetes *Lactarius vellereus* and *L. pergamenus* (Russulaceae). Spectroscopic evidence and chemical synthesis of a degradation product showed that these two compounds had the basic structures I and 2, respectively, but did not permit assignment of the stereochemical configuration. The relative stereostructure of “velleral” 1 was determined by applying extensive NMR techniques and is shown in formula 3. By chemical interrelation of lactone I and “velleral” we have now been able to deduce the stereoarrangement of the two lactones.

It was realised that a comparison of compounds I and 3 could be based on their reduction products, preferably the diols. The reduction agent of choice seemed to be AlH₃ known to give pure 1,2-addition to α,β-unsaturated carbonyl systems without secondary rearrangements. 3 AlH₃ reduction of “velleral” (3) gave as anticipated the diol 4 in moderate yield. A similar reduction of lactone I also yielded a diol with the same \( R_F \) value on TLC as 4 and with IR and NMR spectra superimposable on those of 4. Furthermore, these diols had practically the same optical rotation: \([\alpha]_D^{25} +201^\circ\) for the diol from I and \([\alpha]_D^{25} +205^\circ\) for 4. The identity was thus firmly established.

It has previously been shown that lactone I can be converted to lactone 2 by heat-induced isomerisation. 2 The relative stereostructures of the two lactones are therefore as shown in formulae I and 2, respectively.

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* Part IV, see Ref. 1.
Many of the known sesquiterpenoids of basidiomycetes origin have a fused cyclopentane ring with geminal substituents. Some of these compounds which have been fully elucidated have hydrogens in the ring junction and a methyl group or its equivalent on a carbon atom adjacent to one of the bridgeheads. It is perhaps not surprising that the *Lactarius* compounds "isovelleral" (5),4 the lactones 1 and 2, and "velleral" from *L. vellereus* and *L. pergamenus* and lactarorufin A (6)5 from *L. rufus* have the same relative configuration. However it might be noted that a number of compounds, for instance marasmic acid (7),6,6 illudol (8),7,8 and hirsutic acid (9)8 of diverse structures and origins, have the same steric arrangement at the three carbons concerned even though not always with the same absolute configuration.

**EXPERIMENTAL**

The NMR spectra were recorded on a Varian T-60 spectrometer. The high resolution mass spectrum was measured on a MS 902/DS 30 instrument by the kind cooperation of Dr. G. Hvistendahl, Kjemisk Institut, The University of Oslo, Norway. 

*AlH₃ reduction of "velleral" (3)*.4 "Velleral" (239 mg; 0.001 mol) dissolved in dry ether (5 ml) was added dropwise to a magnetically stirred, ice-cold solution of AlH₃ (0.001 mol) in dry ether (10 ml). After the addition was complete, the reaction mixture was stirred at room temperature for 24 h. Thereafter Na₂SO₄,10H₂O (2 g) was added followed by water (1 ml) and 2 M NaOH (2-3 drops). The mixture was filtered and the organic phase was dried (Na₂SO₄) and evaporated. The residue was chromatographed on a silica gel column with toluene-ethyl acetate (1:1) as eluent to yield diol 4 (80 mg). The diol had b.p. 115°; [α]D 15° +203° (c. 1.6; CHCl₃); IR: max (neat) 3600-3100 (broad, -OH), 3040, 1390, 1380, 1372, 1020, 845, 730, 695 cm⁻¹; NMR: δTMS (CDCl₃) 5.92 (2 H, m; vinyl protons), 4.26 4.08 (4 H, two coincident AB doublets with J =12.5 Hz; -CH₃OH, -CH₂OH), 1.08 (3 H, s; -CH₃), 0.98 (3 H, d J = 6.0 Hz; CH₃-CH₂), 0.93 (3 H, s; -CH₃); MS (70 eV); m/e 236 (M⁺, 11 %; C₁₆H₂₄O₂); 218 (M⁺ - H₂O; 58 %), 203 (44 %), 189 (56 %), 119 (77 %), 105 (100 %), 91 (83 %). (Found: M.wt. 236.1779. Calc.
for C₄H₆O₈: M.wt. 236.1775). The diol 4 gave an oily diacetate and an oily bis-p-nitro-benzoate which were not further characterized.

AIH₃ reduction of lactone 1. The lactone was reduced according to the same procedure as above and gave after work-up a diol which had identical IR and NMR spectra as diol 4 and had the optical rotation [α]D₂⁺₊²₀¹° (c. 1.2; CHCl₃).

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