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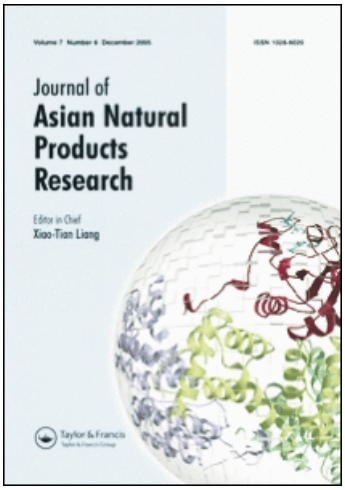

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Two New Caffeyol Glycosides from *Forsythia suspensa*

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TWO NEW CAFFEYOL GLYCOSIDES FROM *FORSYTHIA SUSPENSA*

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Two new caffeoyl glycosides of phenethyl alcohol, suspensaside A (**1**) and suspensaside B (**2**), were isolated from the fruits of *Forsythia suspensa*. Also obtained in this investigation were two known compounds forsythiaside (**3**) and suspensaside (**4**). The structures of compounds **1** and **2** were established by 1D and 2D NMR techniques and chemical methods.

Keywords: *Forsythia suspensa*; Suspensaside A; Suspensaside B; Suspensaside; Forsythiaside

INTRODUCTION

Forsythia suspensa Vahl (Oleaceae) is an important original plant of traditional Chinese medicine "Lian Qiao" which has been used for antiinflammatory, diuretic, drainage and antidotal purposes. Many compounds including caffeyol glycosides, cyclohexyl ethane derivatives, flavonoides, iridoid glycosides, lignans, and triterpenes have been isolated from this plant [1–5]. We have now isolated two new caffeyol glycosides suspensaside A (**1**) and suspensaside B (**2**), together with two known glycosides forsythiaside (**3**) and suspensaside (**4**) from the water soluble part of the 70% EtOH extract of *F. suspensa*. This paper deals with the structure determination of these two new compounds.

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RESULTS AND DISCUSSION

Suspensaside A was isolated as an amorphous powder, m.p. 177–180°C, $[\alpha]_D^{20}$ +15.6 (*c* 0.10, CH_3OH). The HRSIMS spectrum of **1** gave a pseudo-molecular ion at *m/z* 623.1958 $[M+H]^+$ corresponding to a molecular formula of $C_{29}H_{34}O_{15}$. The IR spectrum of **1** indicated the presence of a conjugated ester (1699, 1284 cm^{-1}) and aromatic ring (1605, 1524 cm^{-1}). The ^{1}H-NMR spectrum (in CD_3OD) of **1** showed six aromatic proton resonances, of which the signals at δ 7.00 (1H, d, $J=2.0$ Hz), 6.73 (1H, d, $J=8.2$ Hz) and 6.91 (1H, dd, $J=8.2, 2.0$ Hz) suggested the existence of an 1,3,4-trisubstituted phenyl ring, and the three signals were assigned to H-2′, H-5′, and H-6′, respectively, based on their chemical shifts and coupling-pattern analysis. The three other aromatic protons were observed as two doublets at δ 6.79 (1H, $J=1.2$ Hz, H-2) and 6.67 (2H, d, $J=1.2$ Hz, H-5,6) in the ^{1}H-NMR spectrum run in CD_3OD, while in DMSO-d_6 these signals appeared as two doublets and a double doublet at δ 6.78 (1H, d, $J=1.8$ Hz, H-2), 6.69 (1H, d, $J=8.2$ Hz, H-5) and 6.63 (1H, dd, $J=8.2$, 1.8 Hz, H-6), respectively. The spectral data indicated that there were two 1,3,4-trisubstituted phenyl rings in the structure of **1**. In addition, the ^{1}H-NMR spectrum of **1** (see Table I) also displayed signals for an AB system at δ 7.56 and 6.25 (each 1H, $J=15.9$ Hz) corresponding to the H-7′ and H-8′, respectively. The above information revealed the presence of a caffeoyl partial structure in the molecule.

^{13}C-NMR (Table I) spectrum and DEPT experiments of **1** showed 29 signals: one methyl, two methylenes, 19 methines and seven quaternary carbons, of which the signals at δ 127.8 (C-1′), 115.4 (C-2′), 146.9 (C-3′), 149.8 (C-4′), 116.6 (C-5′), 123.1 (C-6′), 147.8 (C-7′), 114.7 (C-8′), 168.1 (C-9′) were attributed to the caffeoyl group.

