

## Structures of *ent*-2,3-Secoalloaromadendrane Sesquiterpenoids, which have Plant-growth-inhibitory Activity, from *Plagiochila semidecurrens* (Liverwort)

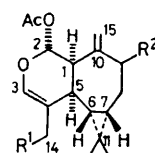
By Akihiko Matsuo,\* Kazunori Atsumi, and Mitsuru Nakayama, Department of Chemistry, Faculty of Science, Hiroshima University, Naka-ku, Hiroshima 730, Japan  
Shûichi Hayashi, Department of Chemistry, Faculty of Science, Okayama University of Science, Okayama 700, Japan

Nine acetyl hemiacetals, (+)-ovalifoliene (1), (+)-ovalifolienal (2), (+)-ovalifolienalone (3), deacetoxyovalifoliene (6), (+)-ovalimethoxy I (7), (+)-ovalimethoxy II (8), (+)-plagiochiline A (9), (+)-plagiochiline B (10), and (+)-9 $\alpha$ -acetoxyovalifoliene (11), which possess the *ent*-2,3-secoalloaromadendrane skeleton and display plant-growth-inhibitory properties, and their bicyclic precursors, (–)-hanegokedial (4) and (+)-hanegoketrial (5), have been isolated from the methanol extract of *Plagiochila semidecurrens* together with the related enantiomeric sesquiterpenoids (12)–(15a). The structures and absolute configurations have been determined on the basis of chemical and spectroscopic evidence and are coincident with the result obtained by X-ray analysis of (+)-ovalifolienalone (3). The biological activity is also described.

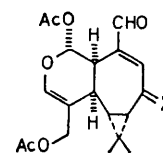
LIVERWORTS (*Hepaticae*) contain several characteristic oil bodies in each cell of the gametophytes which grow from the spores and form the usual plant bodies. They elaborate mono-, sesqui-, and di-terpenoids as well as esters of fatty acids and aromatic acids in high yield. Previously, we reported that almost all the liverwort sesquiterpenoids are enantiomers or similar to the enantiomers of sesquiterpenoids of higher plants,<sup>1–9</sup> a result which has recently been confirmed by other workers.<sup>10,11</sup> The liverworts are, therefore, akin to the fungi and marine invertebrates with respect to the metabolism of sesquiterpenoids, *i.e.* an enzymatic cyclization mechanism occurs in sesquiterpenoid biosynthesis.

In the course of our investigations on terpenoids of the liverworts, we sometimes encountered a kind of allelopathy between the liverworts and some vascular plants and we tested the methanol extracts of several liverworts for plant-growth-inhibitory activity on rice seedlings. The methanol extract of the leafy liverwort, *Plagiochila semidecurrens* Lehm. and Lindenb., which belongs to the Plagiochilaceae of the Jungermanniales, depressed the growth of the leaves and roots of rice seedlings remarkably in biological tests. The present work on the methanol extract was undertaken in order to elucidate the structures of the plant-growth inhibitors. Eight biologically active acetyl hemiacetals, (+)-ovalifoliene (1), (+)-ovalifolienal (2), (+)-ovalifolienalone (3), (+)-ovalimethoxy I (7), (+)-ovalimethoxy II (8), (+)-plagiochiline A (9), (+)-plagiochiline B (10), and (+)-9 $\alpha$ -acetoxyovalifoliene (11), as well as their possible precursors, (–)-hanegokedial (4), (+)-hanegoketrial (5), and deacetoxyovalifoliene (6), were isolated from the extract by a combination of column chromatography and preparative layer chromatography (p.l.c.).<sup>12</sup>† Four enantiomeric sesquiterpenoids, (–)-bicyclogermacrene

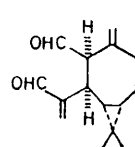
(12),<sup>19</sup> (–)-gymnomitrene ( $\beta$ -pompenne) (13),<sup>20,21</sup> (–)-cuparene (14),<sup>22</sup> and *ent*-3 $\beta$ -acetoxybicyclogermacrene (15a),<sup>16</sup> the last of which was obtained as an alcohol in the pure state, which enabled identification of the structure,<sup>23</sup> were also isolated. The structures and absolute configurations of these novel sesquiterpenoids have been



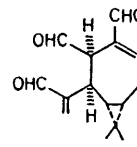
- (1)  $R^1 = \text{OAc}$ ,  $R^2 = \text{H}$   
(6)  $R^1 = R^2 = \text{H}$   
(11)  $R^1 = \text{OAc}$ ,  $R^2 = \alpha\text{-OAc}$



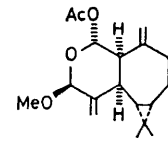
- (2)  $X = \text{H}_2$   
(3)  $X = \text{O}$



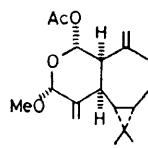
(4)



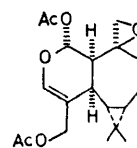
(5)



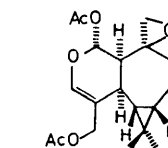
(7)



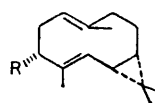
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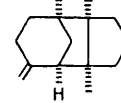
(9)



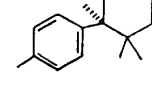
(10)



- (12)  $R = \text{H}$   
(15a)  $R = \text{OAc}$   
(15b)  $R = \text{OH}$

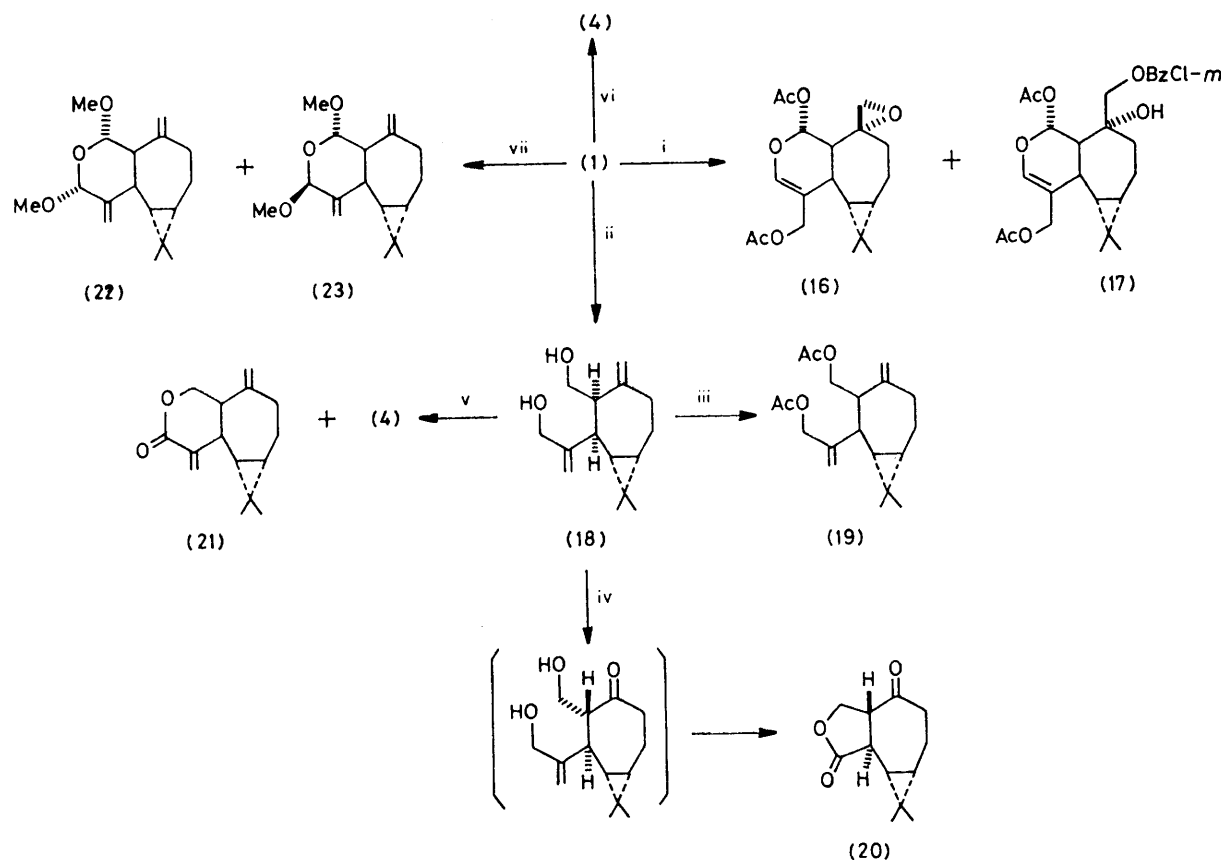


(13)



(14)

† Most of these compounds were also isolated from the other species, *P. ovalifolia* Mitt. in the same genus *Plagiochila*. Recently, Asakawa *et al.* reported the structural assignment of some of these sesquiterpenoids and the chemosystematics of *Plagiochila* species on the basis of their occurrence (see refs. 13–18).



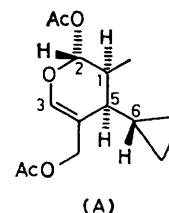
SCHEME 1 Reagents: i,  $m\text{-ClC}_6\text{H}_4\text{CO}_3\text{H}$ ; ii,  $\text{LiAlH}_4$ ; iii,  $\text{Ac}_2\text{O}$ ; iv,  $\text{OsO}_4\text{-NaIO}_4$ ; v,  $\text{CrO}_3\text{-C}_5\text{H}_5\text{N}$ ; vi,  $\text{HCl}$ ; vii,  $\text{MeOH-C}_5\text{H}_5\text{N-}p\text{-MeC}_6\text{H}_4\text{SO}_3\text{H}$

shown to be enantiomeric forms of a novel 2,3-seco-alloaromadendrane skeleton. In this paper we describe in detail the chemical and spectral evidence for the proposed structures and also the biological activity of these compounds.

