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# TERPENOID CONSTITUENTS OF *PELLIA EPIPHYLLA**†

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**Key Word Index**—*Pellia epiphylla*; Metzgeriales; Hepaticae; hydrocarbons; sesquiterpenoids; diterpenoids; sacculatanes; pellialactone.

**Abstract**—An ether extract of the liverwort *Pellia epiphylla* yielded eight sesquiterpenoids: *iso*-α-gurjunene B, 9(15)-africanene, spathulenol, globulol, (+)-α-bisabolol, and the three new compounds, a 4,5-seco-guaiane, epi-swartzianin A, and 1-himachalen-4β-ol; six diterpenoids, three sacculatane-type: with 8(12),17-sacculatadien-11-ol, 7,17-sacculatadien-11-acid as new compounds and sacculaporellin and the phytan-type diterpenes phytol, geranylgeraniol and the new 12,14-dihydroxyphytol. A nor-diterpenoid with an unusual skeleton, named pellialactone is reported. Loliolide has been isolated from a liverwort for the first time. Besides this, some known sterols together with betulin and δ-tocopherol were obtained. © 1997 Elsevier Science Ltd

## INTRODUCTION

The ether extract of *Pellia epiphylla* (L.) Corda, a common thalloid European liverwort, was examined for secondary metabolites. The major constituents were bibenzyls and bisbibenzyls [1]. There were only a few earlier reports on *P. epiphylla* terpenoids, such as α-tocopherol [2], guaiazulene [3], *iso*-α-gurjunene B [4] and several sesquiterpene hydrocarbons [5]. In this paper we present further terpenoid compounds.

## RESULTS AND DISCUSSION

After column chromatography followed by HPLC, the diethyl ether extract of *P. epiphylla* yielded 23 terpenoid compounds. Three were sesquiterpene hydrocarbons *iso*-α-gurjunene B (**1**) [4, 6], the major compound and the two africanane-type compounds 9(15)-africanene (**2**) [7], and *epi*-swartzianin A (**3**) [8, 9]. The other sesquiterpenes were a new 4,5-seco-guaiane (**4**), the known alcohols spathulenol (**5**) [10], globulol (**6**) [11], (+)-6*R*,7*R*-α-bisabolol (**7**) [12], and a new 1-himachalen-4β-ol (**8**). Spathulenol, widespread in liverworts [13], has been shown recently to be an artefact arising from bicyclogermacrene [14]. Both enantiomers of α-bisabolol have already been isolated from liverworts [15, 16, 17]. Sacculatane-type diterpenes are reported for the first time from *P. epiphylla*. These are comprised of the new 8(12),17-sacculatadien-11-ol (**9**) and 7,17-sacculatadien-11-acid (**10**) together with the known sacculaporellin (**11**) [18, 19]. Three phylane-type diterpenes, geranylgeraniol (**12**) [20], phytol (**13**) [21], and the new 12,14-dihydroxyphytol (**14**) were obtained. Additionally, a new nor-diterpenoid with an unusual skeleton, named pellialactone (**15**), was isolated. The carotenoid derived loliolide (**16**) [22] is reported for the first time from a liverwort. Furthermore δ-tocopherol (**17**) [23], which has been reported for *Radula perrottetii* [24], betulin (**18**) [25], β-sitosterol (**19**) [26], stigmast-4-en-3-one (**20**) [27], methylcholest-4-en-3-one (**21**) [27], 5α,8α-epidioxy-methylcholesta-6,22-dien-3β-ol (**22**) [28], and 5α,8α-epidioxy-methylcholesta-6,9(11),22-trien-3β-ol (**23**) [28] were obtained. The known compounds were identified by comparison of their spectroscopic properties with published data. Compound **2**, 9(15)-africanene, which was first isolated from soft corals [7], is reported for the first time from a liverwort.

The $^1$H NMR spectrum of compound **3** ($[M]^+ = m/z$ 204) showed that this too was an africanane sesquiterpenoid i.e. signals of the cyclopropane ring at δ 0.27 (H-3α), 0.68 (H-3β) and 0.75 (H-4). The interpretation of $^1$H NMR, $^{13}$C NMR, and the 2D spectra led to the structure of a 1(11)-africanene. The isolation of such a hydrocarbon, named swartzianin A has been reported from *Porella swartziana* [8, 9]. However, comparison of the published data with those of compound **3** showed a significant difference in the $^1$H NMR spectrum (Table 1) and at C-8 and C-15 of the $^{13}$C NMR spectrum (Table 2). Since all other signals of the $^{13}$C NMR were in good agreement with

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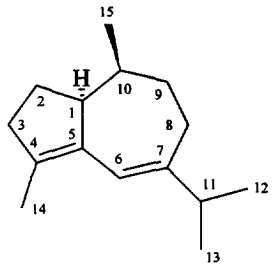
† Dedicated to Prof. Eicher on the occasion of his sixty-fifth birthday.

‡ Author to whom correspondence should be addressed.



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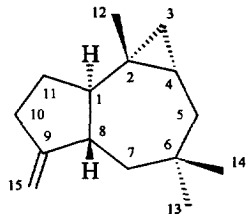

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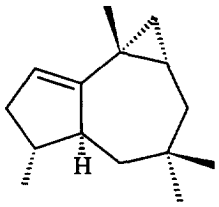

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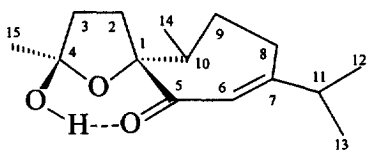

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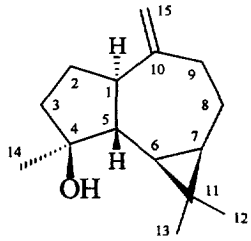

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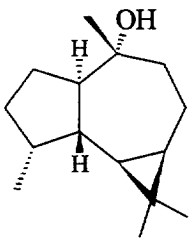

