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NEOLIGNANS, STYRYLPYRONES AND FLAVONOIDS FROM AN *ANIBA* SPECIES

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Key Word Index—*Aniba* sp.; Lauraceae; neolignans; trunk wood, bark; styrylpyrones; flavonoids.

Abstract—The trunk wood and barks from an *Aniba* species contain four esters of benzoic acid with cinnamyl alcohol, five benzofuran neolignans, licarin-A, burchellin, *cis*-burchellin, burchellin-rearranged and *cis*-burchellin-rearranged, one tetrahydrofuran neolignan, aristolignin, three bicyclooctane guianin-type neolignans, (7*S*, 8*S*, 1′*R*, 5′*R*)-4-hydroxy-3,3′-dimethoxy-4′,6′-dioxo-8.1′, 7.5′-neolignan-Δ: 1,3,5,2′,8′ and the new (7*S*, 8*S*, 1′*R*, 4′*R*, 5′*S*)-4′-hydroxy-3,4,3′-trimethoxy-6′-oxo-8.1′, 7.5′-neolignan-Δ: 1,3,5,2′,8′ and (7*S*, 8*S*, 1′*R*, 4′*R*, 5′*S*)-4,4′-dihydroxy-3,3′-dimethoxy-6′-oxo-8.1′, 7.5′-neolignan-Δ: 1,3,5,2′,8′, one new bicyclooctane canellin-type neolignan (7*S*, 8*S*, 1′*S*, 4′*R*, 5′*R*, 6′*S*)-4′,6′-dihydroxy-3,4-dimethoxy-3′-oxo-8.1′, 7.5′-neolignan-Δ: 1,3,5,8′, two styrylpyrones, 4-methoxy-6-(11,12-dimethoxy-*trans*-styryl)-2-pyrone and 6-(11,12-methylenedioxy-*trans*-styryl)-4-methoxy-2-pyrone, two styrylpyrone dimers: 4′-methoxy-8-(11,12-dimethoxyphenyl)-7-[6-(4-methoxy-2-pyronyl)-6-(*E*)-styryl-1′-oxabicyclo[4,2,0]octa-4′-en-2′-one and the new 11,12-dimethoxyphenyl-7,7′-di-[6-(4-methoxy-2-pyronyl)]-cyclobutane and six flavonoids, 3,5-dihydroxy-7,4′-dimethoxyflavone, 5-hydroxy-3,7,4′-trimethoxyflavone, 3,5,4′-trihydroxy-7-methoxyflavone, 2,3-dihydro-5-hydroxy-7,4′-dimethoxyflavone, 2,3-dihydro-3,5-dihydroxy-7-methoxyflavone, 2,3-dihydro-3,5-dihydroxy-7,4′-dimethoxyflavone and a new flavan, 6,7,3′,4′,5′-pentamethoxyflavan.

INTRODUCTION

The secondary metabolites in *Aniba* species are based mainly on either mono- and dioxygenated benzoic acids and cinnamic acids or on di- and trioxygenated cinnamic acids. The former group of precursors leads to pyrones, the latter to neolignans. Based on these two types of compounds, *Aniba* species can be divided between two different groups [1]. Flavonoids, whose precursor is cinnamic acid, were detected in wood of *A. riparia*, which also contains pyrones [1]. However, some unusual co-occurrences of styrylpyrones and neolignans have been observed in fruits of *A. riparia* [2].

RESULTS AND DISCUSSION

A specimen was collected in the vicinity of Belém, in the state of Pará. The material was identified provisionally by Prof. Klaus Kubitzki, Hamburg University, as an *Aniba* sp., and barks and wood separated. The hexane extract of the trunk wood yielded benzoyl esters (**1a–1d**), five benzofuran neolignans: licarin-A (**2**), burchellin (**3a**), *cis*-burchellin (**3b**), burchellin and *cis*-burchellin-rearranged (**4a** and **4b**), the tetrahydrofuran neolignan, aristolignin (**5**), four bicyclooctane guianin-type neolignans: (**6a**, **6b** and **6c**) and one of the canellin-type (**7a**), together with a flavonol (**11a**), two dihydroflavonols (**12b**, **12c**) and a flavan (**13**).

The hexane extract of the barks afforded, besides compounds **1a–1d**, **11a**, **12c**, **3b** and **6a** previously identified, the flavonol **11b**, the dihydroflavonol **12a**, two styryl α-pyrones (**8a**, **8b**) and a dimer of pyrone **8a** (**9**). The chloroform extract of the bark gave, besides **11a** and **11b** another dimer of **8a** (**10**). After acetylation of a chromatographic fraction, four acetylated flavonols (**11c–11e**, **11g**) were also obtained.

Among these substances which were isolated from this *Aniba* sp., benzoyl esters and their derivatives are common constituents of most *Aniba* sp. studied previously [3]. They produce both bicyclooctane and benzofuran neolignans. Licarin-A (**2**) [4], burchellin (**3a**), *cis*-burchellin (**3b**) [4–8] and rearranged burchellins (**4a** and **4b**) [4–7] and the bicyclooctane, neolignan **6c** [9], have been isolated from *A. affinis* [4], *A. burchellii* [5, 6], *A. terminalis* [7], *A. ferrea* [8] and an *Aniba* sp. [9].

