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CARBOXYLATED α-PYRONE DERIVATIVES AND FLAVONOIDS FROM THE LIVERWORT *DUMORTIERA HIRSUTA**

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Key Word Index—*Dumortiera hirsuta*; Hepaticae; carboxylated α-pyrone derivatives; dumortins A–C; flavonoids; synthesis.

Abstract—Three new carboxylated α-pyrone derivatives, dumortins A–C, and a new flavone glycoside have been isolated from the liverwort, *Dumortiera hirsuta*, together with the known flavonoids, luteolin, luteolin-5-*O*-β-D-glucuronide and luteolin-7-*O*-β-D-glucuronide. The structures of the new α-pyrones were confirmed spectroscopically as 4-(3′,4′-dihydroxy-*E*-styryl)-6-carboxy-α-pyrone,4-[2-(3′,4′-dihydroxyphenyl)-ethyl]-6-carboxy-α-pyrone and 3-[1-hydroxy-2-(3′,4′-dihydroxyphenyl)-ethyl]-6-carboxy-α-pyrone. The new flavonoid was elucidated as luteolin-5-*O*-β-D-glucuronide-6″-methyl ester. The structures of dumortins A and B were confirmed by independent chemical synthesis. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

The thalloid liverwort *Dumortiera hirsuta* is a subcosmopolitan species occurring in oceanic and warm to tropical areas [1]. Its taxonomic status based on morphological and chemical studies has been widely discussed [2, 3]. Apart from monoterpene and especially sesquiterpene hydrocarbons [4–6], which are typical for many liverworts, only lunularic acid, lunularin and the unusual flavonoid, luteolin-5-*O*-glucuronide, have been reported from this species as phenolic compounds [2, 7]. However, a reinvestigation by TLC and HPLC gave indications of the presence of further phenolic metabolites; these are the aim of the present work. We report herein the isolation and structural elucidation of three novel carboxylated α-pyrone derivatives, dumortins A–C (**1–3**), and of four flavonoids (**4–7**). A synthetic route to dumortins A and B is also presented.

RESULTS AND DISCUSSION

The phenolic patterns of nine samples from different localities in Europe and South America were compared by 2D TLC and HPLC. Four of the samples exhibited identical profiles of secondary metabolites and were combined for extraction and isolation of phenols. The patterns of the other samples were not completely different, only some spots or peaks of phenolic compounds were missing or less concentrated in the chromatograms. However, **1** and luteolin-5-*O*-glucuronide (**4**) could also be identified in those samples which were not used for the isolation of the phenolics described in this paper.

A combination of VLC and MPLC on RP-18 and column chromatography on Sephadex LH-20 afforded seven phenolic compounds. Among the flavonoids, the previously known compound **4** represented the major secondary metabolite (yield: 250 mg from 16 g of dry plant material = 1.6%). Moreover, we isolated and identified luteolin-7-*O*-glucuronide (**5**), luteolin (**7**) and the new luteolin-5-*O*-β-D-glucuronide-6″-methyl ester (**6**) (NMR data for **4** and **6**: Tables 4 and 5). The latter compound was not an artefact of **4** because it could be detected by HPLC immediately after work-up of a crude 70% aq. acetone extract.

The bright green fluorescence of **1** on TLC plates in UV light and its UV/VIS spectrum with absorption maxima at 252, 300 and 370 nm indicated an extended chromophoric system. The presence of a phenolic *ortho*-dihydroxy group was revealed by Naturstoff-reagenz A on TLC and by the $AlCl_3$-induced shift of 66 nm. The molecular formula was supposed to be $C_{14}H_{10}O_6$ on account of the EI ($[M]^+$ *m/z* 274) and the FAB-mass spectra ($[M-H]^-$ *m/z* 273). The ^1H NMR spectrum afforded signals (Table 1) which could be attributed to a 3,4-di-*O*-substituted *E*-styryl moiety [8] and to two further *meta*-coupled protons. Regarding the signals in the ^{13}C NMR spectrum (seven methines and seven quaternary carbons; DEPT), comparison of literature data [8–10] still required a carboxylated α-pyrone moiety for **1** apart from the signals for the

