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# Plagiochilines T and U, 2,3-secoaromadendranes from the liverwort *Plagiochila carringtonii* from Scotland[1]

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**Abstract**

NMR fingerprinting of five samples of *Plagiochila carringtonii* has shown that the species in Scotland is characterized by the presence of plagiochilines T and U, two new 2,3-secoaromadendranes, in the ratio 2:1, respectively. Plagiochilines T and U were isolated, characterized by GC–MS and $^1$H NMR and the structures elucidated as 2α,15-diacetoxy-2,3-epoxy-2,3-seco-(1α,5α,6β,7β)-aromadendra-3,10(14)-dien-13-al and methyl 2α,15-diacetoxy-2,3-epoxy-2,3-seco-(1α,5α,6β,7β)-aromadendra-3,10(14)-dien-13-oate, respectively. They differ from plagiochiline C by oxidation of the cyclopropyl β-methyl substituent to an aldehyde and a methyl ester respectively and are the first recorded examples with oxidation beyond the alcohol level at this position. *P. carringtonii* may be assigned to the most common *Plagiochila* chemotype, the 2,3-secoaromadendrane group. 

*Keywords:* *Plagiochila carringtonii*; Hepaticae; Liverworts; NMR fingerprinting; GC–MS; $^1$H NMR parameters; Sesquiterpenoid; Plagiochiline T and U

## 1. Introduction

As part of our systematic investigation of the British members of the liverwort genus *Plagiochila* (Rycroft & Cole, 1998; Rycroft, Cole, & Aslam, 1998; Connolly et al., 1999; Rycroft et al., 1999) using NMR fingerprinting (Rycroft, 1996) and GC–MS, we now report the structural elucidation and isolation of two new 2,3-secoaromadendranes, plagiochilines T and U, from *Plagiochila carringtonii* (Balfour) Grolle. Known originally from the British Isles and the Faroes (Averis, 1991), and first described as *Adelanthus carringtonii*, this taxon is a typical member of the community forming the North Atlantic hepatic mat (Averis, 1992). It has had a chequered taxonomic career because for a long period female plants were unknown and male plants were poorly known. It was assigned to the genus *Jamesoniella* for over 70 years until eventually female plants of a related subspecies were found in Nepal and the perianth structure showed clearly that the species belonged to the genus *Plagiochila* rather than *Jamesoniella* (Grolle, 1964). Chemosystematic studies looking at acyclic polyols, including one of unknown structure, provided a picture consistent with this placing (Lewis, 1970). The lipophilic compounds described in this paper provide further support.

## 2. Results and discussion

We have investigated the lipophilic constituents of five specimens of *P. carringtonii* from sites in three different vice-counties of Scotland, including Ben Vorlich (Macvicar, 1902), the locality of the lectotype

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(Grolle, 1964). The $^1$H NMR spectra of $CDCl_3$ extracts showed two sets of signals in the ratio 2:1, each consisting in part of a doublet and a singlet in an otherwise clear region around $\delta$ 6.5 where the signals characteristic of H-2 and H-3 of 2,3-secoaromadendranes are observed. However, the chemical shifts did not correspond to data published for known plagiochilines. GC–MS studies of the same solutions confirmed the presence of two dominant compounds ($R_i$ 2335 and 2398) and also gave profiles of the more volatile lipophilic components of the extracts (Table 1; extract 96016, prepared two years before the GC–MS work was performed, gave inconsistent results and is not included). Assignments of known compounds are based on our previous work and comparison with the literature (Adams, 1995). Derivatization experiments monitored by GC–MS showed that none of the compounds in Table 1 formed acetates, but that the major compound, plagiochiline T, formed a methyl oxime. HR GC–MS studies suggested that plagiochiline T had the formula $C_{19}H_{24}O_6$ and that the minor compound, plagiochiline U, had the formula $C_{20}H_{26}O_7$ (on the basis that the ions measured at 319.1543 and 318.1469 resulted from loss of $CH_3CO_2$ and $CH_3CO_2H$). Plagiochilines T and U were each isolated using TLC. In the $^1$H NMR spectra, features common to the two compounds in addition to the characteristic H-2 and H-3 signals are two acetates, a trisubstituted double bond, an exomethylene and a cyclopropyl methyl group. The molecular formulae therefore indicate that an extra double bond equivalent has to be accommodated if the usual tricyclic plagiochiline ring system is present.