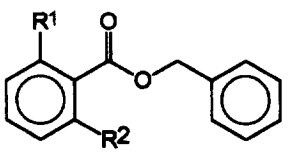
The styrylpyrones, **8a** and **8b**, have also been isolated from various *Aniba* sp. [2, 4, 10–14]. Among the *Aniba* sp. which synthesize styrylpyrones, only *A. cylindriflora* [4] and *A. parviflora* [15] contain styrylpyrones without an *O*-Me at C-4.

Aniba species which contain flavonoids are uncommon. Flavonoids are found only in *A. kappleri* [12], *A. riparia* [1, 2], *A. rosaeodora* [16] and an *Aniba* sp. [17]. The flavonoid **12b** has been isolated from *A. riparia* [1], while flavonoids **11a**, **11b**, **11f**, **12a**, **12c**, neolignan **5** and dimer **10** have not been reported in other *Aniba* sp. Compounds **6a**, **6b**, **7a**, **9** and **13** are new natural products.

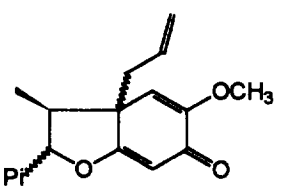
Nomenclature and numbering of neolignans follow the rules outlined in a recent review [18].

Tetrahydrofuran neolignan aristolignin (**5**) had not been isolated from *Aniba* sp. before but was first isolated from *Aristolochia chilensis* (Aristolochiaceae) [19]. The relative positions of the methyl and aryl groups were confirmed by ^{13}C NMR data, by comparison with model compounds, veraguensin [20] and verrucosin [21].

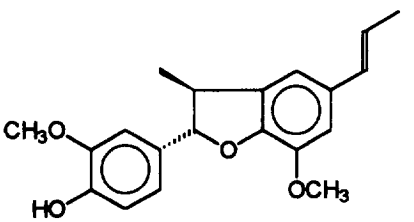
The molecular formulae of **6a** ($C_{21}H_{26}O_5$), **6b** ($C_{20}H_{24}O_5$) and **7a** ($C_{20}H_{26}O_5$) were determined by mass spectrometry, together with proton and carbon counts from NMR spectra. Thus, **6a** and **6b** were thought to be new guianin-type bicyclooctane neolignans and **7a**, a bicyclooctane canellin-type neolignan. Structural assignments for **6a**, **6b** and **7a** were evident in IR, mass, ^1H and ^{13}C NMR spectral data



	R_1	R_2
1a	H	H
1b	OH	H
1c	OH	OH
1d	OCH_3	H



3a α– Pi, β–allyl
3b β–Pi, α–allyl



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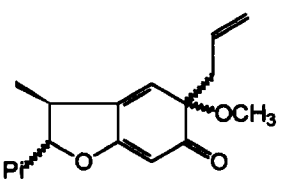
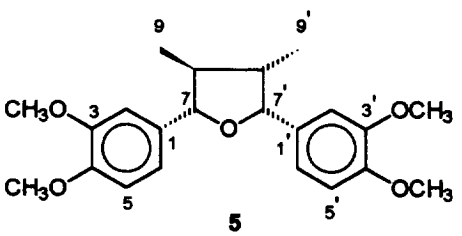


4a α–Pi, β–allyl, α–OCH_3
4b β–Pi, α–allyl, β–OCH_3



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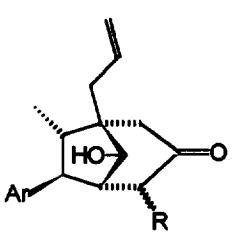
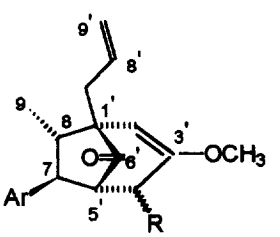


7a Ar=Ve, R= β–OH
7b Ar=Pi, R= β-OH



6a Ar= Ve, R= α–OH
6b Ar= Gu, R= α-OH
6c Ar= Gu, R= =O
6d Ar= Pi, R= β-OH

Gu= Guaiacyl (4-hydroxy- 3-methoxyphenyl)
Pi= Piperonyl (3,4-methylenedioxyphenyl)
Ve= Veratryl (3,4-dimethoxyphenyl)

and comparison with known bicyclooctane neolignans of these two types, previously isolated from *Ocotea porosa* [22], *A. burchellii* [6] and an *Aniba* sp. [9]. The doublets at δ 1.0 ($J = 6.5$ Hz) (**6a**), δ 1.0 ($J = 6.6$ Hz) (**6b**) and δ 0.89 ($J = 6.6$ Hz) (**7a**) showed that the methyl (C-8) and aryl (C-7) groups are *trans*. The methyl groups at C-8 are *endo*-oriented, as confirmed by ^{13}C NMR chemical shifts of *ca* δ 12. According to ^{1}H and ^{13}C NMR data, the hydroxyl group at C-4′ is *endo*-oriented in **6a** and **6b** (H-7 *ca* δ 3.0, H-4′ *ca* δ 4.7, C-2′ *ca* δ 100 and C-4′ *ca* δ 73) and *exo*-oriented in **7a** (H-7 *ca* δ 2.4, H-4′ *ca* δ 4.2 and C-4′ *ca* δ 78) [23–26]. The signal at δ 4.26 (*s*) was attributed to H-6′ (**7a**) and it must form, with H-5′, a dihedral angle of 90°. Another difference between **6a**, **6b** and **7a** was the signal for H-2′, which is ethylenic in **6a** and **6b** (δ 4.43, *s*, 1H) and methylenic in **7a** (δ 2.39, *s*, 2H). Analyses of ^{13}C NMR spectra of **6a**, **6b** and **7a** were based on the model compounds, **6d** and **7b** [22]. IR spectra provided evidence for the oxo group in a five-membered ring [1747 cm^{-1} (**6a**), 1745 cm^{-1} (**6b**) and 1714 cm^{-1} (**7a**)]. Mass spectra included peaks at *m/z* 358 (100%), 344 (100%) and 346 (100%) for **6a**, **6b** and **7a**, respectively, which corresponded with the $[M]^+$. In addition, peaks at *m/z* 151 (41%) (**6a**), 137 (16%) (**6b**) and 151 (40%) (**7a**), due to tropilium ion derivatives, thus confirming guaiacyl and veratryl groups.

