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HIGHLY OXYGENATED NAPHTHALENES AND ACETOPHENONES FROM THE LIVERWORT *ADELANTHUS DECIPIENS* FROM THE BRITISH ISLES AND SOUTH AMERICA†

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Key Word Index—*Adelanthus decipiens*; *Adelanthus crossii*; Adelanthaceae; Jungermanniales; Hepaticae; liverwort; NMR fingerprinting; ^{1}H NMR parameters; GC-MS; naphthalene and acetophenone derivatives.

Abstract—Ten highly oxygenated naphthalene and acetophenone derivatives, including five new natural products, have been identified in $CDCl_3$ extracts of *Adelanthus decipiens* from Scotland, Wales, Ireland, Colombia and Ecuador. Although not all ten compounds were detected in the extracts of all the eight liverwort gatherings examined (two fresh and six herbariumn specimens), the general picture is one of different distributions of compounds rather than the presence or absence of particular compounds in the different samples of liverwort. 1,2-Dimethoxy-3,4-methylenedioxynaphthalene (wettstein A) is the major component in material from the British Isles whereas 1,2,4-trimethoxynaphthalene is the major component in one Colombian specimen and 1,2,3-trimethoxynaphthalene is the major naphthalene derivative in another (the subject of a GC-MS study in 1980). Pentamethoxyacetophenone is the major component in the specimen from Ecuador. The feasibility of using small amounts of herbarium material to undertake this type of study has been demonstrated.

INTRODUCTION

Many liverworts are notable in that they occur in populations that have been highly disjunct globally for millions of years. Often these populations do not reproduce sexually and the hypothesis that each population might be based on a single genotype has been proposed [1], but never tested. Investigation of secondary metabolites is an indirect method of studying plant variability and here we report the results of an investigation of eight different gatherings (from both the northern and southern hemispheres, and including six herbarium specimens) of the liverwort *Adelanthus decipiens* (Hook.) Mitt. In Europe this occurs as one of two species belonging to a genus found largely in the southern hemisphere [2]; the northern limit of its occurrence is in Scotland, where it is confined to the western side of the country [3]. Some of the forms found in South America approach *A. crossii* Spruce, 'which may actually be a synonym' (Gradstein, S.R., personal communication).

Recently we demonstrated that NMR spectroscopy could provide not only a useful fingerprint of an extract of a small amount of plant material, but also useful structural information about individual components: wettsteins A (**1**) and B (**2**) were shown to be the major constituents of the $CDCl_3$ extract of one gathering of *A. decipiens* from Scotland [4]. The information derived from NMR spectra is often complementary to that provided by GC-MS, and combined application of the two techniques constitutes a more powerful means of identifying components of plant extracts than either technique alone. This approach is adopted here in conjunction with preparative TLC to identify several other compounds in extracts of *A. decipiens*.

The only previous report of a chemical study of *A. decipiens* relates to one gathering from Colombia and is restricted to brief GC-MS details, with only β-barbatene and three sterols identified [5]; a voucher specimen of this gathering provided plant material that has been re-investigated as part of this work.

RESULTS AND DISCUSSION

The ^{1}H NMR spectrum of extract GL1 showed that wettsteins A and B were present in the ratio 4:1 [4].

† Part 2 in the series 'NMR Fingerprinting of Liverworts'. For Part 1, see ref. 4.

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GC-MS confirmed the presence of wettsteins A and B (both $[M]^+$ 232) and showed the presence of two other compounds ($[M]^+$ 256 and 240) comparable in amount to wettstein B. Acetylation of the extract increased R_t of the compound with $[M]^+$ 256 by 1 min, indicating the presence of one hydroxyl group. In contrast, GC-MS of extract 96279 showed the compound with $[M]^+$ 256 was the only abundant component in addition to wettsteins A and B; this being so, it was clear that in the ^{1}H NMR spectrum of extract 96279 this compound gives rise to signals from one methyl (acetyl) and four methoxyl groups as well as a deshielded signal from a strongly hydrogen-bonded hydroxyl group. These observations lead to the conclusion that this compound is 2-hydroxy-3,4,5,6-tetramethoxyacetophenone (**3**).

