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A POLYPHENOL AND TWO BIBENZYLS FROM *PLEIONE BULBOCODIOIDES*

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Key Word Index—*Pleione bulbocodioides*; Orchidaceae; tubers; bibenzyl; 10,11-dihydrodibenzo[a,d]cycloheptene; *p*-hydroxybenzyl.

Abstract—From tubers of *Pleione bulbocodioides*, one new polyphenol, pleionol, and two new bibenzyls, bulbocodin and bulbocol were isolated together with three known compounds, 3,3′-dihydroxy-4-(*p*-hydroxybenzyl)-5-methoxybibenzyl, 3,3′-dihydroxy-2-(*p*-hydroxybenzyl)-5-methoxybibenzyl, 3′,5-dihydroxy-2-(*p*-hydroxybenzyl)-3-methoxybibenzyl. The new structures were elucidated as 2,8-dihydroxy-5-(4′-hydroxy-3′-methoxyphenyl)-4-methoxy-10,11-dihydrodibenzo[a,d]cycloheptene, 2′,3-dihydroxy-5-methoxy-2,5′,6-tri(*p*-hydroxybenzyl)bibenzyl and 3,3′-dimethoxy-5-hydroxy-2-(*p*-hydroxybenzyl)bibenzyl from their spectroscopic data.

INTRODUCTION

In the course of our investigations on *Pleione bulbocodioides* (Chinese name "Shan ci-gu"), we have reported the isolation and characterization of several structural types, dihydrophenanthropyrans [1], dihydrophenanthrenes, bibenzyls [2, 3] and ligands [4]. In the present paper, we now report the structural elucidation of one new polyphenol, pleionol (**1**) and two new bibenzyls, bulbocodin (**2**) and bulbocol (**3**), together with three known bibenzyls (**4**)–(**6**) [5].

RESULTS AND DISCUSSION

Pleionol (**1**) exhibited UV maxima at 207 sh, 240 sh and 281 nm. The IR spectrum showed absorptions at 3350 (OH), 1600, 1510 and 1450 cm^{-1} (benzenoids). The mass spectrum exhibited an $[M]^+$ at *m/z* 378 ($C_{23}H_{22}O_5$) and a base peak at *m/z* 255 from loss of a hydroxymethoxyphenyl moiety. The ^{13}C NMR spectrum displayed signals for all 23 carbons in the molecule: one methine, two methylenes and two methoxyls, along with 18 aromatic carbons, of which eight were protonated, five quaternary and five bearing oxygen. Acetylation of **1** afforded a triacetate ($[M]^+$ *m/z* 504), suggesting the presence of three hydroxyl groups. The ^1H NMR spectrum of **1** showed the signals of two methoxyls and eight aromatic protons including two sets of an ABX-system and a pair of doublets, corresponding to three aromatic rings (A–C), from their coupling patterns and integration. The signals forming one ABX-system appeared at δ 7.04 (*d*, J = 7.9 Hz), 6.58 (*dd*, J = 7.9, 2.8 Hz) and 6.56 (*d*, J = 2.8 Hz) due to H-6, H-7, H-9 on the B ring. Those for the second ABX-system were at δ 6.38 (*m*), 6.57 (*d*, J = 8.6 Hz) and 6.22 (*dd*, J = 8.6, 1.9 Hz) due to H-2′, H-5′ and H-6′ on the C ring, together with a pair of doublets at δ 6.20 (*d*, J = 2.6 Hz) and 6.36 (*d*, J = 2.6 Hz) due to H-1 and H-3 on the A ring. The location of the three hydroxyl groups was determined by acetylation shifts. In the ^1H NMR spectrum of the triacetate, the signals due to H-1, H-3, H-5′, H-7 and H-9 were all shifted down-field by ca 0.35 ppm, compared with those for corresponding protons of **1** (see Experimental). Hence, the hydroxyls were located at C-2, C-4′ and C-8, respectively. Additionally, the location of the methoxyl groups was confirmed by NOE enhancement experiments. Irradiation of the methoxyl group at δ 3.80 gave NOE enhancement of H-3 (16%) and irradiation of the other at δ 3.59, gave NOE enhancement of H-2′ (11%), revealing that the methoxyl groups were at C-4 and C-3′.