The dimers **9** and **10**, could be photochemical artifacts. Exposure of crystals of styryl pyrones to sunlight or to a tungsten lamp has been reported to lead to the production of dimers [27–29]. The mass spectrum of **9** did not show peaks at *m/z* 576 corresponding with the $[M]^+$. Furthermore, it did not show peaks at *m/z* 274 and 302 and, thus, **9** cannot possess vicinal phenyls and pyronyls groups. However, the mass spectrum showed a peak at *m/z* 288 (100%) that corresponded with the monomer **8a**. The mid-point of the high-field AA′BB′ ^{1}H NMR signals of **9** (δ 4.24) is compatible with that exhibited by cyclobutanes of the *r*-8, *c*-7′, *t*-8′ and *t*-7 configuration (δ 4.43) but not of the *r*-8, *t*-7′, *c*-8′ and *t*-7 configuration (δ 3.64) [30]. Only in one of the three possible *r*-8, *c*-7′, *t*-8′ and *t*-7 diphenyldipyronyl isomers, do the substituents occupy alternative positions throughout, as required by the mass spectrum of **9**. The ^{13}C NMR spectrum confirmed the presence of 11 sp^2 carbons, two sp^3 carbons of methoxyls groups (δ 55.8 and 56) and two other sp^3 carbons in **9**. The chemical shifts of the sp^3 carbons (δ 45.5 and 43.5) are comparable with those of the cyclobutane ring of acoradin (δ 43.5 and 44.5) [29]. Dimer **10** is identical to a photo-dimer of tri-*O*-methylhispidin [31]; this stereochemical formula must be identical to that of aniba dimer-A, previously isolated from *A. gardneri* and identified from X-ray diffraction data [32, 33].

The spectroscopic data of flavonoids **11a** [34], **11b** [35], **12a** [36] and **12c** [37] were identical to those described in the literature. The ^{1}H NMR spectra of acetylated flavonoids showed one acetoxyl group in **11c** and **11d** (δ 2.35 and 2.38, respectively), two acetoxyl groups for **11e** (δ 2.31 and 2.39) and three acetoxyl groups for **11g** (δ 2.31, 2.34 and 2.39). Comparisons between these acetylated flavonoids and **11a** allowed the assignment of the positions of the acetoxyl groups. Concerning **11a**, when the OAc is in C-3 position (**11c**, **11e** and **11g**), the signals of both H-2′ and H-6′ shift *ca* 0.33 ppm upfield. When the OAc is at C-5 position (**11d**, **11e** and **11g**), the signals for H-6 and H-8 move downfield to 0.27 and 0.42 ppm, respectively, due to a deprotecting effect. When OAc is at C-4′ (**11g**), the signals for H-3′ and H-5′ move 0.28 ppm downfield. In **11g**, if the acetoxyl groups were located at C-5 and C-7, H-6 and H-8 would be less protected from the diamagnetic effects of the carbonyl groups; and signals due to H-6 and H-8 were moved to downfield (δ 6.81 for H-6 and δ 7.28 for H-8) [38]. The mass spectra of **11c**, **11e** and **11g** did not show the $[M]^+$; these molecules showed corresponding losses of OAc groups and show only ions at $[M-42]^+$: *m/z* 314 (**11c**), 356 (**11e**) and 384 (**11g**).

The molecular formula by mass spectrometry, allied to hydrogen and methoxyl counts by NMR, revealed the formula $C_{20}H_{24}O_6$ for compound **13**. The ^{1}H NMR spectrum shows four aromatic and four aliphatic hydrogens. The signals near δ 3.80, which corresponded with 15 H, can be attributed to five aromatic methoxyls. In addition, the ^{1}H NMR spectrum showed a *dd* at δ 4.90, which corresponds with an oximethine hydrogen (H-2) in the vicinity of two other hydrogens (2H-3); H-2 exhibits 2H-3 axial–axial ($J = 9.5$ Hz) and axial–equatorial ($J = 3.2$ Hz) coupling constants. The signal at δ 2.23–2.00 (*m*) was attributed to H-3. In the aromatic region, the NMR spectrum exhibits three distinct singlets. The singlet at δ 6.68, which corresponds with 2 H, was attributed to H-2′ and H-6′. H-8 is located downfield in relation to H-6, because it is in the vicinity of an additional oxygen atom in the C-ring.

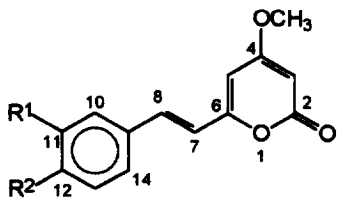
The chemical constitution of this *Aniba* sp. is thus different from other *Aniba* species which have been studied previously. Its botanical classification is complicated by the ambiguity of some of its morphological characteristics [39].

