Chromenes and Prenylated Benzoic Acid Derivatives from the Liverwort *Pedinophyllum interruptum*

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The chemical composition of a diethyl ether extract of the Scottish liverwort *Pedinophyllum interruptum* has been examined. Two new prenylated benzoic acid derivatives, methyl 2,6-dihydroxy-4-methoxy-3-(3'-methyl-2'-butenyl)benzoate and methyl 2,4,6-trihydroxy-3-(3'-methyl-2'-butenyl)benzoate, two new chromenes, methyl 5,7-dihydroxy-2,2-dimethyl-2*H*-chromene-6-carboxylate and methyl 7-hydroxy-5-methoxy-2,2-dimethyl-2*H*-chromene-8-carboxylate, and the two known chromenes methyl 8-hydroxy-2,2-dimethyl-2*H*-chromene-6-carboxylate and methyl 8-methoxy-2,2-dimethyl-2*H*-chromene-6-carboxylate were isolated. Methyl 2,4,6-trihydroxy-3-(3'-methyl-2'-butenyl)benzoate was unstable in air and was quickly converted into methyl 2,4,6-trihydroxy-3-(2'-hydroperoxy-3'-methyl-3'-butenyl)benzoate. All structures were elucidated by means of NMR spectroscopic techniques and mass spectrometry.

Key words: Pedinophyllum interruptum, Prenylated Benzoic Acid Derivatives, Chromenes

Introduction

Pedinophyllum interruptum (Nees) Kaal., is one of only four species of the genus *Pedinophyllum* (Plagiochilaceae). It grows in Europe, West Russia and Eastern North America. The plant is rare in Europe and has been over-recorded in the past because of confusion with certain forms of *Plagiochila porelloides* that often occur in the same habitat [1]. No previous phytochemical studies have been carried out on this species. In continuing our investigations on the constituents of liverworts [2 – 4] we now report the identification of six simple phenolic compounds, the prenylated benzoic acid derivatives **1** and **2** and the chromenes **4** – **7**, from a diethyl ether extract of *P. interruptum*. Chromenes **6** and **7** are known compounds [5].

Results

A small sample of the liverwort *P. interruptum* was extracted with diethyl ether and six uv active compounds were isolated: the new natural products **1**, **2**, **4** and **5** and two known substances, methyl 8-hydroxy-2,2-dimethyl-2*H*-chromene-6-carboxylate **6** and methyl 8-methoxy-2,2-dimethyl-2*H*-chromene-6-carboxylate **7** (Fig. 1). Assignments of the ^{1}H and ^{13}C data for **1, 3, 4** and **5** were carried out with the aid of HMQC, HMBC and NOESY experiments. Only the ^{1}H NMR spectrum of **2** was obtained before it was transformed to the hydroperoxide **3** (Fig. 1). Compounds **6** and **7** were identified by their ^{1}H NMR data which were consistent with the literature values [5]. This is the first report of **7** as a natural product.

Compound **1** was obtained as a colourless oil which slowly solidified to crystals, m.p. 72 – 73 °C. HREIMS analysis gave a parent ion at m/z 266.1154 which supported the molecular formula $C_{14}H_{18}O_5$. The ^{1}H and ^{13}C NMR spectra in $CDCl_3$ showed the signals of a di-C-substituted phloroglucinol moiety with three oxygenated aromatic carbons at δ_C 164.6, 161.3 and 159.1 and only one aromatic proton at δ_H 6.06. The two substituents were revealed as a carbomethoxyl group (δ_C 170.3, 52.6; δ_H 4.03, *s*) and a prenyl side chain [δ_H 3.25 (d, $J = 6.9$ Hz, 2 × H-1'), δ_C 21.9 (C-1'); δ_H 5.16 (t, $J = 6.9$ Hz, H-2'), δ_C 123.2 (C-2'); δ_C 131.4 (C-3'); δ_H 1.76 (s, 3 × H-5'), δ_C 18.0 (C-5'); δ_H 1.67 (s, 3 × H-4'), δ_C 26.0 (C-4')]. In addition, the resonances of a methoxy group (δ_C 55.9, δ_H 3.83, *s*) were observed. The HMBC spectrum showed it was attached to the oxygenated aromatic carbon at δ_C 164.6. A NOE difference experiment showed an effect between the aromatic proton and the protons of the methoxy group, hence the two were vicinal. Since H-1' corre-