Comparison of the ^{1}H NMR spectra of extracts GL1 and 96279 showed that the fourth component ($[M]^+$ 240) in GL1 has an aromatic proton in addition to one acetyl and four methoxyl groups, consistent with structure **4**, 2,3,4,6-tetramethoxyacetophenone. The substitution pattern was deduced from NOE difference experiments which showed that irradiation of two different methoxyl signals (δ 3.799 and 3.891) caused enhancement of the aromatic proton signal.

Preparative TLC of the combined extracts enabled sub-milligram quantities of **3** and **4** to be isolated and characterised using GC, GC-MS and ^{1}H NMR spectroscopy. The data obtained are consistent with published MS and low field ^{1}H NMR data for **3** [6, 7] and **4** [8]. A third TLC band contained a mixture of **1** and **2**.

The major constituents of extract 97003 (from a third Scottish gathering) were found to be compounds **1**, **2** and **3** in addition to a compound ($[M]^+$ 272) with R_i = 1967, thought to be fusicoccadiene on the basis of comparisons with *Plagiochila spinulosa* extracts (Rycroft, D. S. and Cole, W. J., unpublished work).

The ^{1}H NMR spectrum of the extract of one Colombian specimen (Gr. 4254) showed a set of signals from four adjacent, but non-equivalent, aromatic protons. Three corresponding signals from methoxyl groups as well as a shielded aromatic proton singlet suggested the presence of a trimethoxynaphthalene, which was confirmed by the observation of $[M]^+$ = 218 for the major peak in the GC-MS TIC trace. NOE difference experiments showed that two methoxyl groups (δ 3.996 and 4.012) are *ortho* to the isolated aromatic proton. The major constituent in this extract is therefore 1,2,4-trimethoxynaphthalene (**5**); comparison with the residual $^{12}C^1\underline{H}Cl_3$ signal (29.6 mM) showed the concentration of **5** to be 7.6 mM. The ^{1}H NMR parameters obtained using this dilute solution are within the ranges indicated by the rather discrepant sets of published parameters [9–12], that presumably relate to solutions that are considerably more concentrated.

Wettsteins A (1.4 mM) and B (0.3 mM) were visible as minor components in the ^{1}H NMR spectrum of this Colombian extract, but GC/GC-MS showed that the other major components had $[M]^+$ = 170 (R_i = 1271) and $[M]^+$ = 226 (R_i = 1785). The peak with R_i = 1271 gave a database match with 2-undecanone, confirmed by the observation in the ^{1}H NMR spectrum of a singlet at δ 2.133 and a triplet at δ 2.414 (J = 7.5 Hz) from the protons adjacent to the carbonyl group in 2-undecanone (4.0 mM) in agreement with the literature [13]. Homonuclear decoupling confirmed the presence of an unresolved four-bond coupling between the methyl singlet and the methylene triplet. Acetylation of the extract increased R_t of the peak with R_i = 1785 by 1.2 min, indicating the presence of one hydroxyl group. Observation of a set of proton signals representing a concentration of 3.5 mM and comprising three methoxyl groups, an acetyl group, a highly shielded aromatic singlet and a strongly hydrogen-bonded hydroxyl group suggested, in conjunction with the molecular weight, that the compound (R_i = 1785) is a 2-hydroxy-trimethoxyacetophenone. NOE difference experiments showed that two methoxyl groups (δ 3.899 and 3.942) are *ortho* to the aromatic proton; the chemical shift of this proton (δ 5.970) suggests that it is not *para* to the acetyl group. The conclusion that the compound is 2-hydroxy-3,4,6-trimethoxyacetophenone (**6**) was confirmed by isolation of 0.3 mg using preparative TLC, characterisation using GC and ^{1}H NMR spectroscopy, and comparison with literature data [14, 15].