**Structure of (+)-Ovalifoliene (1).**—(+)-Ovalifoliene (1),  $\text{C}_{19}\text{H}_{26}\text{O}_5$ , has been isolated from, and found to be a major component of, the methanol extract of the liverwort *P. semidecurrans*.<sup>24</sup> It was shown by spectroscopy to have a tricyclic sesquiterpenoid skeleton which contains an acetyl hemiacetal group [ $\nu$  1 760  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  2.08 (3 H, s) and 6.53 (1 H, d,  $J$  10.0 Hz)], a  $\beta$ -substituted vinyl ether group [ $\nu$  1 670  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  6.29 (1 H, s)], a primary acetoxy-group [ $\nu$  1 740  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  2.06 (3 H, s) and 4.35 and 4.58 (each 1 H, d,  $J$  12.5 Hz)], an exocyclic methylene group [ $\nu$  895  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  4.78 (2 H, s)], a cyclopropane ring [ $\delta_{\text{H}}$  0.3—1.0 (2 H, complex)], and one geminal dimethyl group [ $\nu$  1 380, 1 370, and 1 360  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  1.02 and 1.08 (each 3 H, s)]. (+)-Ovalifoliene (1) was converted into the monoepoxide (16),  $\text{C}_{19}\text{H}_{26}\text{O}_6$ , and the hydroxy-benzoate (17),  $\text{C}_{26}\text{H}_{31}\text{ClO}_8$ , by oxidation with  $m\text{-ClC}_6\text{H}_4\text{CO}_3\text{H}$  (Scheme 1). The oxiran ring [ $\delta_{\text{H}}$  2.62 and 2.77 (each 1 H, d,  $J$  5.0 Hz)] was introduced with *cis*-orientation to the tertiary acetoxy-group on C-2 by attack of the peracid at the less hindered site<sup>25</sup> and it has the reverse configuration to that of the natural product, (+)-plagiachiline A (9).<sup>13,17,26</sup> By treatment with

lithium aluminium hydride, compound (1) also gave the bicyclic diol (18),  $\text{C}_{15}\text{H}_{24}\text{O}_2$ , which contains two primary hydroxy-groups [ $\nu$  3 600 and 3 400  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  3.76 and 3.87 (each 1 H, br s) and 4.12 (2 H, s)], two exocyclic methylene groups, two tertiary methyl groups, and a cyclopropane ring, the last two of which occurred in the original molecule. The existence of two hydroxy-groups was confirmed by conversion of compound (18) into the diacetate (19),  $\text{C}_{19}\text{H}_{28}\text{O}_4$  [ $\nu$  1 735  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  1.98 and 2.07 (each 3 H, s), 4.0—4.5 (2 H, complex), and 4.62 (2 H, br s)].

The formation of such a bicyclic diol suggests that compound (1) contains the partial structure (A) with an



acetyl hemiacetal ring whose relative configuration has been revealed by  $^1\text{H}$  n.m.r. spectroscopy; the ring junction is shown to be *cis* by the 1-H signal ( $\delta_{\text{H}}$  2.81) which appears as a doublet of doublets [ $J_{1,2}$  10.0 and  $J_{1,5}$  4.0 Hz] and is coupled with the other ring-junction hydrogen

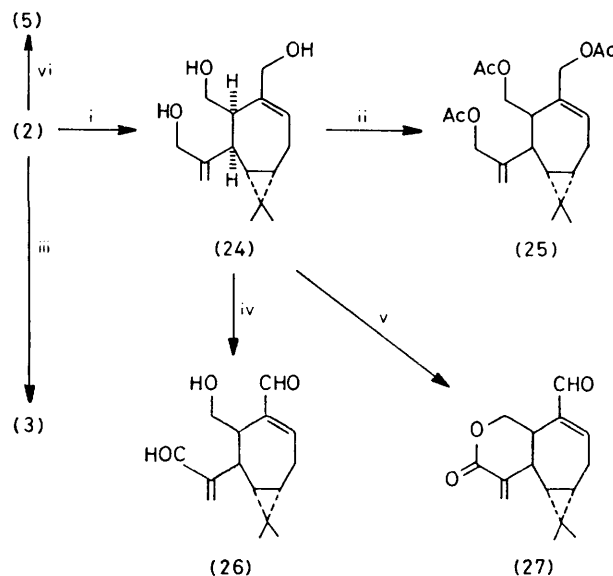
5-H [ $\delta_{\text{H}}$  2.18 (1 H, dd,  $J_{5,6}$  6.0 and  $J_{5,1}$  4.0 Hz)], and with the hydrogen atom, 2-H [ $\delta_{\text{H}}$  6.53 (1 H, d,  $J_{2,1}$  10.0 Hz)], associated with the acetoxy-group. Since another coupling constant of 5-H is observed as  $J_{5,6}$  6.0 Hz, 6-H is *trans* to 5-H, *i.e.* C-5 is bonded to C-6 of the cyclopropane ring. When compound (18) was oxidized with  $\text{OsO}_4\text{-NaIO}_4$  (Scheme 1),<sup>27</sup> it produced the trisnor- $\gamma$ -lactone (20),  $\text{C}_{12}\text{H}_{16}\text{O}_3$  [ $\nu$  1775 and 1720  $\text{cm}^{-1}$ ], which contains a seven-membered ketone. The structure was elucidated on the basis of the  $^1\text{H}$  n.m.r. spectrum which shows characteristic signals for 1-H [ $\delta_{\text{H}}$  3.73 (1 H, ddd,  $J_{1,5}$  11.0,  $J_{1,2a}$  7.5, and  $J_{1,2b}$  4.5 Hz)] and 5-H [ $\delta_{\text{H}}$  2.87 (1 H, dd,  $J_{5,1}$  11.0 and  $J_{5,6}$  7.0 Hz)] together with 2-H<sub>2</sub> [ $\delta_{\text{H}}$  4.23 (1 H, dd,  $J$  9.0 and 7.5 Hz) and 4.77 (1 H, dd,  $J$  9.0 and 4.5 Hz)] and 9-H<sub>2</sub> [ $\delta_{\text{H}}$  2.65 (2 H, dd,  $J$  9.5 and 4.5 Hz)] whose couplings were confirmed by decoupling experiments. These results indicate that the inversion at C-1 occurs during the oxidation which converts the ring junction into a *trans*-fused form. In  $[\text{C}_6\text{H}_6]$ benzene solution the two protons on the cyclopropane ring, furthermore, appear clearly at  $\delta_{\text{H}}$  0.73 (1 H, t,  $J$  7.0 Hz) and 0.37 (1 H, 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 a geminal dimethyl group, was shown to have the *cis*-configuration.<sup>28</sup> By application of the octant and lactone rules to this oxo-lactone,<sup>29,30</sup> the absolute configuration was elucidated as structure (20).

Accordingly, the structure and absolute configuration of (+)-ovalifoliene is *ent*-2 $\beta$ ,14-diacetoxy-2,3-epoxy-2,3-secoalloaromadendra-3,10(15)-diene (1) or the enantiomeric form with the cyclopropane ring in the  $\alpha$ -configuration. The absolute configuration is consistent with the c.d. spectra of the original hemiacetal (1) and the epoxide derivative (16).<sup>31</sup>

**Structures of (+)-Ovalifolienal (2) and (+)-Ovalifolienalone (3).**—(+)-Ovalifolienal (2) and (+)-ovalifolienalone (3)<sup>32</sup> were isolated as oily and crystalline substances, respectively. The elemental compositions show that two hydrogen atoms of ovalifoliene,  $\text{C}_{19}\text{H}_{26}\text{O}_5$ , exchanged with one oxygen atom to form the ovalifolienal,  $\text{C}_{19}\text{H}_{24}\text{O}_6$ , and then a further two hydrogen atoms of ovalifolienal exchanged with one oxygen atom to create ovalifolienalone,  $\text{C}_{19}\text{H}_{22}\text{O}_7$ .

The spectroscopic properties show that the ovalifolienal (2) contains an  $\alpha,\beta$ -disubstituted  $\alpha,\beta$ -unsaturated aldehyde moiety [ $\lambda$  215 and 227 nm (each  $\epsilon$  3410);  $\nu$  1700 and 1645  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  6.79 (1 H, dd,  $J$  8.0 and 4.0 Hz) and 9.33 (1 H, s)] instead of the exocyclic methylene group of (+)-ovalifoliene (1), and that the ovalifolienalone (3) has an additional ketone group [ $\delta_{\text{C}}$  198.0, s] as well as the conjugated aldehydes [ $\lambda$  204 and 233 nm ( $\epsilon$  22400 and 6880);  $\nu$  1705 and 1640  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  6.62 (1 H, s) and 9.57 (1 H, s)]. Furthermore, the spectral data of the acetyl hemiacetal and cyclopropane units in compounds (2) and (3) are similar to those of the ovalifoliene (1). The presence of the acetyl hemiacetal ring in compounds (2) and (3) was confirmed by the transformation of the ovalifolienal (2), using  $\text{LiAlH}_4$  (Scheme 2), into the bicyclic triol (24),  $\text{C}_{15}\text{H}_{24}\text{O}_3$  [ $\nu$  3300  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  4.02 (2 H, br s), 4.15

(2 H, s), and 5.12 and 5.23 (each 1 H, br s)] which gave, on acetylation (Scheme 2) the triacetate (25),  $\text{C}_{21}\text{H}_{30}\text{O}_6$  [ $\nu$  1730 and 1715  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  1.99 (3 H, s), 2.08 (6 H, s), and 4.43, 4.62, and 5.17 (each 2 H, br s)]. The  $^1\text{H}$  n.m.r. spectrum of the ovalifolienalone (3) shows chemical shifts and coupling constants for all the signals in good agreement with structure (3) which contains the same novel carbon skeleton as compound (1). The structure of the ovalifolienal (2) is shown to be 7-deoxyovalifolienalone by comparison of the spectra: the 9-H signals



SCHEME 2 Reagents: i,  $\text{LiAlH}_4$ ; ii,  $\text{Ac}_2\text{O}$ ; iii,  $\text{CrO}_3\text{-C}_5\text{H}_5\text{N-CH}_2\text{Cl}_2$ ; iv,  $\text{CrO}_3\text{-C}_5\text{H}_5\text{N}$ , 6 h; v,  $\text{CrO}_3\text{-C}_5\text{H}_5\text{N}$ , 22 h; vi,  $\text{HCl}$

of compounds (2) and (3) appear, respectively, as a doublet of doublets [ $\delta_{\text{H}}$  6.79 ( $J$  8.0 and 4.0 Hz)] and a singlet [ $\delta_{\text{H}}$  6.62] in the  $^1\text{H}$  n.m.r. spectra, and the C-8 signals appear at  $\delta_{\text{C}}$  39.8 (t) and 198.8 (s) in the  $^{13}\text{C}$  n.m.r. spectra (assignments of all the carbon atoms have been reported in a previous paper<sup>26</sup>). In order to correlate the structure with that of (+)-ovalifolienalone (3), compound (2) was submitted to Collins oxidation and afforded the ketone (3).<sup>33</sup>

Finally, on the basis of analysis of the c.d. spectrum of the ketone (3),<sup>34</sup> the absolute configuration of (+)-ovalifolienalone is *ent*-2 $\beta$ ,14-diacetoxy-2,3-epoxy-15-oxo-2,3-secoalloaromadendra-3,9-dien-8-one (3) and that of (+)-ovalifolienal is *ent*-2 $\beta$ ,14-diacetoxy-2,3-epoxy-15-oxo-2,3-secoalloaromadendra-3,9-diene (2). The X-ray analysis of (+)-ovalifolienalone (3) supported this structure<sup>32</sup> and a full paper on the analysis will be written.