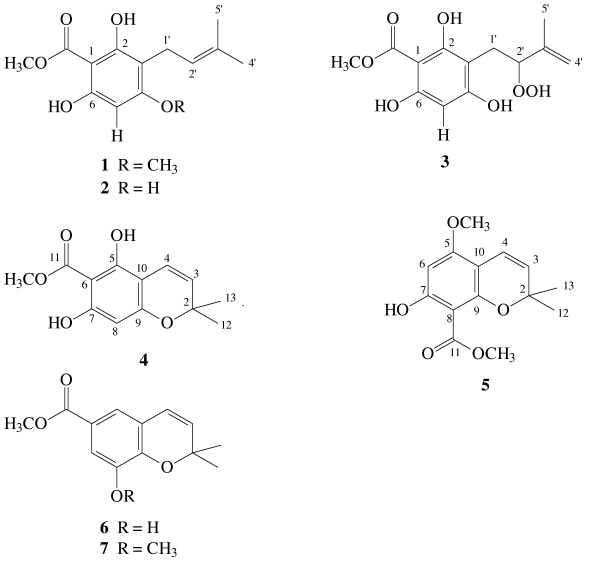

Fig. 1. Structures of methyl 2,6-dihydroxy-4-methoxy-3-(3'-methyl-2'-butenyl)benzoate (**1**), methyl 2,4,6-trihydroxy-3-(3'-methyl-2'-butenyl)benzoate (**2**), methyl 2,4,6-trihydroxy-3-(2'-hydroperoxy-3'-methyl-3'-butenyl)benzoate (**3**), methyl 5,7-dihydroxy-2,2-dimethyl-2H-chromene-6-carboxylate (**4**), methyl 7-hydroxy-5-methoxy-2,2-dimethyl-2H-chromene-8-carboxylate (**5**), methyl 8-hydroxy-2,2-dimethyl-2H-chromene-6-carboxylate (**6**) and methyl 8-methoxy-2,2-dimethyl-2*H*-chromene-6-carboxylate (**7**).

lated with the oxygenated carbon at δ_C 164.6 in the HMBC the prenyl side chain was also vicinal to the methoxy group. Hence the carbomethoxyl group had to be positioned between the two remaining hydroxyl groups leading to structure **1**, methyl 2,6-dihydroxy-4-methoxy-3-(3'-methyl-2'-butenyl)benzoate, for this compound, which is a new natural product. It has already been mentioned in a publication on the synthesis of phloroglucinol derivates but no data except for the melting point were given [6].

Compound **2** was detected in the GC-MS spectrum of the crude extract (*m/z* 252 $[M]^+$) but could not be isolated at first due to its instability. Therefore another small sample of the same plant was extracted and **2** was isolated immediately. A HREIMS (m/z = 252.0999 $[M]^+$, $C_{13}H_{16}O_5$) and a ^{1}H NMR spectrum in C_6D_6 could be recorded before the molecule decomposed to give compound **3**. For better comparison, the NMR data of **1** in C_6D_6 are also given in the experimental. The ^{1}H NMR spectrum of compound **2** was very similar to that of **1** and revealed an aromatic proton at δ_H 5.99 (s, H-5), a prenyl side chain [δ_H 3.56 (d, J = 7.3 Hz, 2 × H-1'); δ_H 5.47 (t, J = 7.3 Hz, H-2'); δ_H 1.73 (s, 3x H-5'); δ_H 1.61 (s, 3 × H-4')] and, in contrast to **1**, only one methoxy group at δ_H 2.94. Since the structural elucidation of **3**, described below, clearly showed the presence of a methyl ester the structure of **2** was established as methyl 2,4,6-trihydroxy-3-(3'-methyl-2'-butenyl)benzoate.

