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Unusual naphthoquinones, catechin and triterpene from *Byrsonima microphylla*

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Abstract

The new triterpene Δ^1-lupenone (**1**), together with lupeol, β-amyrin and betulin were isolated from the wood of *Byrsonima microphylla* (Malpighiaceae). The new compounds 3-hydroxy-2-methoxy-8,8,10-trimethyl-8H-antracen-1,4,5-trione (**2**), 3,7-dihydroxy-2-methoxy-8,8,10-trimethyl-7,8-dihydro-6H-antracen-1,4,5-trione (**3**), (2S*,10aR*)-2,8-dihydroxy-6-methoxy-1,1,7-trimethyl-2,3,10,10a-tetrahydro-1H-fenantren-9-one (**4**) and (2S,3S)-3′-hydroxy-4′,5,7-trimethoxy-flavan-3-ol (**5**) were also isolated through monitored TLC using the antioxidant β-carotene reagent. The antioxidant potential of the compounds **2**–**5** was measured and none of them showed activity. The structures of these compounds were elucidated by chemical and spectroscopic analysis based on NMR techniques (^{1}H, ^{13}C NMR, COSY, nOe difference, HMQC and HMBC), UV and MS.

Keywords: *Byrsonima microphylla*; Malpighiaceae; Naphthoquinones, Δ^1-lupenone; Flavan-3-ol; Antioxidant activity

1. Introduction

The genus *Byrsonima*, which is composed of approximately 150 species, belongs to the Malpighiaceae family and is found primarily from Mexico throughout South America. This family is constituted by approximately 800 species distributed in 60 genera and about 50% of these species are concentrated in Brazil (Joly, 1998). It possesses genus well studied, *Banisteriopsis* for example, which is used in indigenous rituals due to their narcotic and hallucinogenic effects (Hashimoto and Kawanishi, 1976). Several species of the genus *Byrsonima* grow in the Brazilian northeast and are known mainly by the use of their fruits in native feeding and for medicinal purposes, as anti-asthmatics, against the fever and in infections of the skin. Among the 150 species that encompass the genus, there are limited chemical studies. It was previously isolated from them, proantocyanidins, glycolipids, triterpenes and derivatives, gallic acid, flavonoids, pyrogallol and pyrocatechol (Mendes et al., 1999). *B. microphylla* A. Juss. is a small tree that occurs in the northeastern region of Brazil, specially in the "restinga" (sand banks) of the State of Bahia. This paper describes studies regarding the isolation from the chloroform extract from the wood of *B. microphylla* two new naphthoquinones (**2**,**3**), a possible derivative (**4**) and new triterpene (**1**) and flavanol (**5**).

2. Results and discussion

Compound **1** showed a blue spot with Lieberman–Bouchard's compatible with the triterpene structure. The HREIMS of **1** exhibited a molecular ion peak at *m*/*z* 422.3559 indicating a molecular formula of $C_{30}H_{46}O$ (requires 422.3549). The ^{1}H NMR data (Section 3) showed characteristic signals of seven methyl

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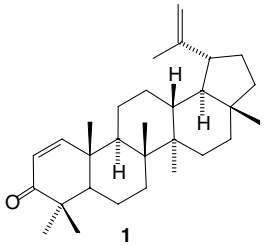
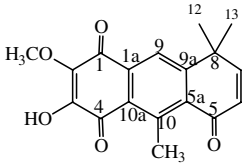
groups, one isopropenyl (δ 4.5, 4.7 and 1.59), two doublets ($J = 10$ Hz) at δ 5.7 and δ 7.1, implying an α,β-unsaturated ketone. The ^{13}C NMR spectra (PND and DEPT 135°) displayed 30 peaks and confirmed the above data through the resonances displayed at δ 19.32, 109.49, 150.77, as well as at δ 205.63, 159.94 and 125.13 for the isopropenyl and α,β-unsaturated carbonyl groups, respectively. The absence of the methyne signal for a hydroxyl group at C-3 left no doubt about the location of the carbonyl group. Therefore, to complete the α,β-carbonyl system, the double bond could only be located at the C1 and C2 positions.