In the ^{1}H-^{1}H COSY NMR spectrum of **1**, a double doublet at δ 3.91 (H-8a) showed a correlation with another double doublet at δ 3.62 (H-8b), and they both showed correlation with a double doublet at δ 4.51 (H-7). The two anomeric protons at δ 4.44 (d, $J=7.7$ Hz), 4.57 (d, $J=1.7$ Hz) in ^{1}H-NMR, and corresponding carbon signals at 99.5, 102.4 in ^{13}C-NMR indicated that compound **1** contained two sugar residues. Using ^{1}H-^{1}H COSY NMR experiments, from the anomeric protons H-1″, the assignments of H-2″ (δ 3.23, m), H-3″ (δ 3.82, m), H-4″ (δ 4.99, t, $J=9.7$ Hz), H-5″ (δ 3.81, m), H-6″ (δ 3.45, dd, $J=11.4, 5.6$ Hz; 3.72, dd, $J=11.4$, 1.7 Hz) could be made; and from the methyl protons H-6‴; (δ 1.14, d, $J=6.2$ Hz), it was possible to assign H-5‴ (δ 3.51, m), H-4‴ (δ 3.28, m), H-3‴ (δ 3.60, m), H-2‴ (δ 3.80, m) and H-1‴. The corresponding carbon signals

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TABLE I NMR data for suspensaside A(1)

Position	δ_C (*in* CD_3OD)	δ_H (*in* CD_3OD)	δ_H (*in DMSO-*d_6)
1	129.9		
2	115.1	6.79 t (1.2)	6.78 d (1.8)
3	146.3		
4	146.6		
5	116.2	6.67 d (1.2)	6.69 d (8.2)
6	119.4	6.67 d (1.2)	6.63 dd (8.2, 1.8)
7(β)	78.8	4.51 dd (10.5, 2.8)	4.50 m
8(α)	72.8	3.91 dd (12.0, 2.8)	3.90 dd (11.8, 2.6)
		3.62 dd (12.0, 10.5)	3.55 m
1′	127.8		
2′	115.4	7.00 d (2.0)	7.04 d (1.9)
3′	146.9		
4′	149.8		
5′	116.6	6.73 d (8.2)	6.76 d (8.2)
6′	123.1	6.91 dd (8.2, 2.0)	7.00 dd (8.2, 1.9)
7′	147.8	7.56 d (15.9)	6.25 d (15.9)
8′	114.7	6.25 d (15.9)	7.51 d (15.9)
9′	168.1		
1″	99.5	4.44 d (7.7)	4.44 d (7.3)
2″	80.9	3.23 m	3.13 m
3″	73.1	3.82 m	3.67 t (9.2)
4″	72.4	4.99 t (9.7)	4.78 t (9.5)
5″	76.5	3.81 m	3.78 m
6″	67.6	3.45 dd (11.4, 5.6)	3.38 dd (12.8, 4.7)
		3.72 dd (11.4, 1.7)	3.56 dd (12.8, 1.9)
1‴	102.4	4.57 d (1.7)	4.51 d (1.6)
2‴	72	3.80 m	3.53 m
3‴	72.5	3.60 m	3.52 m
4‴	74	3.28 m	3.14 m
5‴	69.9	3.51 m	3.41 m
6‴	17.9	1.14 d (6.2)	1.02 d (6.2)

Spectra were recorded at 500 MHz for ^1H and 125 MHz for ^{13}C, with chemical shifts (δ) in ppm relative to internal TMS and coupling constants in Hz are in parentheses.

were assigned as δ 99.5 (C-1″), 80.9 (C-2″), 73.3 (C-3″), 72.4 (C-4″), 76.5 (C-5″), 67.6 (C-6″); and 17.9 (C-6‴), 69.9 (C-5‴), 74.0 (C-4‴), 72.5 (C-3‴), 72.0 (C-2‴), 102.4 (C-1‴), respectively by the ^{13}C-^1H COSY NMR spectrum. These spectral data indicated that the disaccharide part of **1** was composed of glucose and rhamnose. The configurations of the anomeric protons of glucose and rhamnose were proposed as β and α, respectively, on the basis of their coupling constants.

