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NEOLIGNANS FROM A *NECTANDRA* SPECIES*

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Key Word Index—*Nectandra* sp.; Lauraceae; hydrobenzofuranoid neolignans; bicyclo[3.2.1]octanoid neolignans.

Abstract—The trunk wood of an Amazonian *Nectandra* (Lauraceae) species contains one bicyclo[3.2.1]octanoid and four hydrobenzofuranoid neolignans. The latter comprise representatives of the mirandin, the rearranged burchellin and the burchellin types. The former was characterized as (1*S*, 4*R*, 5*S*, 6*R*, 7*R*)-3-allyl-4-hydroxy-1-methoxy-(3′, 4′, 5′-trimethoxyphenyl)-7-methyl-8-oxobicyclo[3.2.1]oct-2-ene (macrophyllin-B), a new representative of the seemingly rare macrophyllin type.

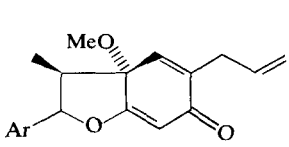
INTRODUCTION

Trunk wood for the present study was collected from a lauraceous tree at Rosa de Maio, a locality on the Manaus–Itacoatiara highway (km 8), Amazonas, by Dionísio Coelho. According to Dr. Klaus Kubitzki, Hamburg, the specimen, voucher Herbarium INPA, Manaus, No. 46.534 (20 February 1974), belongs to an unclassified *Nectandra* species. Indeed mirandin-A (**1a**), which proved to be its major neolignan, is known to occur additionally in *Nectandra miranda* [2]. For reasons stated in a previous paper of this series [3], nomenclature and numbering of this and other neolignans follow the rules which were outlined in a recent review [4].

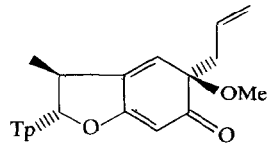
RESULTS AND DISCUSSION

Fractionation of the C_6H_6 extract gave crystalline mirandin-A (**1a**), besides minor quantities of burchellin-type [4, 5] (**2**, **3a**, **3b**) and macrophyllin-type [4, 6] (**4a**) neolignans. While **1a**, **2** and **3a** had been isolated previously from *Nectandra miranda Sandw.* [2]; *from N. miranda* [2] and *Aniba simulans* Allen [7]; and from *A. affinis* [8] and *A. burchellii* Kosterm. [9], respectively, and were thus identifiable by direct comparison with known compounds, **3b** and **4a** were novel neolignans.

Compounds **3a** and **3b** were isolated as a mixture whose separation was not achieved by Si gel chromatography. The IR and UV characteristics of this product and pure **3a** [8] were closely comparable. The MS, however, showed, besides peaks at *m/e* 356 ($M^{+\cdot}$), 315 [(M-allyl)$^+$] and 178 [$(MeO)_2C_6H_3CH{=}CHMe^{+\cdot}$], diagnostic of **3a**, corresponding peaks at *m/e* 386, 345 and 208 of comparable heights. Since all other neolignans of the species under scrutiny sustain a tri-*O*-methylpyrogallyl substituent, it was immediatly suspected that this may be the case also for **3b**, and account for the observed MS peaks. Indeed, the 60 MHz ^{1}H NMR contained, besides the broad singlet at δ 6.85 typical of the C-2, C-5 and C-6 protons of a veratryl group, a fine singlet at δ 6.55, compatible with the C-2 and C-6 protons of a pyrogallyl group. With the exception of the typical 3H-9 and 2H-7′ signals, which appeared at slightly different frequencies, all other peaks for **3a** and **3b** in the spectrum of the mixture were coincident. A conclusive carbon-count for both compounds was given by a proton-decoupled ^{13}C NMR spectrum. Significant differences of signal frequencies were noted solely for the carbons of the aromatic rings. All assignments