**Structures of (−)-Hanegokedial (4) and (+)-Hanegoketrial (5).**—Two sesquiterpene aldehydes, (−)-hanegokedial (4)<sup>24</sup> and (+)-hanegoketrial (5), were isolated from the methanol extract and were unstable, especially compound (5). The spectral data of compound (4),  $\text{C}_{15}\text{H}_{20}\text{O}_2$ , show that it is a bicyclic sesquiterpene dialdehyde which comprises an aldehyde conjugated with an

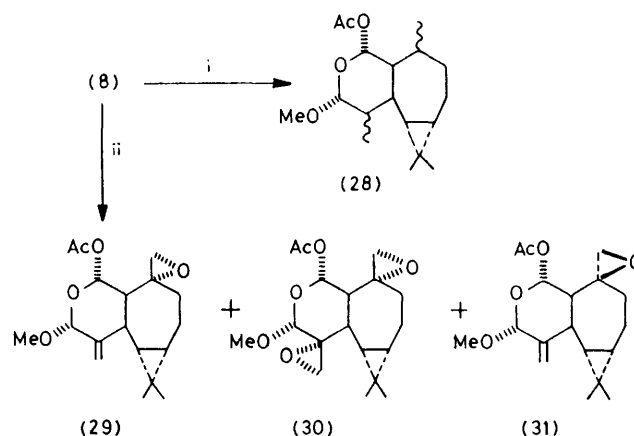
exocyclic methylene group [ $\nu$  2 720, 1 690, and 950  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  6.20 (1 H, d,  $J$  1.0 Hz), 6.54 (1 H, d,  $J$  1.5 Hz), and 9.62 (1 H, s)] and an isolated aldehyde group [ $\nu$  2 720 and 1 720  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  9.77 (1 H, d,  $J$  1.5 Hz)] along with another exocyclic methylene group [ $\nu$  906  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  4.87 (1 H, d,  $J$  2.0 Hz) and 4.95 (1 H, br s)] and a geminal dimethyl group [ $\nu$  1 375 and 1 360  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  0.90 and 1.10 (each 3 H, s)]. From the similarity of these spectra with those of compounds (18) and (19) it may be deduced that compound (4) might be an oxidized form of the diol (18). In fact, the spectral and physical properties are identical with those of the dialdehyde (4),  $\text{C}_{15}\text{H}_{20}\text{O}_2$ , obtained by the Sarett oxidation of compound (18).<sup>35</sup> The  $\alpha$ -methylene- $\delta$ -lactone (21),  $\text{C}_{15}\text{H}_{20}\text{O}_2$ , [ $\nu$  1 712  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  5.39 (1 H, br s) and 6.22 (1 H, d,  $J$  1.5 Hz)] was also formed in this oxidation (Scheme 1). The structure of (–)-hanegokedial is, therefore, *ent*-2,3-secoalloaromadendra-4(14),10(15)-diene-2,3-dione (4).

(+)-Hanegoketrial (5),  $\text{C}_{15}\text{H}_{18}\text{O}_3$ , is also bicyclic and contains an additional aldehyde group conjugated with a trisubstituted double bond [ $\nu$  1 685  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  7.04 (1 H, dd,  $J$  8.0 and 3.0 Hz) and 9.43 (1 H, s)] together with the two aldehyde groups [ $\delta_{\text{H}}$  9.63 (1 H, d,  $J$  1.0 Hz) and 9.72 (1 H, s)], also present in compound (4). The spectral evidence suggests, furthermore, structure (5) as the hanegoketrial molecule, which corresponds with a dialdehyde derivative of ovalifolienal (2). For confirmation of the structure the following chemical reactions were carried out. Compound (24), described above, was oxidized as for the oxidation of the diol (18) and gave the hydroxy-dialdehyde (26),  $\text{C}_{15}\text{H}_{20}\text{O}_3$ , only (Scheme 2). Despite the use of a prolonged reaction time, the trialdehyde was not obtained; the  $\delta$ -lactone (27),  $\text{C}_{15}\text{H}_{18}\text{O}_3$ , was obtained however since any trialdehyde which formed was probably decomposed by acidification as the solvent, pyridine, was removed from the reaction mixture. The formation of the trialdehyde was, however, recognized by t.l.c. by comparison with authentic hanegoketrial.

When compounds (1) and (2) were treated with acid, the dialdehyde and the trialdehyde were produced, respectively. The spectral properties and optical rotations of these products coincided with those of (–)-hanegokedial (4) and (+)-hanegoketrial (5). Since they were easily formed from compounds (1) and (2) by acid treatment, it is not certain whether both the compounds are natural products or artifacts. However, consideration of the biogenesis of the acetyl hemiacetals (1) and (2) from *ent*-alloaromadendrane derivatives *via* oxidative cleavage of the C(2)–(3) bond, indicates that the compounds may be unstable precursors of the hemiacetals (1) and (2).

**Other Acetyl Hemiacetals.**—We obtained a monoacetoxy-sesquiterpenoid, deacetoxyovalifolien (plagiochiline H) (6),  $\text{C}_{17}\text{H}_{24}\text{O}_3$ ,<sup>16</sup> as a minor constituent. The spectral data show the structure to be 14-deacetoxy-ovalifolien, with an acetyl hemiacetal group, an exocyclic methylene group, and a cyclopropane ring substituted by a geminal dimethyl group, which might be a precursor of (+)-ovalifolien (1). Two methoxy-com-

pounds, (+)-ovalimethoxy I (7),  $\text{C}_{18}\text{H}_{26}\text{O}_4$ , and (+)-ovalimethoxy II (methoxyplagiochiline C) (8),  $\text{C}_{18}\text{H}_{26}\text{O}_4$ ,<sup>16</sup> were also isolated from the methanol extract, together with three acetyl hemiacetals, (+)-plagiochiline A (9), (+)-plagiochiline B (10),<sup>14,17</sup> and (+)-9 $\alpha$ -acetoxyovalifolien (11), described in a previous paper.<sup>26</sup> Compounds (7) and (8) are tricyclic compounds which contain a methoxy-group, an acetoxy-group, two exocyclic methylene groups, and a geminal dimethyl group, as well as acetyl hemiacetal-, cyclopropane-, and cycloheptane-rings. They are epimers with respect to the methoxy-group at C-3 because the spectral data are similar, except for the signals due to the methoxy-groups. The configuration of the methoxy-group is tentatively assigned as  $\alpha$  for the major component (8) and as  $\beta$  for the minor component (7) on the basis of chemical shifts of the C-3 protons [ $\delta_{\text{H}}$  5.27 (1 H, s) for (7);  $\delta_{\text{H}}$  5.22 (1 H, s) for (8)] and of the exocyclic C-14 protons [ $\delta_{\text{H}}$  4.93 and 5.10 (each 1 H, s) for (7);  $\delta_{\text{H}}$  5.02 (2 H, s) for (8)]. Hydrogenation



SCHEME 3 Reagents: i,  $\text{H}_2\text{O}$ – $\text{PtO}_2$ ; ii, *m*- $\text{ClC}_6\text{H}_4\text{CO}_3\text{H}$

of (+)-ovalimethoxy II (8) gave compound (28) and epoxidation of compound (8) gave the three products (29)–(31) (Scheme 3). Though (+)-ovalifolien (1), the major component of the liverwort, was treated with methanol under the same conditions as for the extraction process, ovalimethoxy I (7) and ovalimethoxy II (8) were not obtained at all, under either acidic or basic conditions. Two dimethoxy-compounds, (22) and (23), whose structures have been tentatively assigned, were only obtained by treatment of compound (1) with methanol in the presence of pyridinium toluene-*p*-sulphonate.<sup>36</sup>

**The Biological Activity.**—The plant-growth-inhibitory activity of the novel acetyl hemiacetals (1), (2), and (3), and the methoxy-compounds (7) and (8), was tested on rice seedlings. Compounds (1), (2), and (3) inhibit the growth of leaves and roots in concentrations of 25, 50, and 500 p.p.m., respectively. The methoxy-compounds (7) and (8) also inhibit at concentrations of 25 and 100 p.p.m., respectively. (+)-Ovalifolien (1), (+)-ovalifolienal (2), and (+)-ovalimethoxy I (7) are very strong growth inhibitors, and their concentrations for 50%



growth inhibition ( $I_{50}$ ) are *ca.* 7, 15, and 13 p.p.m., respectively. The details of the growth-inhibitory activity and the relationship between activity and chemical structure are described in a separate paper.\* These compounds are a new variety of plant growth inhibitors<sup>37</sup> and they may act as allomones in ecological systems.<sup>38</sup>

# EXPERIMENTAL

Melting points are uncorrected. For column chromatography Merck Kieselgel 60 was used and Merck Keisegel 60 PF<sub>254</sub> was used for t.l.c. and p.l.c. Analytical plates were visualized under u.v. light or were sprayed with 10% sulphuric acid in ethanol and then heated at 100 °C for 10 min. I.r. spectra were recorded on a grating spectrometer and optical rotations were taken on an automatic polarimeter in chloroform solution, unless otherwise stated. <sup>1</sup>H n.m.r. spectra were measured at 60 MHz or 90 MHz and <sup>13</sup>C n.m.r. at 22.63 MHz for CDCl<sub>3</sub> solutions with SiMe<sub>4</sub> as the internal standard. Low- and high-resolution mass spectra were determined at 70 eV (the relative intensities given herein are those of the low-resolution mass spectra).

