The Isolation of New Pyrano-2-arylbenzofuran Derivatives from the Root of *Glycyrrhiza glabra*

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Two new pyrano-2-arylbenzofuran derivatives named glabrocoumarones A and B were isolated from commercially available licorice of *Glycyrrhiza glabra* origin, and their structures were elucidated as 4′,6-dihydroxy-[6″,6″-dimethylpyrano(2″,3″ : 2′,3′)]-2-arylbenzofuran and 2′,6-dihydroxy-[6″,6″-dimethylpyrano(2″,3″ : 4′,3′)]-2-arylbenzofuran, respectively, on the basis of spectroscopic evidence. Six known compounds were also obtained and identified spectroscopically as glabrol, 3-hydroxyglabrol, shinflavanone, [6″,6″-dimethylpyrano(2″,3″ : 7,8)]-[6‴,6‴-dimethylpyrano(2‴,3‴ : 4′,3′)]-flavanone (xambioona), 3,3′-di-γ,γ-dimethylallyl-2′,4,4′-trihydroxychalcone and [6″,6″-dimethylpyrano(2″,3″ : 4,5)]-3′-γ,γ-dimethylallyl-2′,3,4′-trihydroxychalcone.

Key words 2-arylbenzofuran; chalcone; flavanone; licorice; *Glycyrrhiza glabra*; Fabaceae

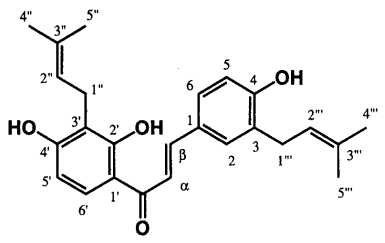
Glycyrrhiza glabra L. (Fabaceae) is the origin of the crude drug licorice that has been used widely in Europe and its vicinity since ancient times. We reported earlier the isolation of antimicrobial and antioxidant principles from licorice root of Russian origin.[1] In recent years the number of reports referring to biological activity of licorice constituents has dramatically increased, and either flavonoids or isoflavonoids were identified as the active principles.[1,2] These findings motivated us to undertake further chemical investigation on commercially available *G. glabra* root, and the isolation of isoflavan derivatives was reported.[3] In this report we describe the isolation and structure of new 2-arylbenzofuran derivatives along with six known compounds.

Results and Discussion

Several fractions obtained through the separation process of the dichloromethane extract of commercially available *G. glabra* root as reported previously[3] were subjected to a series of column chromatographic separation to yield four known phenolic compounds, two pigments (**1** and **2**) and two new compounds (**3a** and **4a**).

Four flavanone derivatives were obtained as known compounds, and readily identified with glabrol,[4] shinflavanone,[5] 3-hydroxyglabrol[2b] and [6″,6″-dimethylpyrano-(2″,3″ : 7,8)]-[6‴,6‴-dimethylpyrano(2‴,3‴ : 4′,3′)]-flavanone (xambioona).[6] The former three compounds were previously obtained from *G. glabra* root.[2b,4,5] Xambioona was a dipyrano-3-hydroxyflavanone that has been reported from *Calopogonium mucunoides*[6] and *Euchresta formosana* (both belong to Fabaceae).[7] The present study confirmed the occurrence of this compound in *G. glabra* from which biogenetically related flavanones were obtained.

Pigments **1** and **2** were obtained in pure crystalline forms of mp 134—137 °C and 153—156 °C, respectively. Pigment **1** was spectroscopically characterized as 3,3′-di-γ,γ-dimethylallyl-2′,4,4′-trihydroxychalcone, and was finally identified with the pigment prepared from the



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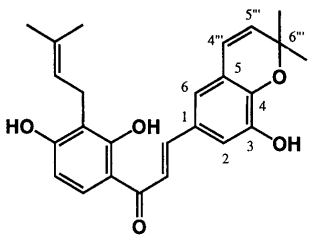

