

## Fungal Extractives

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

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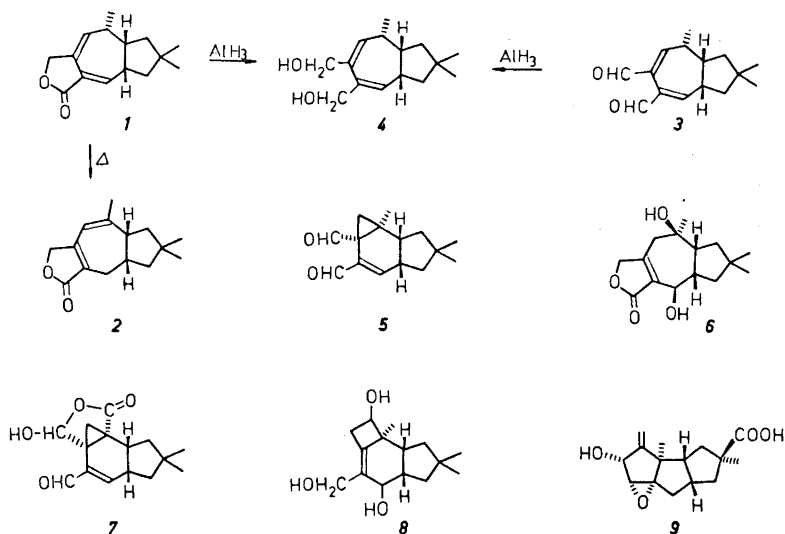
The stereostructures of two sesquiterpene lactones from *Lactarius vellereus* and *L. pergamenus* have been determined by interrelation with the dialdehyde "velleral" of known relative configuration.

In a previous publication<sup>2</sup> 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 *1* and *2*, respectively, but did not permit assignment of the stereochemical configuration. The relative stereostructure of "velleral"<sup>1</sup> was determined by applying extensive NMR techniques and is shown in formula *3*. By chemical interrelation of lactone *1* and "velleral" we have now been able to deduce the stereoarrangement of the two lactones.

It was realised that a comparison of compounds *1* and *3* could be based on their reduction products, preferably the diols. The reduction agent of choice seemed to be  $\text{AlH}_3$  known to give pure 1,2-addition to  $\alpha,\beta$ -unsaturated carbonyl systems without secondary rearrangements.<sup>3</sup>  $\text{AlH}_3$  reduction of "velleral" (*3*) gave as anticipated the diol *4* in moderate yield. A similar reduction of lactone *1* 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 *1* and  $[\alpha]_D^{25} + 203^\circ$  for *4*. The identity was thus firmly established.

It has previously been shown that lactone *1* can be converted to lactone *2* by heat-induced isomerisation.<sup>2</sup> The relative stereostructures of the two lactones are therefore as shown in formulate *1* and *2*, respectively.

\* 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),<sup>4</sup> the lactones 1 and 2, and "velleral" from *L. vellereus* and *L. pergamenus* and lactarorufin A (6)<sup>5</sup> from *L. rufus* have the same relative configuration. However it might be noted that a number of compounds, for instance marasmic acid (7),<sup>6,9</sup> illudol (8),<sup>7,9</sup> and hirsutic acid (9),<sup>8</sup> 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 Institutt, The University of Oslo, Norway.

*AlH<sub>3</sub> reduction of "velleral" (3).*<sup>3</sup> "Velleral" (239 mg; 0.001 mol) dissolved in dry ether (5 ml) was added dropwise to a magnetically stirred, ice-cold solution of  $\text{AlH}_3$  (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  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  (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 ( $\text{Na}_2\text{SO}_4$ ) 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.<sub>0.001</sub> 115°;  $[\alpha]_{\text{D}}^{25} + 203^\circ$  (c. 1.6;  $\text{CHCl}_3$ ); IR:  $\nu_{\text{max}}$  (neat) 3600–3100 (broad, –OH), 3040, 1390, 1380, 1372, 1020, 845, 730, 695  $\text{cm}^{-1}$ ; NMR:  $\delta_{\text{TMS}}$  ( $\text{CDCl}_3$ ) 5.92 (2 H, m; vinyl protons), 4.26–4.08 (4 H, two coincident AB doublets with  $J=|12.5|$  Hz; – $\text{CH}_2\text{OH}$ , – $\text{CH}_2\text{OH}$ ), 1.08 (3 H, s; – $\text{CH}_3$ ), 0.98 (3 H, d  $J=6.0$  Hz;  $\text{CH}-\text{CH}_3$ ), 0.93 (3 H, s; – $\text{CH}_3$ ); MS (70 eV):  $m/e$  236 ( $\text{M}^+$ , 11 %;  $\text{C}_{16}\text{H}_{24}\text{O}_2$ ), 218 ( $\text{M}^+ - \text{H}_2\text{O}$ ; 58 %), 203 (44 %), 189 (56 %), 119 (77 %), 105 (100 %), 91 (83 %). (Found: M.wt. 236.1779. Calc.

for  $C_{16}H_{24}O_2$ ; M.wt. 236.1775). The diol 4 gave an oily diacetate and an oily bis-*p*-nitrobenzoate which were not further characterized.

*AlH<sub>3</sub> reduction of lactone I.* 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  $[\alpha]_D^{25} + 201^\circ$  (c. 1.2;  $CHCl_3$ ).

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