1



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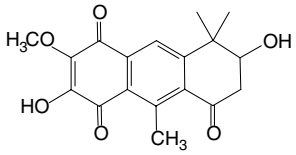

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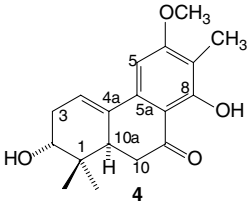

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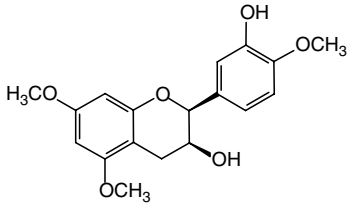

5

The TLC of compounds **2** and **3** turned into pale brown spot after being sprayed with a β-carotene/$CHCl_3$ solution (0.02% m/v). Their ^{1}H and ^{13}C NMR spectra demonstrated their quinone nature. The HREIMS exhibited a molecular ion peak at m/z 312.0990 for **2**, indicating molecular formula of $C_{18}H_{16}O_5$ (requires 312.0998) and, for **3** an ion peak at m/z 330.11031 indicated a molecular formula $C_{18}H_{18}O_6$ (requires 330.11034).

The ^{1}H NMR spectrum of **2** exhibited characteristic singlets for a methoxyl, three methyl groups and three hydrogens at Csp^2 (δ 7.1, 6.3, 6.7), as well as one chelated hydroxyl group at δ 12.4. The ^{13}C NMR spectrum displayed 18 peaks and confirmed the presence of three sp^2 methine carbons, one methoxyl and three methyl groups, through the resonances displayed at δ 118.52, 127.11, 154.74, 60.46, 7.74, 30.00 and 30.00, respectively. Analysis of the DEPT spectra also indicated the presence of 11 non-hydrogenated carbons. Among them, the most relevant resonances in this spectra were the signals attributed to three carbonyl groups (δ 183.4, 183.61 and 190.33) which were compatible with the naphthoquinone framework, in which one carbonyl is chelated with hydroxyl group (Budzianowski, 1997; Khan and Mlungwana, 1999). The UV–VIS spectrum exhibited absorptions similar to the general pattern observed for naphthoquinones (Al-Hazimi and Haque, 2002). The unambiguous assignments of the carbon chemical shifts were made from an HMQC experiment, and nOe difference and HMBC spectra data permitted to disclosure of the spatial relationships among the functional groups of **2**. Thus, it was observed that through nOe irradiation of H-9 led to 20% enhancement of CH_3-12 and CH_3-13, and irradiation of CH_3-12 led to a 7% enhancement of H-9 and H-7. The irradiation of H-7 led to 6% and 4% enhancement of CH_3-12 and H-6, respectively (Fig. 1). The HMBC spectrum, besides confirming the spatial distribution of the groups mentioned above, also showed other significant correlations. For instance, the correlations between δ 1.9 (CH_3-13), δ 6.3 (H-6) and δ 7.1 (H-9) with δ 140.67 (C-5a) permitted the location of the remaining methyl group at C-10. The hydrogens of this methyl showed correlations with C-10a/C-5a confirming the out-of-plane shielding effect of the aromatic ring (Fig. 1). The localization of the methoxyl group was determined by analysis of the effect observed of the 3-acetyl derivative on C-1a ($\Delta\delta = -8.8$ ppm). This deshielding is indicative that the hydroxyl group is at C-3 (Ulubelen et al., 1997).