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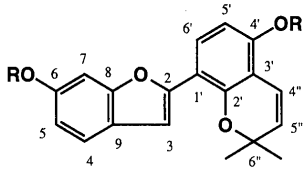
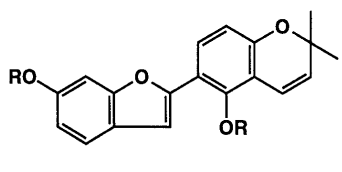


3a R=H
3b R=CH$_3$



4a R=H
4b R=CH$_3$

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Table 1. ^{13}C-NMR[a] Data for 3,3′-Di-γ,γ-dimethylallyl-2′,4,4′-trihydroxychalcone (**1**) and [6″, 6″-Dimethylpyrano(2″,3″:4,5)]-3′-γ,γ-dimethylallyl-3,2′,4′-trihydroxychalcone (**2**)

	Carbon	**1**	**2**
Chalcone moiety	C-1′	114.1[b]	114.0[b]
	C-2′	161.5	161.5
	C-3′	114.3[b]	114.5[b]
	C-4′	163.9	163.9
	C-5′	107.7	107.8
	C-6′	129.2	129.2
	C-α	117.7	118.4
	C-β	144.6	144.4
	C=O	192.3	192.2
	C-1	127.7	127.9
	C-2	130.9	114.3
	C-3	127.7	144.7
	C-4	157.0	142.0
	C-5	116.3	121.2
	C-6	128.3	119.6
A-Ring prenyl moiety	C-1″	21.8	21.8
	C-2″	121.2	121.3
	C-3″	135.6	135.0
	C-4‴	25.8	25.8
	C-5‴	17.9	17.9
B-Ring prenyl moiety	C-1‴	29.6	—
	C-2‴	121.2	—
	C-3‴	135.4	—
	C-4‴	25.8	—
	C-5‴	17.9	—
B-Ring chromene moiety	C-4‴	—	121.6
	C-5‴	—	131.2
	C-6‴	—	78.3
	CH_3	—	28.2
		—	28.2

a) Spectra were measured in $CDCl_3$ at 100 MHz with TMS as internal standard. Assignments were based on ^{13}C–^{1}H COSY and long-range ^{13}C–^{1}H COSY correlation. *b*) Assignments may be interchangeable in the same column.

alkaline treatment of glabrol. A chalcone derivative with the same structure as **1** has been reported as a synthetic compound with antiulcer activity,[8] and has also been isolated as an antileishmanial principle from Chinese licorice root[9] (plant species not specified). It is also known to occur in *G. eurycarpa* root, a licorice with no medicinal value.[10] The structure of pigment **2** was determined to be [6″,6″-dimethylpyrano(2″,3″ : 4,5)]-3′-γ,γ-dimethylallyl-2′,3,4′-trihydroxychalcone using ^{13}C–^{1}H long-range correlation spectroscopy (COSY) spectral analysis. Its ^{1}H-NMR data was in good agreement with those of a prenylpyranochalcone derivative isolated from Chinese licorice root as an antileishmanial substance.[9] Both chalcones **1** and **2** have been obtained only in extremely small quantities and in non-crystalline forms, and detailed spectral data were not available. Thus a full set of the spectral and physical properties for these two compounds is described for the first time in this report (Table 1 for ^{13}C-NMR data).

Compound **3a** was a new compound obtained as colorless needles of mp 192—194 °C, and thus the name of glabrocoumarone A was proposed. Its molecular formula was determined to be $C_{19}H_{16}O_4$ based on mass spectroscopy and elementary analysis. The IR spectrum showed no band in the carbonyl region. The UV spectrum exhibited absorption maxima at 280, 292 and 317 nm, resembling that of a 2-arylbenzofuran derivative.[11] A

Table 2. ^{13}C-NMR[a] Data for Glabrocoumarone A (**3a**), Glabrocoumarone A Dimethyl Ether (**3b**), Glabrocoumarone B (**4a**) and Glabrocoumarone B Dimethyl Ether (**4b**)