The parent ion of **3** in the EIMS was at m/z 284 ($C_{13}H_{16}O_7$) and thus **3** contained two more oxygens than compound **2**. The ^{1}H and ^{13}C NMR spectra (C_6D_6) showed resonances for an aromatic proton (δ_H 6.24, s), three oxygenated aromatic carbons (δ_C 162.3, 160.9, 156.3) and a carbomethoxyl group (δ_C 170.2, 51.5; δ_H 2.94, s) revealing that the two molecules had the same aromatic moiety but differed in the prenyl side chain. The double bond was now between C-3' and C-4' (δ_C 144.3, 113.0) as deduced from the ^{1}H NMR spectrum which showed signals for the two methylene protons (δ_H 5.05, brs, 2 × H-4') and for the methyl group C-5' (δ_H 1.81) attached to it. The carbon at C-2' was oxidised to a hydroperoxide which resulted in a characteristic downfield shift for C-2' to δ_C 88.7. These assignments were also confirmed by comparison with the data for similar side chains [7]. The hydroperoxide was also not stable and eventually decomposed to a complex mixture of products.

The ^{1}H NMR of **4** showed signals for two methyl groups (both δ_H 1.39, H-12 and H-13) attached to an oxygen-bearing carbon and two olefinic protons at δ_H 5.54 and 6.50 (J = 10.1 Hz each) indicating the heterocyclic part of a 2,2-dimethyl-2*H*-chromene moiety. The ^{13}C NMR spectrum in $CDCl_3$ showed only four signals for the aromatic ring subunit: three aromatic carbons (δ_C 125.8, 115.9, 102.2) and one oxygenated carbon (δ_C 160.5). However, in a different solvent (DMSO-d_6) the signals of three oxygenated carbons (δ_C 160.8, 158.7, 156.8) were revealed, indicating a phloroglucinol moiety. The highfield chemical shift of the only aromatic proton at δ_H 5.90 (*s*, H-8) supported this conclusion. The ring carried a carbomethoxyl group (δ_C 170.3, 52.4, δ_H 3.84) that should be attached either to C-6 or to C-8. In the ^{1}H NMR spectrum in DMSO-d_6 the signals of two chelated hydroxyls appeared at δ_H 10.99 and 10.21, indicating that the carbomethoxyl group had to be at C-6, vicinal to both hydroxyls. Further proof of this structure was provided by a NOESY experiment in DMSO-d_6 in which correlations of H-8 with the proton of C-7-OH and the geminal methyls H-12 and H-13 were observed. Thus the structure of **4** was elucidated

as methyl 5,7-dihydroxy-2,2-dimethyl-2*H*-chromene-6-carboxylate.

Compound **5** was also a chromene derivative. Initially we thought it was a methyl ether of **4** because of the similarity of the ^{1}H and ^{13}C NMR spectra: there was a phloroglucinol moiety with three oxygenated carbons (δ_C 164.6, 160.1 and 155.6) and a highfield aromatic proton (δ_H 6.00). One of the hydroxyls was methylated (δ_C 55.6, δ_H 3.76) and the second hydroxyl (δ_H 11.82) was vicinal to the methyl ester (δ_C 171.6, 51.8, δ_H 3.84). However, the correlations in the HMBC showed that the position of the methyl ester was not at C-6 as in **4** but at C-8. The oxygenated carbons at δ_C 160.1 and 155.6 had $^3J_{CH}$-correlations from the double bond proton H-4 at δ_H 6.46 and should therefore be either C-5 or C-9. The methoxy group was attached to the carbon at δ_C 160.1. Since it is impossible for C-9 to carry a methoxy group the carbon at δ_C 160.1 was assigned to C-5. Accordingly, the carbon at δ_C 155.6 had to be attributed to C-9. Thus the remaining hydroxyl bearing carbon (δ_C 164.6) was assigned to C-7. C-5 and C-7 had $^2J_{CH}$-correlations from the aromatic proton. If this were H-8 it should correlate with C-7 and C-9, while H-6 should correlate with C-5 and C-7. Hence the aromatic proton had to be at position 6 and the methyl ester attached to C-8. This structure was further supported by a NOESY experiment which revealed effects between the aromatic proton and the protons of the methoxy group at C-5. Thus the structure of **5** was established as methyl 7-hydroxy-5-methoxy-2,2-dimethyl-2*H*-chromene-8-carboxylate. It seems likely that the prenylated benzoic acids **1** and **2** are the biogenetic precursors of the chromenes **5** and **4** respectively.