The second Colombian specimen (Gr. 3688) was the European voucher specimen from the previous chemical investigation of *A. decipiens* [5]. This specimen, a small form of this species, is limited in quantity, and heterogeneous, but a few strands of *A. decipiens* (amounting to 7 mg) were picked out and extracted. The GC-MS data were similar to those reported previously, although after more than 16 years there was no evidence of any β-barbatene. There are six major components, of which **6** (0.03 mM) is the least abundant; the presence of **6** with $[M]^+$ 226 (base peak) suggests that the peak reported [5] as 280 (226) may in fact have risen from **6**, with the peak at m/z 280 arising from an underlying minor component. Wettsteins A (**1**, 0.09 mM) and B (**2**, 0.04 mM) are also present. The ^{1}H NMR spectrum of the major component (0.11 mM, $[M]^+$ = 196) in the mixture shows a pair of *meta*-coupled protons, an acetyl group, and a strongly hydrogen-bonded hydroxyl group at δ 14.029. Together with two methoxyl signals, the parameters correspond to those of 2-hydroxy-4,6-dimethoxyacetophenone (**7**, brevifolin, xanthoxylin) [16, 17]. The presence of a hydroxyl group in **7** (and **6**) was confirmed by GC/GC-MS of the acetylated extract. The remaining two components have $[M]^+$ = 218 and 248. One set of signals (0.10 mM) including an aromatic singlet at δ 6.953 and three methoxyls corresponds to that of 1,2,3-trimethoxynaphthalene (**8**, $[M]^+$ = 218) [18, 19], while another set (0.07 mM) including two methoxyl peaks (each representing two methoxyl groups) and an AA′XX′ spin system corresponds to that expected for

1,2,3,4-tetramethoxynaphthalene (**9**, $[M]^+ = 248$) and is consistent with literature data [20, 21].

Wettsteins A (2.2 mM) and B (0.3 mM) were again identifiable in the ^1H NMR spectrum of the Ecuadorian extract, but another significant component (2.0 mM), with an acetyl group and three methoxyl signals with intensities 1:2:2, appeared to be the pentamethoxylated derivative of acetophenone. GC/GC-MS showed that this component had $R_i = 1620$ and $[M]^+ = 270$. Isolation of 0.1 mg using preparative TLC and characterisation using GC, GC-MS, HR-EIMS and ^1H NMR spectroscopy confirmed that this compound is 1,2,3,4,5-pentamethoxyacetophenone (**10**). The hydroxyacetophenones **3** (0.7 mM) and **6** (0.4 mM) and the naphthalenes **8** (0.4 mM) and **9** (0.1 mM) were identified in the ^1H NMR spectrum of the extract; **3** and **6** were confirmed by GC-MS comparison of the extract and the acetylated extract.

Two old herbarium specimens were investigated. The ^1H NMR spectrum of the extract of a Welsh specimen (over 80 years old) showed only **1** (0.10 mM) and **2** (0.07 mM), but an Irish specimen (over 50 years old) showed **1** (0.25 mM), **2** (0.15 mM), **3** (0.09 mM) and **4** (0.02 mM). The different ratios of **1** and **2** compared to those in the recent specimens may reflect differential rates of slow oxidation of the electron-rich naphthalene derivatives. During the course of the present work we noticed effects attributed to oxidation [22, 23] (probably accentuated by exposure to light in the dilute solutions), especially of **1** and **5**, but were unable to reach firm conclusions on the identity of the reaction products (see Experimental).