	Carbon	**3a**[b,c]	**3b**[b,d]	**4a**[b,c]	**4b**[d]
2-Arylbenzofuran moiety	C-2	152.2	151.7	153.2	151.7
	C-3	104.4	103.9	103.9	103.5
	C-4	121.6	120.8	121.6	120.8
	C-5	112.7	111.3	112.9	111.6
	C-6	156.1	157.6	156.2	157.8
	C-7	98.2	95.7	98.4	95.8
	C-8	155.5	154.7	155.8	154.9
	C-9	123.4	123.4	122.8	123.2
	C-1′	112.1	112.7	112.4	115.4[e]
	C-2′	151.5	150.4	150.4	153.2
	C-3′	110.5	110.7	112.2	116.8[e]
	C-4′	153.9	154.9	154.8	154.1
	C-5′	108.8	103.2	109.9	112.9
	C-6′	126.7	126.1	127.6	127.1
Chromene moiety	C-4″	117.8	117.0	117.2	116.9
	C-5″	129.3	128.8	130.3	130.8
	C-6″	77.4	76.6	76.5	76.3
	CH_3	28.2	28.0	27.9	27.9
		28.2	28.0	27.9	27.9
	OCH_3	—	55.7	—	55.8
		—	55.8	—	61.1

a) Spectra were measured at 100 MHz with TMS as internal standard. *b*) Assignments were based on ^{13}C–^{1}H COSY and long-range ^{13}C–^{1}H COSY correlation. *c*) Measured in acetone-d_6. *d*) Measured in $CDCl_3$. *e*) Assignments may be interchangeable in the same column.

significant bathochromic shift (19 nm) was also observed by the addition of sodium methoxide, indicating that either 6- or 4′-hydroxyl of a 2-arylbenzofuran skeleton is free. The ^{1}H-NMR spectrum revealed a set of resonances characteristic of a chromene ring [δ 1.54 (6H, s), 5.74 (1H, d, J=10.0 Hz) and 6.75 (1H, d, J=10.0 Hz)] along with the AB [δ 6.57 (1H, d, J=8.7 Hz) and 7.64 (1H, d, J=8.7 Hz)] and ABX [δ 6.78 (1H, dd, J=8.5, 2.1 Hz), 6.96 (1H, dd, J=2.1, 1.0 Hz) and 7.38 (1H, d, J=8.5 Hz)] systems in the aromatic region. The doublet at δ 7.21 was assignable to the furanic proton at the 3-position, and long-range coupling between 3-H and 7-H was observed (J=1.0 Hz). This spectral evidence coupled with the ^{13}C–^{1}H long-range COSY spectral analysis led to the assignment of either 4′,6-dihydroxy-[6″,6″-dimethylpyrano(2″,3″ : 2′,3′)]-2-arylbenzofuran (**3a**) or 2′,6-dihydroxy-[6″,6″-dimethylpyrano(2″,3″ : 4′,3′)]-2-arylbenzofuran (**4a**) for the structure of glabrocoumarone A. Dhami and Stothers reported that the methoxyls of *ortho*-disubstituted anisoles in the ^{13}C resonances appear downfield at *ca.* 60 ppm whereas those of *ortho*-monosubstituted or non-substituted anisoles usually appear at *ca.* 55 ppm.[12] Using these reported results, it is possible to distinguish the structure **3a** from **4a**. Thus glabrocoumarone A dimethyl ether was prepared, and its ^{13}C-NMR spectrum was analyzed (Table 2). The observed chemical shifts for two methoxyls of glabrocoumarone A dimethyl ether were δ 55.7 and 55.8 ppm, suggesting that both methoxyls occur as either *ortho*-nonsubstituted or *ortho*-monosubstituted anisole. Thus the structure of glabrocoumarone A was assigned unequivocally as 4′,6-dihydroxy-[6″,6″-dimethylpyrano(2″,3″ : 2′,3′)]-2-arylbenzofuran (**3a**). This structure was further substantiated by an irradiation experiment in which significant nuclear Overhauser effects

(NOEs) on 5-H (δ 6.85), 7-H (δ 7.05) and 5′-H (δ 6.54) of the aromatic rings and on 4″-H (δ 6.72) of the chromene ring were observed (17, 13, 20 and 23%, respectively) on irradiation of methoxyl signals at δ 3.87 (unresolved).

