

**(+)-Ovalifoliene and (–)-Hanegokedial, Two Novel Sesquiterpenoids of the  
ent-2,3-seco-Alloaromadendrane Skeleton from the Liverwort  
*Plagiochila semidecurrans***

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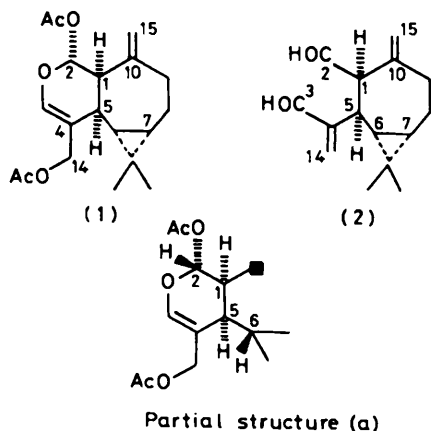
**Summary** Two novel sesquiterpenoids have been isolated from the liverwort *Plagiochila semidecurrans*, and their structures and absolute configurations have been shown to be **(1)** and **(2)**, ent-2,3-seco-alloaromadendrane derivatives.

DURING our studies on terpenoids of the liverworts (*Hepaticae*),<sup>1</sup> two novel sesquiterpenoids (+)-ovalifoliene (**1**) and

(–)-hanegokedial (**2**)† were isolated from a leafy liverwort, *Plagiochila semidecurrans* Lehm. and Lindenb. together with three known enantiomeric sesquiterpenoids, (–)-bicyclogermacrene,<sup>2</sup> (–)-β-pompene (synonym gymnomitrene),<sup>3,4</sup> and (–)-cuparene.<sup>5</sup> The novel metabolites were isolated from a methanol extract of the plant by a combination of column chromatography and preparative t.l.c., and their structures and absolute configurations were

† These compounds were also isolated from another liverwort *P. ovalifolia* of the same genus, and most recently the isolation of some derivatives has been reported by Asakawa *et al.* (see Y. Asakawa, M. Toyota, and T. Takemoto, *Tetrahedron Letters*, 1978, 1553; *Phytochemistry*, 1978, **17**, 1794).

determined to be *ent*-2,3-*seco*-2,3-epoxy-2 $\beta$ ,14-diacetoxy-alloaromadendra-3,10(15)-diene (1) and *ent*-2,3-*seco*-alloaromadendra-4(14), 10(15)-diene-2,3-dial (2) by the following chemical and spectral evidence.