The NMR spectral data of compound **3** were comparable with those observed for **2**. The main differences between compounds **3** and **2** concerned the ^{1}H and ^{13}C NMR data observed for carbons and hydrogens at positions 5, 6 and 7. Accordingly, the signals for H-6 were recorded at δ 2.8 (*dd*, $J = 17$ and 5 Hz) and 3.1 (*dd*, $J = 17$ and 5 Hz) and, for H-7 at δ 4.1 (*t*, $J = 5$ Hz) in the ^{1}H NMR spectrum. On the other hand, the ^{13}C NMR spectra displayed these signals at δ 44.73 and 74.05, respectively, in which the deshielding effect observed at C-8 ($\Delta\delta + 1.5$ ppm) confirms the location of the hydroxyl group at C-7.

Compound **4** also appeared as a pale brown spot in the TLC sprayed with β-carotene solution, and the ^{1}H and ^{13}C NMR spectra exhibited signals for three methyl

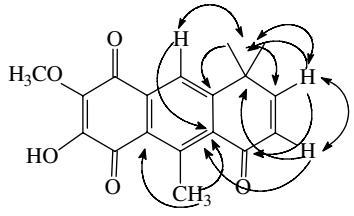

Fig. 1. nOe enhancements (two head arrows) and key HMBC correlations (one head arrows) observed for isolate **2**.

groups, one methoxyl and one chelated hydroxyl group at δ 12.6, among others. The ^{13}C NMR spectrum displayed signals for 18 carbons and, partially by a DEPT 135° experiment was possible to deduce the presence of one carbonyl, one methoxyl, one oxy methine, one methine, three methyl, two methylene, two sp^2-methine and seven quaternary carbons. The structural data of **4** differed from **2** and **3** by the presence of just one carbonyl group. The HREIMS of **4** corroborated the above groups indicating a molecular formula of $C_{18}H_{22}O_4$ ($[M]^+$ *m/z* 302.1508; requires 302.1518). The HMQC and HMBC experiments allowed accurate attribution of chemical shifts, and a determination of the spatial relationships of the above groups. Correlations were observed in the HMBC spectrum between H-4, H-5 and H-10 with C-4a (δ 133.39) and between H-5 and H-10 (δ 2.6 and δ 2.7) with C-8a at δ 109.69. However, the methoxyl and hydroxyl groups were located in the C-ring through the correlations observed between the resonances at δ 3.9 and δ 12.6 with the resonances at δ 163.49 (C-6) and δ 109.69 (C-8a), respectively. On other hand, the C-13 shift of the methyl (δ 7.38) is indicative that this group is placed in di-ortho oxygenated functions (Diaz et al., 1987). Fig. 2 indicates other correlations observed for compound **4** in the HMBC spectrum. This fundamental evidence permitted a proposal for a like-phenanthrene-like skeleton for **4**. The EIMS corroborated the substitution pattern proposed for the A-ring through a base peak at *m/z* 230 relative to Retro Diels–Alder fragment.

Compound **5** exhibited the molecular formula $C_{18}H_{20}O_6$, as established by HREIMS ($[M]^+$ *m/z* 332.1269; requires 332.1260) and its ^{13}C and ^{1}H NMR spectra. The ^{1}H NMR spectrum of **5** indicated its catechin skeleton through resonances displayed for A ring at δ 6.1 (*d*, $J = 2.0$ Hz, H-6) and δ 6.2 (*d*, $J = 2.0$ Hz, H-8) and for ring B at δ 6.9–7.0 (*m*, H-2′, H-6′ and H-5′). Ring C was identified through the resonances at δ 4.9, 4.2 and 2.9 displayed for the oxy benzyl, oxy methine and methylene hydrogens. The ^{13}C NMR spectra defined the catechin skeleton through the carbon signals observed for one oxy methine (δ 66.51), one oxy benzyl (δ 78.51) and one methylene (δ 28.12) carbon relative to ring C. In addition, these spectra (PND and DEPT 135°) displayed resonance signals of three methoxyl groups, six quaternary and five methine sp^2 carbons. The base peak at *m/z* 167 observed in the EIMS, regarded as a Retro Diels–Alder fragment allowed the establishment of two methoxyl groups on ring A. The unique substitution pattern of the ring B and the free hydroxyl group at C-3 in **5** were confirmed by the NMR spectral data of its diacetyl derivative **5a**. Therefore the ^{13}C NMR spectra of the **5a** showed distinguished chemical shifts for C-2′ (δ 118.73), C-41 (δ 152.00) and C-61 (δ 122.52), as well as C-2 (δ 77.41) and C-4 (δ 25.72). These latter changes of chemical shift in accordance with literature (Mukherjee et al., 1994; Geiss et al., 1995) data permitted to recognize the relative stereochemistry of the hydroxyl and benzyl group at C-3 and C-2, as axial, establishing the *cis* relationship between them. The absolute stereochemistry 2*S*, 3*S* was obtained after comparing the positive $[\alpha]_D$ with those negative values found in literature (Mukherjee et al., 1994).