Compound **4a** was obtained as colorless needles of mp 168—169 °C in a small quantity. Its spectroscopic data including ^{1}H- and ^{13}C-NMR spectra were very similar to those of glabrocoumarone A (Table 2). High-resolution mass spectroscopic analysis revealed that compound **4a** has the same molecular formula ($C_{19}H_{16}O_4$) as glabrocoumarone A. Since methoxyl signals were well resolved in the ^{1}H-NMR spectrum of its dimethyl ether, irradiation experiments were carried out. Though significant 17% and 11% NOEs on 5-H (δ 6.86) and 7-H (δ 7.05), respectively, were observed on irradiation of one methoxyl at δ 3.87, irradiation of another methoxyl at δ 3.79 produced 27% NOE on 4″-H (δ 6.68) but no NOE on the B-ring protons. The above evidence suggested that the structure of this compound is expressed as a geometrical isomer (**4a**) of glabrocoumarone A. The observed chemical shifts (δ 55.8 and 61.1 ppm) for methoxyls in the ^{13}C-NMR (Table 2) of its dimethyl ether were also supportive of the structure **4a**. This was also a new compound and thus the name of glabrocoumarone B was proposed.

Experimental

All melting points were measured on a Yanagimoto melting point apparatus and are uncorrected. Spectral data were obtained using the following apparatus: proton and carbon-13 nuclear magnetic resonance (^{1}H- and ^{13}C-NMR) spectra with JEOL JNM GSX-400 (^{1}H, 400 MHz; ^{13}C, 100 MHz) spectrometer with tetramethylsilane (TMS) as an internal standard; mass spectra (MS) with a JEOL SX-102A mass spectrometer; infrared (IR) spectra with a JASCO FT/IR-8000 infrared spectrometer; ultraviolet (UV) spectra with a Shimadzu UV-240 spectrometer; optical rotations with a JASCO DIP-370 polarimeter. Column chromatography was carried out with the following materials: Wakogel C-200 or Merck Kieselgel 60, Sephadex LH-20 (Pharmacia) and RP-8 reversed-phase silica gel (Merck). Thin-layer chromatography (TLC) was conducted on a 0.25 mm pre-coated silica gel plate ($60GF_{254}$, Merck), and spots were detected by inspection under short (254 nm) or long (360 nm) wavelength UV lights, or by the colors developed with 10% H_2SO_4 spraying followed by heating on a hot plate.

Plant Material Commercially available licorice roots derived from *G. glabra* were obtained from central Asian countries through Maruzen Pharmaceutical Co., Ltd., Onomichi, Japan.