1a Ar = α-Tp
1b Ar = β-Tp



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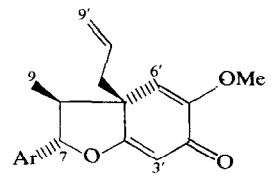
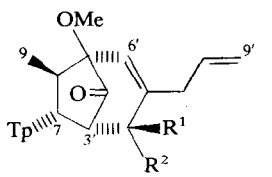


3a Ar = Ve
3b Ar = Tp



4a R^1 = H, R^2 = OH
4b $R^1 + R^2$ = O

*Part 56 in the series "The Chemistry of Brazilian Lauraceae". For Part 55 see ref. [1]. Based on part of the M.S. thesis submitted by R.F., Instituto Nacional de Pesquisas da Amazônia, CNPq, Manaus, AM, to Universidade Federal Rural do Rio de Janeiro (1978).

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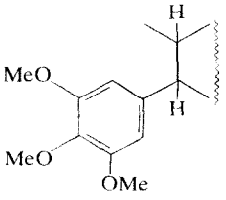
Abbreviations: Tp = 3,4,5-trimethoxyphenyl (tri-*O*-methylpyrogallyl); Ve = 3,4-dimethoxyphenyl (veratryl); Pi = 3,4-methylenedioxyphenyl (piperonyl).

were checked by single frequency off-resonance decoupling which led to the expected band multiplicities.

The relative configuration of **3a** was established by consideration of chemical shifts for atoms at positions 7, 9 and 7′ [10]. As the analogous values for **3b** are substantially identical, both compounds must possess identical relative configurations and conformations. Since, furthermore, the ORD curves of the mixture and of pure **3a** [8, 11] were closely comparable, the absolute configuration shown in **3b** represents the novel neolignan.

Determination of the MW by MS, allied to hydrogen, carbon and methoxyl counts by NMR, revealed the formula $C_{18}H_{16}O_2$ $(OMe)_4$ for compound **4a** suggesting another bis-arylpropanoid compound. Indeed, as in analogous cases [4], a prominent MS fragment ion at *m/e* 208 (45%) and the symmetry of the aryl substitution indicated by NMR data revealed the constitution of one of the C_6C_3-moieties (**5**).

The additional C_6C_3-group had an allyl on a trisubstituted double bond (2H-7′, δ 3.00, *d*, $J = 7$ Hz). The fact that the only vinylic proton (H-6′, δ 5.62) was represented by a singlet with only allylic broadening indicated vicinality of this methine to a tetrasubstituted carbon. This double bond was part of a secondary allyl alcohol since oxidation of the compound with MnO_2 led to an α,β-unsaturated ketone (**4b**, ν_{max} 1680 cm^{-1}), a transformation which produced a 1.13 ppm paramagnetic shift of the olefinic β (H-6′) proton. The secondary nature of the alcohol was confirmed by acetylation. The doublet (δ 4.72, $J = 5$ Hz) due to the carbinolic proton (H-2′) suffered a 1.08 ppm paramagnetic shift. The multiplicity of this signal indicated the vicinity of a further methine. Since the signal of the corresponding proton appeared at δ 2.60, the yet unassigned methoxyl (δ 3.54) could only be situated at the previously mentioned tetrasubstituted carbon. The carbonyl (ν_{max} 1750 cm^{-1}), which must link these trisubstituted and tetrasubstituted carbons in order to complete the C_6-unit **6**, was also part of the



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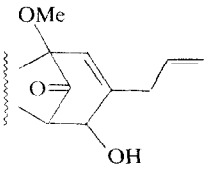
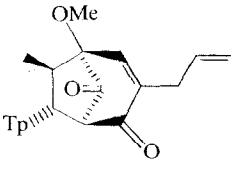


6

pentacycle formed by joining **5** and **6**. Of the two ways this can be done, **4a** alone must represent the correct alternative. Indeed, there was a slight coupling ($J_{H7,H-3'} = 0.8$ Hz) between the bridgehead and the benzylic protons. The interpretations of this, as well as all other proton couplings, were confirmed by a complete series of decoupling experiments at 270 MHz.

