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## New $\alpha$ -Tetralone Galloylglucosides from the Fresh Pericarps of *Juglans sigillata*

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### Abstract

Three new  $\alpha$ -tetralone galloylglucosides (**1–3**), were isolated from the fresh pericarps of *Juglans sigillata* (Juglandaceae), together with the six known ones. The structures of the new compounds were determined as 4,6-dihydroxy- $\alpha$ -tetralone-4-*O*-[6-*O*-(3,4,5-trihydroxybenzoyl)]- $\beta$ -D-glucopyranoside (**1**), (4*S*)-4,5-dihydroxy- $\alpha$ -tetralone-4-*O*-[6-*O*-(3,4,5-trihydroxybenzoyl)]- $\beta$ -D-glucopyranoside (**2**) and (4*S*)-4,5,6-tri-hydroxy- $\alpha$ -tetralone-4-*O*-[6-*O*-(3,4,5-trihydroxybenzoyl)]- $\beta$ -D-glucopyranoside (**3**), respectively, on the basis of detailed spectroscopic analyses, and acidic and enzymatic hydrolysis. The antimicrobial activities of the isolated compounds (**2**, **4** and **7–9**) were evaluated.

### Keywords

*Juglans sigillata*; Juglandaceae;  $\alpha$ -tetralone galloylglucosides; antimicrobial activity

### Introduction

The genus *Juglans* (Juglandaceae) comprising about 20 species is widely distributed in the temperate and subtropical areas of the world [1]. The seeds of *Juglans* species, particularly *J. regia*, known as walnuts, are excellent sources of unsaturated fatty acids and polyphenols, and used as folk remedies for cancer and kidney and stomach diseases in Asia and Europe [2]. The fresh pericarp of some species, e.g. *J. mandshurica* and *J. regia*, commonly named as “Qing-Long-Yi”, have been medicinally used for thousands of years in China, Japan and Korea, owing to its anti-tumor, anti-inflammatory, antinociceptive and antioxidant effects. The roots and leaves of these plants are also used as folk medicine for the treatment of cancer, rheumatic pains and eczema [3,4]. Some naphthalene glucosides [5],  $\alpha$ -tetralones and their derivatives [6–8] and diarylheptanoids [9] have been reported from the fresh pericarps or fruits of *Juglans* species.

*Juglans sigillata* Dode, known as the iron walnut, has been widely cultivated for its edible nuts in the southwest of China. To date, no chemical work has been carried out on this species. Our detailed chemical investigation on the fresh pericarps of *J. sigillata* led to the isolation of three new  $\alpha$ -tetralone galloylglucosides (**1–3**), together with six known ones (**4–**

9) (Figure 1). The isolated compounds **2**, **4** and **7–9** were evaluated for their antimicrobial activities.

## Results and Discussion

The fresh pericarps of *J. sigillata* were extracted three times with 80% aqueous acetone at room temperature. After removal of the organic solvent, the aqueous fraction was extracted with  $\text{CHCl}_3$  and EtOAc, successively. The EtOAc fraction was subjected to column chromatography (CC) over *Sephadex LH-20*, silica gel and *MCI-gel CHP20P* to afford compounds **1–9**. Of them, the known compounds **4–9** were identified as (4*S*)-4-hydroxy-*β*-tetralone-4-*O*-[6-*O*-(3,4,5-tri-hydroxybenzoyl)]-*β*-D-glucopyranoside (**4**) [6], (4*S*)-4,5-dihydroxy-*β*-tetralone-4-*O*-*β*-D-glucopyranoside (**5**) [7], (4*S*)-4-hydroxy-*β*-tetralone (**6**) [7], (4*S*)-4,5-dihydroxy-*β*-tetralone (**7**) [7], (4*S*)-4,5,8-trihydroxy-*β*-tetralone (**8**) [7], and 3,4-dihydro-naphthalen-1(2*H*)-one (**9**) [8], respectively, by comparison of their spectroscopic and physical data with those reported previously in literatures.