EXPERIMENTAL

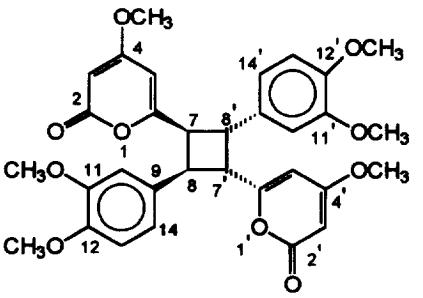
General. Prep. TLC was carried out on silica gel PF-254 (Merck) and CC on silica gel 60 H (0.005–0.045 mm). Mps are uncorr. ^{1}H (200 MHz) and ^{13}C NMR (50 MHz) spectra were recorded in $CDCl_3$ with TMS as int. standard. EIMS were obtained at 70 eV.

Plant material. A trunk sample was collected in the vicinity of Belém, Pará State, and provisionally classified by Prof. Klaus Kubitzki, Hamburg University, as an *Aniba* sp.

Isolation of constituents. Air-dried and powdered wood (2.9 kg) was extracted with hexane at room temp. The extract (45 g) was dissolved in MeOH–H_2O (9:1) and extracted with hexane. Part (100 mg) of the



8a $R^1 = R^2 = OCH_3$
8b $R^1R^2 = O_2CH_2$



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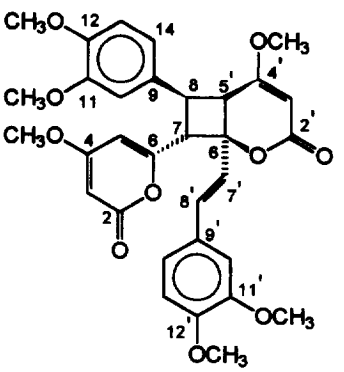

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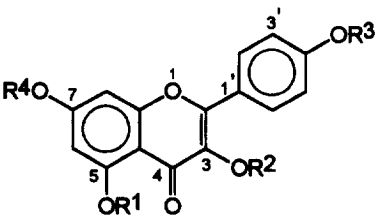
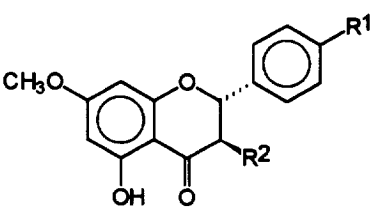
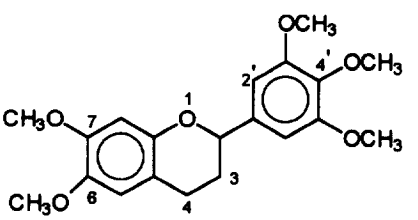


	R^1	R^2	R^3	R^4
11a	H	H	CH_3	CH_3
11b	H	CH_3	CH_3	CH_3
11c	H	Ac	CH_3	CH_3
11d	Ac	H	CH_3	CH_3
11e	Ac	Ac	CH_3	CH_3
11f	H	H	H	CH_3
11g	Ac	Ac	Ac	CH_3



	R^1	R^2
12a	OCH_3	H
12b	H	OH
12c	OCH_3	OH



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hexane extract (29 g) gave by TLC, **1c** (94 mg). The MeOH layer was concd under vacuum yielding 14 g, which was submitted to flash CC (silica gel, hexane–EtOAc, 49:1) providing frs A (12 g) and B (1.2 g). Part of fr. A (100 mg) gave by TLC (hexane–EtOAc, 49:1) **1a** (80 mg) and **1b** (15 mg). Fr. B (1.2 g) was submitted to flash CC and elution with hexane–EtOAc mixts of increasing polarity gave 11 frs. The following frs submitted to prep. TLC (silica gel) afforded from fr. B3, **1d** (20 mg), fr. B4, **11a** (18 mg), fr. B6, **2** (15 mg), fr. B9, **5** (8 mg), fr. B10, **12c** (108 mg), **6a** (49 mg), **6b** (13 mg), **6c** (16 mg), fr. B11, **3b** (186 mg) and **7a** (13 mg). Fr. B5, submitted to HPLC (Si-60 column, 10 μm, 250 × 4.6 mm column, hexane–EtOAc, 49:1), yielded **12b** (28 mg). Fr. B8, submitted to HPLC (Si-60 column, 10 μm, 250 × 4.6 mm column, hexane–EtOAc, 17:3), gave **13** (1.5 mg), **3a** (3 mg) and a mixt. of **4a** and **4b** (8.6 mg).

Air-dried and powdered bark (2.65 kg) was extracted successively with hexane and EtOH at room temp. The hexane extract (43 g) was dissolved in MeOH–H_2O (9:1) and extracted with hexane and the hexane layer evapd. The residue (29 g) gave by TLC of 100 mg, **1c** (70 mg). The MeOH layer was concd under vacuum, yielding 5 g, which was submitted to flash CC. Elution with hexane–EtOAc mixts of increasing polarity gave six frs. The following frs, submitted to prep. TLC, yielded from fr. A, **1a** (11 mg), **1b** (38 mg) and **1c** (83 mg), fr. B, **1d** (14 mg), fr. C, **12a** (59 mg), fr. D, **11a** (172 mg) and **11b** (19 mg), fr. E, **8a** (130 mg), fr. F, **8b** (28 mg), **9** (21 mg), **3b** (3 mg) and **6a** (9 mg). The EtOH extract (100 g), was partitioned between $CHCl_3$–MeOH (3:2). The $CHCl_3$ layer was concd under vacuum yielding 12 g, which was sepd by flash CC (hexane–EtOAc, 49:1 and EtOAc), to give frs A (122 mg), B (2.5 g), C (128 mg)