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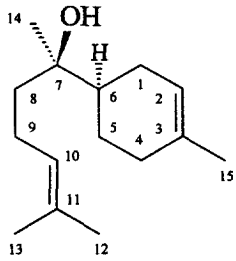

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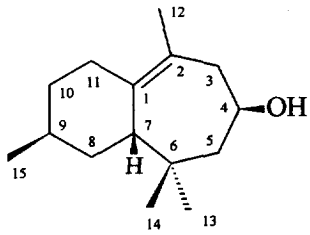

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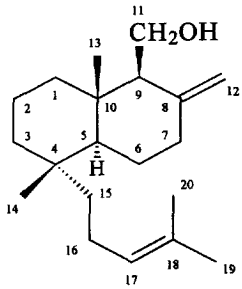

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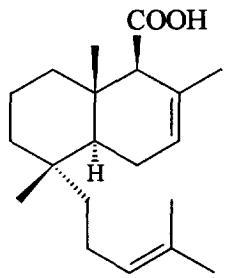

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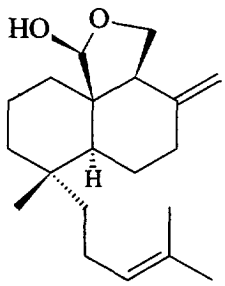

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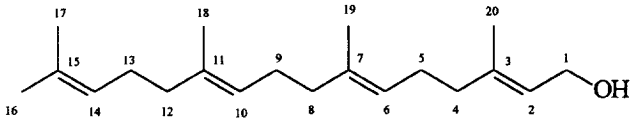
swartzianin A, compound **3** has to be the C-8 epimer of swartzianin A. As with swartzianin A, the NOE measurements gave no significant enhancements, but as the stereochemistry of swartzianin A was elucidated unambiguously by chemical transformation, the methyl group of compound **3** must be in an α position. Compound **3** is therefore *epi*-swartzianin A.

The EI-mass spectrum of compound **4** ($[M]^+ = m/z$ 256) was in agreement with a molecular formula of $C_{15}H_{24}O_3$. The IR spectrum showed the presence of a hydroxyl group (3440 $cm^{-1}$) and an α,β-unsaturated carbonyl group (1670 $cm^{-1}$). The $^1H$ NMR spectrum (Table 1) had a close similarity to that of the guaiane-type *iso*-α-gurjenene B (**1**). Since the amount isolated was too small to obtain a $^{13}C$ NMR spectrum, 2D spectra were measured and the $^{13}C$ NMR data were obtained from the $^{13}C$ projection of the HSQC and HMBC spectra (Table 2). The analysis of the $^1H$–$^1H$



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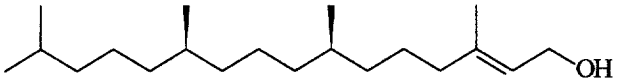

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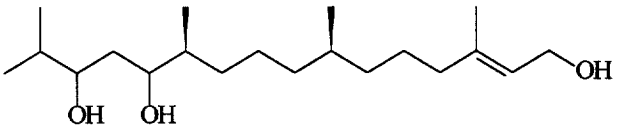

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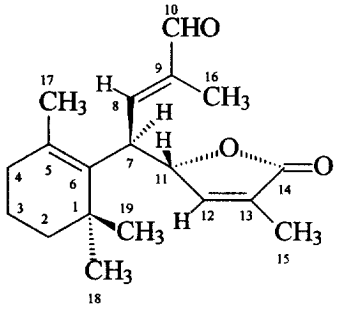

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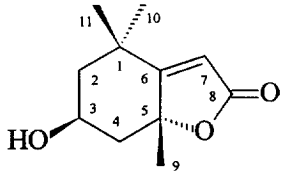

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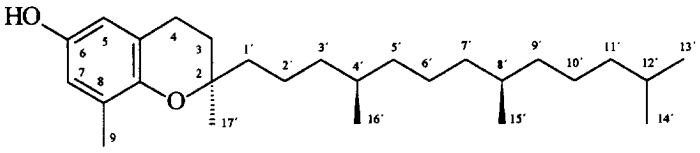

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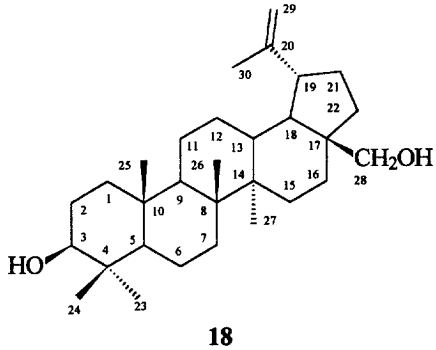

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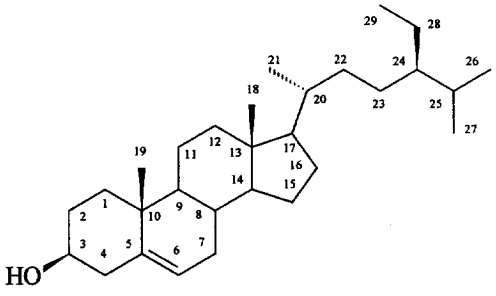