Compound **1** was obtained as a white amorphous powder. Its molecular formula  $\text{C}_{23}\text{H}_{24}\text{O}_{12}$  was determined on the basis of the HR-ESI-MS ( $m/z$  491.1210,  $[M-H]^-$ ). The IR spectrum showed absorption at 3439, 1627, and 1606  $\text{cm}^{-1}$ , suggesting the presence of hydroxyl and carbonyl groups. Acidic hydrolysis of **1** gave D-glucose as the sole sugar residue. The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR data of **1** exhibited the signals arising from a carbonyl (C) 197.8, a benzene ring (H) 7.74, 7.08 and 6.81, a  $\beta$ -glucopyranosyl (anomeric proton at (H) 4.60 (1H, *d*,  $J = 7.9$  Hz, H-C(1)), and carbon signals at (C) 103.7 (C(1)), 76.5 (C(2)), 74.3 (C(3)), 71.1 (C(4)), 77.1 (C(5)) and 63.4 (C(6)), a galloyl (H) 7.11 (2H, *s*) group, two methylenes (C) 35.0 (C(2)) and 31.2 (C(3)) and one oxygen-bearing methine (C) 74.4 (C(4)). These NMR characteristics resembled those observed in **4**. However, instead of a 1,2-disubstituted benzene ring in **4**, compound **1** had a 1,2,4-trisubstituted benzene ring in view of the coupling patterns of the aromatic protons (H) 7.74 (1H, *d*,  $J = 8.6$  Hz, H-C(8)), 7.08 (1H, *d*,  $J = 2.4$  Hz, H-C(5)), and 6.81 (1H, *dd*,  $J = 8.6, 2.4$  Hz, H-C(7)). In the HMBC spectrum of **1**, correlations of (H) 7.74 (H-C(8)) with (C) 197.8 (C(1)) and (H) 7.08 (H-C(5)) with (C) 74.4 (C(4)) were observed. These HMBC correlations in conjunction with the multiplicities in the  $^1\text{H}$  NMR spectrum of **1** demonstrated that C(6) of the benzene ring was substituted with a hydroxyl group. In addition, the HMBC correlations of H-C(4) (H) 4.82) with C(1) (C) 103.7, glucosyl unit) indicated the glucose moiety to be attached to C(4) of the aglycone. The location of the galloyl group at the C(6) hydroxyl group of the glucosyl unit was also determined by the HMBC experiment, in which correlations of  $\text{CH}_2(6)$  (H) 4.57, 4.36, glucosyl unit) with the carboxyl carbon C(7) (C) 167.3) of the galloyl group were displayed. Other HMBC correlations (Figure 2) also confirmed the structure of **1**. The configuration at C(4) could not be established due to insufficient amounts of compound **1**. Accordingly, compound **1** was determined to be 4,6-dihydroxy-*β*-tetralone-4-*O*-[6-*O*-(3,4,5-trihydroxybenzoyl)]-*β*-D-glucopyranoside.

Compound **2** was isolated as a white amorphous powder. The molecular formula  $\text{C}_{23}\text{H}_{24}\text{O}_{12}$  was deduced from the HR-ESI-MS ( $m/z$  491.1191,  $[M-H]^-$ ) data. The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of **2** were very similar to those of **1**, except for the substitution of the benzene ring, which showed proton signals at (H) 7.37 (1H, *dd*,  $J = 9.5, 1.0$  Hz, H-C(8)), 7.26 (1H, *dd*,  $J = 10.0, 9.5$  Hz, H-C(7)), and 7.14 (1H, *dd*,  $J = 10.0, 1.5$  Hz, H-C(6)). These observations indicated that the benzene ring was a 1,2,3-trisubstituted system. In the HMBC spectrum of **2** (Figure 2), correlations of H-C(4) (H) 5.24) with C(5) (C) 156.0), C(9) (C) 133.5) and C(10) (C) 128.7), and H-C(8) (H) 7.37) with C(1) (C) 199.7) revealed that a hydroxyl group was attached to the C(5) position. Connectivities of the sugar moiety with the 4-hydroxy-*β*-tetralone skeleton and the galloyl unit were confirmed by the HMBC experiment, in which correlations of H-C(4) (H) 5.24) with C(1) (C) 103.5), and H-

C(6) (H) 4.57, 4.35) with C(7) (C) 167.3) were observed. Furthermore, enzymatic hydrolysis of **2** gave **7** as the aglycone, whose absolute configuration was determined as 4*S* by the positive  $[\alpha]_D$  value [7]. Acidic hydrolysis, followed by GC analysis, revealed D-glucose as the sugar residue. Thus, the structure of **2** was established as (4*S*)-4,5-dihydroxy-*O*-tetralone-4-*O*-[6-*O*-(3,4,5-trihydroxy-benzoyl)]-*O*-D-glucopyranoside.