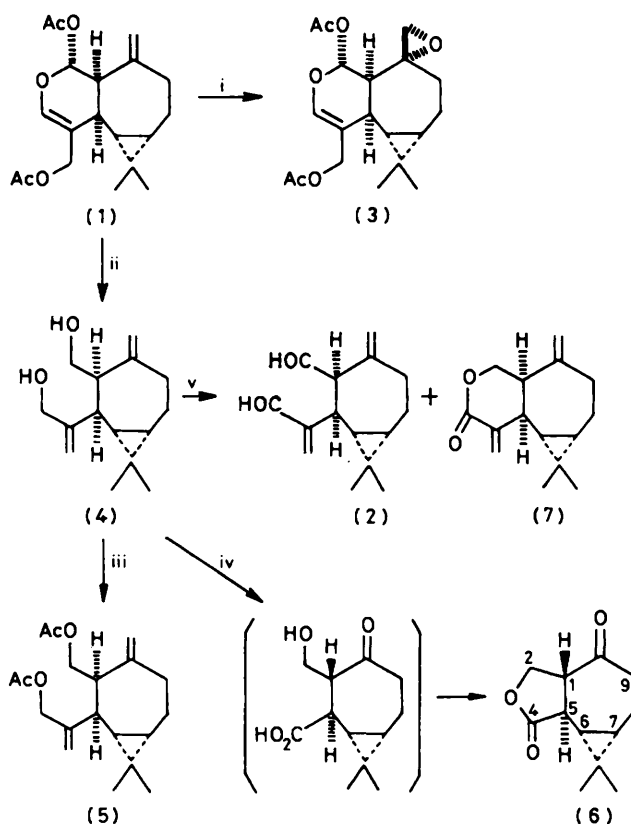


(+)-Ovalifoliene (1),  $C_{19}H_{26}O_5$ ,  $[\alpha]_D^{25} + 24.5^\circ$ , was characterized by its spectroscopic properties $\ddagger$  as a tricyclic sesquiterpenoid containing a cyclopropane ring [ $\delta$  0.4–1.0 (2H)], an acetyl hemiacetal [ $\nu$  1760  $cm^{-1}$ ;  $\delta$  2.08 (3H, s) and 6.53 (1H, d,  $J$  10.0 Hz)], a  $\beta$ -substituted vinyl ether [ $\nu$  1670  $cm^{-1}$ ;  $\delta$  6.29 (1H, s)], a primary acetoxy [ $\nu$  1740  $cm^{-1}$ ;  $\delta$  4.35 and 4.58 (each 1H, d,  $J$  12.5 Hz), 2.06 (3H, s)], an exocyclic methylene [ $\nu$  895  $cm^{-1}$ ;  $\delta$  4.78 (2H, s)], and geminal dimethyl groups [ $\nu$  1380, 1370, and 1360  $cm^{-1}$ ;  $\delta$  1.02 and 1.08 (each 3H, s)].

On oxidation with  $m\text{-ClC}_6\text{H}_4\text{CO}_2\text{H}$ , (1) gave the mono-epoxide (3),  $C_{19}H_{26}O_6$ , m.p. 82–84  $^\circ\text{C}$ , in which the oxirane ring [ $\delta$  2.62 and 2.77 (each 1H, d,  $J$  5.0 Hz)] was introduced *cis* to the tertiary acetoxy group on C-2.<sup>6</sup> Compound (1) was also treated with  $\text{LiAlH}_4$  to give the bicyclic diol (4),  $C_{15}H_{24}O_2$ , m.p. 87.5–88.5  $^\circ\text{C}$ , which showed the presence of two primary hydroxy groups [ $\nu$  3600 and 3400  $cm^{-1}$ ;  $\delta$  3.76 and 3.87 (each 1H, s), 4.12 (2H, s)]. The diol (4) was then converted into the diacetate (5),  $C_{19}H_{26}O_4$  [ $\nu$  1735  $cm^{-1}$ ;  $\delta$  4.16 (1H, dd,  $J$  10.0 and 5.0 Hz), 4.32 (1H, d,  $J$  10.0 Hz), and 4.62 (2H, s)] (see Scheme).

The formation of such a bicyclic compound suggested that (1) contained the partial structure (a) whose relative configuration was revealed by  $^1\text{H}$  n.m.r. spectroscopy; the ring juncture was shown to be *cis* by the 1-H signal ( $\delta$  2.81) which appeared as a doublet of doublets ( $J_{1,2}$  10.0 and  $J_{1,5}$  4.0 Hz), coupling both with the other ring junction methine group (5-H) ( $\delta$  2.18, 1H, dd,  $J_{5,6}$  6.0 and  $J_{5,1}$  4.0 Hz) and with 2-H ( $\delta$  6.53, 1H, d,  $J_{2,1}$  10.0 Hz), the acetoxy group being attached to C-2. Since another coupling constant of the 5-H group was observed as  $J_{5,6}$  6.0 Hz, it was certain that the 6-H methine was *trans* to that of the 5-H, *i.e.* C-5 was connected to the cyclopropane ring.

Compound (4) was oxidized with  $\text{OsO}_4\text{-NaIO}_4$  to produce the trino- $\gamma$ -lactone (6),  $C_{12}H_{16}O_3$ , m.p. 134–135.5  $^\circ\text{C}$  ( $\nu$  1775 and 1720  $cm^{-1}$ ), containing a seven-membered ketone. The  $^1\text{H}$  n.m.r. spectrum exhibited characteristic



SCHEME. i,  $m\text{-ClC}_6\text{H}_4\text{CO}_2\text{H-CH}_2\text{Cl}_2$ ; ii,  $\text{LiAlH}_4\text{-Et}_2\text{O}$ ; iii,  $\text{Ac}_2\text{O-pyridine}$ ; iv,  $\text{OsO}_4\text{-NaIO}_4$  in  $\text{H}_2\text{O-tetrahydrofuran}$  (1:1); v,  $\text{CrO}_3\text{-pyridine}$ .