1 and **2** have been reported previously in *Wettsteinia schusterana* from New Zealand [24]. *Adelanthus* and *Wettsteinia* are the only genera belonging to the family Adelanthaceae [2] and the finding of **1** and **2** in both these genera emphasises their close relationship. This is the first report of **3**, **4**, **5**, **9** and **10** as natural products. **6** and **7** have been reported in one New Zealand sample of the liverwort *Plagiochila fasciculata* [25], but were not found in another [26]. **8** has been isolated from *Wettsteinia inversa* from Taiwan [18] as well as from the New Zealand *Wettsteinia schusterana* [19]. 2-Undecanone, detected in only one of the extracts, is well known as a natural product but this is the first report of its occurrence in a liverwort extract; contamination by, for example, an exudate from another plant prior to collection of the liverwort ('on twigs in wet *Weinmannia* relict woodland' according to the herbarium packet) resulting in the high level of 2-undecanone observed is thought to be unlikely, but cannot be excluded. In contrast, the diverse origins of the liverwort samples and the presence of two different families of compounds (acetophenones and naphthalenes) militate against any idea that adventitious contamination (fungal or otherwise) might be responsible for the presence of compounds **1**–**10**.

Having determined the nature of the major constituents, we re-examined the GC-MS and NMR data of all the extracts to see if there was evidence for the presence of the eleven identified compounds. The results, summarised in Table 1, show that, in broad terms, most of the compounds are present in most of the extracts. For example, nine of the compounds are identifiable in the extracts from two of the liverwort samples (GL1 and 96279). Thus the differences between the samples are more a matter of degree than of kind, and on the evidence of the secondary metabolites of a limited number of samples, the European