Extraction and Isolation The dichloromethane extract (150 g) of *G. glabra* root was separated into eight fractions (Fr. I—VIII) on a silica gel column chromatography as reported in the previous paper.[3] Fractionation of Fr. I (30.32 g) into Fr. A—J was also described previously.[3] Fraction C was further separated by silica gel (chloroform–benzene), Sephadex LH-20 (chloroform–methanol) and RP-8 reversed-phase silica gel column chromatography to give xambioona (30 mg) [amorphous; $[\alpha]_D$ −74.0°; lit.[6] undescribed]. Fraction E was subjected to silica gel (hexane–ethyl acetate) followed by RP-8 column chromatography to give glabrocoumarone B (**4a**; 10 mg). A silica gel column chromatographic separation of Fr. F on elution with hexane–ethyl acetate followed by LH-20 and RP-8 afforded shinflavanone (137 mg). Fraction H was subjected to silica gel column chromatography on elution with hexane–ethyl acetate to furnish thirty fractions. Fractions 28—29 were combined and rechromatographed successively over Sephadex LH-20 and RP-8 to afford 3,3′-di-γ,γ-dimethylallyl-2′,4,4′-trihydroxychalcone (**1**; 21 mg) and [6″,6″-dimethylpyrano(2″,3″ : 4,5)]-3′-γ,γ-dimethylallyl-2′,3,4′-trihydroxychalcone (**2**; 54 mg). Fraction J was separated by Sephadex LH-20 column chromatography to give glabrol (1.09 g) [mp 128—130 °C; lit.[4] 90 °C]. Fraction III (50.98 g) was chromatographed over silica gel (600 g; column size: 824 cm) and the column was eluted with the following solvent system: benzene, 1 l; benzene–acetone (B-A) (99 : 1), 1 l; B-A (97 : 3), 1 l; B-A (95 : 5), 1 l; B-A (94 : 6), 1 l; B-A (93 : 7), 1 l; B-A (92 : 8), 2 l; B-A (91 : 9), 1 l; B-A (90 : 10), 1 l; B-A (88 : 12), 1 l; acetone, 3 l. Twenty-four fractions (500 ml each/fr.) were collected and combined as follows: fr. 1—6 (0.1 g); fr. 7—8 (0.70 g); fr. 9—10 (9.97 g); fr. 11—13 (13.61 g); fr. 14—18 (12.0 g); fr. 19—24 (4.68 g). Fractions 9—10 were combined and repeatedly chromatographed over silica gel, LH-20 and RP-8 to furnish glabrocoumarone A (**3a**; 220 mg). Fractions 19—24 were combined and further separated by a combination of silica gel, LH-20 and RP-8 column chromatography to afford 3-hydroxyglabrol (40 mg) [mp 102—105 °C; lit.[2b] 117—119 °C].

3,3′-Di-γ,γ-dimethylallyl-2′,4,4′-trihydroxychalcone (1) Yellow needles from MeOH–H_2O, mp 134—137 °C. IR ν_{max}^{KBr} cm^{-1}: 3490, 3185, 2913, 1622, 1605, 1559, 1441, 1373, 1310, 1242, 1221. UV λ_{max}^{MeOH} nm (log ε): 243 sh (4.18), 374 (4.60); $\lambda_{max}^{MeOH+AcONa}$ nm: 378; $\lambda_{max}^{MeOH+MeONa}$ nm: 443; $\lambda_{max}^{MeOH+AlCl_3}$ nm: 255 sh, 335 sh, 345 sh, 427. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.76, 1.79, 1.83 (12H, s, 4″-, 4‴-, 5″-, 5‴-CH_3), 3.38 (2H, d, J=7.2 Hz, 1″-C<u>H</u>$_2$), 3.47 (2H, d, J=7.2 Hz, 1‴-C<u>H</u>$_2$), 5.30 (1H, m, 2″-C<u>H</u> or 2‴-C<u>H</u>), 5.32 (1H, m, 2‴-C<u>H</u> or 2″-C<u>H</u>), 5.74 (1H, br s, 4-OH, disappeared on exchange with D_2O), 6.27 (1H, br s, 4′-OH, disappeared on exchange with D_2O), 6.42 (1H, d, J=9.0 Hz, 5′-H), 6.83 (1H, d, J=8.2 Hz, 5-H), 7.38 (1H, d, J=2.0 Hz, 2-H), 7.42 (1H, dd, J=8.2, 2.0 Hz, 6-H), 7.43 (1H, d, J=15.5 Hz, α-H), 7.72 (1H, d, J=9.0 Hz, 6′-H), 7.82 (1H, d, J=15.5 Hz, β-H), 13.88 (1H, s, 2′-OH, disappeared on exchange with D_2O). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: see Table 1. EI-MS m/z (rel. int., %): 392 (M^+, 100), 349 (92), 337 (26), 293 (14), 236 (19), 149 (81). *Anal.* Calcd for $C_{25}H_{28}O_4$: C, 76.50; H, 7.19. Found: C, 76.27; H, 7.24.