**Extraction and Isolation.**—The liverwort *Plagiochila semidecurrens* was collected in a forest in Kochi Prefecture, Japan. The whole plant (3.2 kg) was dried in the shade for several days then digested with methanol at room temperature, and the solvent was removed under reduced pressure. This was then extracted with ether and the solvent was distilled off under reduced pressure to obtain a viscous, brownish oil (80 g). The extract (70 g) was chromatographed through a silica-gel column to give 12 fractions, from which the following compounds were isolated by a further combination of column chromatography and p.l.c. using silica gel: (+)-ovalifoliene (1) (1.47 g), (+)-ovalifolienal (2) (0.49 g), (+)-ovalifolienalone (3) (0.32 g), (–)-hanegokedial (4) (1.12 g), (+)-hanegoketrial (5) (0.035 g), deacetoxyovalifoliene (6) (0.025 g), (+)-ovalimethoxy I (7) (0.11 g), (+)-ovalimethoxy II (8) (0.84 g), (+)-plagiochiline A (9) (0.49 g), (+)-plagiochiline B (10) (0.030 g), (+)-9 $\alpha$ -acetoxy-ovalifoliene (11) (0.21 g), (–)-bicyclogermacrene (12) (0.42 g), (–)-gymnomitrene (13) (1.60 g), (–)-cuparene (14) (0.35 g), and *ent*-3 $\beta$ -acetoxybicyclogermacrene (15) (0.21 g). The physical properties of these compounds are listed below.

**(+)-Ovalifoliene** [*ent*-2 $\beta$ ,14-diacetoxy-2,3-epoxy-2,3-secoalloaromadendra-3,10(15)-diene] (1), an oil, gave [ $\alpha$ ]<sub>D</sub> +24.5 (*c.* 2.1),  $\nu$ (CCl<sub>4</sub>) 1 760, 1 740, 1 670, 1 635, 1 380, 1 370, 1 360, 1 185, 1 158, 954, 895, and 855 cm<sup>–1</sup>;  $\delta_{\text{H}}$  0.3–1.0 (2 H, m), 1.02, 1.08, 2.06, and 2.08 (each 3 H, s), 2.18 (1 H, dd, *J* 6.0 and 4.0 Hz), 2.81 (1 H, dd, *J* 10.0 and 4.0 Hz), 4.35 and 4.57 (each 1 H, d, *J* 13.0 Hz), 4.78 (2 H, s), 6.29 (1 H, s), and 6.53 (1 H, d, *J* 10.0 Hz); *m/e* 334.1746 (*M*<sup>+</sup>, C<sub>19</sub>H<sub>26</sub>O<sub>5</sub> requires *M*<sup>+</sup>, 334.1778, 9%), 291.1249 [*(M*<sup>+</sup> – 43), C<sub>16</sub>H<sub>19</sub>O<sub>5</sub> requires 291.1231, 3], 274.1584 [*(M*<sup>+</sup> – 60), C<sub>17</sub>H<sub>22</sub>O<sub>3</sub> requires 274.1568, 33], 231 (38), 214.1335 [*(M*<sup>+</sup> – 120), C<sub>15</sub>H<sub>18</sub>O requires 214.1356, 87], 199.1109 [*(M*<sup>+</sup> – 135), C<sub>14</sub>H<sub>16</sub>O requires 199.1122, 27], 189.0935 [*(M*<sup>+</sup> – 145), C<sub>12</sub>H<sub>13</sub>O<sub>2</sub> requires 189.0915, 38], 172.0860 [*(M*<sup>+</sup> – 162), C<sub>12</sub>H<sub>12</sub>O requires 172.0887, 33], 161.0951 [*(M*<sup>+</sup> – 173), C<sub>11</sub>H<sub>13</sub>O requires 161.0965, 24], 150 (49), 143 (33), 135 (41), 119 (35), 109 (47), 91 (49), 79 (41), 69 (31), 55 (29), and 43 (100); [ $\theta$ ]<sub>209</sub> (MeCN) +13 400.

\* The biological activity of the acetyl hemiacetals isolated from *P. ovalifolia* and the reaction products derived from compound (1) have been reported (A. Matsuo, K. Nadaya, M. Nakayama, and S. Hayashi, *Nippon Kagaku Kaishi*, 1981, 665).

**(+)-Ovalifolienal** [*ent*-2 $\beta$ ,14-diacetoxy-2,3-epoxy-15-oxo-2,3-secoalloaromadendra-3,9-diene] (2), an oil, gave [ $\alpha$ ]<sub>D</sub> +93.7° (*c.* 3.7);  $\nu$  2 720, 1 760, 1 740, 1 700, 1 675, 1 645, 1 385, 1 375, 1 235, 1 165, 1 023, 963, 870, and 840 cm<sup>–1</sup>;  $\delta_{\text{H}}$  1.11 and 2.04 (each 6 H, s), 2.38 (1 H, dd, *J* 9.0 and 4.0 Hz), 2.75 (1 H, t, *J* 7.0 Hz), 3.45 (1 H, ddd, *J* 10.0, 4.0, and 2.0 Hz), 4.35 and 4.57 (each 1 H, d, *J* 13.0 Hz), 6.38 (1 H, s), 6.45 (1 H, d, *J* 10.0 Hz), 6.79 (1 H, dd, *J* 8.0 and 4.0 Hz), and 9.33 (1 H, s);  $\delta_{\text{C}}$  21.0, 115.5, 140.1, 169.9, and 171.1 (each s), 24.4, 28.4, 30.8, 32.1, 92.5, 141.4, 154.4, and 194.1 (each d), 39.8 and 63.3 (each t), 15.6, 20.0, 21.0, and 25.6 (each q); *m/e* 348.1624 (*M*<sup>+</sup>, C<sub>19</sub>H<sub>24</sub>O<sub>6</sub> requires 348.1572, 6%), 306.1479 [*(M*<sup>+</sup> – 42), C<sub>17</sub>H<sub>22</sub>O<sub>5</sub> requires 306.1466, 7], 288.1384 [*(M*<sup>+</sup> – 60), C<sub>17</sub>H<sub>20</sub>O<sub>4</sub> requires 288.1360, 65], 228.1182 [*(M*<sup>+</sup> – 120), C<sub>15</sub>H<sub>16</sub>O<sub>2</sub> requires 228.1150, 42], 213.0926 [*(M*<sup>+</sup> – 135), C<sub>14</sub>H<sub>13</sub>O<sub>2</sub> requires 213.0915, 23], 199.1103 [*(M*<sup>+</sup> – 149), C<sub>14</sub>H<sub>15</sub>O requires 199.1122, 39], 185.0822 [*(M*<sup>+</sup> – 163), C<sub>9</sub>H<sub>13</sub>O<sub>4</sub> requires 185.0813, 32], 171.1116 [*(M*<sup>+</sup> – 177), C<sub>13</sub>H<sub>15</sub> requires 171.1172, 26], 159.0793 [*(M*<sup>+</sup> – 189), C<sub>11</sub>H<sub>11</sub>O requires 159.0808], 145 (23), 136 (91), 129 (36), 121 (51), 105 (39), 91 (64), 79 (46), 69 (42), 55 (42), and 43 (100);  $\lambda$ (EtOH) 215 and 227 nm (each  $\epsilon$  3 410).

**(+)-Ovalifolienalone** [*ent*-2 $\beta$ ,14-diacetoxy-2,3-epoxy-15-oxo-2,3-secoalloaromadendra-3,9-diene-8-one] (3), m.p. 203 °C, gave [ $\alpha$ ]<sub>D</sub> +149.8° (*c.* 1.6) (Found: C, 62.69; H, 6.16. C<sub>19</sub>H<sub>22</sub>O<sub>7</sub> requires: C, 62.97; H, 6.12);  $\nu$  2 720, 1 760, 1 740, 1 705, 1 670, 1 640, 1 385, 1 367, 1 230, 1 165, 1 118, 1 083, 1 050, 1 017, 964, 907, and 830 cm<sup>–1</sup>;  $\delta_{\text{H}}$  1.12 and 1.30 (each 3 H, s), 1.37 (1 H, dd, *J* 8.0 and 6.0 Hz), 2.00 and 2.07 (each 3 H, s), 2.37 (1 H, d, *J* 8.0 Hz),  $\dagger$  2.65 (1 H, dd, *J* 6.0 and 4.0 Hz), 3.58 (1 H, dd, *J* 10.0 and 4.0 Hz), 4.43 and 4.68 (each 1 H, d, *J* 12.0 Hz), 6.35 (1 H, d, *J* 10.0 Hz), and 6.48, 6.62, and 9.57 (each 1 H, s);  $\delta_{\text{C}}$  29.6, 116.0, 145.2, 160.6, 169.1, and 198.8 (each s), 32.3, 35.4, 37.9, 39.1, 92.2, 141.6, 146.5, and 193.5 (each d), 63.5 (t), 16.6, 20.6, 21.0, and 23.9 (each q); *m/e* 362 (*M*<sup>+</sup>, 8%), 320.1264 [*(M*<sup>+</sup> – 42), C<sub>17</sub>H<sub>20</sub>O<sub>6</sub> requires 320.1259, 13], 302.1201 [*(M*<sup>+</sup> – 60), C<sub>17</sub>H<sub>18</sub>O<sub>5</sub> requires 302.1153, 31], 260.0997 [*(M*<sup>+</sup> – 102), C<sub>15</sub>H<sub>16</sub>O<sub>4</sub> requires 260.1047, 92], 242.0917 [*(M*<sup>+</sup> – 120), C<sub>15</sub>H<sub>14</sub>O<sub>3</sub> requires 242.0999, 37], 232.1045 [*(M*<sup>+</sup> – 130), C<sub>14</sub>H<sub>16</sub>O<sub>3</sub> requires 232.1097, 67], 214.0972 [*(M*<sup>+</sup> – 148), C<sub>14</sub>H<sub>14</sub>O<sub>2</sub> requires 214.0992, 49], 203.0926 [*(M*<sup>+</sup> – 117), C<sub>9</sub>H<sub>15</sub>O<sub>5</sub> requires 203.0919, 48], 199.0723 [*(M*<sup>+</sup> – 163), C<sub>13</sub>H<sub>11</sub>O<sub>2</sub> requires 199.0758, 31], 189.0631 [*(M*<sup>+</sup> – 173), C<sub>11</sub>H<sub>9</sub>O<sub>3</sub> requires 189.0551, 43], 185.0852 [*(M*<sup>+</sup> – 177), C<sub>9</sub>H<sub>13</sub>O<sub>4</sub> requires 185.0813, 43], 177.0884 [*(M*<sup>+</sup> – 185), C<sub>11</sub>H<sub>13</sub>O<sub>2</sub> requires 177.0914, 33], 161.0664 [*(M*<sup>+</sup> – 201), C<sub>10</sub>H<sub>9</sub>O<sub>2</sub> requires 161.0602, 36], 159.0790 [*(M*<sup>+</sup> – 203), C<sub>11</sub>H<sub>11</sub>O requires 159.0808, 14], 145 (33), 136 (82), 121 (71), 105 (49), 91 (100), 83 (80), 69 (57), and 55 (84);  $\lambda$ (EtOH) 204 and 233 nm ( $\epsilon$  22 400 and 6 880); [ $\theta$ ]<sub>378</sub> (MeCN) +13 700 and [ $\theta$ ]<sub>267</sub> +6 470.