In addition, the ^1H NMR and ^1H-^1H COSY spectrum showed the signals of one methine at δ 5.74 (*brs*, H-5) in the down-field and a pair of benzylic methylenes coupled with each other at δ 2.46–2.61 (*m*, H-10) and 2.96–3.01 (*m*, H-11), when irradiation of the former led to enhancement of H-9 (3%) and irradiation of the latter led to enhancement of H-1 (8%), respectively. These results indicated that one of

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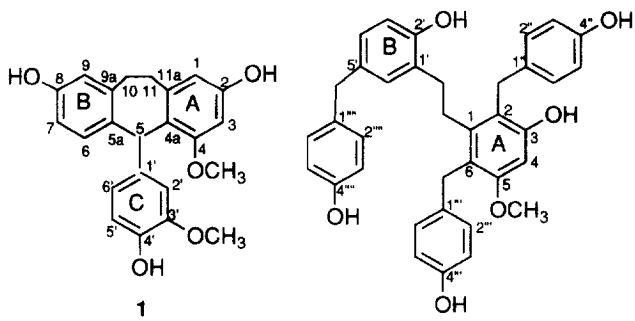

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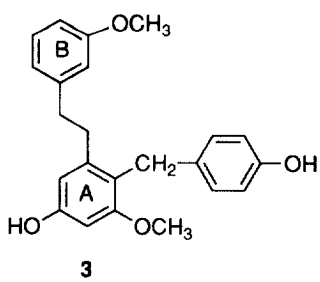

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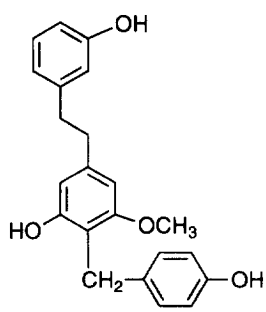

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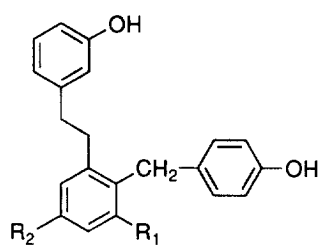

5 R_1=OH R_2=OCH_3

6 R_1=OCH_3 R_2=OH

the methylenes might be adjacent to C-9a, the other to C-11a. Furthermore, in the HMBC spectrum, clear long-range correlations between H-5 and C-1′, C-4a, C-5a; and weak correlations with C-4, C-6, C-9a, C-11a were observed and, in the NOE experiment, enhancements of the signals for H-2′ (2%), 6 (16%), 6′ (2%) and 4-methoxyl (1%) were observed on irradiation of H-5. From these findings, the two methylenes and one methine were considered to make up of a cycloheptane ring involving C-4a, C-11a of A-ring and C-5a, C-9a of B ring, to which 4′-hydroxy-3′-methoxyphenyl (C ring) was attached at C-5.

Therefore, pleionol **1** was decided to be 2,8-dihydroxy-5-(4′-hydroxy-3′-methoxyphenyl)4-methoxy-10,11-dihydrodibenzo-[a,d]cycloheptene. Pleionol, cassigarol [6] and balanocarpol [7] possess a common structural skeleton, 10,11-dihydro-5H-dibenzo[a,d] cycloheptene. However, from a biosynthetic point, pleionol might be derived from 3″-*O*-methyl **6** by intramolecular cyclization, not the condensation of several stilbene units by phenol oxidative coupling [7].