Conversion of Glabrol into 3,3′-Di-γ,γ-dimethylallyl-2′,4,4′-trihydroxychalcone (1) A mixture of ethanol (6 ml), 50% sodium hydroxide (1 ml) and glabrol (100 mg) was heated at 100 °C under argon atmosphere for 2 h. The reaction mixture was then poured into ice water, acidified with hydrochloric acid and extracted with ethyl acetate. The workup in the usual manner afforded a reddish residue, which was then subjected to a column of Sephadex LH-20 on elution with chloroform–methanol (2 : 1). The resulting yellow band was collected and the eluant was evaporated. The residue was recrystallized from aqueous methanol to give yellow needles (70 mg). This semi-synthetic compound melted at 137 °C. It was completely identical to **1** in mixed melting point and spectroscopic properties.

[6″,6″-Dimethylpyrano(2″,3″ : 4,5)]-3′-γ,γ-dimethylallyl-2′,3,4′-trihydroxychalcone (2) Yellow needles from $CHCl_3$–hexane, mp 153—156 °C. IR ν_{max}^{KBr} cm^{-1}: 3399, 2973, 1626, 1561, 1489, 1441, 1372, 1275, 1107. UV λ_{max}^{MeOH} nm (log ε): 243 (4.29), 300 (4.07), 382 (4.49); $\lambda_{max}^{MeOH+AcONa}$ nm: 384; $\lambda_{max}^{MeOH+MeONa}$ nm: 272, 423; $\lambda_{max}^{MeOH+AlCl_3}$ nm: 247, 437. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.47 (6H, s, 6‴-*gem*-CH_3), 1.74 (3H, s, 4″-CH_3), 1.82 (3H, s, 5″-CH_3), 3.45 (1H, br d, J=7.0 Hz, 1″-C<u>H</u>$_2$), 5.29 (1H, m, 2″-C<u>H</u>), 5.65 (1H, d, J=10.0 Hz, 5‴-H), 6.32 (1H, d, J=10.0 Hz, 4‴-H), 6.41 (1H, d, J=8.8 Hz, 5′-H), 6.83 (1H, d, J=1.9 Hz, 6-H), 7.12 (1H, d, J=1.9 Hz, 2-H), 7.40 (1H, d, J=15.3 Hz, α-H), 7.68 (1H, d, J=8.8 Hz, 6′-H), 7.73 (1H, d, J=15.3 Hz, β-H), 13.83 (1H, s, 2′-OH, disappeared on exchange with D_2O). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: see Table 1. EI-MS m/z (rel. int., %): 406 (M^+, 45), 391 (44), 363 (20), 279 (14), 167 (25), 149 (100). *Anal.* Calcd for $C_{25}H_{26}O_5$: C, 73.87; H, 6.45. Found: C, 74.15; H, 6.41.