**(–)-Hanegokedial** [*ent*-2,3-secoalloaromadendra-4(14), 10(15)-diene-2,3-dione] (4), m.p. 66–67 °C, gave [ $\alpha$ ]<sub>D</sub> –10.4° (*c.* 0.8) (Found: C, 76.32; H, 8.77. C<sub>13</sub>H<sub>20</sub>O<sub>2</sub> requires C, 76.44; H, 8.68);  $\nu$  2 720, 1 720, 1 690, 1 632, 1 452, 1 375, 1 360, 950, and 906 cm<sup>–1</sup>;  $\delta_{\text{H}}$  0.90 and 1.10 (each 3 H, s), 3.37 (1 H, br s), 4.87 (1 H, d, *J* 2.0 Hz), 4.95 (1 H, br s), 6.20 (1 H, d, *J* 1.0 Hz), 6.54 (1 H, d, *J* 1.5 Hz), 9.63 (1 H, s), and 9.77 (1 H, d, *J* 1.5 Hz); *m/e* 232 (*M*<sup>+</sup>, 25%), 217 (18), 214 (13), 203 (39), 199 (14), 189 (47), 171 (26), 161 (34), 150 (83), 143 (40), 134 (50), 121 (43), 105 (63), 91 (96), 79 (57),

$\dagger$  This signal was observed when the shift reagent Eu(fod)<sub>3</sub> (7.6 mg) (fod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione) was added to the ketone (3) (30 mg).

69 (53), 55 (40), 43 (53), and 41 (100);  $\lambda(\text{EtOH})$  208 nm ( $\epsilon$  4 880).

(+)-*Hanegoketrial* [ent-15-oxo-2,3-secoalloaromadendra-4(14),9-diene-2,3-dione] (5), an oil, gave  $[\alpha]_D^{20} + 200^\circ$  ( $c$ , 1.0);  $\nu$  2 715, 1 720, 1 685, 1 635, 1 375, 1 365, 1 205, 1 138, 945, and 875  $\text{cm}^{-1}$ ;  $\delta_H$  0.97 and 1.12 (each 3 H, s), 3.97 (1 H, br s), 6.28 (1 H, d,  $J$  1.0 Hz), 6.52 (1 H, d,  $J$  2.0 Hz), 7.04 (1 H, dd,  $J$  8.0 and 3.0 Hz), 9.43 (1 H, s), 9.63 (1 H, d,  $J$  1.0 Hz), and 9.72 (1 H, s);  $m/e$  246 ( $M^+$ , 25%), 232 (20), 228 (14), 217 (31), 203 (30), 199 (29), 182 (46), 171 (25), 151 (60), 129 (49), 123 (71), 118 (65), 105 (70), 91 (100), 77 (86), 69 (73), and 43 (62).

*Deacetoxyovalifoliene* [ent-2 $\beta$ -acetoxy-2,3-epoxy-2,3-secoalloaromadendra-3,10(15)-diene] (6), an oil, gave  $[\alpha]_D^{20} 0^\circ$ ;  $\nu$  1 750, 1 380, 1 370, 1 240, 1 190, 1 135, 1 100, 1 060, 1 010, 905, and 835  $\text{cm}^{-1}$ ;  $\delta_H$  1.02 and 1.07 (each 3 H, s), 1.57 (3 H, d,  $J$  2.0 Hz), 1.78 (1 H, dd,  $J$  10.0 and 4.0 Hz), 2.05 (3 H, s), 2.77 (1 H, dd,  $J$  10.0 and 4.0 Hz), 4.72 (2 H, br s), 5.88 (1 H, q,  $J$  2.0 Hz), and 6.47 (1 H, d,  $J$  10.0 Hz);  $m/e$  276 ( $M^+$ , 18%), 233.1517 [ $(M^+ - 43)$ ,  $C_{15}H_{21}O_3$  requires 233.1540, 19], 216.1472 [ $(M^+ - 60)$ ,  $C_{15}H_{20}O$  requires 216.1512, 47], 201.1279 [ $(M^+ - 75)$ ,  $C_{14}H_{17}O$  requires 201.1278, 28], 191.1453 [ $(M^+ - 85)$ ,  $C_{13}H_{15}O$  requires 191.1435, 12], 191.1104 [ $(M^+ - 85)$ ,  $C_{12}H_{15}O_2$  requires 191.1071, 13], 173.0969 [ $(M^+ - 103)$ ,  $C_{12}H_{18}O$  requires 173.0966, 66], 163.1086 [ $(M^+ - 113)$ ,  $C_{11}H_{15}O$  requires 163.1121, 6], 163.0736 [ $(M^+ - 113)$ ,  $C_{10}H_{11}O_2$  requires 163.0757, 15], 161.0940 [ $(M^+ - 115)$ ,  $C_{11}H_{13}O$  requires 161.0965, 18], 159.1144 [ $(M^+ - 117)$ ,  $C_{12}H_{15}$  requires 159.1172, 12], 159.0783 [ $(M^+ - 117)$ ,  $C_{11}H_{11}O$  requires 159.0808, 11], 147 (31), 145 (31), 139 (27), 135 (28), 121 (31), 109 (44), 95 (39), 91 (35), 81 (29), 79 (29), 69 (29), 67 (27), 55 (32), and 43 (100).

(+)-*Ovalimethoxy I* [ent-2 $\beta$ -acetoxy-2,3-epoxy-3 $\alpha$ -methoxy-2,3-secoalloaromadendra-4(14),10(15)-diene] (7), an oil, gave  $[\alpha]_D^{20} + 55.8^\circ$  ( $c$ , 2.2);  $\nu$  3 040, 1 740, 1 660, 1 635, 1 380, 1 370, 1 235, 1 112, 1 092, 1 083, 1 020, 925, and 865  $\text{cm}^{-1}$ ;  $\delta_H$  1.05, 1.08, and 2.06 (each 3 H, s), 2.71 (1 H, dd,  $J$  10.0 and 3.0 Hz), 3.51 (3 H, s), 4.73 (2 H, s), 4.93, 5.10, and 5.27 (each 1 H, s), and 6.52 (1 H, d,  $J$  10.0 Hz);  $m/e$  306 ( $M^+$ , 4%), 274 (7), 263 (5), 246 (50), 231 (13), 218 (25), 203 (69), 188 (39), 175 (62), 171 (61), 161 (32), 143 (97), 133 (41), 121 (54), 105 (69), 91 (100), 79 (74), 69 (72), and 55 (68).

(+)-*Ovalimethoxy II* [ent-2 $\beta$ -acetoxy-2,3-epoxy-3 $\beta$ -methoxy-2,3-secoalloaromadendra-4(14),10(15)-diene] (8), an oil, gave  $[\alpha]_D^{20} + 2.0^\circ$  ( $c$ , 1.5);  $\nu$  3 040, 1 740, 1 660, 1 637, 1 380, 1 370, 1 360, 1 245, 1 118, 1 100, 1 057, 1 005, 975, 945, 915, and 863  $\text{cm}^{-1}$ ;  $\delta_H$  1.04, 1.12, and 2.08 (each 3 H, s), 3.17 (1 H, dd,  $J$  10.0 and 3.0 Hz), 3.51 (3 H, s), 4.77 (2 H, s), 5.02 (2 H, br s), 5.22 (1 H, s), and 6.45 (1 H, d,  $J$  10.0 Hz);  $m/e$  306 ( $M^+$ , 6%), 274 (13), 263 (43), 246.1591 [ $(M^+ - 60)$ ,  $C_{16}H_{22}O_2$  requires 246.1618, 79], 231 (14), 218.1645 [ $(M^+ - 88)$ ,  $C_{15}H_{22}O$  requires 218.1668, 32], 215.1490 [ $(M^+ - 91)$ ,  $C_{15}H_{19}O$  requires 215.1434, 22], 204.1473 [ $(M^+ - 102)$ ,  $C_{14}H_{20}O$  requires 204.1512, 34], 188.1596 [ $(M^+ - 118)$ ,  $C_{14}H_{20}$  requires 188.1564, 51], 175.1141 [ $(M^+ - 131)$ ,  $C_{12}H_{15}O$  requires 175.1122, 63], 171.1109 [ $(M^+ - 135)$ ,  $C_9H_{15}O_3$  requires 171.1020, 63], 159.1148 [ $(M^+ - 147)$ ,  $C_{12}H_{15}$  requires 159.1172, 11], 159.0798 [ $(M^+ - 147)$ ,  $C_{11}H_{11}O$  requires 159.0808, 11], 143 (100), 135 (38), 121 (43), 117 (43), 105 (56), 91 (76), 79 (52), 69 (44), 55 (42), 43 (94), and 91 (94).

(+)-*Plagiochiline A* [ent-2 $\beta$ ,14-diacetoxy-2,3:10 $\alpha$ ,15 $\alpha$ -diepoxy-2,3-secoalloaromadendr-3-ene] (9), an oil, gave  $[\alpha]_D^{20} + 32.3^\circ$  ( $c$ , 1.6);  $\nu(\text{CCl}_4)$  1 760, 1 745, 1 695, 1 675, 1 382,

1 370, 1 365, 1 230, 1 190, 1 170, 1 010, 885, and 845  $\text{cm}^{-1}$ ;  $\delta_H$  1.06 and 1.11 (each 3 H, s), 1.72 (1 H, dd,  $J$  10.0 and 4.0 Hz), 2.08 and 2.23 (each 3 H, s), 2.48 (2 H, s), 4.35 and 4.57 (each 1 H, d,  $J$  13.0 Hz), 6.53 (1 H, s), and 6.83 (1 H, d,  $J$  10.0 Hz);  $m/e$  350 ( $M^+$ , 3%), 307 (2), 290 (9), 262 (3), 247 (17), 230.1274 [ $(M^+ - 120)$ ,  $C_{15}H_{18}O_2$  requires 230.1305, 15], 201 (13), 187 (19), 175.1124 [ $(M^+ - 175)$ ,  $C_{12}H_{15}O$  requires 175.1123, 8], 159.0829 [ $(M^+ - 191)$ ,  $C_{11}H_{11}O$  requires 159.0810, 18], 133 (17), 121 (16), 105 (25), 91 (30), 85 (67), 83 (96), 74 (39), 69 (36), 59 (45), and 43 (100);  $[O]_{20}^{20}$  (MeCN) + 24 300.