The relative configurations of the substituents of the bicyclo[3.2.1]oct-2-ene skeleton of **4a** were deduced from the 3H-9 proton signal at relatively low field (δ 1.05) indicative of the Me/Ar *trans*-relationship, and the coupling constant between H-2′, H-3′ (5 Hz) which was, according to the Karplus equation, compatible only with the *endo*-configuration for the hydroxyl at C-2′.

The absolute configurational details indicated in **4** were determined by comparison with the bicyclo[3.2.1]oct-2-ene (**7**). This compound was obtained by acid-catalysed rearrangement of mirandin-A (**1a**) of known stereochemistry [2,11]. The reaction proceeds by way of an intermediate benzylic ion **8**



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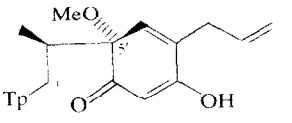


8

[12]. The centre at C-5′ is not affected, i.e. the methoxyl is not eliminated, since not only in MeOH, but also in EtOH, **7** is the sole reaction product. The aryl substituent in the end product **7** could thus appear *cis*- or *trans*-oriented with respect to Me-8. Only the *trans* derivative (3H-9′, δ 1.09) was obtained. All other substituents, however, must retain the absolute configurational identity during the transformation of **1a** into **7**.

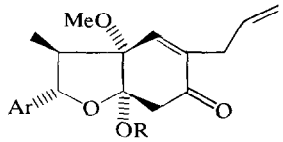
Spectral comparison of **7** and **4b**, the oxidation product of **4a**, showed the compounds to be configurationally different. H-7 resonated at higher field in **7** (δ 2.47) than in **4a** (δ 2.60), a reflection of the relative situations with respect to the C-2′ carbonyl: H-7 is *endo* in **7**, where it receives anisotropic shielding by the carbonyl and so H-7 is *exo* in **4b**. Analogously, H-6′ resonated at lower field in **7** (δ 7.05) than in **4b** (δ 6.75), a reflection of the relative situations with respect to the C-7 aryl and the C-8 methyl: Ar-7 must be *exo* in **7**, where it cannot exert anisotropic shielding on H-6′ and must be *endo* in **4b**; Me-8 which is *endo* in **7**, where it exerts electronic repulsion on H-6′, must be *exo* in **4b**. The clearest evidence for the orientation of Ar-7 related to Me-8 on one hand and to the carbonyl at C-2′ on the other, however, was given by ^{13}C NMR data. C-9 of **7** (δ 13.8) and C-2′ of **4b** (δ 189.3) resonated at higher field than their counterparts in the alternative compounds (C-9 of **4b** at δ 15.6; C-2′ of **7** at δ 194.2), as reflections of stronger γ-effects within the cyclic systems. Contrasting electronic interactions between the aryl and ring system are evidenced also by the IR carbonyl absorptions of **7** (ν_{max} 1667 cm^{-1}) vs **4b** (ν_{max} 1680 cm^{-1}) (cf. [9]).

With the establishment of the relative configuration of **4b** its absolute configuration could be deduced. Indeed, the ORD curve of **7** showed a positive Cotton effect at 307 nm and a negative Cotton effect at 282 nm assigned to the aryl and enone chromophores, respectively. Both these effects were positive in the case of **4b**, revealing identical chirality for the benzylic C-7 and antipodal chirality for C-3′ and C-5′ vicinal to the enone group. According to these facts, and the above deduction of the relative configuration of the hydroxyl at C-4′, structure **4a** is proposed for the natural neolignan.

The novel compound **4a** is designated macrophyllin-B since it belongs to a neolignan type so far represented only by macrophyllin, now suffixed A, from *Licaria macrophylla* [6].