The known triterpenes (β-amyrin, betulin and lupeol) were identified by TLC comparison with authentic samples and published data (Mahato and Kundu, 1994). Besides the simple structures of compounds **2** and **3**, the additional ring of naphthoquinone moiety is unexpectable. So, the molecular formula of **4** indicates that it is probably a biosynthetic derivative of the previous compounds. This is the first occurrence of naphthoquinones in Malpighiaceae. The antioxidant activities of the compounds **2**–**5** were estimated by employing the assay of inhibition of autooxidation of β-carotene in linolenic acid suspension (Barreiros et al., 2000) and by DPPH radical scavenging (Malterud et al., 1993). Despite the TLC/β-carotene spots indicating inhibition of oxidation, none of the isolates showed significant activity when compared with the results obtained from the commercial antioxidants, propyl gallate and α-tocopherol.

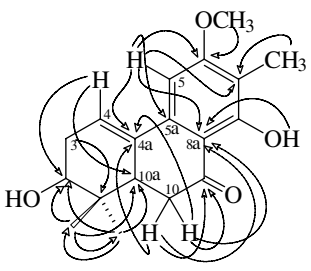

Fig. 2. HMBC correlations observed for **4**.

3. Experimental section

3.1. General experimental procedures

The ^{1}H and ^{13}CNMR, DEPT, COSY, HETEROCOSY ($J = 140$ and 9 Hz) and, spectra were obtained on a Varian Gemini 300 and gHMQC and gHMBC on a Brucker 500 MHz instrument employing $CDCl_3$ as solvent and reference. The MS were recorded on a Micromass Autospec spectrometer (HRMS) and a HP model 5973 spectometer (EIMS). Melting points were measured in a Microquímica MIAPF 301 apparatus and are uncorrected. Column chromatography was carried out on silica gel 60 and, TLC on Si gel monitored the fractions and the spots were revealed with β-carotene solution (Merck) and UV light (254/366 nm).

3.2. Plant material

The stems of *B. microphylla* were collected in September, 2001 in the Reserve of "Parque Metropolitano do Abaeté" (Salvador-BA, Brazil). Prof. Maria Lenise S. Guedes identified the plant material and a voucher specimen was deposited at the Herbarium Alexandre Leal Costa of the Universidade Federal da Bahia under the number 027883.