The above information suggested that **1** bore a marked structural resemblance in the linkage between a glucose and a phenethyl moiety to that of the known compound oraposide which contains, besides the glycosidic linkage, an ether linkage between a glucose and a phenethyl moiety [7,8]. The

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spectrum of **1** supported the attachments of the caffeyol and rhamnose moieties at the C-4″ and C-6″, respectively, of the glucose moiety. The linkage positions of substituents were also deduced from HMBC data of **1** (see Fig. 1), in which long-range heteronuclear correlations were observed between the following carbons and protons: C-9′ (δ 168.1) and H-4″ (δ 4.99), C-1‴ (102.4) and H-6″ (δ 3.45, 3.72), C-8 (δ 72.8) and H-1″ (δ 4.44), C-1″ (δ 99.5) and H-8a (δ 3.91). Based on the foregoing analysis, the structure of suspensaside A has been concluded to be 1″,2″-[β-3,4,-dihydroxylphenyl-α,β-dioxoethanol]-4″-O-caffeoyl-O-α-rhamnopyranosyl-(1 → 6)-β-glucopyranoside.

Suspensaside B (**2**) was obtained as an amorphous powder, m.p. 156–160°C, $[\alpha]_D^{23}$ −13.3 (*c* 0.26, CH_3OH). Its molecular formula was established as $C_{33}H_{44}O_{16}$ by FABMS and elemental analysis. Characteristic absorptions for conjugated ester at 1695, 1284 cm^{-1} and aromatic ring at 1603, 1510 cm^{-1} were observed in the IR spectrum of **2**. The ^{1}H-NMR spectra of **2** displayed six aromatic proton signals at δ 6.79 (1H, d, J = 1.8 Hz), 6.82 (1H, d, J = 8.2 Hz), 6.70 (1H, dd, J = 8.2, 1.8 Hz), 7.10 (1H, d, J = 1.9 Hz), 6.80 (1H, d, J = 8.2 Hz) and 7.00 (1H, dd, J = 8.2, 1.8 Hz), which were ascribed to H-2, H-5, H-6 and H-2′, H-5′, H-6′, respectively, and indicated the presence of two 1,3,4-trisubstituted phenyl rings. A singlet at δ 1.24 (3H, d, J = 6.2 Hz) was due to the C-6‴ CH_3 protons of Rhamnose. Two doublets of an AB system at δ 7.64 and 6.33 (each 1H, d, J = 15.9 Hz) were due to the double-bond protons of C-7′ and C-8′.

The ^{13}C-NMR spectrum of **2** displayed resonances for 33 carbons. The DEPT spectrum indicated that the compound contained two methyls, five methylenes, 19 methines and seven quaternary carbons, of which the signals at δ 105.0 and 102.0 indicated that compound **2** contained two sugar residues. Comparison of the ^{13}C-NMR spectrum of **2** with that of the known

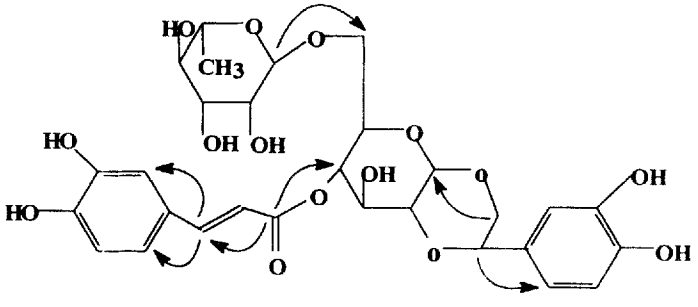

FIGURE 1 Selective HMBC observations for suspensaside A. Arrows denote HMBC correlation from C to H.