The acid-(TsOH) catalysed rearrangement of mirandin-A (**1a**) to the 4,8-dioxobicyclo[3.2.1]oct-2-ene **7** (76% yield), the central feature of the structure

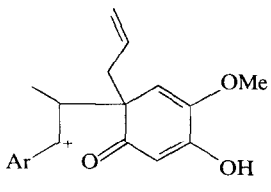
elucidation of the neolignan **4a**, required reflux in MeOH. A previous hydrobenzofuranoid–bicyclo[3.2.1]octanoid rearrangement [12] was performed at room temperature [13]. Under the milder conditions, however, **1a** isomerized to **1b** [2] (32%), and added the elements of water and methanol leading to the products **9a** (18%) and **9b** (31%). Relevant features of the ^{1}H NMR data of **9a** and **9b** were comparable with those for pipernone (**9c**), an antifeeding neolignan of *Piper futokadzura* for which



9a Ar = Tp, R = H
9b Ar = Tp, R = Me
9c Ar = Pi, R = Me

only a constitutional formula is available [14]. All three derivatives should thus possess the same relative stereochemistry. This is defined by experimental evidence for C-6, C-7, and C-5′, while construction of a model reveals the *trans*-ring juncture to be highly strained.

Alternative cyclization modes of benzylic ions such as **10**, whose preferred direction seems to be governed mainly by stereochemical factors [12], rationalizes the co-occurrence of 8.1′-linked neolignans of the burchellin (**3**) and guianin (**11**) type in extracts of



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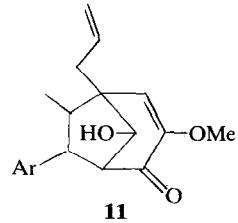

11

Lauraceae species (cf. [9, 11, 13]). Now that the co-occurrence of mirandin (**1**) and marcophyllin (**4**) types has been established, the relationship of the 8.5′-linked neolignans can be assumed to be mediated by intermediates such as **8**.

EXPERIMENTAL

Isolation of the constituents. Trunk wood reduced to saw dust (4.5 kg) was percolated with C_6H_6 at room temp. A powdery mixture of extract (100 g) and Si gel (200 g) was washed successively with petrol, C_6H_6 and $CHCl_3$ and MeOH giving respectively fractions A_1, A_2 and A_3. A_1 (18 g) was separated by filtration into crystalline **1a** (9 g) and oily aliphatic material. A_3 (4 g) in EtOH deposited a solid which, after separation by centrifugation and washing with EtOH, gave a colourless powder of aliphatic esters (350 mg). A_2 (35 mg) was in part (15 g) chromatographed on Si gel (200 g), elution with C_6H_6–Me_2CO of indicated proportions giving fractions B_1 (1:0), B_2 (9.5:0.5), B_3 (9:1), B_4 (8.5:1.5), B_5 (8:2). B_1 (2.2 g) and B_2 (2.7 g) were composed respectively of **1a**, **4a** and **2**, **4a**, which were separated by repeated TLC (Si gel, $CHCl_3$): **1a** (750 mg, R_f 0.80), **2** (810 mg, R_f 0.71), **4a** (160 mg, R_f 0.76). B_3 (1.4 g), B_4 (1.9 g) and B_5 (2.2 g) were respectively **2**, and mixtures of **2**, **3a**, **3b** and **3a**, **3b**. The latter mixture could not be resolved by TLC on Si gel.