and D (6 g). Frs A–C gave **1a**. Fr. D (1.0 g) was acetylated (Ac_2O–pyridine), yielding six frs by flash CC (silica gel, hexane–EtOAc, 3:2). The following frs, submitted to prep. TLC (silica gel) afforded from fr. A, **11a** (4 mg) and **11d** (12 mg), fr. B, **11g** (35 mg), fr. C, **12c** (2 mg) and **8b** (11 mg), fr. D, **11c** (15 mg) and **11e** (9 mg), fr. E, **8a** (62 mg) and fr. F, **10** (7 mg).

(7S, 8S, 1′R, 4′R, 5′S)-4′-*Hydroxy*-3,4,3′-*trimethoxy*-6′-*oxo*-8.1′,7.5′-*neolignan*-Δ: 1,3,5,2′,8′ (**6a**). Oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}. 3470, 1747, 1635, 1607, 1517, 1467. ^1H NMR (200 MHz, $CDCl_3$): δ 6.75 (*d*, J = 8.0 Hz, H-5), 6.61–6.68 (*m*, H-2, H-6), 5.90 (*ddd*, J = 2.8, 7.3, 17.0 Hz, H-8′), 5.02–5.10 (*m*, H-9′), 4.67 (*d*, J = 5.2 Hz, H-4′), 4.43 (*s*, H-2′), 3.82 (*s*, 3-OMe, 4-OMe), 3.61 (*s*, 3′-OCH_3), 3.02 (*dd*, J = 1.7, 8.7 Hz, H-7), 2.72 (*dd*, J = 1.7, 5.2 Hz, H-5′), 2.37 (*dd*, J = 7.0, 14.1 Hz, H-7′), 2.24 (*dd*, J = 7.3, 14.1 Hz, H-7′), 1.99 (*dq*, J = 6.6, 8.7 Hz, H-8), 1.00 (*d*, J = 6.6 Hz, H-9). ^{13}C NMR (50 MHz, $CDCl_3$): δ 210.4 (C-6′), 153.9 (C-3′), 148.9 (C-3), 147.5 (C-4), 137.1 (C-1), 134.0 (C-8′), 119.3 (C-6), 117.8 (C-9′), 111.3 (C-5), 110.8 (C-2), 98.6 (C-2′), 74.1 (C-4′), 58.3 (C-5′), 52.9 (C-1′), 48.3 (C-8), 45.5 (C-7), 35.3 (C-7′), 12.1 (C-9), 55.2, 55.8, 55.9 (OMe). MS *m/z* (rel. int.): 358 $[M]^+$ (100), 206 (5), 205 (5), 180 (8), 178 (64), 151 (41), 91 (46).

(7S, 8S, 1′R, 4′R, 5′S)-4,4′-*Dihydroxy*-3,3′-*dimethoxy*-6′-*oxo*-8.1′,7.5′-*neolignan*-Δ: 1,3,5,2′,8′ (**6b**). Oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3454, 1745, 1636, 1611, 1518, 1454. ^1H NMR (200 MHz, $CDCl_3$): δ 6.75 (*d*, J = 8.2 Hz, H-5), 6.58–6.63 (*m*, H-2, H-6), 5.84–6.02 (*m*, H-8′), 5.01–5.10 (*m*, H-9′), 4.68 (*d*, J = 5.2 Hz, H-4′), 4.43 (*s*, H-2′), 3.82 (*s*, 3,4-OMe), 3.61 (*s*, 3′-OMe), 2.99 (*dd*, J = 1.7, 8.7 Hz, H-7), 2.72 (*dd*, J = 1.7, 5.2, H-5′), 2.37 (*dd*, J = 7.1, 14.2, H-7′), 2.23 (*dd*, J = 7.5, 14.2 Hz, H-7′), 1.98 (*dq*, J = 6.6, 8.7 Hz, H-8), 1.00 (*d*, J = 6.6 Hz, H-9). ^{13}C NMR (50 MHz, $CDCl_3$): δ 210.5 (C-6′), 153.8 (C-3′), 146.5 (C-3), 144.1 (C-4), 136.4 (C-1), 134.1 (C-8′), 120.1 (C-6), 117.8 (C-9′), 114.4 (C-5), 110.1 (C-2), 98.6 (C-2′), 74.1 (C-4′), 58.3 (C-5′), 55.2, 55.9 (OMe), 52.9 (C-1′), 48.5 (C-8), 45.7 (C-7), 35.4 (C-7′), 12.1 (C-9). MS *m/z* (rel. int.): 344 $[M]^+$ (100), 206 (2), 205 (5), 180 (8), 178 (11), 137 (16).

(7S, 8S, 1′R, 5′R)-4-*Hydroxy*-3,3′-*dimethoxy*-4′,6′-*dioxo*-8.1′, 7.5′-*neolignan*-Δ: 1,3,5,2′,8′ (**6c**). ^{13}C NMR (50 MHz, $CDCl_3$): δ 203.7 (C-6′), 191.1 (C-4′), 152.8 (C-3′), 147.2 (C-3), 145.3 (C-4), 133.7 (C-8′), 133.5 (C-1), 120.3 (C-6), 119.4 (C-2′), 118.2 (C-9′), 109.7 (C-5), 109.0 (C-2), 57.3 (C-5′), 55.9, 55.2 (OMe), 53.6 (C-1′), 49.9 (C-7), 46.7 (C-8), 35.4 (C-7′), 13.6 (C-9).