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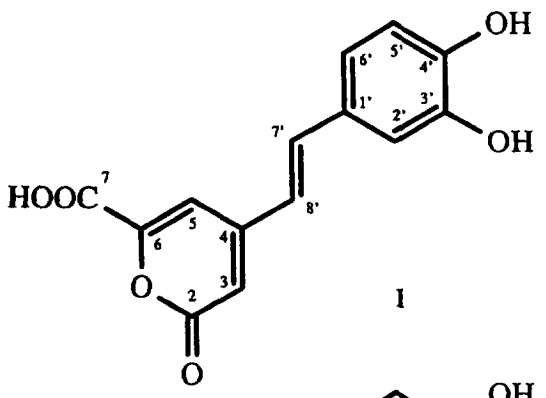
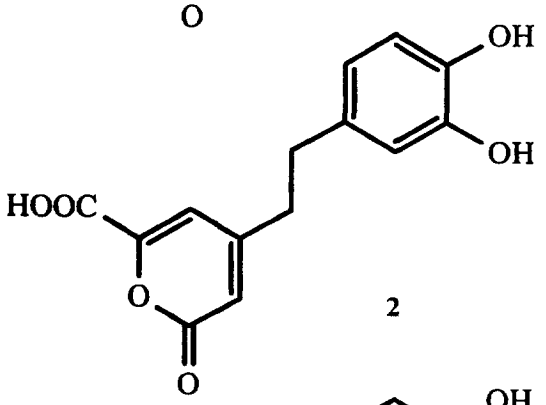
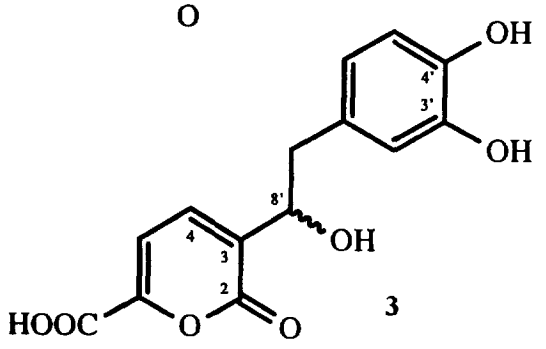






oxygenated styryl part. The complete structure of **1** was confirmed by 2D NMR spectroscopy (HMQC; HMBC, Table 3) and NOE difference spectroscopy (Fig. 1) as 4-(3′,4′-dihydroxy-*E*-styryl)-6-carboxy-α-pyrone.

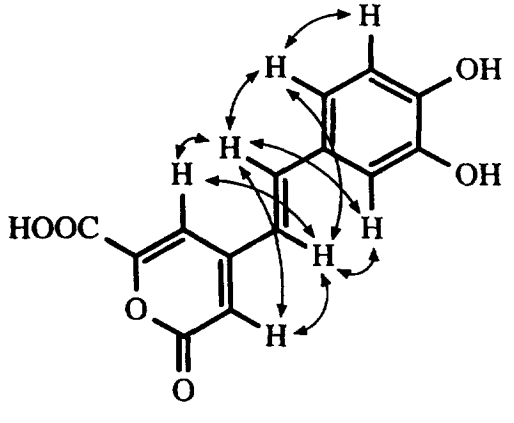


Fig. 1. NOE interactions of dumortin A (**1**).

Compound **2** was elucidated to be 4-[2-(3′,4′-dihydroxyphenyl)-ethyl]-6-carboxy-α-pyrone (1D NMR spectroscopy and especially NOEs between H-3/H-5 and the protons of the ethyl bridge). The lack of a *trans*-configurated double bond, as in **1**, coincided with the appearance of **2** as a dark absorbing spot on TLC in UV light. Also the EI-mass spectrum with $[M]^+$ at *m/z* 276 ($C_{14}H_{12}O_6$) supported the above structure.