3.3. Extraction and isolation

The powdered and dried stem material (4.4 kg) was extracted with MeOH and the methanolic extract was successively partitioned between hexane/MeOH:H_2O (9:1), $CHCl_3$/MeOH:H_2O (6:4) and EtOAc/H_2O. After solvent evaporation, the $CHCl_3$ extract (4.1 g) was subjected to column chromatography over silica gel eluted with hexane and mixtures of hexane/EtOAc 9:1, 7:3, 6:4 and 1:1 as well as EtOAc. The fractions obtained were further combined on the basis of TLC revealed with Lieberman–Burchard and β-carotene solution. From the fraction eluted with hexane/EtOAc 9:1 and revealed with Lieberman–Burchard reagent the Δ^1-lupenone (**1**, 12.8 mg), β-amyrin (10.8 mg) and lupeol (15.0 mg) were isolated. The compound **2** (11.0 mg) and betulin (17.0 mg) were obtained from the fraction of initial CC eluted with hexane/EtOAc (7:3) followed by another CC over silica gel eluted with $CHCl_3$/EtOAc (9:1). The fraction from the main CC eluted with hexane/EtOAc (6:4) was fractionated on CC over silica gel and eluted with hexane/EtOAc (4:6) followed by preparative TLC using CH_2Cl_2/EtOAc (9:1) as eluant to afford compound **3** (19.5 mg). Compound **4** (9.4 mg) was obtained from the fraction of main CC eluted with hexane/EtOAc (1:1) followed by preparative TLC over silica gel using $CHCl_3$/EtOAc (9:1) as mobile phase. The fraction from the initial CC eluted with hexane/EtOAc (4:6) afforded compound **5** (25 mg) following purification with preparative TLC over silica gel plates eluted with hexane/acetone/acetic acid (8:2:0.3).

3.3.1. Δ^1-Lupenone (*1*)

Pale yellow oil; $[\alpha]_D^{25}$ −9.6° (*c* 2.5×10^{-4} CH_3OH)UV (CH_3OH)λ_{max} 227 nm; EIMS: 70 eV (rel. int.) *m/z*: 422 [M^+] (26); 229 (100), 191 (42), 150 (73), 137 (63), 121 (47); HREIMS: 70 eV *m/z* 422.3559 (calc. for $C_{30}H_{46}O$, requires 422.3549); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.13 (Me-23), 1.07 (*s*, 3H, Me-24), 1.08 (*s*, 3H, Me-25), 1.10 (*s*, 3H, Me-26), 0.96 (*s*, 3H, Me-27), 0.65 (*s*, 3H, Me-28), 1.59 (*s*, 3H, Me-30), 4.5 (*d*, $J = 1.1$ Hz, 1H, H-29a), 4.7 (*d*, $J = 1.1$ Hz, 1H, H-29 b), 5.7 (*d*, $J = 10$ Hz, 1H, H-2), 7.1 (*d*, $J = 10$ Hz, 1H, H-1); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.94 (C-1), 125.13 (C-2), 205.63 (C-3), 44.65 (C-4), 53.42 (C-5), 19.01 (C-6), 33.75 (C-7), 41.75 (C-8), 44.42 (C-9), 39.55 (C-10), 21.24 (C-11), 25.09 (C-12), 38.22 (C-13), 43.01 (C-14), 27.36 (C-15), 35.48 (C-16), 43.10 (C-17), 48.14 (C-18), 47.29 (C-19), 150.77 (C-20), 29.78 (C-21), 39.96 (C-22), 27.79 (C-23), 21.41 (C-24), 19.20 (C-25), 16.45 (C-26), 14.42 (C-27), 18.03 (C-28), 109.49 (C-29), 19.32 (C-30).

3.3.2. 3-Hydroxy-2-methoxy-8,8,10-trimethyl-8H-antracen-1,4,5-trione (*2*)

Yellow crystals, m.p. 140–141 °C; UV (CH_3OH) λ_{max} 212, 275, 401 nm; EIMS: 70 eV (rel. int.) *m/z*: 312 [M^+] (11); 279 (10), 259 (19), 185 (34), 165 (23), 149 (74), 129 (22), 105 (41), 71 (60), 57 (100); HREIMS: 70 eV *m/z* 312.0990 (calc. for $C_{18}H_{16}0_5$, requires 312.0998); ^{1}H NMR (300 MHz, $CDCI_3$) δ 6.33 (*d*, $J = 10.0$ Hz, 1H, H-6), 6.7 (*d*, $J = 10.0$ Hz, 1H, H-7), 7.1 (*s*, 1H, H-9), 1.4 (*s*, 6H, Me-11, Me-12), 1.9 (*s*, 3H, Me-13), 4.2 (*s*, 3H, OMe-2), 12.4 (*s*, 1H, OH-3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.61 (C-1), 116.02 (C- 1a), 161.88 (C-2), 162.45 (C-3), 190.33 (C-4), 183.24 (C-5), 124.62 (C-5a), 127.11 (C-6), 154.74 (C-7), 38.38 (C-8), 118.52 (C-9), 157.46 (C-9a), 138.27 (C-10), 123.66 (C-10a), 7.70 (C-11), 30.00 (C-12), 30.00 (C-13), 60.46 (OCH_3).