Glabrocoumarone A (3a) Colorless needles from MeOH–H_2O, mp 192—194 °C. IR ν_{max}^{KBr} cm^{-1}: 3499, 3323, 1626, 1593, 1503, 1447, 1306, 1119. UV λ_{max}^{MeOH} nm (log ε): 248 (4.12), 273 sh (4.41), 280 (4.46), 292 (4.44), 317 (4.56); $\lambda_{max}^{MeOH+MeONa}$ nm: 294, 336. ^{1}H-NMR (400 MHz, acetone-d_6) δ: 1.54 (6H, s, 6″-*gem*-CH_3), 5.74 (1H, d, J=10.0 Hz, 5″-H), 6.57 (1H, d, J=8.7 Hz, 5′-H), 6.75 (1H, d, J=10.0 Hz, 4″-H), 6.78 (1H, dd, J=8.5, 2.1 Hz, 5-H), 6.96 (1H, dd, J=2.1, 1.0 Hz, 7-H), 7.21 (1H, d, J=1.0 Hz, 3-H), 7.38 (1H, d, J=8.5 Hz, 4-H), 7.64 (1H, d, J=8.7 Hz, 6′-H), 8.40, 8.80 (1H each, br, 6′-, 2′-OH, disappeared on exchange with D_2O). ^{13}C-NMR (100 MHz, acetone-d_6) δ: see Table 2. EI-MS m/z (rel. int., %): 308 (M^+, 36), 293 (100), 147 (10). *Anal.* Calcd for $C_{19}H_{16}O_4$: C, 74.01; H, 5.23. Found: C, 74.26; H, 5.28. Glabrocoumarone A was methylated with diazomethane and the reaction mixture was worked up in the usual manner to give a dimethyl ether (**3b**). Amorphous. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.54 (6H, s, 6″-*gem*-CH_3), 3.87 (6H, s, 6-, 4′-OCH_3), 5.65 (1H, d, J=10.1 Hz, 5″-H), 6.54 (1H, d, J=8.8 Hz, 5′-H), 6.72 (1H, d, J=10.1 Hz, 4″-H), 6.85 (1H, dd, J=8.5, 2.1 Hz, 5-H), 7.05 (1H, d, J=2.1 Hz, 7-H), 7.19 (1H, br s, 3-H), 7.43 (1H, d, J=8.5 Hz, 4-H), 7.79 (1H, d, J=8.8 Hz, 6′-H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ:

see Table 2.

Glabrocoumarone B (4a) Colorless needles from MeOH–H_2O, mp 168—169 °C. IR ν_{max}^{KBr} cm^{-1}: 3412, 2361, 1620, 1489, 1354, 1289, 1219, 1113. UV λ_{max}^{MeOH} nm (log ε): 237 (4.39), 277 (4.54), 286 sh (4.46), 310 sh (4.48), 320 (4.56); $\lambda_{max}^{MeOH+MeONa}$ nm: 265 sh, 273, 285 sh, 325, 370. ^{1}H-NMR (400 MHz, acetone-d_6) δ: 1.42 (6H, s, 6″-*gem*-CH_3), 5.75 (1H, d, J=9.9 Hz, 5″-H), 6.47 (1H, d, J=8.8 Hz, 5′-H), 6.80 (1H, dd, J=8.4, 2.2 Hz, 5-H), 6.84 (1H, d, J=9.9 Hz, 4″-H), 7.00 (1H, dd, J=2.2, 1.1 Hz, 7-H), 7.10 (1H, d, J=1.1 Hz, 3-H), 7.39 (1H, d, J=8.4 Hz, 4-H), 7.58 (1H, d, J=8.8 Hz, 6′-H), 8.41, 8.43 (1H each, s, 6′-, 2′-OH, disappeared on exchange with D_2O). ^{13}C-NMR (100 MHz, acetone-d_6) δ: see Table 2. EI-MS m/z (rel. int., %): 308 (M^+, 85), 290 (100), 265 (8), 147 (20). HR-MS: Calcd for $C_{19}H_{16}O_4$: 308.1049. Found: 308.1048. Glabrocoumarone B dimethylether (**4b**) was prepared as stated above. Amorphous. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.46 (6H, s, 6″-*gem*-CH_3), 3.79, 3.87 (3H each, s, 2′-, 6-OCH_3), 5.70 (1H, d, J=10.1 Hz, 5″-H), 6.68 (1H, d, J=10.1 Hz, 4″-H), 6.69 (1H, d, J=8.5 Hz, 5′-H), 6.86 (1H, dd, J=8.5, 2.1 Hz, 5-H), 7.05 (1H, dd, J=2.1, 0.9 Hz, 7-H), 7.11 (1H, d, J=0.9 Hz, 3-H), 7.44 (1H, d, J=8.5 Hz, 4-H), 7.71 (1H, d, J=8.5 Hz, 6′-H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: see Table 2.

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