Bulbocodin **2** showed the UV absorption maxima characteristic of the bibenzyl series at 207, 230 sh and 281 nm [2]. The IR spectrum had absorptions at 3250 (OH), 1590, 1510 and 1440 cm^{-1} (benzenoids). The mass spectrum exhibited an $[M]^+$ at *m/z* 562 ($C_{36}H_{34}O_6$) and three significant peaks at *m/z* 456, 349 and 241 formed by sequential losses of three hydroxybenzyl groups. Acetylation of **2** afforded a pentaacetate ($[M]^+$ *m/z* 772) indicating the presence of five hydroxyl groups. The ^1H NMR spectrum showed five doublets at δ 6.60 (2H), 6.64 (4H), 6.76 (2H), 6.78 (2H) and 6.86 (2H), due to three pairs of A_2B_2 system characteristic of *p*-substituted aromatic ring, and three singlets at 3.58, 3.81, 3.86 due to three benzylic methylenes, supporting the presence of three *p*-hydroxybenzyl groups. In addition, the ^1H NMR spectrum exhibited the signals of one methoxyl group at δ 3.73 and four aromatic protons on two benzene rings of bibenzyl. Among them, one appeared as a singlet at δ 6.45 due to H-4 on A ring, the remaining three appeared as an ABX-system at δ 6.57 (*d*, J = 8.2 Hz), 6.53 (*dd*, J = 8.2, 3.3 Hz) and 6.58 (*d*, J = 3.3 Hz) due to H-3′, H-4′ and H-6′ on the B ring. Furthermore, in the ^1H NMR spectrum, four aliphatic protons due to bibenzyl methylenes appeared as a pair of splitting multiplets at δ 2.45 (2H) and 2.68 (2H), different from their usual splitting pattern, which could be explained by the influence of large substituents at C-2 and C-6, confirming that the two *p*-hydroxybenzyls were located at C-2 and C-6 [2, 5, 8]. This conclusion was also supported by the ^{13}C NMR spectrum, in which the symmetrical substituted *p*-hydroxybenzyls on C-2 and C-6 were observed as similar chemical shifts at δ

134.1, 130.0, 116.0, 156.1 and 134.3, 130.7, 116.1, 156.3 due to C-1″, C-2″, 6″, C-3″, 5″, C-4″ and C-1‴, C-2‴, 6‴, C-3‴, 5‴ and C-4‴, respectively, along with δ 31.2 and 31.8 due to two benzylic methylenes. The signal assignments and the locations of the remaining *p*-hydroxybenzyl, methoxyl and hydroxyl groups were determined by NOE enhancements and acetylation shifts. Irradiation of the benzylic methylene at δ 3.86, caused NOE with H-2‴, 6‴ at δ 6.86 (11%), the methoxyl (1%) and one methylene at δ 2.68 (5%), and irradiation of H-4 caused NOE with the methoxyl (8%) only, indicating that the methoxyl at C-5 and one hydroxyl at C-3 are on the same A ring. In turn, selective irradiation of one methylene at δ 2.45 enhanced the NOEs with the other methylene at δ 2.68 (6%) and H-6′ (7%). Irradiation of H-4′, enhanced the NOE with H-2⁗, 6⁗ at δ 6.76 (7%), indicating the remaining *p*-hydroxybenzyl at C-5′ and the hydroxyl at C-2′ on B ring, in good agreement with the downfield shift of H-3′ in the ^{1}H NMR spectrum of the acetate (see Experimental). Therefore, bulbocodin **2** was assigned to be 2′,3-dihydroxy-5-methoxy-2,5′,6-tri(*p*-hydroxybenzyl)bibenzyl.

Bulbocol **3** showed UV and IR spectra very similar to those of **2**, suggesting that it was also a bibenzyl. Acetylation of **3** afforded a diacetate ($[M]^+$ *m/z* 448) indicating the presence of two hydroxyl groups. The mass spectrum exhibited the $[M^+]$ at *m/z* 364 and one intense peak at *m/z* 257, due to the loss of one hydroxybenzyl group as in **2**, together with *m/z* 137 and 121, which corresponded with $C_8H_9O_2$ (hydroxymethoxytropylium) and C_8H_9O (methoxytropylium), resulting from the cleavage of the benzylic linkage. The ^{1}H NMR spectrum showed the signals due to one *p*-hydroxybenzyl group, two methoxyl groups and signals due to a pair of methylenes and six aromatic protons of a bibenzyl moiety. Two of them appeared as one pair of doublets at δ 6.34 and 6.27 due to H-4 and H-6 on a 1,2,3,5-tetrasubstituted A ring; the remaining four appeared at δ 6.55, 6.69, 7.11 and 6.64 assignable to H-2′, 4′, 5′ and 6′ on a 1′,3′-disubstituted B ring from their chemical shifts and splitting patterns. Considering the mass fragmentation, one methoxyl, one hydroxyl and one *p*-hydroxybenzyl groups might be attached to the A ring, and another methoxyl should be attached at the C-3′ position on B-ring, which was also supported by comparison with the spectral data of known 3′-substituted bibenzyls [2, 3, 5]. This assumption was further proved by NOE enhancements. Irradiation of the methylene at δ 2.73 enhanced H-6 (10%) and the benzylic methylene at δ 3.83 (6%), confirming the *p*-hydroxy-benzyl group at C-2. In turn, irradiation of the methoxyl group at δ 3.74, enhanced only H-4 (15%), indicating the methoxyl group at C-3 and, hence, the hydroxyl at C-5. From the above spectral evidence, bulbocol **3** was concluded to be 3,3′-dimethoxy-5-hydroxy-2-(*p*-hydroxybenzyl)bibenzyl.