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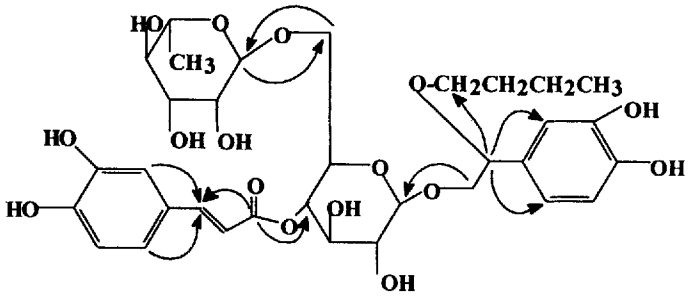

FIGURE 2 Selective HMBC observations for suspensaside B. Arrows denote HMBC correlation from C to H.

compound suspensaside (**4**) showed that there were additional carbon signals at δ 14.7 (CH_3), 20.4 (CH_2), 32.9 (CH_2), 69.6 (CH_2) in the spectrum of **2**. The corresponding protons in ^{13}C-^{1}H COSY spectrum were δ 0.94 (3H, t, $J = 7.3$ Hz), 1.40 (2H, m), 1.60 (2H, m), 3.42 (2H, t, $J = 6.5$ Hz), respectively, which showed correlations in the ^{1}H-^{1}H COSY spectrum. Considering the above data and molecular formula, the difference between suspensaside B (**2**) and suspensaside (**4**) was that in the former the hydroxyl group at C-7 was replaced by a butoxy group. The respective positions of the substituents were determined using long-range heteronuclear correlations observed by HMBC (see Fig. 2). Therefore, the structure of suspensaside B was elucidated as 3,4-dihydroxy-7-butoxy-phenethyl-4″-O-caffeoyl-O-α-rhamnopyranosyl-(1 → 6)-β-glucopyranoside. It must be noted that compounds **1** and **2** are possible to be artificial products formed in the processes of isolation and extraction from suspensaside (**4**) through the intermediate **5** (Scheme 1).

Compounds **3** and **4** were obtained as amorphous powder. They were identified as forsythiaside [2] and suspensaside [6], respectively, on the basis of their spectral data (IR, MS, NMR, etc.).

EXPERIMENTAL SECTION

General Experimental Procedures

Melting points were determined with an XT4-100X micromelting point apparatus and were uncorrected. Optical rotations were obtained on a Perkin-Elmer 241 polarimeter. IR spectra were recorded on a Perkin-Elmer 683 spectrophotometer. NMR spectra were run on a Bruker AM-500 spectrometer. HRSIMS and FABMS were recorded on APEX-II-FTMS and

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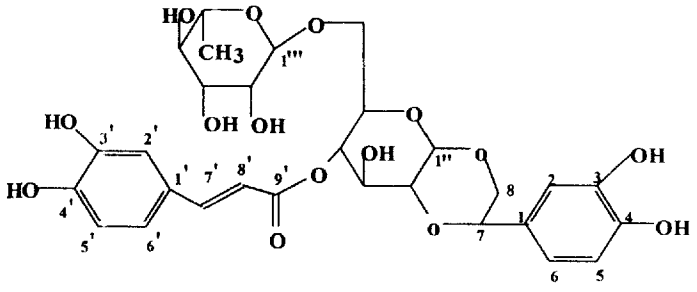

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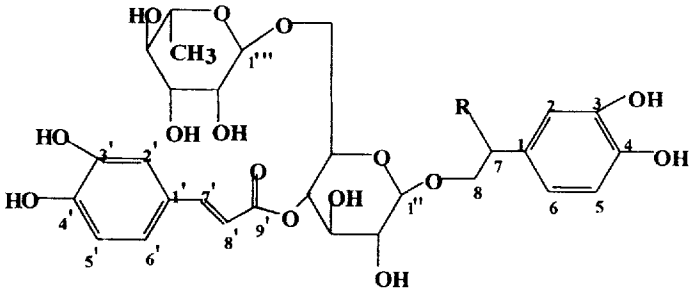
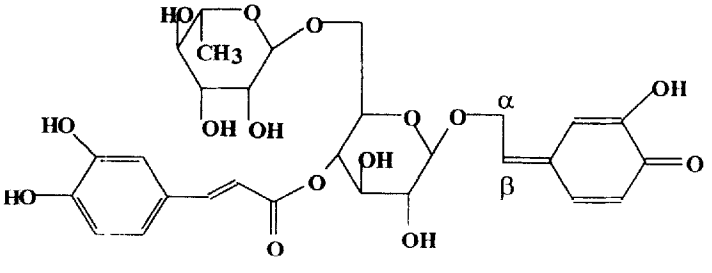


2 R = $OCH_2CH_2CH_2CH_3$
3 R = H
4 R = OH



5

SCHEME 1

ZAB-2F instruments. Elemental analysis was performed on a MOD1106 elemental analyzer. Si gel (Haiyang 180–200 mesh, produced by Qingdao Haiyang Chemical Group Co., Qingdao) was used for column chromatography. Precoated Si gel plates (GF 254) were used for analytical and preparative TLC.