The M_r of **3** ($[M-H]^-$ at *m/z* 291) was 18/16 mu higher than those of **1** and **2**, respectively, suggesting the presence of a hydroxyethyl bridge (Tables 1 and 2) between the phenyl and the pyrone part. Regarding the pyrone ring itself, two *ortho*-coupled protons (H-4 and H-5, Table 1) were visible. Hence, the attachment of the substituent at the pyrone ring could not be C-4 (as in **1** and **2**) if we assumed a 6-carboxy-α-pyrone again. The observed heteronuclear couplings (Table 3) and also the spatial vicinity of H-4 and not H-5 to the protons of the hydroxyethyl bridge (shown by irradiation experiments) were in accord with the structure of a 3-[1-hydroxy-2-(3′,4′-dihydroxyphenyl)-ethyl]-6-carboxy-α-pyrone for **3**.

Such α-pyrones with 3-substitution are already known from some liverworts [11, 12; Schöneborn, R., personal communication], but to the best of our knowledge α-pyrones with substitution at C-4 are so far unknown in the plant kingdom. According to Hegnauer and Hegnauer [13], α-pyrones are so far reported from various members of the Piperaceae and Lauraceae, and fungi. Recent results show that these compounds also occur in the genus *Equisetum* [8, 14].

The independent synthesis of **1**/**2** (Scheme 1) was based on a carbonyl olefination reaction between veratraldehyde (**10**) and a 2*H*-pyrone ylide moiety prepared *in situ* from the phosphonium salt (**9**), which was obtained from methyl 4-(bromomethyl)-2-oxo-2*H*-pyrane-6-carboxyalte (**8**) [15, 16]. Wittig reaction with **10** under mild crown ether catalysis [17] yielded the *E*-(**11a**) and *Z*-styrylpyrone (**11b**), which were separated. Demethylation of **11a** [18] afforded **12**, which was saponified to yield **1**. Hydrogenation of **12** in methanol [19] resulted in direct formation of **2**.

EXPERIMENTAL

Plant material. Gametophytic plant material of the investigated samples of *D. hirsuta* (Sw.) Nees (=Dh) originated from the following localities: Dh 1: Bandujo, Asturia, Spain, 1.9.80, no. 1575; Dh 2: La Palma, Canary Islands, March 1982, no. 1576; Dh 3: road from Quito to Santo Domingo, Pichincha, Ecuador, 29.9.88, no. 2513; Dh 4: road from Lloa to Rio Cristal, Pichincha, Ecuador, 1.10.88, no. 2514; Dh 5: locality near sample Dh 4, no. 2515; Dh 6: Rio Palenque Science Center, Los Rios, Ecuador, 15.10.88, no. 2516; Dh 7: road to Santo Domingo, Pichincha, Ecuador, 16.10.88, no. 2517; Dh 8: rainforest in Oaxaca state, Mexico, 9.8.91, no. 2639; Dh 9: road from Ribeiro Frio to Balcões, Madeira, 9.10.90, no. 3085. Voucher speci-

Table 1. ^{1}H NMR spectral data for compounds **1**–**3** (400 MHz, DMSO-d_6)

H	1	2	3
3	6.47 *d* (1.0)	6.32 *d* (1.0)	—
4	—	—	7.47 *d* (6.8)
5	7.51 *d* (1.4)	7.11 *d* (1.4)	7.15 *d* (6.8)
2′	7.09 *d* (2.0)	6.58 *d* (2.0)	6.58 *d* (2.1)
5′	6.77 *d* (8.1)	6.60 *d* (8.0)	6.57 *d* (7.3)
6′	7.00 *dd* (2.0, 8.2)	6.45 *dd* (2.0, 8.0)	6.38 *dd* (1.9, 8.0)
7′	7.52 *d* (16.2)	2.69 *s*	2.82 *dd* (3.4, 13.8)
			2.50 *dd* (7.3, 13.0)*
8′	6.88 *d* (16.2)	2.69 *s*	4.64 *dd* (3.2, 7.2)

*Partially overlapped by DMSO-signal.