**19**

and $^{1}H$–$^{13}C$ COSY spectra revealed the existence of four partial structures A–D (Fig. 1). The connection of these partial structures was deduced from the HMBC spectrum (Fig. 2). The two methyl groups of segment B ($\delta_H$ 0.91, 0.89, *d* both) were correlated to the quaternary olefinic carbon atom of segment D ($\delta_C$ 165.0, *s*). This olefinic centre showed also correlations to the two methylene protons of segment A ($\delta_H$ 2.55, *m*; 1.90, *dd*). Both the methyl group of segment A ($\delta_H$ 0.65, *d*) and the olefinic proton of segment D ($\delta_H$ 6.04) were correlated to an oxygen-bearing quaternary carbon atom ($\delta_C$ 91.8) to give a seven membered ring. The remaining singlet methyl group ($\delta_H$ 1.06, *s*) showed a correlation to a quaternary hemiacetal carbon atom ($\delta_C$ 98.6, *s*) and to the methylene centre of segment C. The protons of the second methylene group of this segment ($\delta_H$ 2.31, *ddd*; 1.36, *td*) correlated to the ketone group, the oxygen-bearing quaternary carbon atom and the methine group of segment A. Thus all C-C attachments were obvious. To explain the existence of the hemiacetal group and the coupling systems of segment C (i.e. fixed geometry), there had to

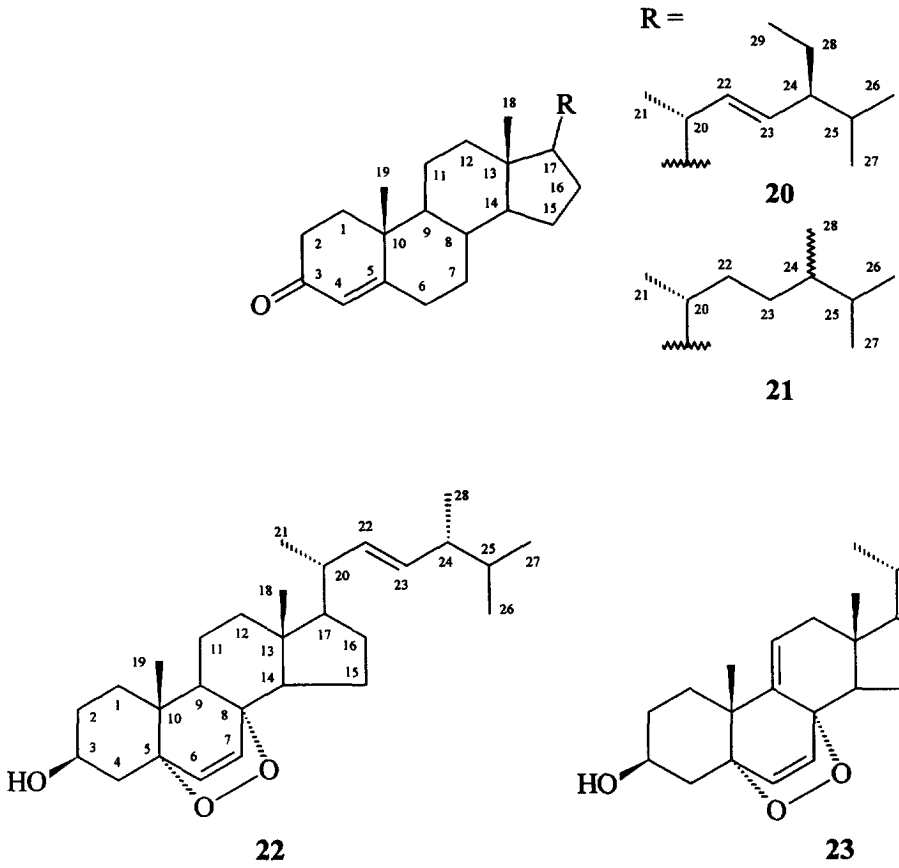


Table 1. $^1$H NMR spectral data and coupling constants (in Hz in parentheses) for compounds **3** (in $CDCl_3$), **4** (Benzene-$d_6$) and **8** ($CDCl_3$)

| H | 3 | 4 | 8 |
|---|---|---|---|
| 2 | — | 2.31 *ddd* (13.0, 5.3, 2.4) α<br>1.36 *td* (13.4, 4.9) β | — |
| 3 | 0.27 *dd* (4.0, 4.0) α<br>0.68 *dd* (8.3, 4.0) β | 1.78 *td* (13.4, 5.3) α<br>1.51 *m* β | 2.45 *dd* (10.7, 3.2) α<br>2.40 *dd* (10.7, 7.0) β |
| 4 | 0.75 *m* | — | 3.96 *m* |
| 5 | 1.04 *dd* (14.8, 9.8)<br>1.72 *m* | — | 1.63 *dd* (11.6, 3.6) α<br>1.56 *dd* (11.6, 5.4) β |
| 6 | — | 6.04 *m* | — |
| 7 | 1.20 *dd* (13.5, 3.0) α<br>1.28 *dd* (13.5, 10.8) β | — | 2.11 *m* |
| 8 | 1.86 *m* | 2.55 *m* α<br>1.90 *dd* (17.7, 6.6) β | 1.41 *m*<br>1.32 *dd* (11.3, 2.2) |
| 9 | 1.72 *m* | 1.56 *m* α<br>1.09 *m* β | 1.54 *m* |
| 10 | 1.82 *m* α<br>2.38 *m* β | 1.48 *m* | 1.86 *m* α<br>1.22 *m* β |
| 11 | 5.53 *br s* | 2.10 *m* | 2.15 *m* α<br>2.28 *m* β |
| 12 | 1.15 *s* | 0.91* *d* (6.6) | 1.66 *br s* |
| 13 | 0.82 *s* | 0.89* *d* (6.6) | 0.89 *s* |
| 14 | 0.96 *s* | 0.65 *d* (6.8) | 1.03 *s* |
| 15 | 0.98 *d* (6.6) | 1.06 *s* | 0.88 *d* (6.7) |
| C-4-OH | | 2.93 *br s* | |

* Interchangeable signals.