(+)-*Plagiochiline B* (ent-2 $\beta$ ,13,14-triacetoxy-2,3:10 $\alpha$ ,15 $\alpha$ -diepoxy-2,3-secoalloaromadendr-3-ene) (10), m.p. 104–105  $^\circ\text{C}$ , gave  $[\alpha]_D^{20} + 25.7^\circ$  ( $c$ , 1.3) (Found: C, 62.03; H, 7.07.  $C_{21}H_{28}O_8$  requires C, 61.75; H, 6.91%);  $\nu$  1 740, 1 675, 1 385, 1 370, 1 240, 1 190, 1 165, 1 120, 1 085, 1 010, 980, 960, and 885  $\text{cm}^{-1}$ ;  $\delta_H$  1.18 (3 H, s), 1.73 (1 H, dd,  $J$  10.0 and 4.0 Hz), 2.07, 2.11, and 2.22 (each 3 H, s), 2.47 (2 H, s), 4.07 and 4.32 (each 1 H, d,  $J$  12.0 Hz), 4.43 and 4.65 (each 1 H, d,  $J$  12.0 Hz), 6.40 (1 H, s), and 6.85 (1 H, d,  $J$  10.0 Hz);  $m/e$  408 ( $M^+$ , 3%), 348 (4), 288 (23), 265 (14), 247 (16), 228 (16), 199 (10), 187 (18), 171 (8), 91 (16), 81 (15), 55 (12), and 43 (100).

(+)-*9 $\alpha$ -Acetoxyovalifoliene* [ent-2 $\beta$ ,9 $\beta$ ,14-triacetoxy-2,3-epoxy-2,3-secoalloaromadendra-3,10(15)-diene] (11), an oil, gave  $[\alpha]_D^{20} + 53.2^\circ$  ( $c$ , 0.6);  $\nu$  1 760, 1 740, 1 675, 1 640, 1 380, 1 370, 1 240, 1 153, 1 112, 1 020, 960, and 915  $\text{cm}^{-1}$ ;  $\delta_H$  0.97 and 1.07 (each 3 H, s), 2.02 (6 H, s), 2.09 (3 H, s), 2.89 (1 H, dd,  $J$  9.5 and 4.5 Hz), 4.33 and 4.51 (each 1 H, d,  $J$  12.5 Hz), 4.92 and 5.07 (each 1 H, s), 5.02 (1 H, dd,  $J$  9.0 and 3.0 Hz), 6.33 (1 H, s), and 6.51 (1 H, d,  $J$  9.5 Hz);  $\delta_C$  19.7, 113.3, 146.8, 170.0, and 170.9 (each s), 28.5, 29.7, 33.7, 48.4, 73.7, 90.3, and 140.5 (each d), 31.8, 63.5, and 115.0 (each t), 15.8, 21.0, 21.0, 21.0, and 24.0 (each q);  $m/e$  392 ( $M^+$ , 3%), 332.1649 [ $(M^+ - 60)$ ,  $C_{19}H_{24}O_5$  requires 332.1622, 33], 289 (7), 272.1394 [ $(M^+ - 120)$ ,  $C_{17}H_{20}O_3$  requires 272.1411, 100], 257 (9), 230.1283 [ $(M^+ - 162)$ ,  $C_{15}H_{18}O_2$  requires 230.1305, 48], 215.1044 [ $(M^+ - 177)$ ,  $C_{14}H_{15}O_2$  requires 215.1070, 23], 212.1168 [ $(M^+ - 180)$ ,  $C_{15}H_{16}O$  requires 212.1200, 72], 201.1273 [ $(M^+ - 191)$ ,  $C_{14}H_{17}O$  requires 201.1278, 41], 187.0770 [ $(M^+ - 205)$ ,  $C_{12}H_{15}O_2$  requires 187.0758, 46], 169.1035 [ $(M^+ - 223)$ ,  $C_{13}H_{13}$  requires 169.1016, 8], 169.0628 [ $(M^+ - 223)$ ,  $C_{12}H_9O$  requires 169.0653, 16], 159.0825 [ $(M^+ - 233)$ ,  $C_{11}H_{11}O$  requires 159.0808, 36], 149 (16), 135 (27), 119 (21), 105 (29), 95 (30), 91 (33), 79 (27), 69 (31), 55 (24), and 47 (20).

(-)-*Bicyclogermacrene* (12), an oil, gave  $[\alpha]_D^{20} - 71.5^\circ$  ( $c$ , 1.6);  $\nu(\text{CCl}_4)$  3 025, 1 656, 1 395, 1 375, 850, and 830  $\text{cm}^{-1}$ ;  $\delta_H(\text{CCl}_4)$  1.02 and 1.13 (each 3 H, s), 1.45 and 1.63 (each 3 H, d,  $J$  2.0 Hz), 4.28 (1 H, d,  $J$  12.0 Hz), and 4.73 (1 H, br d,  $J$  8.0 Hz).

(-)-*Gymnomitrene* (1,2,6-trimethyl-8-methylenetricyclo-[5.3.1.0 $^{2,6}$ ]undecane) (13), an oil, gave  $[\alpha]_D^{20} - 24.3^\circ$  ( $c$ , 1.8);  $\nu(\text{CCl}_4)$  3 050, 1 640, 1 385, 1 375, 1 365, and 890  $\text{cm}^{-1}$ ;  $\delta(\text{CCl}_4)$  0.85, 0.92, and 1.05 (each 3 H, s) and 4.53 (2 H, d,  $J$  2.5 Hz).

(-)-*Cuparene* (14), an oil, gave  $[\alpha]_D^{20} - 35.7^\circ$  ( $c$ , 1.0);  $\nu(\text{CCl}_4)$  1 515, 1 500, 1 460, 1 388, 1 375, 1 367, 1 250, and 860  $\text{cm}^{-1}$ ;  $\delta(\text{CCl}_4)$  0.55, 1.05, 1.25, and 2.28 (each 3 H, s), and 6.92 and 7.13 (each 2 H, d,  $J$  8.0 Hz).

ent-3 $\beta$ -Acetoxycyclogermacrene (15a), gave  $\delta(\text{CCl}_4)$  1.05 and 1.12 (each 3 H, s), 1.45 and 1.67 (each 3 H, d,  $J$  2.0 Hz), 1.97 (3 H, s), 4.59 (1 H, d,  $J$  12.0 Hz), 4.91 (1 H, br d,  $J$  8.0 Hz), and 5.15 (1 H, t,  $J$  3.0 Hz).

*Epoxidation of (+)-Ovalifoliene* (1).—To a solution of (+)-



ovalifoliene (1) (95 mg) in chloroform (10 ml), *m*-chloroperbenzoic acid (50 mg) and disodium hydrogenphosphate (50 mg) (as a buffer reagent) were added, and the mixture was stirred at 2–10 °C for 13 h. The reaction mixture, after decomposition of the peracid with potassium iodide, was washed with 5% sodium thiosulphate, 5% sodium hydrogencarbonate, and water. Two products, the mono-epoxide (16) (18 mg) and the hydroxy-benzoate (17) (19 mg), were obtained by p.l.c., together with unchanged ovalifoliene (1) (40 mg).

ent-2 $\beta$ ,14-Diacetoxy-2,3:10 $\beta$ ,15 $\beta$ -diepoxy-2,3-secoalloaromadendr-3-ene (16), m.p. 82–84 °C, gave  $[\alpha]_D^{25} +25.0^\circ$  (*c*, 0.9) (Found: C, 64.91; H, 7.60. C<sub>19</sub>H<sub>26</sub>O<sub>6</sub> requires C, 65.12; H, 7.48%);  $\nu$  1 760, 1 740, 1 670, 1 382, 1 375, 1 365, 1 240, 1 190, 1 152, 1 062, 1 110, 960, 914, and 850 cm<sup>-1</sup>;  $\delta_H$  1.10, 1.12, 2.06, and 2.15 (each 3 H, s), 2.22 (1 H, dd, *J* 10.0 and 4.0 Hz), 2.62 and 2.77 (each 1 H, d, *J* 5.0 Hz), 4.35 and 4.55 (each 1 H, d, *J* 13.0 Hz), 6.28 (1 H, s), and 6.62 (1 H, d, *J* 10.0 Hz);  $\delta_C$  20.3, 59.3, 116.5, 169.7, and 171.3 (each s), 28.8, 29.6, 31.4, 50.7, 91.7, and 140.3 (each d), 21.7, 33.7, 57.4, and 63.3 (each t), 15.7, 21.0, 21.0, and 28.8 (each q); *m/e* 350 (*M*<sup>+</sup>, 5%), 290 (7), 247 (35), 230 (33), 215 (13), 201 (21), 187 (30), 173 (17), 142 (30), 128 (31), 121 (30), 105 (37), 91 (43), 79 (38), 69 (51), 55 (40), and 43 (100);  $[\theta]_{207}^{MeCN} +19\ 100$ .

ent-2 $\beta$ ,14-Diacetoxy-2,3-epoxy-10 $\beta$ -hydroxy-2,3-secoalloaromadendr-3-en-15-yl *m*-chlorobenzoate (17), an oil, gave  $[\alpha]_D^{22} +22.0^\circ$  (*c*, 1.0);  $\nu$  3 580, 1 740, 1 630, 1 570, 1 450, 1 420, 1 240, 1 052, 940, 908, and 855 cm<sup>-1</sup>;  $\delta_H$  1.05, 1.23, 2.00, and 2.07 (each 3 H, s), 3.43 (1 H, dd, *J* 10.0 and 3.0 Hz), 4.08 and 4.55 (each 1 H, d, *J* 12.0 Hz), 4.82 and 4.90 (each 1 H, br d, *J* 3.0 Hz), 6.33 (1 H, s), 6.50 (1 H, d, *J* 10.0 Hz), 7.48 (1 H, t, *J* 8.0 Hz), 7.57 (1 H, dt, *J* 8.0 and 2.0 Hz), 7.87 (1 H, dt, *J* 8.0 and 2.0 Hz), and 7.93 (1 H, t, *J* 2.0 Hz); *m/e* 506 and 508 (*M*<sup>+</sup>, 0.6 and 0.2%), 446 and 448 (9.5 and 3), 350 (0.5), 308 (2), 290 (20), 261 (11), 248 (7), 230 (21), 219 (13), 201 (29), 187 (18), 176 (15), 156 and 158 (38 and 15), 149 (19), 148 (18), 147 (16), 139 and 141 (100 and 46), 133 (21), 119 (14), 111 and 113 (38 and 11), 105 (23), 91 (21), 79 (17), 69 (31), 57 (19), and 43 (87).