2,2-Dimethyl-2*H*-chromenes are widespread in many higher plants, especially in Asteraceae [8–9] and Rutaceae [10]. However, they are rare liverwort constituents. The only chromene derivatives that have been reported are structural variations of prenylated bibenzyls in which a prenyl side chain of the bibenzyl is cyclised to give 2,2-dimethylchromene derivatives. These were isolated from the liverworts *Radula kojana* [11], *R. perrottetii* and *R. complanata* [12], *R. laxiramea* [3] and *Lethocolea glossophylla* [13]. Recently methyl 5,7-dihydroxy-2,2-dimethyl-2*H*-chromene-6-carboxylate and methyl 7-hydroxy-5-methoxy-2,2-dimethyl-2*H*-chromene-8-carboxylate were also isolated from another Hepaticae species, *Adelanthus lindenbergianus* [14].

Experimental Section

Spectroscopy

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a BRUKER DPX-400 spectrometer. The chemical shifts are given in δ values (ppm) relative to TMS as internal standard; 2D spectra were recorded as H,H-COSY, HMQC and HMBC experiments. The UV spectra were recorded on a Shimadzu UV mini-1240 UV-vis spectrophotometer, while IR spectra were recorded on a Jasco FR-IR-410 spectrophotometer. Mass spectra were recorded in the positive EI mode on a Jeol JMS-700 instrument.

Plant material

P. interruptum (Nees) Kaal. was collected in Glen Stockdale, Scotland and identified by DSR in September 1998. A voucher specimen is retained in the Chemistry Department, University of Glasgow.

Extraction and isolation

2.5 g powdered, air dried plant material was extracted with Et_2O. The extract (230 mg) was separated by VLC on diol silica (diol silica gel 40–63 μm, stepwise with a *n*-hexane-EtOAc gradient) gel to give 9 fractions (A-I). HPLC of fraction B (1–1.5% EtOAc) on silica gel (LiChrospher Si 100, 5 μm, 4 × 250; *n*-hexane:EtOAc 96:4) gave **4** (1 mg), **5** (1 mg) and **1** (6 mg). Fraction C (8–10% EtOAc) was methyl 8-methoxy-2,2-dimethyl-2*H*-chromene-6-carboxylate **7** (1 mg), HPLC (LiChrospher Si 100, 5 μm, 4 × 250; *n*-hexane:EtOAc 90:10) of fraction E (7–10% EtOAc) yielded methyl 8-hydroxy-2,2-dimethyl-2*H*-chromene-6-carboxylate **6** (1 mg) (Orjala *et al.*, 1993). Fraction H (18–20% EtOAc) was also pure and yielded **2** (1 mg).