(7S,8S,1′R)-$\Delta^{8'}$-3,4,5′-*Trimethoxy*-(*and* 3,4,5,5′-*tetramethoxy*)-1′,4′-*dihydro*-4′-*oxo*-6.O.2′,7.1′-*neolignan* (**3a**+**3b**). Viscous oil, IR ν_{max}^{Film} cm^{-1}: 1658. UV λ_{max}^{EtOH} nm (log ε): 234, (4.68), 277 (5.49), 305 (3.98). ^{1}H NMR **3a**/**3b** (60 MHz, $CDCl_3$): δ 6.85/6.55 (*br s/s*, 3H-2,5,6/2H-2,6), 5.38 (*d*, *J* = 9 Hz, H-7), 2.4–2.55 (*m*, H-8), 1.19/1.17 (*d*, *J* = 7 Hz, 3 H-9), 5.82 (*s*, H-3′), 5.50 (*s*, H-6′), 2.4–2.6 (*m*, 2H-7′), 5.6–6.2 (*m*, H-8′), 4.9–5.3 (*m*, 2H-9′), 3.85 (*s*, 2 OMe-3,4/2 OMe-3,5), —/3.82 (*s*, —/OMe-4), 3.65 (*s*, OMe-5′). ^{13}C NMR **3a**/**3b** (25.2 MHz, $CDCl_3$): δ 129.9/133.1 (*s*, C-1), 109.2/103.4 (*d*, C-2), 149.6/153.3 (*s*, C-3), 149.2/131.5 (*s*, C-4), 110.9/153.3 (*d/s*, C-5), 119.4/103.4 (*d*, C-6), 91.1 (*d*, C-7), 49.4 (*d*, C-8), 8.5 (*q*, C-9), 51.0 (*s*, C-1′), 181.4 (*s*, C-2′), 101.9 (*d*, C-3′), 182.7 (*s*, C-4′), 153 (*s*, C-5′), 107.9 (*d*, C-6′), 36.7 (*t*, C-7′), 130.8 (*d*, C-8′), 119.9 (*t*, C-9′), 55.9/56.1 (*q*, 2 OMe-3,4/2 OMe-3,5), —/60.7 (*q*, —/OMe-4), 55.2 (*q*, OMe-5). MS **3a**/**3b** *m/e* (rel. int.): 356/386 (6%/4%) M^+, 315/345 (4/1), 178/208 (6/4). ORD (4.9 mg/10 ml MeOH): $[\phi]_{400}$ +410, $[\phi]_{355}$ +600, $[\phi]_{320}^{pk}$ +4700, $[\phi]_{303}$ 0, $[\phi]_{280}^{tr}$ −8400, $[\phi]_{260}$ −4900, $[\phi]_{249}$ 0.

(7R,8R,2′R,3′S,5′S)-$\Delta^{8'}$-2′-*Hydroxy*-3,4,5,5′-*tetramethoxy*-2′,3′,4′,5′-*tetrahydro*-4′-*oxo*-7.3′,8.5′-*neolignan* (**4a**). Viscous oil, $C_{22}H_{28}O_6$ by NMR C and H counts and MS. IR ν_{max}^{Film} cm^{-1}: 1750. ^{1}H NMR (270 MHz, $CDCl_3$): δ 6.35 (*s*, 2H-2,6), 2.90 (*dd*, *J* = 7, 0.8 Hz, H-7), 2.30 (*quintet*, *J* = 7 Hz, H-8), 1.05 (*d*, *J* = 7 Hz, 3H-9), 4.72 (*d*, *J* = 5 Hz, H-2′), 2.60 (*dd*, *J* = 5, 0.8 Hz, H-3′), 5.62 (*br s*, H-6′), 3.00 (*d*, *J* = 7 Hz, 2H-7′), 5.8–5.95 (*m*, H-8′), 5.0–5.25 (*m*, 2H-9′), 3.81 (*s*, OMe-3,5), 3.79 (*s*, OMe-4), 3.54 (*s*, OMe-5′). ^{13}C NMR (20 MHz, $CDCl_3$): δ 140.3(*s*, 2 C-1,1′), 104.7 (*d*, 2C-2,6), 153.7 (*s*, 2 C-3,5), 45.4, 46.0 (2*d*, 2C-7,8), 11.9 (*q*, C-9), 76.3 (*d*, C-2′), 58.9 (*d*, C-3′), indet. (C-4′), 85.5 (*s*, C-5′), 126.6 (*d*, C-6′), 36.4 (*t*, C-7′), 135.1 (*d*, C-8′), 117.3 (*t*, C-9′), 56.3 (*s*, 2 OMe-3,5), 60.8 (*s*, OMe-4), 52.9 (*s*, OMe-5′). ORD (4.2 mg/10 ml MeOH): $[\phi]_{400}$ 0, $[\phi]_{335}^{tr}$ −1750, $[\phi]_{310}$ 0, $[\phi]_{293}$ +1170, $[\phi]_{275}^{tr}$ +970, $[\phi]_{260}$ +1260, $[\phi]_{250}$ 0, $[\phi]_{245}^{tr}$ −1260, $[\phi]_{235}$ 0. *Acetate*, viscous oil. ^{1}H NMR (60 MHz, $CDCl_3$): δ 6.30 (*s*, 2H-2,6), 2.8–3.0 (*m*, H-7, 2H-7′), 2.2–2.5 (*m*, H-8), 1.05 (*d*, *J* = 7 Hz, 3H-9), 5.78 (*m*, 2H-2′,6′), 2.5–2.7 (*m*, H-3′), 5.6–5.9 (*m*, H-8′), 5.2–5.3 (*m*, 2H-9′) 3.82 (*s*, 3 OMe-3,4,5), 3.58 (*s*, OMe-5′), 2.10 (*s*, OAc-2′).