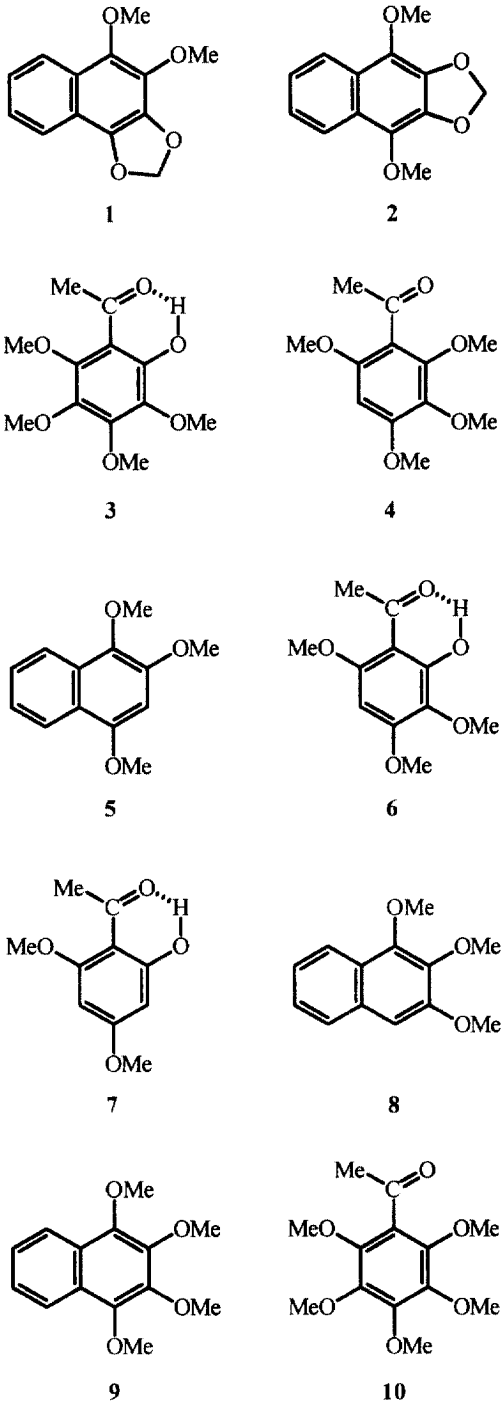

Table 1. Compounds identified in eight extracts of *Adelanthus decipiens*

Country of origin			Scotland	Scotland	Scotland	Wales	Ireland	Colombia	Colombia	Ecuador
Voucher ref. no.			GL1	96279	97003	H3775	H3782	G&S4254	G&A3688	G,M&F 6856
Wt. of material extracted			246 mg	165 mg	73 mg	48 mg	94 mg	81 mg	7 mg	45 mg
	Compound number	R_i	Concentration (mM) determined from NMR spectrum							
2-(HO)-4,6-$(MeO)_2$-acetophenone	**7**	1625							0.11	
2-(HO)-3,4,6-$(MeO)_3$-acetophenone	**6**	1785	0.2	0.1	0.03			3.5	0.03	0.4
2-(HO)-$(MeO)_4$-acetophenone	**3**	1732	2.9	0.6	0.4		0.09			0.7
2,3,4,6-$(MeO)_4$-acetophenone	**4**	1670	2.0	0 01			0.02			
$(MeO)_5$-acetophenone	**10**	1620	0.1	0.03	0.01					2.0
1,2,3-$(MeO)_3$-naphthalene	**8**	1720	0.1	0.01	0.01			0.15	0.10	0.4
1,2,4-$(MeO)_3$-naphthalene	**5**	1752	0.1	0.01	0.005			7.6		
1,2,3,4-$(MeO)_4$-naphthalene	**9**	1764	0.1	0.01	0.02			0.07	0.07	0.1
wettstein A	**1**	1845	12.0	1.7	1.1	0.10	0.25	1.4	0.09	2.2
wettstein B	**2**	1907	3.3	0.5	0.3	0.07	0.15	0.3	0.04	0.3
2-undecanone		1271						4.0		

and South American populations have not diverged greatly and show only minor infraspecific variation.

The present work has established, by developing an idea mooted by Phillipson [27], that it can be feasible to exploit herbarium resources and use NMR spectroscopy, especially in conjunction with GC-MS, to undertake comparative chemical studies of plants, as in this case study of liverworts.

EXPERIMENTAL

General

TLC: precoated silica gel 60 F_{254} plates, layer thickness 0.25 mm for both anal. and prep. work, $CHCl_3$–EtOAc (3:1), visualized by spraying with 10% ceric sulphate in 10% H_2SO_4 and heating, bands from prep. TLC recovered using MeOH. GC: CP Sil 5 CB (Chrompack) fused silica capillary column (25 m × 0.32 mm × 0.12 μm) and FID; the Grob-type injector was operated in split mode (50:1) and the He carrier and make-up gas flow rates were 2 ml min^{-1} and 25 ml min^{-1} respectively; the column temp. was programmed from 80° (held 2 min) to 275° (held 10 min) at 5° min^{-1}; the injection port and detector temp. were 255° and 260°, respectively. The Kováts retention indices of the compounds identified are included in Table 1. GC-MS (70 eV): HP1 fused silica capillary column (12.5 m × 0.2 mm × 0.33 μm); injection and temp. programming conditions were identical to those for GC; retention times from the total ion current (TIC) traces practically matched those of the GC FID chromatograms. ^1H NMR (360 MHz, $CDCl_3$, int. TMS, 25°): under our conditions, the residual $CHCl_3$ signal was at δ 7.261 ± 0.001. HR EI-MS: measured at 70 eV.

Plant material

The samples of *A. decipiens* studied were: (i) Glen Loin, Arrochar (*leg.* D.S. Rycroft, 29th October 1994, no. GL1, *det.* D.G. Long): 246 mg extracted 1st May 1996; 90 mg extracted 7th November 1996. (ii) Glen Stockdale, Appin (*leg.* D.S. Rycroft, 29th September 1996, no. 96279): 165 mg extracted 4th October 1996. (iii) Trilleachan birch woods, Loch Etive (*leg.* D.S. Rycroft, 17th February 1997, no. 97003): 73 mg extracted 21st February 1997. (iv) Colombia (Páramo de Chirgaza, Cundinamarca), (*leg.* S.R. Gradstein & E. Santana, 23-IX-1982, no. Gr. 4254): 81 mg extracted 9th January 1997. (v) Colombia (Páramo de Guasca, Cundinamarca), (*leg.* S.R. Gradstein & J. Aguirre C., 7th August 1980, no. Gr. 3688, *det.* S.R. Gradstein, *teste* R. Grolle): 7 mg extracted 8th May 1997. (vi) Ecuador (Carchi), (*leg.* S.R. Gradstein, R. Mues & J.P. Frahm, 5/6-X-1988, no. 6856): 45 mg extracted 9th January 1997. (vii) Wales (Tyn-y-groes), (*leg.* W. Ingham & J.B. Duncan, August 1914, GL no. H3775): 48 mg extracted 4th March 1997. (viii) Ireland (Slievemore, Achill Island) (*leg. et det.* P.W. Richards,