Spectroscopic data

*Methyl 2,6-dihydroxy-4-methoxy-3-(3'-methyl-2'-butenyl)-benzoate (**1**)*

Colourless oil, which solidifies readily. – M.p. 72–73 °C (CH_2Cl_2). – UV ($CHCl_3$): λ_{max} = 273, 318 nm. – IR (film) ν = 3415, 2960, 2925, 2855, 1675, 1645, 1590, 1430, 1285, 1155, 1105 cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 6.06 (s, H-5), 5.16 (t, J = 6.9 Hz, H-2'), 4.03 (s, $COOCH_3$), 3.83 (s, OCH_3), 3.25 (d, J = 6.9 Hz, 2 × H-1'), 1.76 (s, 3 × H-5'), 1.67 (s, 3 × H-4'). – ^{1}H NMR (C_6D_6): δ = 6.11 (s, H-5), 5.63 (t, J = 7.2 Hz, H-2'), 3.68 (d, J = 7.2 Hz, 2× H-1'), 3.18 (s, OCH_3), 2.97 (s, $COOCH_3$), 1.88 (s, 3× H-5'), 1.71 (s, 3 × H-4'). – ^{13}C {^{1}H} NMR ($CDCl_3$): δ = 170.3 (*C*$OOCH_3$), 164.6 (C-4), 161.3 (C-6), 159.11 (C-2), 131.4 (C-3'), 123.2 (C-2'), 109.4 (C-3), 94.1 (C-1), 92.0 (C-5), 55.9 (OCH_3), 52.6 (*C*$OOCH_3$), 26.0 (C-4'), 21.9 (C-1'), 18.0 (C-5'). – ^{13}C {^{1}H} NMR (C_6D_6): δ = 170.2 (*C*$OOCH_3$), 164.6 (C-4), 161.7 (C-2), 159.0 (C-6), 130.7 (C-3'), 123.9 (C-2'), 109.2 (C-3), 94.3

(C-1), 92.0 (C-5), 55.1 (OCH_3), 51.5 ($COOCH_3$), 26.0 (C-4'), 22.2 (C-1'), 17.9 (C-5'). – MS (EI, 70 eV): *m/z* (%) = 266 (92) $[M]^+$, 251 (21), 234 (28), 219 (100), 206 (44), 191 (46), 179 (84), 166 (17), 149 (7), 69 (13). – HREIMS: $m/z = 266.1154$ $[M]^+$ (calcd. for $C_{14}H_{18}O_5$ 266.1154).

*Methyl 2,4,6-trihydroxy-3-(3'-methyl-2'-butenyl)benzoate (**2**)*

Colourless oil. – ^{1}H NMR (C_6D_6): $\delta = 5.99$ (s, H-5), 5.47 (t, $J = 7.3$ Hz, H-2'), 3.56 (d, $J = 7.3$ Hz, 2× H-1'), 2.94 (s, $COOCH_3$), 1.73 (s, 3 × H-5'), 1.61 (s, 3 × H-4'). – MS (EI, 70 eV): *m/z* (%) = 252 (100) $[M]^+$, 237 (16), 220 (41), 205 (83), 192 (50), 177 (50), 165 (87), 152 (14), 123 (10), 69 (20). – HREIMS: $m/z = 252.0999$ $[M]^+$ (calcd. for $C_{13}H_{16}O_5$ 252.0998).

*Methyl 2,4,6-trihydroxy-3-(2'-hydroperoxy-3'-methyl-3'-butenyl)benzoate (**3**)*

Colourless oil. – ^{1}H NMR (C_6D_6): $\delta = 6.24$ (s, H-5), 5.03 (brs, H-4'a), 4.91 (brs, H-4'b), 4.58 (dd, $J = 3.5$, 8.7 Hz, H-2'), 3.18 (dd, $J = 3.5$, 14.8 Hz, H-1'a), 2.98 (dd, $J = 8.7$, 14.8 Hz, H-1'b), 2.94 (s, $COOCH_3$), 1.81 (s, 3 × H-5'). – ^{1}H NMR ($CDCl_3$): $\delta = 6.06$ (s, H-5), 5.05 (brs, 2 × H-4'), 4.46 (dd, $J = 2.9$, 9.0 Hz, H-2'), 4.04 (s, $COOCH_3$), 3.06 (dd, $J = 2.9$, 15.1 Hz, H-1'a), 2.78 (dd, $J = 9.0$, 15.1 Hz, H-1'b), 1.87 (s, 3 × H-5'). – ^{13}C {^{1}H} NMR (C_6D_6): δ = 170.2 ($COOCH_3$), 162.3 (C-4), 160.9 (C-6*), 156.3 (C-2*), 144.3 (C-3'), 113.0 (C-4'), 104.8 (C-3), 96.8 (C-5), 94.2 (C-1), 88.7 (C-2'), 51.5 ($COOCH_3$), 24.9 (C-1'), 19.0 (C-5'). MS (EI, 70 eV): *m/z* (%) = 284 (2) $[M]^+$, 268 (10), 252 (22), 211 (36), 197 (46), 179 (58), 165 (100), 70 (16), 41 (19).
*Assigments interchangeable.