The known bibenzyls, 3,3′-dihydroxy-4-(*p*-hydroxybenzyl)-5-methoxybibenzyl **4**, 3,3′-dihydroxy-2-(*p*-hydroxybenzyl)-5-methoxybibenzyl **5** and 3′,5-dihydroxy-2-(*p*-hydroxybenzyl)-3-methoxybibenzyl **6** were identified by direct comparison with the corresponding authentic compounds.

EXPERIMENTAL

Mps: uncorr. IR: KBr. UV: MeOH. ^{1}H and ^{13}C NMR: 500 and 125 MHz, respectively, MeOH-d_3 with TMS. MS: EI at 70 eV. CC was performed on Merck silica gel, LH-20, Cosmosil C_{18} and HP-20, TLC on Merck silica gel.

Plant materials

As described in Ref. [1].

Extraction and isolation

As described in Ref. [1]. Fr. 4 was rechromatographed over silica gel, LH-20 and Cosmosil C_{18} to give **1** (4 mg) and **3** (7 mg). Fr. 5 was rechromatographed over HP-20, silica gel and LH-20 to give **2** (10 mg).

Compound **1**. Oil. $[\alpha]_D$ −5.6 (MeOH; c 0.1). IR ν_{max} cm^{-1}: 3350, 1600, 1510, 1450. UV λ_{max} nm (log ε): 207 sh (4.70), 240 sh (4.04), 281 (3.76). MS *m/z* (rel. int.): 378 $[M]^+$ (65), 347 (4), 255 (100). ^{1}H NMR: δ 2.46–2.61 (2H, *m*, H-10), 2.96–3.01 (2H, *m*, H-11), 3.59 (3H, *s*, 3′-OMe), 3.80 (3H, *s*, 4-OMe), 5.74 (1H, *brs*, H-5), 6.20 (1H, *d*, *J* = 2.6 Hz, H-1), 6.22 (1H, *dd*, *J* = 8.6, 1.9 Hz, H-6′), 6.36 (1H, *d*, *J* = 2.6 Hz, H-3), 6.38 (1H, *m*, H-2′), 6.56 (1H, *d*, *J* = 2.8 Hz, H-9), 6.57 (1H, *d*, *J* = 8.6 Hz, H-5′), 6.58 (1H, *dd*, *J* = 7.9, 2.8 Hz, H-7), 7.04 (1H, *d*, *J* = 7.9 Hz, H-6). ^{13}C NMR: δ 33.6 (*t*, C-10), 33.7 (*t*, C-11), 46.0 (*d*, C-5), 56.3 (*q*, 3′-OMe), 56.6 (*q*, 4-OMe), 97.9 (*d*, C-3), 110.2 (*d*, C-1), 112.4 (*d*, C-2′), 113.6 (*d*, C-5′), 115.6 (*d*, C-7), 118.1 (*d*, C-9), 120.9 (*d*, C-6′), 123.3 (*s*, C-4a), 133.5 (*s*, C-11a), 134.1 (*d*, C-6), 140.1 (*s*, C-1′), 142.9 (*s*, C-5a), 143.9 (*s*, C-9a), 145.1 (*s*, C-4′), 148.5 (*s*, C-3′), 157.2 (*s*, C-8), 157.7 (*s*, C-2), 159.5 (*s*, C-4). *Triacetate*. Oil. ^{1}H NMR: δ 2.21 (3H, *s*, OAc), δ 2.26 (3H, *s*, OAc), 2.27 (3H, *s*, OAc), 2.64–2.73 (2H, *m*, H-10), 3.06–3.11 (2H, *m*, H-11), 3.56 (3H, *s*, 3′-OMe), 3.86 (3H, *s*, 4-OMe), 6.05 (1H, *s*, H-5), 6.40 (1H, *dd*, *J* = 8.3, 2.1 Hz, H-6′), 6.50 (1H, *m*, H-2′), 6.55 (1H, *d*, *J* = 2.1 Hz, H-1), 6.71 (1H, *d*, *J* = 2.1 Hz, H-3), 6.83 (1H, *d*, *J* = 8.3 Hz, H-5′), 6.91 (1H, *d*, *J* = 2.4 Hz, H-9), 6.93 (1H, *dd*, *J* = 8.1, 2.4 Hz, H-7), 7.32 (1H, *d*, *J* = 8.1 Hz, H-6). MS *m/z* (rel. int.): 504 $[M]^+$ (56), 462 (100), 420 (25), 378 (9), 338 (34), 296 (66), 255 (57).