Table 2. ^{13}C NMR spectral data for compounds **1**–**3** (100 MHz, DMSO-d_6)

C	1	2	3
2	160.9	160.2*	159.8
3	112.5	115.4†	136.7
4	151.2	158.5	137.1
5	107.0	112.0	110.5
6	149.4	148.5	147.7
7	160.8	160.4*	160.5
1′	127.1	130.9	129.3
2′	114.4	115.7†	116.9
3′	145.5	143.4	143.5
4′	147.8	144.9	144.7
5′	115.7	116.2†	115.2
6′	120.7	118.9	120.3
7′	138.6	35.9	41.0
8′	120.2	32.7	68.9

*,†Assignments interchangeable.

mens are deposited in the herbarium of Prof. Dr R. Mues, Saarbrücken, Germany.

Extraction and isolation. For comparative chromatographic analyses 100–200 mg of each sample were extracted with 80% aq. MeOH. For details of 2D TLC and HPLC see refs [20, 21]. Ground plant material (16 g) of combined samples Dh 3 (2 g), Dh 4 (12 g), Dh 5 (0.5 g) and Dh 9 (1.5 g) was extracted ×2 with MeOH and ×3 with 80% aq. MeOH. The extract was bound on RP-18 (Merck). Initial fractionation was performed by VLC using a H_2O–MeOH gradient to yield 4 major frs (1–4). Fr. 1 (eluted with H_2O) was discarded as no phenols could be detected. Fr. 2 (20–40% aq. MeOH) was chromatographed on RP-18 by MPLC (30% aq. MeOH with 2% HOAc) and afforded **3** (yield: 53.2 mg) and **2** (yield: 34.3 mg), which were purified on Sephadex LH-20 using 60% aq. HeOH as solvent. Fr. 3 (40–70% MeOH) was at first passed over a Sephadex LH-20 column (gradient: 30–80% aq. MeOH), resulting in several subfrs (3.1–3.5). From fr. 3.2, **1** (yield: 12.4 mg) was isolated after MPLC on RP-18 (40% aq. MeOH with 2% HOAc) followed by CC on Sephadex LH-20 (60% aq. MeOH). Fr. 3.3 contained **4**–**6**, which were sepd from each other by repeated MPLC on RP-18 using 15–30% aq. MeCN and 40% aq. MeOH (each containing 2% HOAC) and by CC on Sephadex LH-20 using 60% aq. MeOH. Yields: **4**: 250 mg; **5**: 7.5 mg; **6**: 6 mg. Fr. 4 was eluted between 70 and 80% aq. MeOH and was united with fr. 3.5. After MPLC on RP-18 (55% aq. MeOH with 2% HOAc) and CC on Sephadex LH-20 (70% aq. MeOH), **7** was obtained (yield: 2.1 mg).

Table 3. Long-range correlations detected in HMBC spectra of compounds **1** and **3**

	Correlated carbons	
H	1	3
3	2, 5, 8′	—
4	—	2, 3, 5, 6, 8′
5	3, 6, 7, 8′	3, 4, 6, 7
2′	3′, 4′, 6′, 7′	1′, 3′, 6′, 7′
5′	1′, 3′, 4′	1′, 4′, 6′
6′	2′, 4′, 5′, 7′	1′, 2′, 4′, 5′, 7′
7′	3, 2′, 6′	3, 1′, 2′, 6′, 8′
8′	3, 4, 5, 1′	2, 3, 4, 1′, 7′

Chromatography. See ref. [20].