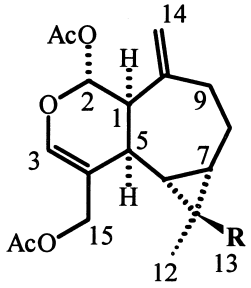
Inspection of the $^1$H NMR spectrum of plagiochiline T aided by homonuclear decoupling and NOE difference experiments enabled the proton connectivity network of almost the entire molecule to be constructed unambiguously. The main sequence traceable starts at the doublet of H-2 and continues through H-1, H-5, H-6, H-7, H-8α and H-8β to H-9α and H-9β of the 2,3-secoaromadendrane skeleton. Irradiation in the vicinity of H-9β removed the 1 Hz allylic coupling of the H-14 exomethylene proton at $\delta$ 4.90. The signal for H-3 displays an unresolved triplet splitting that was removed by decoupling 2H-15 and indicates that C-15 carries one of the two acetoxyl groups. Comparison with the NMR data of plagiochiline C (**1**) (Rycroft, 1996) places the second acetoxyl group at C-2 and suggests that the stereochemistry is the same. The presence of only one cyclopropyl methyl group in conjunction with a singlet at $\delta$ 8.71, formation of an oxime derivative and consideration of the molecular formula suggested that the second cyclopropyl methyl group had been oxidised to an aldehyde. The unusual highly-shielded position of the aldehyde proton is almost the same as that ($\delta$ 8.69) reported previously for the *exo*-aldehyde substituent on the cyclopropane ring of an aristolenal (Wu & Chen, 1992) and contrasts strongly with the more deshielded position ($\delta$ 9.60) observed for the *endo*-aldehyde group present on the cyclopropane ring of a bicyclogermacrenal (Toyota, Nagashima, Fukuyama, Honda, & Asakawa, 1988). Irradiation of the aldehyde proton in an NOE difference experiment produced NOEs at H-6 and H-7 and demonstrated that the configuration is indeed *exo* and that the aldehyde carbon is C-13, on the β-face of the molecule. Plagiochiline T is therefore 2α,15-diacetoxy-2,3-epoxy-2,3-seco-(1α,5α,6β,7β)-aromadendra-3,10(14)-dien-13-al (**2**), with the absolute configuration assumed to be as in plagiochiline C (Matsuo, Atsumi,

Table 1
Occurrence (based on low resolution GC–MS) of ten components[a] in four $CDCl_3$ extracts of *Plagiochila carringtonii*

| Peak No. | Assignment | $R_i$ | $M_r$[b] | Base peak | Percentage abundance from GC–MS TIC integration[c] for collection number | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | 97011 | 97018 | 97135 | 98006 |
| 1 | oct-1-en-3-yl acetate | 1093 | (128) | 43 | 3 | 2 | 2 | 1 |
| 2 | | 1362 | 202 | 159 | + | 12 | 12 | 13 |
| 3 | β-barbatene | 1425 | 204 | 93 | 8 | 5 | 9 | 4 |
| 4 | bicyclogermacrene | 1477 | 204 | 121 | – | 6 | 8 | 9 |
| 5 | spathulenol | 1548 | (205) | 43 | 2 | 2 | – | + |
| 6 | | 1789 | 216 | 43 | 3 | 4 | 2 | 3 |
| 7 | | 1949 | 274 | 124 | – | 5 | 4 | – |
| 8 | | 1978 | 272 | 135 | 2 | 4 | 1 | + |
| 9[d] | plagiochiline T (**2**) | 2335 | 348 | 43 | 26 | 29 | 23 | 33 |
| 10 | plagiochiline U (**3**) | 2398 | 378 | 43 | 14 | 15 | 11 | 15 |

[a] Peaks (except fatty acid peaks) are included if the integrated intensity in any extract was ≥2% of the total integrated intensity.
[b] Numbers in parentheses indicate the peak observed with greatest $m/z$ rather than $M_r$.
[c] Peaks detectable at a low level are indicated by +.
[d] On formation of a methyl oxime, this peak moved: $R_i$ 2366, $m/z$ 346 $[M-OMe]^+$, base peak 43.