(7S, 8S, 1′S, 4′R, 5′R, 6′S)-4′,6′-*Dihydroxy*-3,4-*dimethoxy*-3′-*oxo*-8.1′, 7.5′-*neolignan*-Δ: 1,3,5,8′ (**7a**). Oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3482, 1714, 1609, 1517, 1464. ^1H NMR (200 MHz, $CDCl_3$): δ 7.01 (*d*, J = 1.8 Hz, H-2), 6.86 (*dd*, J = 1.8, 8.2 Hz, H-6), 6.73 (*d*, J = 8.2, H-5), 5.80–6.00 (*m*, H-8′), 5.11–5.19 (*m*, H-9′), 4.26 (*s*, H-6′), 4.18 (*d*, J = 3.4 Hz, H-4′), 3.86 (*s*, OMe), 2.56 (*d*, J = 3.7 Hz, H-5′), 2.27–2.56 (*m*, H-7, H-8), 2.39 (*s*, H-2′), 2.04 (*dd*, J = 8.2, 14.0 Hz, H-7′), 0.89 (*d*, J = 6.4 Hz, H-9). ^{13}C NMR (50 MHz, $CDCl_3$): δ 210.7 (C-3′), 148.9 (C-3), 147.4 (C-4), 137.6 (C-1), 134.2 (C-8′), 119.6 (C-6), 118.7 (C-9′), 111.7 (C-5), 110.9 (C-2), 79.5 (C-6′), 77.2 (C-4′), 55.9 (OMe), 55.8 (OMe), 55.1 (C-5′), 53.2 (C-1′), 52.1 (C-8), 47.9 (C-7), 42.9 (C-2′), 37.6 (C-7′), 11.9 (C-9). MS *m/z* (rel. int.): 346 $[M]^+$ (100), 193 (11), 192 (4), 167 (25), 166 (9), 178 (29), 151 (40).

4-*Methoxy*-6-(11,12-*dimethoxy*-trans-*styryl*)-2-*pyrone* (**8a**). Mp 160–162° (Me_2CO). ^{13}C NMR (50 MHz, $CDCl_3$): δ 171.1 (C-2), 164.1 (C-4), 158.9 (C-6), 150.3 (C-12), 149.1 (C-11), 135.6 (C-8), 128.2 (C-9), 121.5 (C-14), 116.5 (C-7), 111.1 (C-13), 109.2 (C-10), 100.5 (C-5), 88.3 (C-3), 55.9, 55.8 (OMe). MS *m/z* (rel. int.): 288 $[M]^+$ (100), 271 (5), 260 (14), 217 (19), 151 (6), 69 (4).

6-(11,12-*Methylenedioxy*-trans-*styryl*)-4-*methoxy*-2-*pyrone* (**8b**). Mp 245–248° (Me_2CO). ^{13}C NMR (50 MHz, DMSO-d_6): δ 171.1 (C-2), 163.0 (C-4), 158.8 (C-6), 148.6 (C-11), 148.2 (C-12), 134.3 (C-8), 129.8 (C-9), 123.8 (C-14), 117.9 (C-7), 108.8 (C-10), 106.2 (C-13), 101.7 ($O_2\underline{C}H_2$), 100.9 (C-5), 88.6 (C-3), 56.6 (OMe). MS *m/z* (rel. int.): 272 $[M]^+$ (100), 255 (7), 244 (21), 229 (11), 212 (12), 201 (52), 135 (10), 89 (37), 69 (56).

r-8, *c*-7′, *t*-8′, *t*-7-8,8′-11,12-*Dimethoxyphenyl*-7,7′-*di*-[6-(4-*methoxy*-2-*pyronyl*)]-*cyclobutane* (**9**). Mp 112–114° (hexane–EtOAc, 3:2). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3087–3085, 1718, 1645. ^1H NMR (200 MHz, $CDCl_3$): δ 6.77–6.87 (*m*, H-10, H-13, H-14, H-10′, H-13′, H-14′), 5.71 (*d*, J = 2.1, H-5, H-5′), 5.21 (*d*, J = 2.0, H-3, H-3′), 4.32 (*m*, H-8, H-8′), 4.15 (*m*, H-7, H-7′), 3.84, 3.82, 3.77 (*s*, 11′, 11, 12-OMe), 3.75 (*s*, 12′-OMe), 3.67 (*s*, 4,4′-OMe). ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.6 (C-2, C-2′), 164.0 (C-4, C-4′), 162.9 (C-6, C-6′), 148.9 (C-12, C-12′), 148.1 (C-11, C-11′), 129.8 (C-9, C-9′), 119.5 (C-14, C-14′), 111.0 (C-13, C-13′), 110.9 (C-10, C-10′), 101.3 (C-5, C-5′), 87.8 (C-3, C-3′), 55.8, 56.0 (OMe), 45.5 (C-7, C-7′), 43.5 (C-8, C-8′). MS *m/z* (rel. int.): 288 (100), 260 (16), 217 (22), 151 (4).