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Plant Material

The fruits of *F. suspensa* were collected in Beijing in July 1995. The plant material was identified by Professor Wan-Zhi Song, and a voucher specimen has been deposited in the Herbarium of Institute of Materia Medica, Chinese Academy of Medical Sciences.

Extraction and Isolation

The fruits of *F. suspensa* (10 kg) were extracted with hot 70% EtOH three times (3 × 10L) and the solutions were combined and concentrated *in vacuo*. A suspension of the EtOH extract in H_2O was extracted with EtOAc six times. The remaining solutions were evaporated and chromatographed on a Si gel (180–200 mesh) column eluted with a $CHCl_3$/MeOH gradient solvent system. Fractions with similar R_f values (by TLC) were evaporated and combined to give 30 fractions. Each fraction was repeatedly subjected to column chromatography on Sephadex LH-20, Si gel, and MPLC, eluted with CH_3OH, $CHCl_3/CH_3OH$, and CH_3OH/H_2O, respectively, to obtain **1** (30 mg), **2** (16 mg), **3** (1 g), and **4** (9 mg).

Supensaside A (**1**) Compound **1**, yellowish powder, m.p. 176–180°C; $[\alpha]_D^{20}$ +15.6 (*c* 0.10, CH_3OH); IR (KBr) ν_{max} 3398 (OH), 1699 (conjugated CO), 1605 (C=C), 1524, 1284, 1119, 1053, 980, 812 cm $^{-1}$; ^{13}C-NMR, and ^{1}H-NMR, see Table I; HRSIMS *m/z* 623.1958 $[M+H]^+$ (calcd. for $C_{29}H_{35}O_{15}$ 623.1970).

Acid hydrolysis of Suspensaside A Compound **1** (5 mg) in 1% H_2SO_4 solution was heated on a water bath for 2 h, then cooled. The mixture was extracted with EtOAc. The EtOAc layer was washed and evaporated to dryness. Caffeic acid in the residue was identified by comparison with an authentic sample [on TLC with $CHCl_3$–AcOEt–AcOH (1 : 1 : 0.02)]. The aqueous layer was neutralized with 5% NaOH, then filtered. The filtrate showed the presence of glucose and rhamnose [identified by TLC comparison using $CHCl_3$–MeOH–H_2O (7 : 3 : 0.3), detection with anisaldehyde/H_2SO_4 reagent].

Suspensaside B (**2**) yellowish powder, m.p. 155–160°C; $[\alpha]_D^{20}$ −13.3 (*c* 0.26, CH_3OH); IR (KBr) ν_{max} 3369 (OH), 1695 (conjugated CO), 1603 (C=C), 1447, 1283, 1159, 1063, 1045, 980, 812 cm^{-1}; ^{13}C-NMR and ^{1}H-NMR, see Table II; FABMS *m/z* 719.4 $[M+Na]^+$; anal. C 56.80, H 6.38, calcd. for $C_{33}H_{44}O_{16}$, C 56.90, H 6.32.

Acid hydrolysis of Suspensaside B Compound **2** (5 mg) was hydrolyzed by the same method as **1**. Caffeic acid, glucose and rhamnose were identified from the hydrolysis solutions.

TABLE II NMR data for suspensaside B (**2**) (in CD_3OD)

Position	δ_C	δ_H	*Position*	δ_C	δ_H
1	131.8		1″	105.0	4.49 d (7.8)
2	115.0	6.79 d (1.8)	2″	75.3	3.36 m
3	146.5		3″	75.8	3.68 m
4	146.3		4″	72.8	4.97 t (9.7)
5	116.5	6.82 d (8.2)	5″	75	3.70 m
6	119.7	6.70 dd (8.2, 1.8)	6″	67.6	3.79 m
7(β)	81.9	4.48 m			3.52 m
8(α)	75.4	4.02 m	1‴	102.2	4.67 d (1.5)
		3.66 m	2‴	72.0	3.88 m
1′	127.7		3‴	72.3	3.78 m
2′	115.2	7.10 d (1.9)	4‴	73.9	3.41 m
3′	146.9		5‴	69.9	3.65 m
4′	149.8		6‴	18.0	1.24 d (6.2)
5′	116.2	6.80 d (8.2)	Butoxy		
6′	123.1	7.00 dd (8.2, 1.9)	CH_2	69.6	3.42 t (6.5)
7′	147.6	7.64 d (15.9)	CH_2	32.9	1.60 m
8′	114.8	6.33 d (15.9)	CH_2	20.4	1.40 m
9′	168.3		CH_3	14.7	0.94 t (7.3)