& Nakayama, 1981). Carbonyl substituents on cyclopropane rings generally adopt conformations with bisected geometry (Tidwell, 1987). The *exo* or *endo* configuration of an aldehyde substituent will have a strong influence, through changes in the steric interactions, on the conformational equilibrium about the cyclopropyl—carbonyl bond and large changes in the chemical shift of the aldehyde proton are a possible consequence; it is likely that not only conjugation but also magnetic anisotropy make important contributions to the shifts actually observed (cf. Balci, Fischer, & Günther, 1980). In these circumstances shift prediction is difficult; although our observations suggest that, empirically, the aldehyde proton chemical shift may have diagnostic value in distinguishing the *exo* and *endo* configurations, confirmation of this from additional examples would be useful.




| | R |
|---|---|
| **1** | Me |
| **2** | CHO |
| **3** | $CO_2Me$ |
| **4** | $CH(OMe)_2$ |

The $^1H$ NMR spectrum of plagiochiline U differs from that of T by the presence of a methoxyl signal and the absence of the aldehyde signal. The molecular formula indicates that in this case the extra double bond equivalent is present in the form of a methoxycarbonyl substituent on the cyclopropane. The close similarity of the other $^1H$ NMR parameters (assigned using homonuclear decoupling) is taken as evidence that this methoxycarbonyl substituent also has a β-orientation and that plagiochiline U is methyl 2α,15-diacetoxy-2,3-epoxy-2,3-seco-(1α,5α,6β,7β)-aromadendra-3,10(14)-dien-13-oate (**3**).

Some of the plant material was extracted using methanol. The $^1H$ NMR spectrum of one of the TLC bands from this extract showed that it consisted of a ca. 2:1 mixture of plagiochiline T and its dimethyl acetal (**4**). The latter compound is evidently readily hydrolysed because after partial evaporation of a $CDCl_3$ solution in a stream of nitrogen, GC–MS and $^1H$ NMR showed that conversion of **4** to **2** was complete and the methanol produced had been removed by entrainment with the $CDCl_3$.

Derivatives of plagiochiline A (10,14-epoxyplagiochiline C) where cyclopropane methyl groups are oxidised to the alcohol level (and acetylated) were reported twenty years ago from Japanese *Plagiochila hattoriana* (Asakawa, Toyota, & Takemoto, 1978) and from French *P. asplenioides* (Asakawa, Toyota, Takemoto, & Suire, 1979) but plagiochilines O from Colombian *P. cristata* and S from an axenic culture of Panamanian *P. adianthoides* were the first derivatives of plagiochiline C itself (**1**) where similar oxidation was discovered (Valcic, Zapp, & Becker, 1997). Plagiochilines T and U are the first recorded examples where oxidation to the aldehyde and carboxyl level at one of the cyclopropane carbon substituents has occurred. Oxidation of a different methyl group (C-15) to the carboxyl level is known in plagiochilines L & M (Hashimoto, Nakamura, Tori, Takaoka, & Asakawa, 1995), but these have been isolated from *Heteroscyphus planus* only, a member of the family Geocalycaceae rather than Plagiochilaceae. It was possible to detect traces of other plagiochilines in the *P. carringtonii* extracts, with, for example, 1% of plagiochiline C in No. 97018.

The discovery of plagiochilines T and U enables the chemosystematic position of *P. carringtonii* to be established as a 2,3-secoaromadendrane chemotype (Asakawa, 1995). Therefore the *Plagiochila* that for most of the time that it has been known to science was regarded as a *Jamesoniella* turns out chemically to be a member of the most common *Plagiochila* chemotype. As in the cases of 9,10-dihydrophenanthrenes in *P. spinulosa* (Connolly et al., 1999), plagiochiline C and atlanticol in *P. atlantica* (Rycroft & Cole, 1998) and bibenzyls in *P. exigua* (Rycroft, Cole, & Aslam, 1998), the close similarity of the plagiochiline profiles of the five *P. carringtonii* samples studied is consistent with the hypothesis that the extant populations of these vegetatively reproducing liverworts may be derived from single clones (Hill, Collins, & Edwards, 1998).