Oxidation product of macrophyllin-B (**4b**). A suspension of MnO_2 (3 g) in a soln of **4a** (30 mg) in $CHCl_3$ (20 ml) was stirred under N_2 (6 hr), filtered over Si gel ($CHCl_3$) and evapd. The residue (**4b**, 27 mg) was a viscous oil, $C_{22}H_{26}O_6$ by NMR C and H counts and MS. IR ν_{max}^{Film} cm^{-1}: 1750, 1680. ^{1}H NMR (270 MHz, $CDCl_3$): δ6.37 (*s*, 2H-2,6), 2.60 (*d*, *J* = 8 Hz, H-7), 2.45 (*dq*, *J* = 8, 6.5 Hz, H-8), 1.12 (*d*, *J* = 7 Hz, 3H-9), 3.05 (*s*, H-3′), 6.75 *br s*, H-6′), 3.1/3.3 (*m*, 2H-7′), 5.75–5.9 (*m*, H-8′), 5.1–5.2 (*m*, 2H-9′), 3.84 (*s*, 2 OMe-3,5), 3.81 (*s*, OMe-4), 3.58 (*s*, OMe-5′). ^{13}C NMR (20 MHz, $CDCl_3$): δ 136.7 (*s*, 2C-1,4), 104.5 (*s*, 2C-2,6), 153.9 (*s*, 2C-3,5), 45.3, 46.6 (2*d*, 2C-7,8), 15.6 (*q*, C-9), 140.1 (*s*, C-1′), 189.3 (*s*, C-2′), 66.4 (*d*, C-3′), indet. (C-4′), 94.5 (*s*, C-5′), 143.6 (*d*, C-6′), 34.1 (*t*, C-7′), 133.8 (*s*, C-8′), 118.5 (*t*, C-9′), 56.3 (*s*, 2 OMe-3,5), 60.9 (*s*, OMe-4), 51.0 (*s*, OMe-5′). ORD (1 mg/12.5 ml MeOH): $[\phi]_{400}$ −900, $[\phi]_{370}^{tr}$ −1400, $[\phi]_{360}^{pk}$ −1000, $[\phi]_{352}^{tr}$ −1200, $[\phi]_{330}$ 0, $[\phi]_{310}^{pk}$ +800, $[\phi]_{295}^{tr}$ +400, $[\phi]_{290}^{pk}$ +500, $[\phi]_{282}$ 0, $[\phi]_{260}$ −500, $[\phi]_{245}$ −1900.

Isomerization products of mirandin-A (**7**, **1b**, **9a**, **9b**). Solns of **1a** (200 mg) and TsOH (50 mg) in dry MeOH (15 ml) were either refluxed (15 hr) or kept at room temp. (48 hr). In the first case work-up involved concn, cooling to room temp.

and extraction with $CHCl_3$. The extract, filtered through Si gel (C_6H_6), gave **7** (yield 76%). In the second case work-up involved neutralization with $NaHCO_3$ and evapn. The residue was separated by TLC (Si gel, C_6H_6–EtOAc, 8:2) into **1b** (yield 32%) and a mixture. This was fractionated by repeated TLC into **9a** (yield 18%) and **9b** (yield 31%).