August 1933, GL no. H3782): 94 mg extracted 4th March 1997. Voucher specimens of *A. decipiens* collected by D.S.R. (all from Argyll, Scotland) are deposited in the University of Glasgow herbarium (GL), which was also the source of the Welsh and Irish specimens. South American specimens came from the University of Göttingen herbarium (GOET). Extracts were prepared by triturating the dried plant material with sufficient $CDCl_3$ to produce 0.6–0.7 ml of a filtered solution.

Extracts GL1 and 96279

Prep. TLC of combined solns gave (wt from integration of ^1H NMR signals relative to the residual $^{12}C^1\underline{H}Cl_3$ signal): an approximately equimolar mixture of **1** and **2** (0.5 mg) R_f 0.7, **3** (0.3 mg) R_f 0.65, and **4** (0.2 mg) R_f 0.56. ^1H NMR: **3**, δ 2.678 (3H, *s*, MeCO), 3.807, 3.859, 3.952, 4.082 (3H × 4, *s* × 4, MeO × 4), 13.155 (1H, *s*, HO-2); **4** δ 2.479 (3H, *s*, MeCO), 3.799, 3.809 (3H × 2, *s* × 2, MeO × 2), 3.891 (6H, *s*, MeO × 2), 6.260 (1H, *s*, H-5).

Extract Gr. 4254, Columbia

GC/GC-MS, compound (TIC rel. abund.), *m/z* (rel. int.): 2-undecanone (81), 170 $[M]^+$ (4), 58 $[Me_2CO]^+$ (100); 'final' oxidation product of **5** (24), 250 $[M]^+$ (3), 235 $[M-Me]^+$ (4), 219 $[M-MeO]^+$ (9), 203 $[M-47]^+$ (2), 191 $[M-MeOCO]^+$ (100); 'intermediate' oxidation product of **5** (26), 250 $[M]^+$ (3), 219 $[M-MeO]^+$ (6), 191 $[M-MeOCO]^+$ (100); **5** (100), 218 $[M]^+$ (77), 203 $[M-Me]^+$ (100), 175 $[M-43]^+$ (69); **9** (ca 1), 248 $[M]^+$ (89), 233 $[M-Me]^+$ (100); **6** (67), 226 $[M]^+$ (100), 211 $[M-Me]^+$ (88); **1** (7), 232 $[M]^+$ (72), 217 $[M-Me]^+$ (100); **2** (4), 232 $[M]^+$ (91), 217 $[M-Me]^+$ (100).