Compound **3** was obtained as a white amorphous powder. Its molecular formula was determined to be C<sub>23</sub>H<sub>24</sub>O<sub>13</sub> by HR-ESI-MS ( $[M-H]^-$ ,  $m/z$  507.1118). The <sup>1</sup>H- and <sup>13</sup>C-NMR spectra displayed the signals due to a 4-hydroxy-*O*-tetralone skeleton, a glucosyl moiety and a galloyl unit, suggesting that **3** was also a 4-hydroxy-*O*-tetralone derivative. The *ortho* coupled aromatic proton signals at (H) 7.35 and 6.89 (each 1H, *d*, *J* = 8.4 Hz) indicated a 1,2,3,4-tetrasubstituted benzene ring in **3**. Acidic hydrolysis of **3** gave D-glucose as the sole sugar residue. In the HMBC spectrum of **3** (Figure 2), correlations of H-C(8) (H) 7.35) with C(1) (C) 199.0) and C(4) (C) 71.0) and H-C(4) (H) 5.25) with C(5) (C) 143.0) assigned the *ortho* aromatic protons as H-C(7) and H-C(8). Furthermore, HMBC correlations of H-C(4) (H) 5.25) with C(1) (C) 103.2) and H-(6) (H) 4.55, 4.34) with C(7) (C) 167.4) confirmed the connectivities of the sugar moiety with the 4-hydroxy-*O*-tetralone aglycone and the galloyl moiety. Accordingly, the structure of **3** was established as (4*S*)-4,5,6-trihydroxy-*O*-tetralone-4-*O*-[6-*O*-(3,4,5-trihydroxybenzoyl)]-*O*-D-glucopyranoside.

Compounds **1–4**, with a 4-hydroxy-*O*-tetralone aglycone and 6-*O*-galloylglucosyl moiety in molecule, were isolated for the first time from fresh pericarps of *Juglans* species. The known compound **4** was reported to have strong inhibitory activity against the protein tyrosine phosphatase 1B [6], which plays a major role in the dephosphorylation of the insulin receptor. Thus, it may have a potential for the development of new pharmacological agents for the treatment of type-2 diabetes and obesity.

The isolated compounds **2**, **4** and **7–9** were evaluated for *in vitro* antifungal (*Aspergillus fumigatus*, *Candida albicans*, *C. glabrata*, *C. krusei*, *Cryptococcus neoformans*) and antibacterial (*Escherichia coli*, *Mycobacterium intracellulare*, *Pseudomonas aeruginosa*, *Staphylococcus aureus* and methicillin-resistant *S. aureus*) activities using a modified version of the CLSI (formerly NCCLS) methods [11–13]. Only compound **8** exhibited moderate antibacterial activity against *S. aureus* and methicillin-resistant *S. aureus* with 50% inhibitory concentrations (IC<sub>50</sub>)/minimum inhibitory concentrations (MIC) of 4.96/10.0 μg/mL, and 3.46/5.0 μg/mL. The IC<sub>50</sub>/MIC values of the positive antibacterial control ciprofloxacin were 0.13/0.50 μg/mL and 0.14/0.50 μg/mL.

## Experimental Part

### General

FAB-MS (negative ion mode) and HR-ESI-MS (negative ion mode) spectra were measured on *VG AutoSpec 3000* and *API Qstar Pulsar LC/TOF* spectrometers, respectively. The matrix for FAB-MS was glycerol. Optical rotations: *SEPA-3000* automatic digital polarimeter. IR Spectra: *Bio-Rad FTS-135* spectrometer; in cm<sup>-1</sup>. UV Spectra: *JASCO V-560 UV/VIS* spectrophotometer. 1D- and 2D-NMR spectra were run on a *Bruker AM-400* or a *DRX-500* instruments operating at 400 or 500 MHz for <sup>1</sup>H, 100 or 125 MHz for <sup>13</sup>C, respectively. Coupling constants were expressed in Hertz and chemical shifts were given on a ppm scale with tetramethylsilane as internal standard. CC: *Sephadex LH-20* (*Pharmacia Fine Chemical Co., Ltd.*); silica gel (200–300 mesh, *Qingdao Makall Group Co., Ltd.*); *MCI gel CHP 20P* (*Mitsubishi Chemical Co.*). TLC was carried out on silica gel H-precoated plates (*Qingdao Makall Group Co., Ltd.*) with chloroform/methanol/water (8:2:0.2). Spots

were detected by spraying with 10% sulfuric acid reagent followed by heating. GC analysis was run on a *Shimadzu GC-14C* gas chromatograph.

### Plant Material

The fresh pericarps of *J. sigillata* were collected in August 2007 in the botanical garden of Kunming Institute of Botany, Chinese Academy of Sciences, Yunnan province, China, and identified by Prof. *Xiao Cheng* (Botanical Garden, Kunming Institute of Botany, Chinese Academy of Sciences). The voucher specimen (KIB-ZL2007002) has been deposited in the State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences. The fresh material was soaked into 80% aqueous acetone at room temperature as soon as collected.