Compound **2**. Oil. IR ν_{max} cm^{-1}: 3250, 1590, 1510, 1440. UV λ_{max} nm (log ε): 207 (2.80), 230 sh (2.54), 281 (2.03). MS *m/z* (rel. int.): 562 $[M]^+$ (5), 456 (71), 349 (100), 241 (39), 137 (18), 107 (76). ^{1}H NMR: δ 2.43–2.46 (2H, *m*, —CH$_2$—CH$_2$—), 2.67–2.70 (2H, *m*, —CH$_2$—CH$_2$—), 3.58 (2H, *s*, ϕ—CH$_2$—ϕ), 3.73 (3H, *s*, 5-OMe), 3.81 (2H, *s*, ϕ—CH$_2$—ϕ), 3.86 (2H, *s*, ϕ—CH$_2$—ϕ), 6.45 (1H, *s*, H-4), 6.53 (1H, *dd*, *J* = 8.2,

3.3 Hz, H-4′), 6.58 (1H, *d*, *J* = 3.3 Hz, H-6′), 6.57 (1H, *d*, *J* = 8.2 Hz, H-3′), 6.60 (2H, *d*, *J* = 8.3 Hz, H-3‴, 5‴), 6.64 (4H, *d*, *J* = 8.3 Hz, H-3″, 3‴, 5″, 5‴), 6.76 (2H, *d*, *J* = 8.3 Hz, H-2‴, 6‴), 6.78 (2H, *d*, *J* = 8.3 Hz, H-2″, 6″), 6.86 (2H, *d*, *J* = 8.3 Hz, H-2‴, 6‴). ^{13}C NMR: δ 31.1 (*t*, ϕ—CH_2—ϕ), 31.2 (*t*, ϕ—CH_2—ϕ), 31.8 (*t*, ϕ—CH_2—ϕ), 34.7 (*t*, —$\underline{C}H_2$—CH_2—), 37.9 (*t*, —CH_2—$\underline{C}H_2$—), 56.0 (*q*, 5-OMe), 98.4 (*d*, C-4), 113.9 (*d*, C-3′), 115.9 (*d*, C-3‴, 5‴), 116.0 (*d*, C-3″, 5″), 116.1 (*d*, C-3‴, 5‴), 116.6 (*d*, C-4′), 119.5 (*s*, C-6), 120.4 (*s*, C-2), 129.9 (*d*, C-2‴, 6‴), 130.0 (*d*, C-2″, 6″), 130.7 (*d*, C-2‴, 6‴), 131.5 (*s*, C-1′), 132.1 (*d*, C-6′), 133.7 (*s*, C-1‴), 134.1 (*s*, C-1″), 134.3 (*s*, C-1‴), 142.8 (*s*, C-5′), 142.9 (*s*, C-1), 155.9 (*s*, C-2′), 156.0 (*s*, C-4‴), 156.1 (*s*, C-4″), 156.3 (*s*, C-4‴), 156.7 (*s*, C-3), 158.5 (*s*, C-5). *Pentaacetate*. Oil. ^{1}H NMR: δ 2.12 (3H, *s*, OAc), 2.23 (6H, *s*, OAc × 2), 2.24 (3H, *s*, OAc), 2.26 (3H, *s*, OAc), 2.52–2.56 (2H, *m*, —$\underline{C}H_2$—CH_2—), 2.75–2.78 (2H, *m*, —CH_2—$\underline{C}H_2$—), 3.72 (3H, *s*, 5-OMe), 3.77 (4H, *s*, ϕ—CH_2—ϕ × 2), 3.99 (2H, *s*, ϕ—CH_2—ϕ), 6.69 (1H, *d*, *J* = 2.1 Hz, H-6′), 6.74 (1H, *s*, H-4), 6.85 (1H, *dd*, *J* = 8.3, 2.1 Hz, H-4′), 6.90 (1H, *d*, *J* = 8.3 Hz, H-3′), 6.91 (4H, *d*, *J* = 8.1 Hz, H-3″, 3‴, 5″, 5‴), 6.92 (2H, *d*, *J* = 8.1 Hz, H-3‴, 5‴), 6.96 (2H, *d*, *J* = 8.1 Hz, H-2‴, 6‴), 7.00 (2H, *d*, *J* = 8.1 Hz, H-2″, 6″), 7.02 (2H, *d*, *J* = 8.1 Hz, H-2‴, 6‴). MS *m*/*z* (rel. int.): 772 $[M]^+$ (4), 730 (8), 688 (5), 582 (44), 475 (11), 433 (47), 391 (46), 349 (16).