Table 2. $^{13}C$ NMR spectral data of compounds **3** ($CDCl_3$), **4** (Benzene-$d_6$) and **8** ($CDCl_3$)

| C | 3 | 4 | 8 |
|---|---|---|---|
| 1 | 152.7 *s* | 91.8 *s* | 142.3 *s* |
| 2 | 18.9 *s* | 24.6 *t* | 121.9 *s* |
| 3 | 21.9 *t* | 30.6 *t* | 41.9 *t* |
| 4 | 22.7 *d* | 98.6 *s* | 71.4 *d* |
| 5 | 42.0 *t* | 201.0 *s* | 46.2 *t* |
| 6 | 32.8 *s* | 123.3 *d* | 33.0 *s* |
| 7 | 44.8 *t* | 165.0 *s* | 48.0 *d* |
| 8 | 49.4 *d* | 30.8 *t* | 46.7 *t* |
| 9 | 42.3 *d* | 35.4 *t* | 41.3 *d* |
| 10 | 39.3 *t* | 38.3 *d* | 31.6 *t* |
| 11 | 124.4 *d* | 37.2 *d* | 29.7 *t* |
| 12 | 28.5 *q* | 21.0* *q* | 22.2 *q* |
| 13 | 30.4 *q* | 20.5* *q* | 32.0 *q* |
| 14 | 29.7 *q* | 15.4 *q* | 30.1 *q* |
| 15 | 18.9 *q* | 25.3 *q* | 32.0 *q* |

* Interchangeable signals.

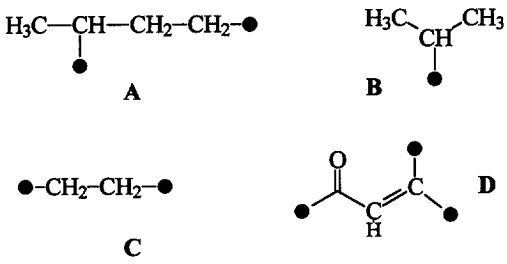


Fig. 1. Partial structures of compound **4**

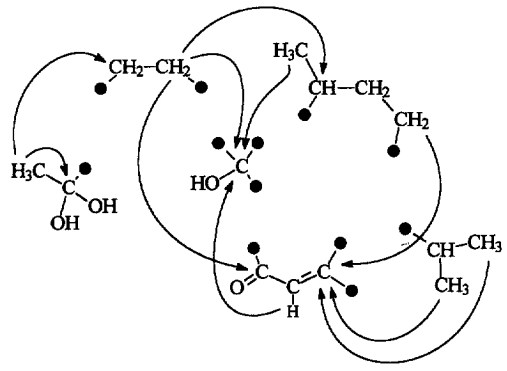

Fig. 2. Most important long-range H—C correlations of compound **4**

be an oxygen bridge between the two oxygen-bearing quaternary carbon atoms, thus giving the structure of a 4,5-seco-guaiane (Fig. 3), which might be theoretically derived from *iso*-α-gurjunene B (**1**) by oxidative bond cleavage between C-4 and C-5, followed by oxidation at C-1 and formation of the hemiacetal. The stereochemistry of compound **4** was derived from a NOESY spectrum. Correlations existed between the methyl group at C-10 and the two methylene protons at C-2. Additionally, only one of the two possible epimers of that hemiacetal which are normally seen in liquid state [see sacculaporellin (**11**)] were observed.

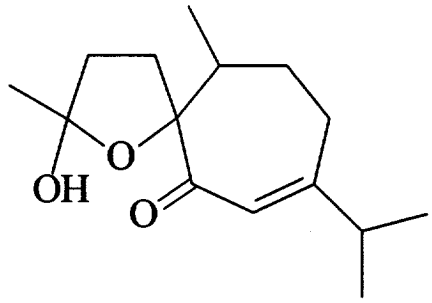

Fig. 3. Plain structure of the 4,5-seco-guaiane **4**

So the hydroxyl group at C-4 had to be in the β-position to form a hydrogen bridge to the ketone at C-5, giving structure **4**.

Compound **8** was a sesquiterpenoid with the formula ($C_{15}H_{26}O$ ($[M]^+ = m/z$ 222), and thus having three degrees of unsaturation. The $^{13}C$ NMR spectrum (Table 2) revealed the existence of a tetrasubstituted double bond ($\delta_C$ 142.3, *s*, C-1; 121.9, *s*, C-2) and an oxygen-bearing methine carbon atom ($\delta_C$ 71.4, *d*, C-4). As no further functional groups could be detected, compound **8** had to be a bicyclic system. The $^1H$ NMR spectrum (Table 1) showed the signal of an oxygen-bearing methine group ($\delta_H$ 3.96, *m*, H-4), and four methyl groups, one of them being olefinic ($\delta_H$ 1.66, *br s*, H-12). The remaining three showed resonances at $\delta$ 1.03 (*s*, H-14), 0.89 (H-13) and 0.88 (H-15).

By analysis of the $^1H$–$^1H$ and $^1H$–$^{13}C$ COSY spectra, three partial structures (A–C) were evident (Fig. 4). The HMBC spectrum showed the following connections (Fig. 5): The methine proton and the neighbouring methylene group of segment A showed connections to the olefinic carbon atom at $\delta$ 121.9 (C-2) of segment B. The second substituent of that carbon atom was the olefinic methyl group, because of the correlation between that methyl group ($\delta_H$ 1.66, *br s*, H-12) and the methylene carbon atom of segment A ($\delta_C$ 41.9, *t*, C-3). Segment C was the third substituent of that double bond, because there were correlations between the protons of the terminating methylene carbon atom of segment C ($\delta_H$ 2.28, *m*; 2.15, *m*, H-11) and the olefinic carbon atoms of segment B. Finally, the two remaining singlet methyl groups ($\delta_H$ 1.03, *s*, H-14; 0.88, *s*, H-15) showed correlations to the last carbon atom ($\delta_C$ 33.0, *s*, C-6), to the methylene group