3.3.3. 3,7-Dihydroxy-2-methoxy-8,8,10-trimethyl-7,8-dihydro-6H-antracen-1,4,5-trione (*3*)

Pale crystals, m.p. 146–147 °C; $[\alpha]_D^{25}$ −10.8° (*c* 2.5×10^{-4} CH_3OH); UV (CH_3OH) λ_{max} 206, 270, 398 nm; EIMS: 70 eV (rel.int.) *m/z* 330: [M^+] (17); 302 (100), 286 (41), 271 (37), 259 (37), 243 (17), 185 (12), 115 (23); HREIMS 70 eV. *m/z* 330.11030 (calc. for $C_{18}H_{18}O_6$, requires 330.11034); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10 (*s*, 1H, H-9), 4.1 (*t*, $J = 5.0$ Hz, 1H, H-7), 2.8 (*dd*, $J = 17.0$, 5.0 Hz, 1H, H-6a), 3.1 (*dd*, $J = 17.0$, 5.0 Hz, 1H, H-6b), 1.33 (*s*, 3H, Me-12), 1.37 (*s*, 3H, Me-11), 1.9 (s, 3H, Me-13), 4.16 (s, 3H, OMe-2), 12.51 (*s*, 1H, OH-3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 182.68 (C-1), 115.14 (C-1a), 161.54 (C-2), 162.87 (C-3), 190.36 (C-4), 195.53 (C-5), 126.75 (C-5a), 44.74 (C-6), 74.05 (C-7), 40.93 (C-8), 118.92 (C-9), 157.07 (C-9a), 136.74 (C-10), 125.04 (C-10a), 7.90 (C-11), 23.77 (C-12), 26.69 (C-13), 60.48 (OCH_3).

3.3.4. (2S*,10aR*)-2,8-Dihydroxy-6-methoxy-1,1,7-trimethyl-2, 3,10,10a-tetrahydro-1H-fenantren-9-one (*4*)

Amophours power, m.p. 156–158 °C; $[\alpha]_D^{25}$ −22.4° (*c* 2.5×10^{-4} CH_3OH); UV (CH_3OH) λ_{max} 242, 290, 333 nm; EIMS: 70 eV (rel. int.) *m/z*: 302 [M^+] (79), 215 (21), 230 (100), 199 (16), 105 (20), 83 (26); HREIMS: 70 eV *m/z* 302.1508 (calc. for $C_{18}H_{22}O_4$, requires 302.1518); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.6 (*dd*, $J = 9.0$, 5.0 Hz, 1H, H-2), 2.3–2.5 (*m*, 2H, H-3), 6.4 (*t*, $J = 2.3$ Hz, 1H, H-4), 6.6 (*s*, 1H, H-5), 2.6–2.7 (*m*, 2H, H-10), 2.6 (*m*, 1H, H-10a), 1.30 (*s*, 3H, Me-11), 0.9 (*s*, 3H, Me-12), 2.1 (*s*, 3H, Me-13), 3.90 (*s*, 3H, OMe-6), 12.6 (*s*, 1H, OH-8); ^{13}C NMR (75 MHz, *CDCl*$_3$) δ

35.89 (C-1), 73.90 (C-2), 31.82 (C-3), 121.47 (C-4), 133.39 (C-4a), 97.35 (C-5), 140.67 (C-5a), 163.49 (C-6), 112.70 (C-7), 161.62 (C-8), 109.69 (C-8a), 203.16 (C-9), 38.69 (C-10), 45.07 (C-10a), 24.50 (C-11), 15.10 (C-12), 7.38 (C-13), 55.59 (OCH_3).