rel-(6*R*, 7*S*, 8*S*, 5′*S*)-4′-*Methoxy*-8-(11,12-*dimethoxyphenyl*)-7-[6-(4-*methoxy*-2-*pyronyl*)]-6-(E)-*styryl*- 1′-*oxabicyclo*[4,2,0]octa-4′-en-2′-one (**10**). Mp 195–197° (hexane–EtOAc, 3:7). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3086–3014, 1713, 1621. ^1H NMR (200 MHz, $CDCl_3$): δ 6.76–6.98 (*m*, H-10, H-13, H-14, H-10′, H-13′, H-14′), 6.93 (*d*, J = 16 Hz, H-8′), 6.47 (*d*, J = 16.0 Hz, H-7′), 5.92 (*d*, J = 2.1 Hz, H-5), 5.32 (*d*, J = 2.1 Hz, H-3), 5.28 (*s*, H-3′), 4.28 (*dd*, J = 9.8, H-8), 4.05 (*d*, J = 11 Hz, H-7), 3.92 (*s*, 12′-OMe), 3.70 (*s*, 4-OMe), 3.56 (*d*, J = 9.7, H-5′), 3.32 (*s*, 4′-OMe), 3.85, 3.86, 3.87 (*s*, 11′, 11, 12-OMe). ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.6, 170.2 (C-2, C-2′), 164.0, 164.8 (C-4, C-4′), 149.2, 149.3 (C-12, C-12′), 148.7, 148.9 (C-11, C-11′), 128.9, 128.3 (C-9, C-9′), 123.3, 122.5 (C-14, C-14′), 111.1, 111.3 (C-13, C-13′), 88.6, 91.6 (C-3, C-3′), 102.8 (C-5), 30.9 (C-5′), 158.6 (C-6), 79.5 (C-6′), 45.9 (C-7), 119.1 (C-7′), 39.1 (C-8), 130.9 (C-8′), 110.7, 108.7 (C-10, C-10′), 55.3, 55.6, 55.9, 56.0 (OMe). MS *m/z* (rel. int.): 288 (100), 260 (17), 245 (18), 217 (36), 151 (15), 69 (39).

3,5-*Dihydroxy*-7,4′-*dimethoxyflavone* (**11a**). Mp 180–181° ($CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ

11.7 (*s*, 5-OH), 8.14 (*d*, $J = 9.0$, H-2′, H-6′), 7.0 (*d*, $J = 9.0$, H-3′, H-5′), 6.58 (*s*, 3-OH), 6.46 (*d*, $J = 2.1$, H-8), 6.35 (*d*, $J = 2.1$, H-6), 3.87 (*s*, OMe). ^{13}C NMR (50 MHz, $CDCl_3$): δ 175.1 (C-4), 165.7 (C-7), 161.1 (C-4′), 160.8 (C-5), 156.8 (C-9), 145.7 (C-2), 135.6 (C-3), 128.8 (C-2′, C-6′), 123.1 (C-1′), 114.0 (C-3′, C-5′), 103.9 (C-10), 97.9 (C-6), 92.2 (C-8), 55.8, 55.4 (OMe). MS *m/z* (rel. int.): 314 $[M]^+$ (100), 313 (11), 285 (8), 271 (20), 135 (17).

5-*Hydroxy*-3,7,4′-*trimethoxyflavone* (**11b**). Mp 138–140° ($CHCl_3$–MeOH). ^{1}H NMR (200 MHz, $CDCl_3$): δ 12.6 (*s*, 5-OH), 8.07 (*d*, $J = 9.0$, H-2′, H-6′), 7.0 (*d*, $J = 9.0$, H-3′, H-5′), 6.43 (*d*, $J = 2.2$, H-8), 6.33 (*d*, $J = 2.2$, H-6), 3.84 (*s*, OMe). ^{13}C NMR (50 MHz, $CDCl_3$): δ 178.8 (C-4), 165.4 (C-7), 162 (C-4′), 161.7 (C-5), 156.8 (C-9), 148.0 (C-2), 138.9 (C-3), 130 (C-2′, C-6′), 122.8 (C-1′), 114.0 (C-3′, C-5′), 106 (C-10), 97.8 (C-6), 92.2 (C-8), 60.1 (3-OMe), 55.8, 55.4 (4′,7-OMe). MS *m/z* (rel. int.): 328 $[M]^+$ (2), 313 (10), 285 (8), 167 (23), 166 (58), 162 (11), 135 (58), 91 (95).

3-*Acetoxy*-5-*hydroxy*-7,4′-*dimethoxyflavone* (**11c**). Mp 177–180° (hexane–EtOAc, 2:3). ^{1}H NMR (200 MHz, $CDCl_3$): δ 12.2 (*s*, 5-OH), 7.81 (*d*, $J = 9.0$, H-2′, H-6′), 6.99 (*d*, $J = 9.0$, H-3′, H-5′), 6.45 (*d*, $J = 2.2$, H-8), 6.35 (*d*, $J = 2.2$, H-6), 3.88 (*s*, OMe), 2.35 (*s*, OAc). MS *m/z* (rel. int.): 314 (100), 299 (21), 271 (25), 243 (13), 135 (73).

5-*Acetoxy*-3-*hydroxy*-7,4′-*dimethoxyflavone* (**11d**). Mp 167–169° (hexane–EtOAc, 1:1). ^{1}H NMR (200 MHz, $CDCl_3$–$(CD_3)_2CO$): δ 9.81 (*s*, OH), 8.06 (*d*, $J = 9.2$, H-2′, H-6′), 7.06 (*d*, $J = 9.2$, H-3′, H-5′), 6.88 (*d*, $J = 2.2$, H-8), 6.58 (*d*, $J = 2.2$, H-6), 3.89 (*s*, OMe), 3.86 (*s*, OMe), 2.38 (*s*, OAc). MS *m/z* (rel. int.): 356 $[M]^+$ (100), 313 (86), 314 (45), 299 (9), 271 (43), 135 (14).