### Extraction and Isolation

The fresh pericarps of *J. sigillata* (37 kg) were extracted three times with 80% aqueous acetone (30 L) at room temperature (each 7 days). After removal of the organic solvent under reduced pressure, the aqueous fraction was extracted with equivoluminal  $\text{CHCl}_3$  and EtOAc, successively, to give a  $\text{CHCl}_3$  fraction (24 g) and an EtOAc fraction (240 g).

The EtOAc fraction (240 g) was subjected to CC over *Sephadex LH-20*, eluted with MeOH/ $\text{H}_2\text{O}$  (0:1–1:0) to afford four fractions (*Frs. 1–4*). Further CC on *MCI-gel CHP20P* and *Sephadex LH-20*, both of which were eluted with MeOH/ $\text{H}_2\text{O}$  (0:1–4:6) gave **1** (2.0 mg) and **3** (3.0 mg) from *Fr. 1* (4.9 g); **2** (44 mg) from *Fr. 2* (3.8 g); and **4** (114 mg) from *Fr. 3* (21.8 g); respectively. *Fr. 4* (3.3 g) was subjected to CC over silica gel, eluted with petroleum ether/ethyl acetate (7:3, 1:1, and 2:8 successively), and then over *Sephadex LH-20* and *MCI-gel CHP20P*, eluted with MeOH/ $\text{H}_2\text{O}$  (0:1–3:7), to afford **5** (35 mg), **6** (6 mg), **7** (48 mg), **8** (25 mg), and **9** (20 mg).

**4,6-Dihydroxy- $\alpha$ -tetralone-4-O-[6'-O-(3'',4'',5''-trihydroxybenzoyl)]- $\beta$ -D-glucopyranoside (1)**—White amorphous powder,  $[\alpha]_{\text{D}}^{16} = 0$  ( $c = 0.08$ , MeOH). UV (MeOH): 290 (3.69), 224 (3.86), 207 (3.85). IR (KBr)  $\text{cm}^{-1}$ : 3439, 1627, 1606, 1042, 577.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR data: Table 1. FAB-MS: 491 ( $[M - \text{H}]^-$ ). HR-ESI-MS: 491.1210 ( $[M - \text{H}]^-$ ,  $\text{C}_{23}\text{H}_{23}\text{O}_{12}^-$ ; calc. 491.1190).

**(4S)-4,5-Dihydroxy- $\alpha$ -tetralone-4-O-[6'-O-(3'',4'',5''-trihydroxybenzoyl)]- $\beta$ -D-glucopyranoside (2)**—White amorphous powder,  $[\alpha]_{\text{D}}^{26} = +10.3$  ( $c = 0.20$ , MeOH). UV (MeOH): 321 (3.87), 235 (4.24), 198 (4.14). IR (KBr)  $\text{cm}^{-1}$ : 3422, 1679, 1609, 1348, 1319, 1232, 1074, 1038, 589.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR data: Table 1. FAB-MS: 491 ( $[M - \text{H}]^-$ ). HR-ESI-MS: 491.1191 ( $[M - \text{H}]^-$ ,  $\text{C}_{23}\text{H}_{23}\text{O}_{12}^-$ ; calc. 491.1189).

**(4S)-4,5,6-Trihydroxy- $\alpha$ -tetralone-4-O-[6'-O-(3'',4'',5''-trihydroxybenzoyl)]- $\beta$ -D-glucopyranoside (3)**—White amorphous powder,  $[\alpha]_{\text{D}}^{16} = 14.2$  ( $c = 0.11$ , MeOH). UV (MeOH): 321 (3.87), 220 (4.03), 203 (4.08). IR (KBr)  $\text{cm}^{-1}$ : 3425, 1611, 1318, 1225, 1038, 592.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR data: Table 1. FAB-MS: 507 ( $[M - \text{H}]^-$ ). HR-ESI-MS: 507.1118 ( $[M - \text{H}]^-$ ,  $\text{C}_{23}\text{H}_{23}\text{O}_{13}^-$ ; calc. 507.1139).