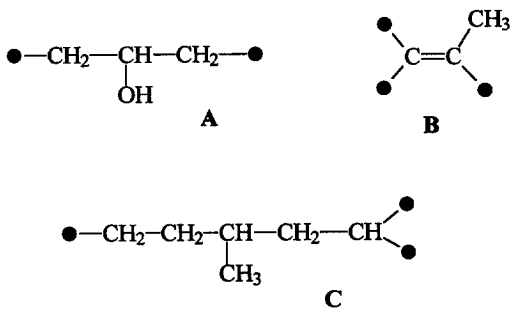


Fig. 4. Partial structures of compound **8**

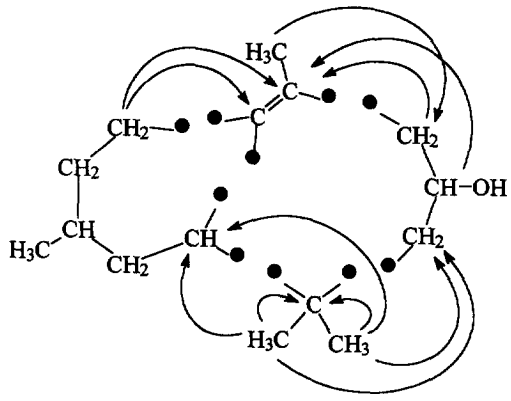

Fig. 5. Most important long-range correlations of compound **8**

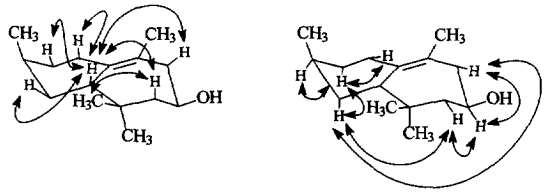

Fig. 6. Relevant NOE-correlations of compound **8**

Table 3. $^{13}C$ NMR spectral data of compounds **9**, **14**, and **15** ($CDCl_3$ each)

| C | 9 | 14 | 15 |
|---|---|---|---|
| 1 | 37.8a *t* | 59.4 *t* | 35.8 *s* |
| 2 | 18.9 *t* | 123.2 *d* | 39.8 *t* |
| 3 | 31.3a *t* | 140.0 *s* | 19.1 *t* |
| 4 | 35.8 *s* | 39.7 *t* | 34.4 *t* |
| 5 | 52.4 *d* | 25.0 *t* | 132.4 *s* |
| 6 | 23.9 *t* | 36.5 *t* | 134.6 *s* |
| 7 | 38.8 *t* | 32.6 *d* | 45.6 *d* |
| 8 | 147.8 *s* | 37.0 *t* | 151.0 *d* |
| 9 | 59.4 *d* | 24.8 *t* | 140.9 *s* |
| 10 | 39.0 *s* | 33.1 *t* | 195.2 *s* |
| 11 | 58.8 *t* | 39.3 *d* | 82.5 *d* |
| 12 | 106.3 *t* | 77.0 *d* | 147.8 *d* |
| 13 | 15.8 *q* | 36.3 *t* | 130.6 *s* |
| 14 | 20.8 *q* | 78.2 *d* | 173.4 *s* |
| 15 | 44.5 *t* | 34.2 *d* | 10.6 *q* |
| 16 | 21.8 *t* | 18.3* *q* | 9.9 *q* |
| 17 | 125.1 *d* | 17.4* *q* | 22.2 *q* |
| 18 | 131.0 *s* | 14.1 *q* | 28.6 *q* |
| 19 | 17.5 *q* | 19.4 *q* | 28.2 *q* |
| 20 | 25.7 *q* | 16.1 *q* | |

* Interchangeable signals.

of segment A ($\delta_C$ 46.2, *t*, C-5) and the methine carbon atom of segment C ($\delta_C$ 48.6, *d*, C-7). The last remaining bond forms the bicyclic system of a 1-himachalen-4-ol. In the NOESY spectrum, two sets of correlations were observed, so the ring system of compound **8** were rigid, giving one set for the protons above and one for the protons below the rings. The most important NOE interactions shown in Fig. 6. As both the protons H-4 and H-9 were below the ring system, the alcohol and the methyl group C-15 had to be in $\beta$-positions, although the methyl group showed no correlations. The methine proton H-7 was also on the same side of the ring. Therefore, compound **8** has to be the 1-himachalen-4$\beta$-ol with the given relative stereochemistry.

Compound **9**, $C_{20}H_{34}O$, ($[M]^+ = m/z$ 290), with four degrees of unsaturation, showed in the $^{13}C$ NMR spectrum (Table 3) the presence of 20 carbon atoms, of which three functional groups were detectable. The first was a secondary alcohol function ($\delta_C$ 58.8, *t*, C-11), the second an exomethylene group ($\delta_C$ 106.3, *t*, C-12, 147.8, *s*, C-8) and finally a trisubstituted double bond with carbon atoms at $\delta$ 125.1 (*d*, C-17) and 131.0 (*s*, C-18). This double bond was characterised in the $^1H$ NMR spectrum (Table 4) by an olefinic proton coupling with a methylene carbon atom ($\delta_H$ 5.06, *t*, 7.1 Hz, H-17) and two olefinic methyl groups at $\delta$ 1.66 (*br s*, H-20) and 1.58 (*br s*, H-19), indicative of an isoprenyl moiety. Additionally, two more methyl groups could be detected at higher field: ($\delta_H$ 0.78, *s*, H-14; 0.73, *s*, H-13). Together these signals indicated a bicyclic carbon skeleton with an isoprenyl side chain and six genuine or oxidized methyl groups. One skeleton with these characteristics is that of the sacculatanes, a skeleton occurring only in liverworts. The substitution pattern and stereochemistry of sacculatanes can be obtained by comparison of the $^{13}C$ NMR data with those of drimane sesquiterpenes, which show a very similar substitution pattern. After comparison with the $^{13}C$ data of albicanol [29], all carbon atoms of the decaline system could be attributed. The remaining signals of the side chain were compared with the data of other sacculatanes [30, 31]. Compound **9** was thus characterized as 8(12),17-sacculatadien-11-ol, the first sacculatane type isolated from *P. epiphylla*. As this skeleton occurs in *P. endiviifolia* [31] and in *P. neesiana* [32] it seems to be characteristic to the genus *Pellia*.