3,5-*Diacetoxy*-7,4′-*dimethoxyflavone* (**11e**). Mp 212–215° (hexane–EtOAc, 3:2). ^{1}H NMR (200 MHz, $CDCl_3$)–$(CD_3)_2CO$): δ 7.82 (*d*, $J = 9.0$, H-2′, H-6′), 7.04 (*d*, $J = 9.0$, H-3′, H-5′), 6.88 (*d*, $J = 2.2$, H-8), 6.62 (*d*, $J = 2.2$, H-6), 3.91 (*s*, OMe), 3.89 (*s*, OMe), 2.39 (*s*, OAc), 2.31 (*s*, OAc). MS *m/z* (rel. int.): 356 (2), 314 (4), 300 (100), 299 (9), 271 (8), 135 (8).

3,5,4′-*Triacetoxy*-7-*methoxyflavone* (**11g**). Mp 222–224° (Me_2CO). ^{1}H NMR (200 MHz, $CDCl_3$–$(CD_3)_2CO$): δ 7.90 (*d*, $J = 8.7$, H-2′, H-6′), 7.28 (*d*, $J = 8.7$, H-3′, H-5′), 6.96 (*d*, $J = 2.3$, H-8), 6.66 (*d*, $J = 2.3$, H-6), 3.94 (*s*, OMe), 2.39 (*s*, OAc), 2.34 (*s*, OAc), 2.31 (*s*, OAc). MS *m/z* (rel. int.): 384 (22), 342 (19), 300 (100), 171 (18), 121 (27).

(2*R*, 3*R*)-2,3-*Dihydro*-5-*hydroxy*-7,4′-*dimethoxyflavone* (**12a**). Mp 114–115° (hexane–EtOAc, 1:1). ^{13}C NMR (50 MHz, $CDCl_3$): δ 196 (C-4), 167.9 (C-7), 164.1 (C-5), 162.9 (C-9), 160 (C-4′), 130.3 (C-1′), 127.7 (C-2′, C-6′), 114.2 (C-3′, C-5′), 103.1 (C-10), 95.0 (C-6), 94.2 (C-8), 78.9 (C-2), 43.2 (C-3), 55.7, 55.4 (OMe). MS *m/z* (rel. int.): 300 $[M]^+$ (100), 299 (60), 193 (17), 166 (20), 134 (76), 121 (65).

(2*R*, 3*R*)-2,3-*Dihydro*-3,5-*dihydroxy*-7-*methoxyflavone* (**12b**). Mp 173–175° (hexane–EtOAc, 4:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ 11.2 (*s*, OH), 7.46 (*m*, H-2′, H-6′, H-3′, H-5′, H-4′), 6.11 (*d*, $J = 2.1$ Hz, H-8), 6.05 (*d*, $J = 2.1$, H-6), 5.08 (*d*, $J = 11.9$ Hz, H-2), 4.55 (*d*, $J = 11.9$ Hz, H-3), 3.84 (*s*, OMe). ^{13}C NMR (50 MHz, $CDCl_3$): δ 195.8 (C-4), 168.9 (C-7), 163.6 (C-5), 136.1 (C-1′), 129.4 (C-4′, C-5′), 128.7 (C-3′), 127.5 (C-2′, C-6′), 100.8 (C-10), 95.5 (C-6), 94.7 (C-8), 83.4 (C-2), 72.4 (C-3), 55.8 (OMe). MS *m/z* (rel. int.): 286 $[M]^+$ (81), 257 (100), 167 (54), 120 (7), 91 (27).

(2*R*, 3*R*)-2,3-*Dihydro*-3,5-*dihydroxy*-7,4′-*dimetoxyflavone* (**12c**). Mp 200–203° (MeOH). ^{13}C NMR (50 MHz, DMSO-d_6): δ 198.6 (C-4), 167.7 (C-7), 163.2 (C-5), 162 (C-9), 159.7 (C-4′), 129.6 (C-1′), 129.3 (C-2′, C-6′), 113.8 (C-3′, C-5′), 101.6 (C-10), 95.1 (C-6), 94.1 (C-8), 83.0 (C-2), 71.7 (C-3), 55.3, 56.1 (OMe). MS *m/z* (rel. int.): 316 $[M]^+$ (15), 287 (31), 167 (100), 150 (27), 121 (59).

6,7,3′,4′,5′-*Pentamethoxyflavan* (**13**). Mp 119–120° (hexane–EtOAc, 4:1). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2926, 2852, 1592, 1512, 1462, 1261, 1126. ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.68 (*s*, H-2′, H-6′), 6.53 (*s*, H-8), 6.49 (*s*, H-5), 4.90 (*dd*, $J = 3.2$, 9.5 Hz, H-2), 3.80 (*s*, OMe), 2.93 (*ddd*, $J = 16.2$, 5.2, 10.2 Hz, H-4 ax), 2.74 (*ddd*, $J = 16.2$, 5.2, 2.9 Hz, H-4 eq), 2.00–2.23 (*m*, H-3). MS *m/z* (rel. int.): 360 $[M]^+$ (72), 194 (68), 180 (100), 166 (23), 151 (44), 106 (10).

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