Spectra were recorded at 500 MHz for ^1H and 125 MHz for ^{13}C, with chemical shifts (δ) in ppm relative to internal TMS and coupling constants in Hz are in parentheses.

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Forsythiaside (**3**) A yellowish powder, m.p. 150–152°C; $[\alpha]_D^{20}$ −25.2 (*c* 0.14, CH_3OH); IR (KBr) ν_{max} 3406 (OH), 1697 (conjugated CO), 1605 (C=C), 1522, 1283, 1159, 1059, 980, 812 cm^{-1}; ^1H-NMR (in CD_3OD) δ 1.14 (3H, d, $J=6.3$ Hz, H-6‴), 2.76 (2H, m, H-7), 4.30 (1H, d, $J=7.8$ Hz, H-1″), 4.58 (1H, d, $J=1.6$ Hz, H-1‴), 7.53 (1H, d, $J=15.9$ Hz, H-7′), 6.23 (1H, d, $J=15.9$ Hz, H-8′), 6.64 (1H, d, $J=2.1$ Hz, H-2), 6.51 (1H, dd, $J=8.1, 2.1$ Hz, H-6), 6.62 (1H, d, $J=8.1$ Hz, H-5), 6.72 (1H, d, $J=8.2$ Hz, H-5′), 6.90 (1H, dd, $J=8.2, 2.0$ Hz, H-6′), 7.00 (1H, d, $J=2.0$ Hz, H-2′); ^{13}C-NMR see Table III; FABMS $[M+H]^+$ 625.1.

Suspensaside (**4**) A yellowish powder, m.p. 175–182°C; $[\alpha]_D^{20}$ −18.8 (*c* 0.10, CH_3OH); IR (KBr) ν_{max} 3389 (OH), 1699 (conjugated CO), 1601 (C=C), 1524, 1383, 1263,1045, 980, 812 cm^{-1}; ^1H-NMR (in CD_3OD) δ 1.14 (3H, d, $J=6.2$ Hz, H-6‴), 4.36 (1H, d, $J=7.7$ Hz, H-1″), 4.58 (1H, d, $J=1.6$ Hz, H-1‴), 4.70 (1H, dd, $J=7.8, 3.0$ Hz, H-7), 7.00 (1H, d, $J=1.5$ Hz, H-2′), 6.90 (1H, dd, $J=7.6$, 1.5 Hz, H-6′), 6.73 (1H, d, $J=7.6$ Hz, H-5′), 6.80 (1H, d, $J=1.4$ Hz, H-2), 6.62 (1H, dd, $J=8.1, 1.4$ Hz, H-6), 6.66 (1H, d, $J=8.1$ Hz, H-5), 7.54 (1H, d, $J=15.9$ Hz, H-7′), 6.24 (1H, d, $J=15.9$ Hz, H-8′); ^{13}C-NMR see Table III; FABMS $[M+H]^+$ 641.1.

TABLE III ^{13}C NMR data for compounds **3** and **4** (in CD_3 OD)

Position	**3**	**4**	*Position*	**3**	**4**
1	131.4	133.8	1″	104.5	104.4
2	116.4	114.7	2″	75.2	75.2
3	146.2	146.1	3″	75.9	75.6
4	144.5	146.2	4″	74.0	73.9
5	117.2	116.2	5″	74.9	74.8
6	121.3	119.1	6″	67.8	67.7
7	36.7	76.5	1‴	102.3	102.3
8	72.2	73.4	2‴	72.1	72.2
1′	127.8	127.6	3‴	72.3	72.4
2′	115.3	115.2	4‴	72.4	73.5
3′	147.6	146.9	5‴	69.9	69.9
4′	149.7	149.8	6‴	18.0	18.0
5′	116.6	116.5			
6′	123.0	123.1			
7′	147.6	147.8			
8′	114.9	114.6			
9′	168.3	168.3			

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