Table 4. $^1H$ NMR spectral data and coupling constants (in Hz in parentheses) for compounds **9** and **10** ($CDCl_3$ each)

| H | 9 | 10 |
|---|---|---|
| 7 | 2.39 *m* | 5.53 *br s* |
| 9 | — | 2.92 *br s* |
| 11 | 3.81 *dd* (10.6, 3.6)<br>3.76 *dd* (10.6, 10.6) | — |
| 12 | 4.91 *s*<br>4.62 *s* | 1.65 *br s* |
| 13 | 0.73 *s* | 1.00 *s* |
| 14 | 0.78 *s* | 0.90 *s* |
| 17 | 5.06 *t* (7.1) | 5.04 *t* (7.1) |
| 19 | 1.58 *br s* | 1.57 *br s* |
| 20 | 1.66 *br s* | 1.65 *br s* |

Compound **10**, $C_{20}H_{32}O_2$ ($[M]^+ = m/z$ 304), gave a similar $^1H$ NMR spectrum (Table 4) to that of compound **9**, indicating a sacculatane derivative. Instead

Table 5. $^1$H NMR spectral data and coupling constants (in Hz in parentheses) for compound **14** ($CDCl_3$)

| H | **14** |
|---|---|
| 1 | 4.12 *d* (6.8) |
| 2 | 5.37 *t* (6.8) |
| 4 | 1.96 *t* (7.5) |
| 12 | 3.74 *m* |
| 13 | 1.42 *m* |
| 14 | 3.58 *m* |
| 15 | 1.63 *m* |
| 16 | 0.89 *d* (6.8) |
| 17 | 0.89 *d* (6.8) |
| 18 | 0.86 *d* (6.7) |
| 19 | 0.83 *d* (6.6) |
| 20 | 1.63 *br s* |

of the two signals of the exomethylene group, there was the signal of an olefinic proton ($\delta_H$ 5.53, *br s*, H-7) and the signal of an olefinic methyl group ($\delta_H$ 1.66, *br s*, H-12), so the double bond had moved into the ring. Additionally, the signals of the alcohol moiety had disappeared, and a new signal was present at $\delta$ 2.92 (*br s*, H-9). This is in accordance with a carboxyl moiety at C-11, explaining the mass spectrum with its additional degree of unsaturation and the unusual upfield shift of H-9. Due to the small amount of the sample (2.4 mg), no $^{13}$C NMR data could be obtained, but the existence of the carboxyl group was proven by the typical absorption in the IR spectrum at 1710 $cm^{-1}$. Thus, compound **10** is 7,17-sacculatadien-11-acid. The stereochemistry shown here was assumed by analogy to the other two sacculatanes presented in this paper.

The $^1$H NMR spectrum (Table 5) of compound **14**, $C_{20}H_{40}O_3$ ($[M+H]^+ = m/z$ 329) was nearly identical to that of phytol (**13**) i.e. an allylic primary alcohol moiety at $\delta_H$ 4.12 (*d*, H-1), an olefinic proton at $\delta_H$ 5.37 (*t*, H-2), an olefinic methyl group at $\delta_H$ 1.63 (*br s*), and four more doublet methyl groups between $\delta$ 0.89 and 0.83 (H-16, H-17, H-18, H-19). Additionally, there were two signals at $\delta$ 3.74 (*m*, H-12) and 3.58 (*m*, H-14) corresponding to two additional methine carbon atoms in the $^{13}$C NMR spectrum ($\delta_C$ 78.2, *d*, C-14; 77.0, *d*, C-12) (Table 3). Therefore, compound **14** appeared to be a dihydroxyphytol. The position of the two additional hydroxy groups was determined from the two-dimensional NMR spectra. The $^1$H–$^1$H-COSY showed a correlation between the signal at $\delta$ 3.74 (H-12) to a methylene group, whose signal appears at $\delta$ 1.42 as an unresolved multiplet. The latter signal was also correlated to the second hydroxy methine group at $\delta$ 3.58 (H-14). Finally, this second signal was correlated to a methine proton at $\delta$ 1.63 (H-15) which in the HMBC spectrum showed correlations to two methyl carbon atoms ($\delta_C$ 18.3, C-16; 17.4, C-17) (Fig. 7). This is only possible, if the hydroxy functions are at C-12 and C-14 of the phytane skeleton, thus compound **14** has to be 12,14-dihydroxyphytol (2-phyten-1,12,14-triol). The stereochemistry of these new stereocentres remains to be confirmed.

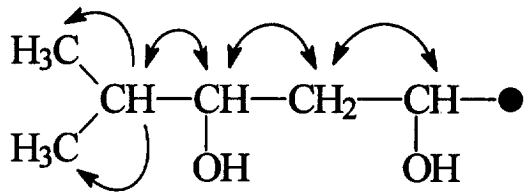


Fig. 7. Significant $^1$H-$^1$H-COSY (↔) and long-range (→) correlations of compound **14**

The NMR spectra of compound **15** indicated an unusual, highly functionalized molecule. The $^{13}$C NMR spectrum (Table 3) showed the signals for 19 carbon atoms. This, together with the $[M]^+$ signal of $m/z$ 302 in the mass spectrum, suggested a molecular formula of $C_{19}H_{26}O_3$, a nor-diterpenoid with seven degrees of unsaturation.

