## SESQUITERPENOIDS FROM THE LIVERWORT LOPHOZIA VENTRICOSA

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Abstract—Two sesquiterpenoids, previously reported as ventricosins A and B, from Lophozia ventricosa have been identified as ent-4(15),7(11)-eudesmadien-8-one and ent-maalioxide, respectively.

Previous work on the liverwort Lophozia ventricosa (Dicks.) Dum. led to the isolation of two sesquiterpenoids, ventricosins A and B, whose structures were not assigned [1]. We have reinvestigated this liverwort and have identified ventricosin A as ent-4(15),7(11)-eudesmadien-8-one (1) and ventricosin B as ent-maalioxide (3).

Ventricosin A (1) was obtained as an oil,  $C_{15}H_{22}O$ ,  $[\alpha]_D - 80.5^\circ$  (c 1.14 in CHCl<sub>3</sub>) (lit. [2]  $[\alpha]_D - 87.4^\circ$ ). Its <sup>13</sup>C NMR spectrum (see Experimental) showed similarities to that of cuauhtemone (2) [2] and suggested the structure 4(15),7(11)-eudesmadien-8-one, which was confirmed by comparison of its <sup>1</sup>H NMR data with literature values [3, 4]. 4(15),7(11)-Eudesmadien-8-one has been previously isolated in both enantiomeric forms, the (+)-form from Actractylodes japonica [4] and the (-)-form from Asarum caulescens [5] and Peteravenia schultzii [3]. The magnitude and sign of the specific rotation of ventricosin A indicate that it belongs to the enantio series [4] and therefore has structure 1.

Ventricosin B,  $C_{15}H_{26}O$ , a crystalline compound, mp  $64-65^{\circ}$ ,  $[\alpha]_D - 36.1^{\circ}$  (c 1.16 in CHCl<sub>3</sub>) (lit. [6] mp  $66^{\circ}$ ,  $[\alpha]_D - 34.5^{\circ}$ ), has two tertiary carbons bearing oxygen ( $\delta_C$  78.6 and 81.4) and four tertiary methyl groups ( $\delta_H$  1.26, 1.07, 0.98 and 0.85;  $\delta_C$  17.9, 22.8, 25.8 and 30.8) which together with one fully substituted carbon ( $\delta_C$  34.2), two methines ( $\delta_C$  43.1 and 58.4) and six methylenes ( $\delta_C$  21.3, 22.3, 27.5, 40.7, 41.1 and 43.4) constitute a tricyclic system. The identity of ventricosin B with *ent*-maalioxide (3), previously isolated [6] from *Plagiochila acanthophylla* subspecies *japonica*, was suggested by the above data and

was readily confirmed by comparison of its physical and spectroscopic properties with literature values [6].

## **EXPERIMENTAL**

The liverwort *L. ventricosa* was collected in the Harz Mountains, G.D.R., in September 1981. Extraction of the airdried liverwort with Et<sub>2</sub>O afforded a crude extract (38 g), which was subjected to CC on Grade III alumina followed by prep. TLC to give two compounds: ent-4(15),7(11)-eudesmadien-8-one (1) (ventricosin A), which was obtained as an oil,  $\delta_{\rm H}$  4.95 and 4.60 (each br s, 2H-15), 2.24 (s, 2H-9), 1.96 and 1.78 (each br s, vinyl methyls);  $\delta_{\rm C}$  37.0 (C-1), 23.4 (C-2), 41.4 (C-3), 149.1 (C-4), 47.1 (C-5), 29.3 (C-6), 131.5 (C-7), 201.8 (C-8), 57.6 (C-9), 38.0 (C-10), 144.1 (C-11), 22.2 and 23.2 (C-12 and C-13), 17.3 (C-14) and 107.0 (C-15) and ent-maalioxide (3) (ventricosin B), which was sublimed and had mp 64–65°.

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