Prep. TLC gave: **5** (ca 0.4 mg) R_f 0.65, and **6** (0.3 mg) R_f 0.54. The ^1H NMR spectrum of the TLC band containing **5** also showed signals attributed to the two oxidation products of **5**; the signals of the 'final' oxidation product (R_i = 1711) increased with time relative to those of the 'intermediate' oxidation product (R_i = 1733) and **5**, and eventually the signals of **5** disappeared; within 2 days, GC-MS of the NMR sample showed essentially one peak and HR-EIMS gave 250.0844 $[M]^+$ (7) ($C_{13}H_{14}O_5$ requires 250.0841), 191.0719 $[M-MeOCO]^+$ (100) ($C_{11}H_{11}O_3$ requires 191.0708), hence broadly confirming the oxidation hypothesis. ^1H NMR: **5** (in the crude extract), δ 3.819 (3H, *s*, MeO-1), 3.996 and 4.012 (3H × 2, *s* × 2, MeO-2 and -3), 6.647 (1H, *s*, H-3), 7.345, 7.493 (1H × 2, *ddd* × 2, J = 8.5, 6.8, 1.2 Hz, H-6, -7), 8.046 (1H, *ddd*, J = 8.5, 1.2, 0.7 Hz, H-8), 8.149 (1H, *ddd*, J = 8.5, 1.2, 0.7 Hz, H-5); **6**, δ 2.625 (3H, *s*, MeCO), 3.819 (3H, *s*, MeO-3), 3.899 and 3.942 (3H × 2, *s* × 2, MeO-4, -6), 5.970 (1H, *s*, H-5), 13.796 (1H, *s*, HO-2); 'intermediate' oxidation product of **5**, δ 3.399 (3H, *s*), 3.723 (3H, *s*), 6.433 (1H, *s*); 'final' oxidation product of **5**, δ 3.522 (3H, *s*), 3.846 (3H, *s*), 5.338 (1H, *s*).

Extract Gr. 3688, Columbia

GC/GC-MS, compound (TIC rel. abund.), *m/z* (rel. int.): **7** (98), 196 $[M]^+$ (32), 181 (100); unknown with R_i = 1677 (31), 206 (9), 163 (100); **8** (100), 218 $[M]^+$ (100), 203 (46), 175 (20), 160 (38); **9** (81), 248 $[M]^+$ (94), 233 (100), 205 (26), 190 (35), 175 (12), 147 (28), 104 (27); **6** (17), 226 $[M]^+$ (100), 211 (96), 183 (49), 165 (47); **1** (37), 232 $[M]^+$ (71), 217 (100), 187 (18), 159 (8), 144 (6), 129 (9), 104 (25); **2** (39), 232 $[M]^+$ (88), 217 (100), 187 (23), 159 (8), 149 (20), 129 (11), 104 (19). ^1H NMR: **7**, δ 2.613 (3H, *s*, MeCO), 3.822, 3.856 (3H × 2, *s* × 2, MeO × 2), 5.924, 6.063 (1H × 2, *d* × 2, J = 2.4 Hz, H-3 and H-5), 14.029 (1H, *s*, HO-2); **8**, δ 3.979, 3.980, 4.051 (3H × 3, *s* × 3, MeO × 3), 6.953 (1H, *s*, H-4); **9**, δ 4.004, 4.028 (6H × 2, *s* × 2, 2 MeO × 2), 7.427, 8.055 (2H × 2, apparent *dd* × 2, 'J = 3.3, 6.5 Hz, H-5,6,7,8 AA'XX' system).

Extract 6856, Ecuador

GC-MS (measurements performed after many NMR experiments, by which time the solution was 3 weeks old and **1** and **2** had decomposed): compound (TIC rel. abund.), *m/z* (rel. int.): **10** (100), 270 $[M]^+$ (100), 255 (77); **8** (7), 218 $[M]^+$ (100), 203 (43), 175 (18), 160 (36); **3** (4), 256 $[M]^+$ (100), 241 (60), 213 (32), 195 (23), 163 (31); **6** (1), 226 $[M]^+$ (100), 211 (88), 183 (43), 165 (39).

Prep. TLC gave **10** (0.1 mg) R_f 0.61. HR-EIMS *m/z* (rel. int.): 270.1097 $[M]^+$ (70) (calc. for $C_{13}H_{18}O_6$: 270.1103), 255.0865 (70), 227.0910 (39), 212.0685 (69), 197.0466 (100), 195.0660 (63); ^1H NMR: δ 2.494 (3H, *s*, MeCO), 3.840 (6H, *s*, OMe × 2), 3.876 (6H, *s*, OMe × 2), 3.949 (3H, *s*, MeO-4).

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