3.3.5. (2S,3S)-3′-Hydroxy-5,7,4′-trimethoxy-flavan-3-ol (5)

White crystals, m.p. 106–107 °C; $[\alpha]_D^{25}$ + 11.0 (*c* 3.5×10^{-3} $CHCl_3$); UV (CH_3OH) λ_{max} 225, 290 nm; EIMS: 70 eV (rel.int.) *m/z*: 332 [M^+] (19); 167 (100), 137 (17); HREIMS: 70 eV *m/z* 332.1269 (calc. for $C_{18}H_{20}O_6$, requires 332.1260); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.9 (s, 1H, H-2), 4.2 (*sl*, 1H, H-3), 2.9 (*m*, 2H, H-4), 6.1 (*d*, $J = 2.0$ Hz, 1H, H-6), 6.2 (*d*, $J = 2.0$ Hz, 1H, H-8), 6.90 (*sl*, 2H, H2′, H-6′), 7.0 (*sl*, 1H, H-5′), 3.70 (*s*, 3H, OMe), 3.80 (*s*, 3H, OMe), 3.90 (*s*, 3H, OMe); ^{13}C NMR (75 MHz, $CDCl_3$) δ 78.51 (C-2), 66.51 (C-3), 28.12 (C-4), 159.28 (C-5), 93.40 (C-6), 158.68 (C-7), 92.21 (C-8), 155.25 (C-9), 100.31 (C-10), 130.23 (C-1′), 114.46 (C-2′), 145.51 (C-3′), 146.69 (C-4′), 109.13 (C-5′), 119.37 (C-6′), 55.38 (5-OCH_3), 55.46 (7-OCH_3), 56.03 (4′-OCH_3).

3.3.6. Acetylation of compound 3 and (2S,3S)-3′-hydroxy-5,7,4′-trimethoxy-flavan-3-ol (5)

The compounds **3** (5.0 mg) and **5** (8.0 mg) were separately added to a solution of pyridine (0.5 ml) and acetic anhydride (0.5 ml) and the mixtures were allowed to stand at room temperature for 36 h. Cold H_2O was added and the acetyl derivatives (**3a**, 5.2 mg; **5a**, 7.8 mg) were extracted with $CHCl_3$.

Compound **3a**. ^{13}C NMR (75 MHz, $CDCl_3$) 183.2 (C-1); 123.9 (C-1a); 160.3 (C-2); 169.2 (C-3); 183.4 (C-4); 183.6 (C-5); 126.9 (C-5a); 38.5 (C-6); 77.0 (C-7); 38.4 (C-8); 124.9 (C-9); 155.8 (C-9a); 139.5 (C-10); 125.9 (C-10a); 8.5 (CH_3-10); 21.1 (CH_3-8a); 22.6 (CH_3-8b); 60.0 (OCH_3-2).

(*2S,3S*)-*3,3′-diacetoxy-5,7,4′-trimethoxy-flavan-3-ol* (**5a**). ^{13}C NMR (75 MHz, $CDCl_3$ δ 78.41 (C-2), 67.76 (C-3), 25.72 (C-4), 159.67 (C-5), 93.29 (C-6), 159.67 (C-7), 92.05 (C-8), 155.25 (C-9), 100.04 (C-10), 136.63 (C-1′), 118.73 (C-2′), 145.94 (C-3′), 152.00 (C-4′), 110.81 (C-5′), 122.52 (C-6′), 55.35 (5-OCH_3), 55.40 (7-OCH_3), 55.94 (4′-OCH_3), 20.5 (CH_3COO), 20.86 (CH_3COO), 170.2 (CH_3COO), 170.9 (CH_3COO).

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