## 3. Experimental

### 3.1. General

TLC, GC, GC–MS and $^1H$ NMR (360 or 400 MHz, $CDCl_3$) were generally performed as described previously (Rycroft, Cole, & Rong, 1998). HR GC-CI/EI(70eV)–MS mass measurements used a CP Sil 8 CB-MS column (25 m × 0.25 mm × 0.12 μ*m*) with He at 1 ml $min^{-1}$ and the same temperature programming as in the other GC work. $R_f$ values relate to the solvent system $CHCl_3$:EtOAc = 5:1.

### 3.2. Plant material

*P. carringtonii* was collected by DSR in W. Scotland. Vouchers have been deposited in the University of Glasgow herbarium (GL). The following were used to prepare solutions for the NMR and GC/GC–MS studies: (i) No. 96016, collected 2nd April 1996 (Sgurr Dubh, Coulin Forest, Kinlochewe, v.-c.

105 West Ross), 77 mg extracted 12th April 1996; (ii) No. 97011, collected 30th March 1997 (An Teallach, v.-c. 105 West Ross), 149 mg extracted 27th October 1997; (iii) No. 97018, collected 1st April 1997 (Conival, v.-c. 107 East Sutherland), 183 mg extracted 1st November 1997; (iv) No. 97135, collected 5th September 1997 (Beinn Eighe, v.-c. 105 West Ross), 51 mg extracted 10th November 1997 and (v) No. 98006, collected 16th February 1998 (Ben Vorlich, v.-c. 99 Dunbarton), 104 mg extracted 1st March 1998.

### 3.3. Extraction

Extracts were prepared by triturating dried plant material with sufficient $CDCl_3$ to produce 0.6–0.7 ml of a filtered solution. The concentration of plagiochiline T in extracts (i), (ii), (iii), (iv) and (v) was 0.2, 1, 1, 0.2 and 1 mM, respectively; the concentration ratio T:U was always ca. 2:1. Compounds in the extracts and derivatives were characterized in situ using GC/GC–MS. The remainder of these solutions was carried over for the TLC studies, which also used a MeOH extract of additional material of No. 98006.

### 3.4. Compound characterization and isolation

#### 3.4.1. Plagiochiline T (**2**)

Isolated (ca. 0.2 mg) from the MeOH extract using TLC ($R_f$ 0.42). $^1$H NMR showed that 31% was present as the dimethyl acetal, Section 3.4.2; after the $CDCl_3$ solution had been concentrated using a stream of $N_2$, GC–MS and $^1$H NMR showed that the dimethyl acetal had been hydrolysed and an essentially pure sample of **2** remained. GC-CI(isobutane)–HRMS (using a TLC fraction containing T and U), $R_i$ 2335: $m/z$ 349.1664 $[MH]^+$ ($C_{19}H_{25}O_6$ requires 349.1651), 289.1427 $[MH - MeCO_2H]^+$ ($C_{17}H_{21}O_4$ requires 289.1440). GC–MS $m/z$ (rel. int.): 348 $[M]^+$ (1), 319 (1), 305 (1), 289 (5), 288 (3), 260 (5), 259 (3), 228 (17), 217 (7), 200 (9), 199 (15), 185 (11), 171 (9), 153 (11), 149 (8), 147 (7), 145 (9), 143 (7), 138 (7), 133 (8), 121 (7), 109 (22), 105 (11), 95 (15), 91 (19), 81 (15), 79 (14), 77 (11), 67 (6), 55 (8), 53 (6), 43 (100), 41 (9). $^1$H NMR (400 MHz): $\delta$ 1.12 (1H, br. dddd, $J$=14, 12, 11, 2 Hz, H-8α), 1.26 (3H, s, $H_3$-12), 1.48 (1H, dd, $J$=10.2, 9.4 Hz, H-6), 1.72 (1H, ddd, $J$=10.6, 10.2, 7.0 Hz, H-7), 2.00 (3H, s, OAc), 2.11 (3H, s, OAc), 2.16 (1H, ddd, $J$=14, 7, 6 Hz, H-8β), 2.23 (1H, dd, $J$=9.4, 3.8 Hz, H-5), 2.24 (1H, br. dd, $J$=14, 12 Hz, H-9β), 2.41 (1H, br. dd, $J$=14, 6 Hz, H-9α), 2.88 (1H, dd, $J$=10.2, 3.8 Hz, H-1), 4.35 (1H, d, $J$=12.4 Hz, H-15), 4.42 (1H, d, $J$=12.4 Hz, H-15), 4.87 (1H, d, $J$=2.1 Hz, H-14), 4.90 (1H, br. dd, $J$=2, 1 Hz, H-14), 6.39 (1H, br. t, $J$=1 Hz, H-3), 6.64 (1H, d, $J$=10.2 Hz, H-2), 8.71 (1H, s, H-13).