**Lithium Aluminium Hydride Reduction of (+)-Ovalifoliene (1).**—Ovalifoliene (1) (250 mg) in dry ether (10 ml) was added to a solution of lithium aluminium hydride (40 mg) in dry ether (10 ml) as drops and the mixture was stirred at room temperature for 2 h. The excess of hydride was decomposed by addition of ice–water (0.1 ml) and 10% sodium hydroxide (0.1 ml) and the white precipitate which formed was filtered off. The diol (18) (167 mg) was obtained from the reaction mixture by p.l.c.

ent-2,3-Secoalloaromadendra-4(14),10(15)-diene-2,3-diol (18), m.p. 87.5–88.5 °C, gave  $[\alpha]_D^{25} -44.0^\circ$  (*c*, 1.9) (Found: C, 75.72; H, 10.25. C<sub>15</sub>H<sub>24</sub>O<sub>2</sub> requires C, 76.22; H, 10.24%);  $\nu$  3 600, 3 400, 1 630, 1 390, 1 380, 1 020, 905, and 860 cm<sup>-1</sup>;  $\delta_H$  0.93 and 1.08 (each 3 H, s), 3.76 and 3.87 (each 1 H, br s), 4.12 and 4.80 (each 2 H, s), and 5.07 and 5.20 (each 1 H, br s); *m/e* 236 (*M*<sup>+</sup>, 7%), 221 (6), 218 (12), 205 (48), 187 (14), 175 (21), 161 (16), 145 (29), 135 (38), 119 (55), 105 (48), 91 (60), 79 (49), 69 (49), 55 (47), 43 (60), and 41 (100).

**Acetylation of the Diol (18).**—The diol (18) (26 mg) in pyridine (1 ml) and acetic anhydride (1 ml) was stirred at room temperature for 2 h. The product, recovered in the usual way, was purified by p.l.c. to afford the diacetate (19) (32 mg).

ent-2,3-Diacetoxy-2,3-secoalloaromadendra-4(14),10(15)-diene (19), an oil, gave  $[\alpha]_D^{25} -59.1^\circ$  (*c*, 1.1);  $\nu$  1 735, 1 645,

1 635, 1 380, 1 370, 1 240, 1 040, and 905 cm<sup>-1</sup>;  $\delta_H$  0.92, 1.08, 1.98, and 2.07 (each 3 H, s), 2.86 (1 H, dd, *J* 10.0 and 5.0 Hz), 4.20 (1 H, d, *J* 12.0 Hz), 4.22 (1 H, dd, *J* 12.0 and 10.0 Hz), 4.0–4.5 (2 H, complex), 4.62 (2 H, br s), 4.69 (2 H, s), and 5.15 (2 H, br s); *m/e* 320 (*M*<sup>+</sup>, 5%), 260 (13), 245 (3), 217 (9), 200 (54), 185 (37), 157 (79), 144 (26), 134 (93), 119 (32), 105 (44), 91 (55), 79 (40), 69 (38), 55 (26), 43 (100), and 41 (56).

**Oxidation of the Diol (18) with Osmium Tetraoxide–Sodium Periodate (Lemieux–Johnson Oxidation).**<sup>27</sup>—A mixture of the diol (18) (84 mg), in tetrahydrofuran–water (1 : 1, 10 ml), one crystal of osmium tetraoxide, and sodium metaperiodate (460 mg) was stirred at room temperature for 2 h. The reaction mixture was extracted with ethyl acetate and the solvent was evaporated off under reduced pressure to give the product. The keto-lactone (20) (48 mg) was purified by p.l.c.

ent-3-Oxa-14,15-dinor-1 $\beta$ -alloaromadendrane-4,10-dione (20), m.p. 134–135 °C, gave  $[\alpha]_D^{25} +21.3^\circ$  (*c*, 2.4) (Found: C, 68.99; H, 7.84. C<sub>12</sub>H<sub>16</sub>O<sub>3</sub> requires C, 69.21; H, 7.74%);  $\nu$  1 775, 1 720, 1 385, 1 360, 1 180, 1 130, 1 067, 1 005, 963, and 865 cm<sup>-1</sup>;  $\delta_H$  1.12 and 1.18 (each 3 H, s), 2.65 (2 H, dd, *J* 9.5 and 4.5 Hz), 2.87 (1 H, dd, *J* 11.0 and 7.0 Hz), 3.73 (1 H, ddd, *J* 11.0, 7.5, and 4.5 Hz), 4.23 (1 H, dd, *J* 9.0 and 7.5 Hz), and 4.77 (1 H, dd, *J* 9.0 and 4.5 Hz);  $\delta_C$  (C<sub>6</sub>D<sub>6</sub>) 0.37 (1 H, ddd, *J* 11.5, 7.0, and 4.5 Hz), 0.73 (1 H, t, *J* 7.0 Hz), 0.90 and 0.93 (each 3 H, s), 2.38 (1 H, dd, *J* 11.0 and 7.0 Hz), 2.90 (1 H, ddd, *J* 11.0, 7.5, and 4.5 Hz), 3.80 (1 H, dd, *J* 9.0 and 7.5 Hz), and 4.63 (1 H, dd, *J* 9.0 and 4.5 Hz); *m/e* 208 (*M*<sup>+</sup>, 10%), 193 (3), 190 (4), 180 (23), 153 (14), 122 (15), 107 (19), 93 (23), 85 (100), 82 (57), 67 (21), 55 (22), and 41 (36);  $[\theta]_{298}^{MeCN} +2\ 500$ ,  $[\theta]_{292} +2\ 470$ , and  $[\theta]_{213} -7\ 270$ .

**Oxidation of the Diol (18) with Chromic Acid (Sarett Oxidation).**<sup>35</sup>—Chromic acid (15 mg) in small portions was stirred into pyridine (0.2 ml) at 15–20 °C. To the slurry of the complex was added the diol (18) (35 mg) in pyridine (3 ml) and the mixture was stirred for 20 h. The reaction mixture was poured into ice–water and extracted with chloroform to give two products which were isolated by p.l.c. and identified as the  $\alpha$ -methylene- $\delta$ -lactone (21) (4 mg) and (–)-hanegokedial (4) (5.5 mg).

ent-2,3-Epoxy-2,3-secoalloaromadendra-4(14),10(15)-diene-3-one (21), m.p. 51–52 °C, gave  $[\alpha]_D^{25} +15.8^\circ$  (*c*, 0.2);  $\nu$  1 712, 1 632, 1 400, 1 310, 1 148, 1 030, 945, and 905 cm<sup>-1</sup>;  $\delta_H$  1.06 and 1.12 (each 3 H, s), 4.81 (2 H, s), 5.39 (1 H, br s), and 6.22 (1 H, d, *J* 1.5 Hz); *m/e* 232 (*M*<sup>+</sup>, 17%), 217 (13), 202 (82), 199 (63), 179 (14), 159 (29), 145 (45), 131 (48), 119 (42), 105 (66), 91 (89), 79 (85), 69 (48), 55 (43), and 43 (100);  $\lambda(EtOH)$  214 nm ( $\epsilon$  8 720).

**Acid Treatment of (+)-Ovalifoliene (1).**—To ovalifoliene (1) (40.5 mg) in methanol (10 ml) one drop of 10% hydrochloric acid was added and the solution (pH *ca.* 4) was allowed to stand for one day. (–)-Hanegokedial (4) (15.5 mg) was obtained from the reaction mixture.

**Reaction of (+)-Ovalifoliene (1) with Methanol in the Presence of Pyridinium Toluene-*p*-sulphonate (PPTS).**<sup>36</sup>—A mixture of (+)-ovalifoliene (1) (45 mg), methanol (10 ml), and PPTS (5 mg) was stirred at room temperature for one week. The solution was washed once with half-saturated sodium chloride and two products, (22) (6 mg) and (23) (10 mg), were obtained by p.l.c. from the reaction mixture together with unchanged ovalifoliene (1) (7 mg).

ent-2,3-Epoxy-2 $\beta$ ,3 $\beta$ -methoxy-2,3-secoalloaromadendra-4(14),10(15)-diene (22) gave  $\delta_H$  1.03, 1.10, 3.50, and 3.53

(each 3 H, s), 4.77 (2 H, s), 4.93 (1 H, s), 4.98 (1 H, s), 5.00 (1 H, d,  $J$  9.0 Hz), and 5.17 (1 H, s).

*ent*-2,3-Epoxy-2 $\beta$ ,3 $\alpha$ -methoxy-2,3-secoalloaromadendra-4(14),10(15)-diene (23) gave  $\delta_{\text{H}}$  0.88, 1.12, 3.28, and 3.30 (each 3 H, s), 4.72 (2 H, s), 4.87 (1 H, d,  $J$  9.0 Hz), and 4.90, 5.17, and 5.30 (each 1 H, s).

*Lithium Aluminium Hydride Reduction of (+)-Ovalifolienal* (2).—The aldehyde (2) (257 mg) was stirred with lithium aluminium hydride (85 mg) in dry ether (10 ml) at room temperature for 2 h. The excess of hydride was decomposed by addition of water (0.2 ml) and 5% sodium hydroxide (0.2 ml) and the mixture was filtered. The filtrate was purified by p.l.c. to yield the triol (24) (90 mg).