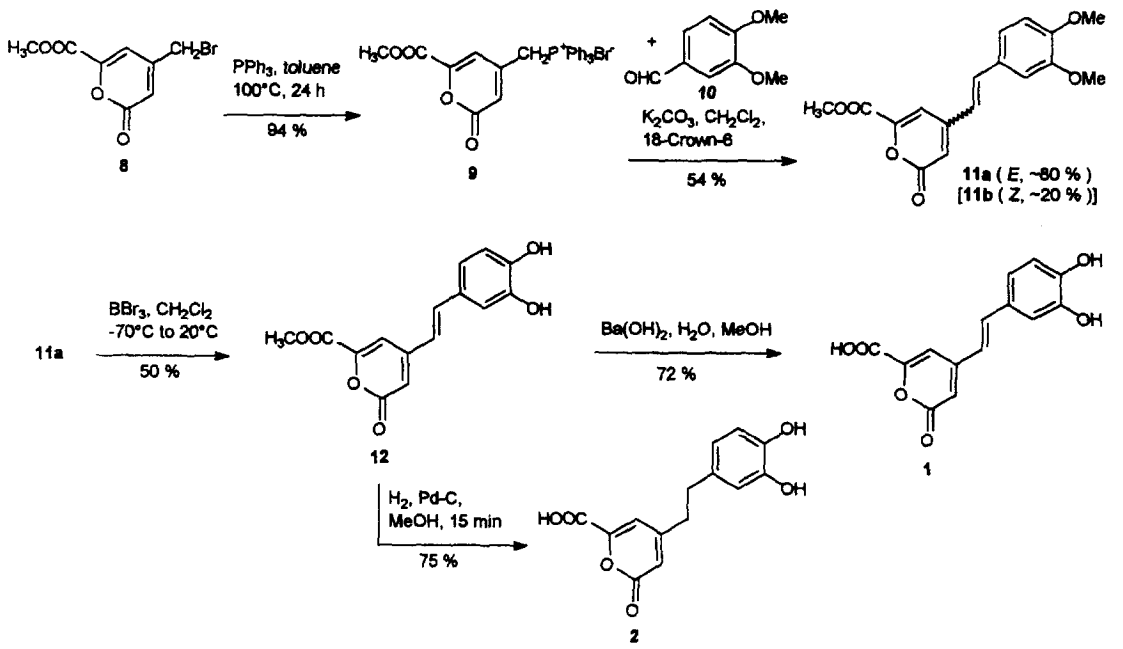
Spectroscopy. NMR were recorded on a Bruker AM 400 (1D) and on a Bruker DRX 500 (2D). NOE difference spectra were recorded using MeOH-d_4 with 1 drop of DMSO-d_6. EI-MS were recorded at 70 eV, and FAB-MS, Xe, 5–7 keV, glycerol as matrix and CI-MS, *iso*-butane, 120 eV.

Dumortin A (**1**). UV: λ_{max}; MeOH: 252, 300, 370; NaOMe: 246, 296, 436; $AlCl_3$: 247, 319, 436; $AlCl_3$/HCl: 250 sh, 300, 381. EI-MS (70 eV), *m/z* (rel. int.): 274 $[M]^+$ (4), 273 (6), 230 (10), 229 (32), 173 (20), 123 (100), 107 (83); FAB-MS, *m/z* 273 $[M-H]^-$. NMR data: Tables 1 and 2.

Dumortin B (**2**). UV: λ_{max}^{MeOH}: 233 sh, 288, 308 sh. EI-MS, *m/z* (rel. int.): 276 $[M]^+$ (4), 232 (2), 123 (100). NMR data: Tables 1 and 2.

Dumortin C (**3**). UV: λ_{max}^{MeOH}: 228 sh, 290 sh, 303. FAB-MS, *m/z* 291 $[M-H]^-$, 247 $[M-H-44]^-$. NMR data: Tables 1 and 2.

Compound **4**. UV: λ_{max}^{MeOH}: 242, 250 sh, 262 sh, 300 sh, 346. NaOMe: 259, 320 sh, 397. $AlCl_3$: 240 sh, 255 sh, 299, 375. $AlCl_3$/HCl: 262 sh, 302 sh, 346,



Scheme 1. Synthesis of dumortins A (**1**) and B (**2**).

410 sh. NaOAc: 261, 316 sh, 373. NaOAC/H_3BO_3: 253, 303 sh, 366. FAB-MS, *m/z* 461 $[M-H]^-$, 285 $[M-H-176]^-$. NMR data: Tables 4 and 5.

Compound **5**. UV: λ_{max}^{MeOH}: 255, 268 sh, 349; NaOMe: 261, 301 sh, 391; $AlCl_3$: 274, 300 sh, 327 sh, 426; $AlCl_3$/HCl: 265, 297 sh, 356, 387 sh; NaOAc: 259, 378; NaOAc/H_3BO_3: 260, 373. FAB-MS, *m/z* 461 $[M-H]^-$, 285 $[M-H-176]^-$. Co-chromatography with authentic luteolin-7-*O*-β-D-glucuronide.