Examination of the 2D NMR spectra revealed two main partial structures A and B (Fig. 8). Moiety A was a trimethylcyclohexene ring, very typical for terpenoid compounds of the cyclofarnesane type. The second partial structure B was a linear chain of four methine carbon atoms: an olefinic proton ($\delta_H$ 6.66, H-8; $\delta_C$ 151.0, C-8) of a trisubstituted double bond showed $^1$H–$^1$H-couplings to an aliphatic proton ($\delta_H$ 3.26, H-7; $\delta_C$ 45.6, C-7), which was correlated to a proton of a carbon atom bearing an oxygen ($\delta_H$ 5.35, H-11; $\delta_C$ 82.5, C-11). The coupling to a second olefinic proton of another trisubstituted double bond ($\delta_H$ 7.00, H-12; $\delta_C$ 147.8, C-12) resulted in the last carbon atom of this chain. The correlations of the HMBC spectrum showed the connections of the partial structures to give the complete molecule (Fig. 9). The correlations

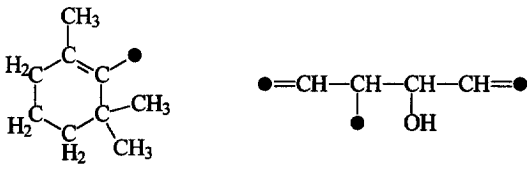


Fig. 8. Partial structures of compound **15**

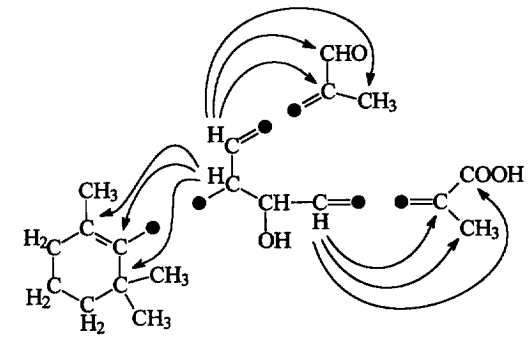


Fig. 9. Important long-range H—C correlations of compound **15**

of the aliphatic methine proton of partial structure B to the quaternary carbon atoms of the cyclohexene ring ($\delta_C$ 35.8, C-1; 132.4, C-5; 134.6, C-6) connected the two partial structures. The two double bonds were assigned as follows: The methine proton next to the alcohol function ($\delta_H$ 7.00, H-12) was correlated to an olefinic carbon atom ($\delta_C$ 130.6, *s*, C-13), a carbonyl group ($\delta_C$ 173.4, *s*, C-14) and a methyl group ($\delta_C$ 10.6, *q*, C-15). The NOE interaction between the methyl group ($\delta_H$ 1.91, H-15) and the olefinic proton proved the *Z*-configuration. The remaining olefinic proton ($\delta_H$ 6.66, H-8) showed analogous correlations to an olefinic atom ($\delta_C$ 140.9, C-9), a formyl group ($\delta_C$ 195.2, *d*, C-10) and again a methyl group ($\delta_C$ 9.9, *q*, C-16). Here, a NOE-interaction between the formyl group ($\delta_H$ 9.44, *s*, H-16) and the olefinic proton established an *E*-configuration. The lowfield shift of the methine proton ($\delta_H$ 5.35, H-11) and the mass spectrum required the presence of a lactone ring between C-11 and the carboxyl group C-14. Additionally, the IR spectrum showed the lactone absorption band at 1760 $cm^{-1}$, in accordance to data from the literature for such a butenolide [33].

The remaining NOE-interactions showed correlations between H-8 and H-11, but no correlation to H-7. This and the $^3J$ coupling constants of 9.9 Hz and H-7 to both H-8 and H-11 suggest a *trans-trans*-configuration of these three protons, resulting in the shown relative stereochemistry.

Due to the complex structure, compound **15** was given the name pellialactone. Pellialactone cannot be assigned to any known diterpene skeleton, but nevertheless it is of terpenoid origin. From C-1 to C-10, a nor-cyclofarnesane skeleton is detectable, C-11 to C-14 forms a further isoprenyl moiety.

## EXPERIMENTAL

*General.* Since the determination of the absolute configuration is not possible by NMR spectroscopy, this remains to be clarified. So the structure drawings of the new terpenoids represent one of the two possible enantiomers.

Solvents used for spectra measurements: $CDCl_3$ and benzene-$d_6$ for NMR [$^1$H NMR: 400 MHz, $^{13}$C NMR: 100 MHz for one-dimensional, 500 MHz and 125 MHz for two-dimensional techniques, respectively, chemical shifts are given in $\delta$ values (ppm) from TMS], $CHCl_3$ for optical rotation.

*Plant material.* See ref. [1].

*Extraction and isolation.* Freeze-dried, powdered gametophytes of *P. epiphylla* (750 g) were extracted with $Et_2O$. The extract was evapd *in vacuo* and chromatographed on Sephadex LH-20 using MeOH–$CH_2Cl_2$ (1:1) as eluent to yield four main frs. Frs 2–4 contained only phenolic compounds, presented in a previous paper [1]. Fr. 1 was chromatographed on silica gel *via* VLC using a hexane–EtOAc gradient to yield 11 frs. Fr. 1, the hydrocarbon fr. was sepd *via* HPLC and argentation chromatography [34] (hexane–TBME, 99.5:0.5, 95:5, and 85:15) to give **3** (9.3 mg), **1** (38.4 mg), and **2** (14.4 mg), respectively.

*Compound* **3**. $[\alpha]_D^{20} = -116°$ (*c* 0.210); IR *v* $cm^{-1}$: 2980, 2960, 2860, 1460, 1380, 1360, 1020, 820; $^1$H NMR: Table 1; $^{13}$C NMR: Table 2; EIMS *m/z* (rel. int.): 204 $[M]^+$ (43), 189 (38), 175 (13), 161 (38), 147 (40), 133 (100), 119 (72), 105 (80), 91 (83), 77 (39), 65 (16), 55 (41).