#### 3.4.2. Plagiochiline T dimethyl acetal [2α,15-diacetoxy-2,3-epoxy-13,13-dimethoxy-2,3-seco-(1α,5α,6β,7β)-aromadendra-3,10(14)-diene] (**4**)

Present initially in a sample of plagiochiline T isolated from the MeOH extract using TLC, Section 3.4.1. $^1$H NMR (400 MHz, assigned signals only): $\delta$ 1.04 (3H, s, $H_3$-12), 2.05 (3H, s, OAc), 2.10 (3H, s, OAc), 2.36 (1H, br. dd, $J$=13, 6 Hz, H-9α), 2.83 (1H, br. dd, $J$=10, 4 Hz, H-1), 3.31 (3H, s, 13-OMe), 3.34 (3H, s, 13-OMe), 3.87 (1H, s, H-13), 4.45 (1H, d, $J$=12.2 Hz, H-15), 4.53 (1H, br. dd, $J$=12.2, 1 Hz, H-15), 4.81 (1H, d, $J$=2.4 Hz, H-14), 4.84 (1H, br. d, $J$=2 Hz, H-14), 6.32 (1H, br. s, H-3), 6.58 (1H, d, $J$=9.9 Hz, H-2).

#### 3.4.3. Plagiochiline T methyl oxime

Prepared by treatment of plagiochiline T with methoxylamine hydrochloride in pyridine. GC–MS, $R_i$ 2366, $m/z$ (rel. int.): 346 $[M–CH_3O]^+$ (6), 286 (13), 244 (19), 226 (14), 215 (2), 198 (5), 153 (7), 148 (3), 145 (4), 135 (3), 124 (25), 117 (5), 105 (4), 94 (16), 91 (12), 81 (7), 79 (8), 77 (9), 67 (5), 55 (6), 53 (6), 43 (100), 41 (9).

#### 3.4.4. Plagiochiline U (**3**)

Isolated (ca. 0.05 mg) using TLC ($R_f$ 0.53) and characterized using GC–MS and $^1$H NMR. GC-EI-HRMS (using the MeOH extract), $R_i$ 2398, $m/z$ (rel. int.): 319.1543 $[M–CH_3CO_2]^+$ (5.5%) ($C_{18}H_{23}O_5$ requires 319.1545), 318.1469 $[M–CH_3CO_2H]^+$ (8.2%) ($C_{18}H_{22}O_5$ requires 318.1467). GC–MS $m/z$ (rel. int.): 378 $[M]^+$ (1), 319 (3), 318 (3), 276 (4), 259 (8), 258 (19), 245 (8), 226 (4), 216 (6), 199 (9), 198 (7), 187 (6), 171 (6), 159 (5), 145 (9), 136 (6), 129 (5), 117 (5), 109 (21), 105 (8), 95 (6), 91 (15), 81 (11), 79 (11), 77 (9), 67 (6), 59 (5), 55 (7), 53 (6), 43 (100), 41 (9). $^1$H NMR (400 MHz, assigned signals only): $\delta$ 1.27 (3H, s, $H_3$-12), 1.57 (1H, dd, $J$=10.5, 9.5 Hz, H-6), 1.80 (1H, td, $J$=10.5, 7.1 Hz, H-7), 2.01 (3H, s, OAc), 2.10 (3H, s, OAc), 2.15 (1H, dd, $J$=9.5, 3.8 Hz, H-5), 2.36 (1H, br. dd, $J$=13, 6 Hz, H-9α), 2.85 (1H, dd, $J$=10.2, 3.8 Hz, H-1), 3.65 (3H, s, $CO_2Me$), 4.37 (1H, d, $J$=12.3 Hz, H-15), 4.45 (1H, d, $J$=12.3 Hz, H-15), 4.83 (1H, d, $J$=2.1 Hz, H-14), 4.87 (1H, br. d, $J$=2 Hz, H-14), 6.36 (1H, br. t, $J$=1 Hz, H-3), 6.63 (1H, d, $J$=10.2 Hz, H-2).

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