signals for 1-H [ $\delta$  3.73 (1H, ddd,  $J_{1,5}$  11.0,  $J_{1,2a}$  7.5, and  $J_{1,2b}$  4.5 Hz)] and 5-H [ $\delta$  2.87 (1H, dd,  $J_{5,1}$  11.0 and  $J_{5,6}$  7.0 Hz)] together with 2-H<sub>2</sub> [ $\delta$  4.23 (1H, dd,  $J$  9.0 and 7.5 Hz)] and 4-77 (1H, dd,  $J$  9.0 and 4.5 Hz)] and 9-H<sub>2</sub> [ $\delta$  2.65 (2H, dd,  $J$  9.5 and 4.0 Hz)] whose coupling constants were also confirmed by decoupling experiments. These results indicate that inversion at C-1 occurs during the oxidation which converts the ring juncture into a *trans*-fused form. In benzene solution the two methine protons on the cyclopropane ring appeared clearly at  $\delta$  0.73 (1H, t,  $J$  7.0 Hz) and 0.35 (1H, ddd,  $J$  11.5, 7.0, and 4.5 Hz), assigned as the 6-H and 7-H signals respectively, and the cyclopropane ring substituted with geminal dimethyl groups was determined to have a *cis*-configuration.

By application of the octant and lactone rules to this oxo-lactone ( $[\theta]_{298} + 2500$ ,  $[\theta]_{392} + 2470$ ,  $[\theta]_{213} - 7270$ ),<sup>7,9</sup> the absolute configuration was shown to be (6). Therefore, the absolute configuration of (+)-ovalifoliene was shown to have the enantiomeric form (1), having a cyclopropane ring with  $\alpha$ -configuration; the configuration is consistent with the c.d. spectra of the original hemiacetal (1) ( $[\theta]_{209} + 13400$ ) and the epoxide (3) ( $[\theta]_{207} + 19100$ ).<sup>9</sup>

The spectral data for (-)-hanegokedial (2),  $C_{15}H_{20}O_2$ , m.p. 66.5–67.5  $^\circ\text{C}$ ,  $[\alpha]_D - 10.4^\circ$ , showed that it was a bicyclic sesquiterpene dial consisting of an aldehyde

$\ddagger$  All new compounds (1)–(7) gave spectral data in good agreement with the assigned structures. Optical rotations and i.r. spectra were measured in  $\text{CHCl}_3$  solutions and  $^1\text{H}$  n.m.r. spectra in  $\text{CDCl}_3$  solutions, unless otherwise stated.

conjugated with an exocyclic methylene group [ $\nu$  2720, 1690, and 950  $\text{cm}^{-1}$ ;  $\delta$  6.20 (1H, d,  $J$  1.0 Hz), 6.53 (1H, d,  $J$  1.5 Hz), and 9.62 (1H, s)] and an isolated aldehyde [ $\nu$  2720 and 1720  $\text{cm}^{-1}$ ;  $\delta$  9.77 (1H, d,  $J$  1.5 Hz)] along with another exocyclic methylene group [ $\nu$  906  $\text{cm}^{-1}$ ;  $\delta$  4.87 (1H, d,  $J$  2.0 Hz) and 4.95 (1H, br s)] and geminal dimethyl groups [ $\nu$  1375 and 1360  $\text{cm}^{-1}$ ;  $\delta$  0.90 and 1.10 (each 3H, s)]. From the similarity of these spectra to those of (4) and (5) it was deduced the compound might be an oxidised form of the diol (4). In fact the spectral and physical properties were identical to those of the dialdehyde  $\text{C}_{18}\text{H}_{20}\text{O}_2$ , m.p. 66–67.5 °C,  $[\alpha]_D -9.5^\circ$ , obtained by oxidation of (4) with  $\text{CrO}_3$ . The  $\alpha$ -methylene- $\delta$ -lactone (7),  $\text{C}_{18}\text{H}_{20}\text{O}_2$ , m.p. 51–52 °C,  $[\alpha]_D +15.8^\circ$  [ $\nu$  1710  $\text{cm}^{-1}$ ;  $\delta$  5.39 (1H, br s), 6.22 (1H, d,  $J$  1.5 Hz)] was also formed in this oxidation (see Scheme). Accordingly, the structure of (–)-hanego-

kedial was shown to be *ent*-2,3-*seco*-alloaromadendra-4(14), 10(15)-diene-2,3-dial (2).

These unique metabolites belong to the enantiomeric sesquiterpenoids, and may be biosynthesized from the *ent*-alloaromadendrane skeleton *via* oxidative cleavage of the C(2)–C(3) bond followed by formation of a cyclic hemiacetal.<sup>10</sup> This is confirmed by the isolation of (–)-taylori-one, *ent*-1,10-*seco*-aromadendra-1(5),4(14)-dien-10-one, from another liverwort.<sup>11</sup> Compound (1) inhibits the growth of roots of rice at a concentration of 50 p.p.m.

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