*ent*-2,3-Secoalloaromadendra-4(14),9-diene-2,3,15-triol (24), an oil, gave  $[\alpha]_{\text{D}} +140.3^{\circ}$  ( $c$ , 1.4);  $\nu$  3 600, 3 300, 1 040, 1 020, 910, 880, and 830  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  0.95 and 1.09 (each 3 H, s), 4.02 (2 H, br s), 4.15 (2 H, s), 5.12 and 5.23 (each 1 H, br s), and 5.74 (1 H, dd,  $J$  7.0 and 4.0 Hz).

*Acetylation of the Triol* (24).—The triol (24) (14 mg) was mixed with pyridine (0.2 ml) and acetic anhydride (0.2 ml), and allowed to stand for 1 h. The triacetate (25) (9 mg) was obtained by p.l.c. from the reaction mixture.

*ent*-2,3,15-Acetoxy-2,3-secoalloaromadendra-4(14),9-diene (25), an oil, gave  $[\alpha]_{\text{D}} +113.3^{\circ}$  ( $c$ , 0.5);  $\nu$  1 730, 1 715, 1 640, 1 365, 1 355, 1 230, 985, 915, and 875  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  0.97, 1.07, and 1.99 (each 3 H, s), 2.08 (6 H, s), 4.20 and 4.30 (each 1 H, s), 4.43, 4.62, and 5.17 (each 2 H, br s), and 5.76 (1 H, dd,  $J$  7.0 and 4.0 Hz);  $m/e$  378 ( $M^{+}$ , 2%), 318 (3), 279 (4), 258 (23), 245 (23), 215 (7), 198 (50), 183 (46), 155 (40), 143 (38), 129 (12), 120 (100), 105 (82), 91 (36), 79 (24), 69 (17), and 55 (19).

*Oxidation of the Triol* (24) with Chromic Acid (Sarett Oxidation).<sup>35</sup>—(a) The triol (24) (28 mg) in pyridine was stirred with the Sarett reagent [see oxidation of the diol (18)] for 6 h. The usual work-up gave a product, the hydroxy-dialdehyde (26) (5 mg), which was purified by p.l.c.

*ent*-2-Hydroxy-3,15-dioxo-2,3-secoalloaromadendra-4(14),9-diene (26), an oil, gave  $[\alpha]_{\text{D}} +244^{\circ}$  ( $c$ , 0.3);  $\nu$  3 570, 3 420, 2 720, 1 690, 1 635, 1 145, 1 035, 950, 920, and 840  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  0.93 and 1.17 (each 3 H, s), 6.19 (1 H, d,  $J$  1.5 Hz), 6.47 (1 H, d,  $J$  2.0 Hz), 6.83 (1 H, dd,  $J$  7.0 and 3.0 Hz), and 9.37 and 9.62 (each 1 H, s);  $m/e$  248 ( $M^{+}$ , 11%), 230 (24), 218 (18), 201 (29), 177 (29), 165 (20), 159 (28), 145 (31), 129 (44), 123 (61), 105 (71), 91 (100), 77 (73), 69 (61), and 55 (68);  $\lambda(\text{EtOH})$  208 and 224 nm ( $\epsilon$  5 830 and 6 940). (b) When the reaction time was prolonged to 22 h the triol (24) (45 mg) gave the  $\delta$ -lactone (27) (7 mg) which was purified by p.l.c.

*ent*-2,3-Epoxy-15-oxo-2,3-secoalloaromadendra-4(14),9-dien-3-one (27), m.p. 118–119  $^{\circ}\text{C}$ , gave  $[\alpha]_{\text{D}} +60.0^{\circ}$  ( $c$ , 0.5);  $\nu$  2 720, 1 715, 1 685, 1 635, 1 145, 1 030, and 950  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  1.10 and 1.25 (each 3 H, s), 5.47 (1 H, d,  $J$  1.0 Hz), 6.33 (1 H, d,  $J$  1.0 Hz), 6.93 (1 H, dd,  $J$  8.0 and 4.0 Hz), and 9.28 (1 H, s).

*Oxidation of (+)-Ovalifolienal* (2) into (+)-Ovalifolienalone (3) with Chromic Acid (Collins Oxidation).<sup>33</sup>—Chromic acid (265 mg) was added to pyridine (420 mg) and dichloromethane (6.5 ml). After 15 min ovalifolienal (2) (150 mg) in dichloromethane was added in portions, with stirring, and the mixture was stirred at 70  $^{\circ}\text{C}$  for 6 h. The solution was passed through a silica-gel column and the filtrate was washed with 5% sodium hydroxide, 5% hydrochloric acid, 5% sodium hydrogencarbonate, and then saturated sodium chloride. The ketone (3) (16 mg) was obtained by p.l.c.

*Acid Treatment of (+)-Ovalifolienal* (2).—The aldehyde (2) (44 mg) in methanol (10 ml) and one drop of 10% hydro-

chloric acid (pH *ca.* 4) was allowed to stand for one day. (+)-Hanegoketrial (5) (6 mg) was obtained by p.l.c. from the reaction mixture.

*Catalytic Hydrogenation of (+)-Ovalimethoxy II* (8).—Adams catalyst (7 mg) was added to a solution of the methoxy-compound (8) (65 mg) in ethyl acetate (2 ml) and the mixture was hydrogenated at room temperature for 2 h. The usual work-up gave the tetrahydro-derivative (28) (44 mg) which was purified by p.l.c.

*ent*-2 $\beta$ -Acetoxy-2,3-epoxy-3 $\beta$ -methoxy-2,3-secoalloaromadendrane (28), an oil, gave  $[\alpha]_{\text{D}} 0^{\circ}$  ( $c$ , 1.8);  $\nu$  1 735, 1 305, 1 240, 1 115, 1 103, 1 060, 994, 967, 925, and 860  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  0.95 and 1.03 (each 3 H, s), 0.98 and 1.01 (each 3 H, d,  $J$  7.0 Hz), 2.08 and 3.35 (each 3 H, s), 4.46 (1 H, d,  $J$  4.0 Hz), and 6.27 (1 H, d,  $J$  9.0 Hz);  $m/e$  310 ( $M^{+}$ , 6%), 250 (66), 235 (5), 219 (17), 207 (20), 190 (19), 178 (73), 163 (21), 148 (58), 135 (48), 126 (64), 107 (56), 93 (43), 81 (38), 72 (49), 55 (44), 43 (100), and 41 (57).

*Epoxidation of (+)-Ovalimethoxy II* (8). The methoxy-compound (8) (86 mg) in chloroform (8 ml) was stirred at room temperature with *m*-chloroperbenzoic acid (90 mg) and disodium hydrogenphosphate (90 mg) for 3 h. The usual work-up gave three products, (29) (29 mg), (30) (14 mg), and (31) (8.5 mg), which were isolated by p.l.c.

*ent*-2 $\beta$ -Acetoxy-2,3:10 $\beta$ ,15 $\beta$ -diepoxy-3 $\beta$ -methoxy-2,3-secoalloaromadendr-4(14)-ene (29), an oil, gave  $[\alpha]_{\text{D}} +1.3^{\circ}$  ( $c$ , 1.5);  $\nu$  1 750, 1 660, 1 245, 1 230, 1 122, 1 065, 1 005, 945, 915, 865, and 830  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  1.04, 1.19, and 2.12 (each 3 H, s), 2.53 and 2.68 (each 1 H, d,  $J$  5.0 Hz), 3.45 (3 H, s), 5.02 (2 H, s), 5.18 (1 H, s), and 6.49 (1 H, d,  $J$  10.0 Hz);  $m/e$  322 ( $M^{+}$ , 5%), 291 (3), 279 (4), 262 (27), 247 (19), 231 (40), 219 (58), 204 (27), 187 (24), 173 (29), 159 (42), 155 (20), 131 (53), 121 (56), 105 (67), 91 (100), 82 (76), 69 (64), 55 (71), and 43 (86).

*ent*-2 $\beta$ -Acetoxy-2,3:4 $\beta$ ,14 $\beta$ :10 $\beta$ ,15 $\beta$ -triepoxy-3 $\beta$ -methoxy-2,3-secoalloaromadendrane (30) gave  $\delta_{\text{H}}$  1.02, 1.07, and 2.15 (each 3 H, s), 2.48 and 2.65 (each 1 H, d,  $J$  5.0 Hz), 2.65 and 2.85 (each 1 H, d,  $J$  5.0 Hz), 3.45 (3 H, s), 4.73 (1 H, s), and 6.50 (1 H, d,  $J$  10.0 Hz).

*ent*-2 $\beta$ -Acetoxy-2,3:10 $\alpha$ ,15 $\alpha$ -diepoxy-3 $\beta$ -methoxy-2,3-secoalloaromadendr-4(14)-ene (31) gave  $\delta_{\text{H}}$  1.05, 1.13, and 2.17 (each 3 H, s), 2.43 (2 H, s), 3.47 (3 H, s), 4.95 (1 H, s), 5.00 and 5.17 (each 1 H, s), and 6.68 (1 H, d,  $J$  10.0 Hz).

*Lithium Aluminium Hydride Reduction of ent*-3 $\beta$ -Acetoxy-bicyclogermacrene (15a).—The crude acetoxy-compound (15a) (*ca.* 85% pure, 30 mg) was added to a solution of lithium aluminium hydride (10 mg) in dry ether (2 ml) and the mixture was stirred for 2 h. The crude product was obtained by the usual work-up and *ent*-3 $\beta$ -hydroxybicyclogermacrene (15b) (19 mg) was isolated by p.l.c.<sup>22</sup> as an oil;  $[\alpha]_{\text{D}} -31.9^{\circ}$  ( $c$ , 0.9);  $\nu$  3 600, 3 420, 1 660, 1 460, 1 385, 1 050, 1 010, 985, 858, and 848  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  1.07 and 1.12 (each 3 H, s), 1.42 and 1.58 (each 3 H, d,  $J$  1.5 Hz), 4.30 (1 H, t,  $J$  3.0 Hz), 4.80 (1 H, d,  $J$  12.0 Hz), and 5.08 (1 H, br d,  $J$  8.0 Hz);  $m/e$  220 ( $M^{+}$ , 36%), 205 (6), 202 (7), 187 (8), 177 (13), 161 (12), 149 (19), 137 (38), 121 (52), 109 (100), 95 (47), 81 (37), 67 (31), and 55 (23).

*Biological Activity*.—The plant-growth-inhibitory activity of the novel acetyl hemiacetals (1), (2), (3), (7), and (8), using rice seedlings (Shin-sen-bon, an ordinary variety of *Oryza sativa* L.) was tested with the same procedure as described in the previous paper.<sup>26</sup>

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