Fr. 3 was chromatographed *via* HPLC on silica gel (hexane–TBME, 19:1) to yield **7** (18.4 mg). Fr. 4 yielded after sepn by HPLC on silica gel (hexane–EtOAc 97:3) **9** (21.4 mg), **5** (4.7 mg), and **17** (2.9 mg).

*Compound* **9**. $[\alpha]_{365}^{20} = -13°$ (*c* 0.394); IR *v* $cm^{-1}$: 3400, 2920, 2860, 1650, 1440, 1380, 1020, 890; $^1$H NMR: Table 4; $^{13}$C NMR: Table 3; EIMS *m/z* (rel. int.): 290 $[M]^+$ (0.6), 205 (5), 161 (10), 149 (8), 135 (10), 133 (12), 121 (17), 119 (14), 109 (29), 107 (19), 105 (26), 95 (28), 93 (28), 91 (27), 81 (32), 69 (50), 67 (23), 55 (48), 43 (100), 41 (98).

Fr. 5 was chromatographed on silica gel *via* HPLC (hexane–EtOAc, 23:2) to give three further frs. Fr. 1 was sepd *via* HPLC (silica gel, $CH_2Cl_2$–EtOAc 97:3) to give a mixture of **20** and **21** (8 mg), which were identified by their mass spectra in the GC-MS. The second fr. was sepd in the same way to yield **11** (13.2 mg). The last fr. was purified by HPLC (silica gel, hexane–*iso*-PrOH, 97:3) to give **8** (9.4 mg) and **13** (5.6 mg).

*Compound* **8**. $[\alpha]_D^{20} = +1°$ (*c* 0.670); IR *v* $cm^{-1}$: 3400, 2920, 2860, 1620, 1460, 1370, 1170, 1080, 1020, 760; $^1$H NMR: Table 1; $^{13}$C NMR: Table 2; EIMS *m/z* (rel. int.): 222 $[M]^+$ (11), 207 (11), 189 (45), 180 (41), 164 (27), 147 (46), 133 (34), 123 (75), 107 (100), 95 (61), 91 (53), 81 (57), 67 (28), 55 (37).

Fr. 6 was sepd by HPLC (silica gel, hexane–*iso*-PrOH, 99.25:0.75) to give **12** (14.5 mg) and two frs, whose purification gave **10** (2.4 mg) and **6** (4.8 mg) (silica gel, hexane–EtOAc, 9:1 and 22:3, respectively).

*Compound* **10**. $[\alpha]_D^{20} = +26°$ (*c* 0.140); IR *v* $cm^{-1}$: 3500, 3020, 2980, 1710, 1500, 1430, 1260, 1230; $^1$H NMR: Table 4; EIMS *m/z* (rel. int.): 304 $[M]^+$ (19), 289 (4), 219 (80), 173 (18), 119 (34), 109 (52), 81 (45), 69 (100), 55 (82).

After recrystallisation of fr. 7 from hexane, **7** (138 mg) was obtained as a pure compound. Fr. 8 was prepurified by HPLC (silica gel, hexane–EtOAc, 41:9) to give three main frs, whose purification yielded **15** (4.7 mg), **4** (1.8 mg) (silica gel, hexane–EtOAc, 7:3), and **18** (6.8 mg) (silica gel, hexane–EtOAc, 17:8).

*Compound* **4**. $[\alpha]_D^{20} = -82°$ (*c* 0.065); IR *v* $cm^{-1}$: 3440, 2970, 2940, 1670, 1450, 1380, 1240, 1010, 940, 910, 880, 850; $^1$H NMR: Table 1; $^{13}$C NMR: Table 2; EIMS *m/z* (rel. int.): 252 $[M]^+$ (9), 207 (10), 169 (16), 151 (100), 141 (49), 135 (15), 128 (56), 123 (36), 118 (26), 109 (26), 99 (94).

*Compound* **15**. $[\alpha]_D^{20} = -117°$ (*c* 0.205); IR *v* $cm^{-1}$: 2940, 2870, 1760, 1690, 1460, 1200, 1090, 1040, 950, 860, 760; $^1$H NMR: Table 6; $^{13}$C NMR: Table 3; EIMS *m/z* (rel. int.): 302 $[M]^+$ (2), 177 (38), 135 (9), 121 (25),

Table 6. $^1$H NMR spectral data and coupling constants (in Hz in parentheses) for compound **15** ($CDCl_3$)

| H | 15 |
|---|---|
| 2 | 1.42 *m* α/β |
| 3 | 1.57 *m* α/β |
| 4 | 2.02 *m* α/β |
| 7 | 3.26 *t* (9.9) |
| 8 | 6.66 *dd* (10.0, 1.2) |
| 10 | 9.44 *s* |
| 11 | 5.35 *dt* (9.9, 1.8) |
| 12 | 7.00 *t* (1.5) |
| 15 | 1.91 *t* (1.7) |
| 16 | 1.81 *d* (1.3) |
| 17 | 1.83 *s* |
| 18 | 0.81 *s* |
| 19 | 0.89 *s* |

109 (16), 107 (21), 105 (17), 97 (38), 91 (36), 69 (51), 55 (30), 41 (100), 39 (73).

Fr. 10 was sepd by HPLC (silica gel, hexane–EtOAc, 7:3, followed by RP18, $H_2O$–MeOH: 2:23) to give **22** (15.8 mg) and **23** (1.0 mg). The last fr. was purified by HPLC on diol modified silica gel (hexane–EtOAc, 3:1) and gave **16** (20.8 mg) and **14** (22.8 mg).

*Compound* **14**. $[\alpha]_D^{20} \pm 0°$ (*c* 0.424); IR *v* $cm^{-1}$: 3360, 2920, 2860, 1410, 1380, 1060, 1010, 850; $^1$H NMR: Table 5; $^{13}$C NMR: Table 3; CIMS$^+$: *m/z* 329 $[M+H]^+$.

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