Compound **6**. UV data almost identical to those for **4**. FAB-MS, *m/z* 475 $[M-H]^-$, 285 $[M-H-208]^-$. NMR data: Tables 4 and 5.

Compound **7**. UV: λ_{max}^{MeOH}: 254, 269 sh, 349; NaOMe: 266, 401; $AlCl_3$: 272, 300 sh, 426; $AlCl_3$/HCl: 261, 276 sh, 296 sh, 355, 390. NaOAc: 268, 401; NaOAc/H_3BO_3: 265, 388. EI-MS, *m/z* (rel. int.): 286 $[M]^+$ (2), 243 (2), 152 A_1^+ (5). ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.16 (*d*, $J = 2.1$ Hz, H-6), 6.42 (*d*, $J =$

Table 4. ^{1}H NMR spectral data for flavonoids **4** and **6** (400 MHz, DMSO-d_6)

H	**4**	**6**
Aglycone		
3	6.55 *s*	6.54 *s*
6	6.67 *d* (2.2)	6.63 *d* (2.2)
8	6.70 *d* (2.3)	6.70 *d* (2.3)
2′	7.36 *br.s*	7.35 *br.s*
5′	6.87 *d* (8.1)	6.86 *d* (8.1)
6′	7.37 *d* (8.2)	7.37 *d* (8.2)
Glucuronic acid		
1″	4.89 *d* (7.3)	4.94 *d* (7.3)
5″	3.90 *d* (8.9)	4.05 *d* (9.7)
OMe	—	3.70 *s*

Assignments according to ref. [22].

Table 5. ^{13}C NMR spectral data for flavonoids **4** and **6** (100 MHz, DMSO-d_6)

C	**4**	**6**
Aglycone		
2	162.5	162.5
3	105.7	105.6
4	176.8	176.7
5	158.4	158.4
6	104.1	104.0
7	161.4	161.3
8	98.4	98.4
9	158.1	158.0
10	108.2	108.1
1′	121.5	121.4
2′	113.2	113.1
3′	145.7	145.6
4	149.3	149.2
5′	116.0	115.9
6′	118.6	118.5
Glucuronic acid		
1″	103.8	103.6
2″	73.4	73.3
3″	75.8	75.4
4″	71.4	71.4
5″	75.0	74.7
6″	170.0	169.2
OMe	—	52.0

Assignments according to refs [23, 24].

1.9 Hz, H-8), 6.65 (*s*, H-3), 6.86 (*d*, $J = 8.2$ Hz, H-5'), 7.37 (*d*, $J = 2.2$ Hz, H-2'), 7.40 (*dd*, $J = 2.2$, 8.2 Hz, H-6').

Synthesis of phosphonoum bromide (**9**). A mixt. of **8** (4.95 g, 20 mM) and triphenyl phosphane (5.25 g, 20 mM) was heated (100°) in dry toluene (50 ml) for 24 hr. The pptd product was filtered off, washed with toluene (20 ml) and petrol (2 × 20 ml) and dried. Yield: 9.35 g (94%), mp 182°. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.97–7.76 (15H, *m*), 6.62 (1H, *s*), 6.42 (1H, *d*, $J = 4.1$ Hz), 5.27 (2H, *d*, $J = 17.3$ Hz), 3.78 (3H, *s*).