Compound **3**. Oil. IR ν_{max} cm^{-1}: 3250, 1600, 1550. UV λ_{max} nm (log ε): 220 sh (4.47), 230 sh (4.44), 280 (3.86). MS *m*/*z* (rel. int.): 364 $[M]^+$ (100), 257 (18), 137 (5), 121 (20), 107 (24), ^{1}H NMR: δ 2.56–2.64 (2H, *m*, —$\underline{C}H_2$—CH_2—), 2.70–2.75 (2H, *m*, —CH_2—$\underline{C}H_2$—), 3.72 (3H, *s*, 3′-OMe), 3.74 (3H, *s*, 3-OMe), 3.83 (2H, *s*, ϕ—CH_2—ϕ), 6.27 (1H, *d*, *J* = 2.6 Hz, H-6), 6.34 (1H, *d*, *J* = 2.6 Hz, H-4), 6.55 (1H, *t*, *J* = 2.1, 1.7 Hz, H-2′), 6.63 (2H, *d*, *J* = 8.6 Hz, H-3″, 5″), 6.64 (1H, *m*, H-6′), 6.69 (1H, *dd*, *J* = 7.9, 1.7 Hz, H-4′), 6.86 (2H, *d*, *J* = 8.6 Hz, H-2″, 6″), 7.11 (1H, *t*, *J* = 7.9 Hz, H-5′). ^{13}C NMR: δ 30.6 (*t*, ϕ—CH_2—ϕ), 36.4 (*t*, —$\underline{C}H_2$—CH_2—), 38.6 (*t*, —CH_2—$\underline{C}H_2$—), 55.6 (*q*, 3′-OMe), 56.1 (*q*, 3-OMe), 98.1 (*d*, C-4), 109.5 (*d*, C-6), 112.6 (*d*, C-4′), 114.9 (*d*, C-2′), 116.0 (*d*, C-3″, 5″), 120.0 (*d*, C-6′), 121.8 (*s*, C-2), 130.0 (*d*, C-2″, 6″), 130.2 (*d*, C-5′), 134.3 (*s*, C-1″), 143.7 (*s*, C-1), 144.9 (*s*, C-1′), 156.1 (*s*, C-4″), 157.6 (*s*, C-5), 160.3 (*s*, C-3′), 161.2 (*s*, C-3). *Diacetate*. Oil. ^{1}H NMR ($CDCl_3$): δ 2.25 (3H, *s*, OAc), 2.29 (3H, *s*, OAc), 2.69–2.74 (2H, *m*, —$\underline{C}H_2$—CH_2—), 2.81–2.86 (2H, *m*, —CH_2—$\underline{C}H_2$—), 3.76 (6H, 3, 3′-OMe), 4.0 (2H, *s*, ϕ—CH_2—ϕ), 6.56 (1H, *dd*, *J* = 2.1, 2.1 Hz, H-2), 6.62 (2H, *d*, *J* = 2.1 Hz, H-4.6), 6.67 (1H, *dd*, *J* = 7.9, 2.1 Hz, H-6′), 6.72 (1H, *dd*, *J* = 7.9, 2.1 Hz, H-4′), 6.92 (2H, *d*, *J* = 8.3 Hz, H-3″, 5″), 7.07 (2H, *d*, *J* = 8.3 Hz, H-2″, 6″), 7.17 (1H, *t*, *J* = 7.9 Hz, H-5′). MS *m*/*z* (rel. int.): 448 $[M]^+$ (80), 406 (100), 364 (78), 257 (24).

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