*Methyl 5,7-dihydroxy-2,2-dimethyl-2H-chromene-6-carboxylate (**4**)*

Yellow oil. – UV ($CHCl_3$): λ_{max} = 264, 337 nm. – IR (film) ν = 3400, 2950, 1650, 1580, 1450, 1375, 1050, 950 cm^{-1}. – ^{1}H NMR ($CDCl_3$): $\delta = 6.58$ (d, $J = 10.0$ Hz, H-4), 5.90 (s, H-8), 5.42 (d, $J = 10.0$ Hz, H-3), 3.99 (s, $COOCH_3$), 1.39 (s, 3 × H-12, 3 × H-13). – ^{1}H NMR (DMSO-d_6): $\delta = 10.99$ (s, OH-5), 10.21 (s, OH-7), 6.50 (d, J = 10.1 Hz, H-4), 5.86 (s, H-8), 5.54 (d, $J = 10.1$ Hz, H-3), 3.86 (s, $COOCH_3$), 1.35 (s, 3 × H-12, 3 × H-13); ^{13}C {^{1}H} NMR ($CDCl_3$): $\delta = 169.7$ (C-11), 160.5 (C-5, C-7, C-9), 125.8 (C-3), 115.9 (C-4), 102.2 (C-10), 96.6 (C-8), 93.4 (C-6), 77.6 (C-2), 52.4 ($COOCH_3$), 28.2 (C-12, C-13). – ^{13}C {^{1}H} NMR (DMSO-d_6): $\delta = 170.3$ (C-11), 160.8 (C-7), 158.7 (C-9), 156.8 (C-5), 125.9 (C-3), 115.5 (C-4), 101.3 (C-10), 95.8 (C-8), 95.0 (C-6), 77.2 (C-2), 52.4 ($COOCH_3$), 27.7 (C-12, C-13). – MS (EI, 70 eV): *m/z* (%) = 250 (12) $[M]^+$, 235 (24), 217 (10), 203 (100), 175 (2), 147 (1), 135 (2), 117 (1), 101 (2), 91 (3), 69 (7), 55 (1). – HREIMS: m/z = 250.0841 $[M]^+$ (calcd. for $C_{13}H_{14}O_5$ 250.0841).

*Methyl 7-hydroxy-5-methoxy-2,2-dimethyl-2H-chromene-8-carboxylate (**5**)*

Yellow oil. – UV ($CHCl_3$): $\lambda_{max} = 285$, 332 (nm). – IR (film) ν = 3435, 2925, 2855, 1635, 1445, 1260, 1125, 1100, 810 cm^{-1}. – ^{1}H NMR ($CDCl_3$): $\delta = 11.82$ (s, OH-7), 6.46 (d, $J = 9.8$ Hz, H-4), 6.00 (s, H-6), 5.39 (d, $J = 9.8$ Hz, H-3), 3.84 (s, $COOCH_3$), 3.76 (s, OCH_3), 1.36 (s, 3× H-12, 3 × H-13). – ^{13}C {^{1}H} NMR ($CDCl_3$): $\delta = 171.6$ (C-11), 164.6 (C-7), 160.1 (C-5), 155.6 (C-9), 125.2 (C-3), 116.4 (C-4), 103.7 (C-10), 96.9 (C-8), 92.0 (C-6), 76.8 (C-2), 55.6 (OMe-7), 51.8 ($COOCH_3$), 27.6 (C-12, C-13). – MS (EI, 70 eV): *m/z* (%) = 264 (10) $[M]^+$, 249 (19), 235 (6), 217 (100), 202 (4), 173 (11), 147 (1), 132 (1), 114 (1), 103 (2), 91 (2), 69 (4), 55 (1). – HREIMS: $m/z = 264.0996$ $[M]^+$ (calcd. for $C_{14}H_{16}O_5$ 264.0998).

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