Compound **7**. Crystals, mp 141–143° (C_6H_6-hexane), $C_{22}H_{26}O_6$, by NMR C and H counts and MS. IR ν_{max}^{Film} cm^{-1}: 1757, 1667. ^1H NMR (270 MHz, $CDCl_3$): δ 6.70 (*s*, 2H-2,6), 2.46–2.48 (*m*, 2H-7,8), 1.09 (*d*, $J = 7$ Hz, 3H-9), 3.54 (*s*, H-3'), 7.05 (*br s*, H-6'), 3.12 (*dt*, $J = 5.1$ Hz, 2H-7'), 5.8–5.9 (*m*, H-8'), 5.15–5.21 (*m*, 2H-9'), 3.84 (*s*, 2 OMe-3,5), 3.82 (*s*, OMe-4), 3.65 (*s*, OMe-5'). ^{13}C NMR (20 MHz, $CDCl_3$): δ 137.2 (*s*, 2C-1,4), 104.6 (*d*, 2C-2,6), 153.8 (*s*, 2C-3,5), 45.4, 49.5 (2*d*, 2C-7,8), 13.9 (*q*, C-9), 140.6 (*s*, C-1'), 202.2 (*s*, C-2'), 69.9 (*d*, C-3'), 194.3 (*s*, C-4'), 89.4 (*s*, C-5'), 147.3 (*d*, C-6'), 32.8 (*t*, C-7'), 134.1 (*d*, C-8'), 118.0 (*t*, C-9'), 56.3 (*s*, 2 OMe-3,5), 60.8 (*s*, OMe-4), 54.0 (*s*, OMe-5'). ORD (1.2 mg/25 ml MeOH): $[\phi]_{400}$ −400, $[\phi]_{365}^{tr}$ −1400, $[\phi]_{355}$ 0, $[\phi]_{330}^{pk}$ +3800, $[\phi]_{307}$ 0, $[\phi]_{292}^{tr}$ −1600, $[\phi]_{283}$ 0, $[\phi]_{252}$ + 10200, $[\phi]_{235}$ 0.

Compound **1b**. This is compound **7c** in ref. [2].

Compound **9a**. Crystals, mp 173–175° (C_6H_6–hexane). IR ν_{max}^{KBr} cm^{-1}: 1665. UV λ_{max}^{EtOH} nm (log ε): 230 (4.02), 282 (3.54), 302 (3.76). MS *m/e* (rel. int.): 404 M^+ (52), 317 (20), 276 (8), 208 (100), 139 (34), 181 (8), 151 (19). *Compound* **9b**. Crystals, mp 98–100° (C_6H_6–hexane). IR ν_{max}^{KBr} cm^{-1}: 1675. UV λ_{max}^{EtOH} nm (log ε): 235 (4.02), 284 (3.84), 295 (3.78). MS *m/e* (rel. int.): 418 M^+ (22), 317 (42), 276 (12), 208 (100), 193 (42), 181 (7), 179 (5), 151 (51). ^1H NMR **9a**/**9b** (100 MHz, $CDCl_3$): δ6.62/6.54 (*s*, 2H-2,6), 4.12/4.10 (*d*, $J = 11$ Hz, H-7), 2.5–2.9 (*m*, H-8), 1.06/1.02 (*d*, $J = 7$ Hz, 3H-9), 2.75/2.64 (*d*, $J = 16$ Hz, H−3'ax), 3.22/3.28 (*d*, $J = 16$ Hz, H-3' eq), 6.50/6.44 (*br s*, H-6'), 3.17 (*d*, $J = 7$ Hz, 2H-7'), 5.7–6.1 (*m*, H-8'), 5.1–5.3 (*m*, 2H-9'), 3.82 (*s*, 2 OMe-3,5), 3,85/3.86 (*s*, OMe-4), —/3.56 (*s*, OMe-4'), 3.44/3.42 (*s*, OMe-5').

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