Synthesis of styrylpyrone (**11a**). A mixt. of **10** (1.6 g, 10 mM), **9** (7.45 g, 15 mM), K_2CO_3 (2.75 g, 20 mM) and 18-crown-6 (100 mg) in dry CH_2Cl_2 (50 ml) was heated to reflux for 48 hr. The mixt. was cooled, acidified (dil. HOAc), washed with H_2O (3 × 30 ml) and dried ($MgSO_4$). CC of the crude product (silica gel, Et_2O–cyclohexane, 1:1–3:1) gave starting material (**10**, 320 mg, 20%), a mixt. of **11a** and **11b** (630 mg, 20%) and **11a** (1.70 g, 54%) as bright yellow crystals; mp 170°. IR (KBr) ν cm^{-1}: 2350, 1725, 1700, 1655, 1540, 1530, 1420, 1340, 1270, 1170, 1140, 1110, 1025, 980, 880. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (1H, *d*, $J = 1.2$ Hz), 7.27 (1H, *d*, $J = 16.0$ Hz), 7.14 (1H, *dd*, $J = 1.2$, 8.4 Hz), 7.10 (1H, *s*), 6.90 (1*H*, *d*, $J = 8.4$ Hz), 6.77 (1H, *d*, $J = 16.3$ Hz), 6.37 (1H, *s*), 3.96 (3H, *s*), 3.95 (3H, *s*), 3.93 (3H, *s*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.0, 160.3, 151.2, 150.4, 149.5, 148.3, 138.2, 128.1, 122.3, 121.2, 114.6, 111.5, 109.7, 107.8, 56.1, 53.1. CI-MS (120 eV), *m/z* (rel. int.): 317 $[M + 1]^+$ (6), 279 (57), 277 (11), 257 (6), 219 (23), 182 (64), 167 (100), 149 (57), 109 (58), 95 (16), 71 (18).

Synthesis of **12**. To a soln of **11a** (1.6 g, 5 mM) in dry CH_2Cl_2 (150 ml) was added dropwise BBr_3 (1 M in CH_2Cl_2, 50 ml) at −78°. The mixt. was allowed to come to 20° overnight and then extracted with 0.5 N NaOH (3 × 25 ml). The aq. layer was acidified with conc. HCl and extracted with EtOAc (3 × 50 ml). The combined organic layers were dried ($MgSO_4$) and concd. The crude product was recrystallized from EtOH–H_2O (1:3), yielding **12** (720 mg, 50%). Yellow crystals, mp 199° IR (KBr) ν cm^{-1}: 3425, 2350, 1725, 1700, 1540, 1500, 1425, 1340, 1270, 1170, 1140, 1115, 1025, 970, 875. CI-MS (120 eV), *m/z* (rel. int.): 288 $[M]^+$ (26), 229 (100), 200 (32), 173 (47), 155 (23), 127 (31), 115 (30). ^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6): δ 3.38 (1H, *s*), 9.00 (1H, *s*), 7.55 (1H, *s*), 7.47 (1H, *d*, $J = 16.0$ Hz), 7.10 (1H, *d*, $J = 1.6$ Hz), 6.99 (1H, *dd*, $J = 1.6$, 8.0 Hz), 6.85 (1H, *d*, $J = 16.0$ Hz), 6.78 (1H, *d*, $J = 8.0$ Hz), 6.49 (1H, *s*), 3.90 (3H, *s*). ^{13}C NMR (100 MHz, $CDCl_3$/DMSO-d_6): δ 160.4, 169.8, 151.0, 148.0, 147.6, 145.6, 138.9, 127.1, 120.9, 120.0, 115.8, 114.4, 113.2, 108.0, 52.8.

Synthesis of dumortin A (**1**). To a soln of **12** (288 mg, 1 mM) in MeOH (10 ml) was added $Ba(OH)_2 \cdot H_2O$ (1.26 g, 4 mM) in H_2O (25 ml). The mixt. was stirred for 15 hr at 20°, acidified with 2 N HCl and extracted with EtOAc (3 × 50 ml). The combined organic layers were dried ($MgSO_4$) and concd. The crude product was purified by flash CC on RP-18 using 40% aq. MeOH containing 2% HOAc as eluent. Yield: 195 mg (72%), mp 260° (decomp.). The synthetic product was identical in all spectroscopic (NMR and MS) and chromatographic (TLC and HPLC) data with the natural compound.

Synthesis of dumortin B (**2**). Compound **12** (288 mg, 1 mM) was hydrogenated (1.5 bar, 15 min) in MeOH (30 ml), in presence of 5% Pd–C (300 mg). After filtration from catalyst, the solvent was removed and the residue purified by flash CC on RP-18 using 35% aq. MeOH containing 2% HOAc as eluent. Yield: 215 mg (72%), yellow oil not crystallized. The synthetic product was identical in all spectroscopic (NMR and MS) and chromatographic (TLC and HPLC) data with the natural compound.

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