### Acidic Hydrolysis of Compounds 1–3

Compounds **1** (1.5 mg), **2** (4.0 mg) and **3** (1.5 mg) were separately hydrolyzed with 2 M HCl/dioxane (1:1, 4 mL) under reflux for 6 h. The reaction mixture was extracted with EtOAc for 4 times. The aqueous layer was neutralized with 2 M NaOH and dried under reduced pressure. The residue was dissolved in pyridine (2 mL). L-cysteine methyl ester hydrochloride (about 1.5 mg) was added and the mixture was kept at 60 °C for 1 h. Next,

trimethylsilylimidazole (about 1.5 mL) was added to the reaction mixture in ice water and kept at 60 °C for 30 min. Then, the mixture was subjected to GC analysis, run on a *Shimadzu GC-14C* gas chromatograph equipped with a 30 m × 0.32 mm i.d. *30QC2/AC-5* quartz capillary column and an H<sub>2</sub> flame ionization detector with the following conditions: column temperature, 180–280 °C; programmed increase, 3 °C/min; carrier gas, N<sub>2</sub> (1 mL/min); injector and detector temperature, 250 °C; injection volume, 4 μL; and split ratio, 1/50. The configuration of the sugar moiety was determined by comparing the retention time with the derivatives of authentic samples. The retention times of D-/L-glucose were 19.21/14.94 min.

### Enzymatic Hydrolysis of Compound 2

A solution of **2** (10 mg) in H<sub>2</sub>O was incubated with α-glucosidase (*Sigma Chemical Co.*, 8.92 U/mg, 8 mg) at 37 °C for 7 days. The reaction mixture was extracted with CHCl<sub>3</sub> for 5 times. The CHCl<sub>3</sub> fraction was evaporated to dryness and subjected to column chromatography over *MCI-gel CHP20P*, eluted successively with water and methanol, to afford **7** (2 mg), [α]<sub>D</sub><sup>18</sup> = +16.7 (*c* = 0.03, MeOH).

### Antifungal and Antibacterial Bioassays

All organisms are obtained from the American Type Culture Collection (Manassas, VA) and include the fungi *Candida albicans* ATCC 90028, *C. glabrata* ATCC 90030, *C. krusei* ATCC 6258, *Cryptococcus neoformans* ATCC 90113, and *Aspergillus fumigatus* ATCC 204305 and the bacteria *Staphylococcus aureus* ATCC 29213, methicillin-resistant *S. aureus* ATCC 33591 (MRS), *Escherichia coli* ATCC 35218, *Pseudomonas aeruginosa* ATCC 27853, and *Mycobacterium intracellulare* ATCC 23068. Susceptibility testing is performed using a modified version of the CLSI methods [11] [12]. *M. intracellulare* is tested using a modified method of *Franzblau et al* [14]. Samples (**2**, **4**, and **7–9**) are serially-diluted in 20% DMSO/saline and transferred in duplicate to 96-well flat bottom microplates. Microbial inocula are prepared by correcting the OD<sub>630</sub> of the microbe suspensions in incubation broth to afford final target inocula after addition to the samples. All organisms are read spectrometrically prior to and after incubation. The detailed protocol has been described in a previous paper [15].

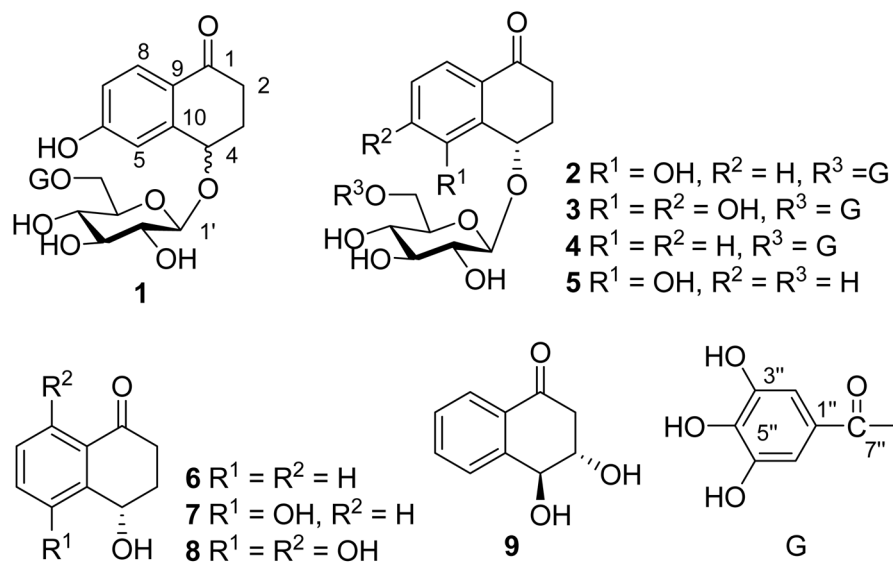
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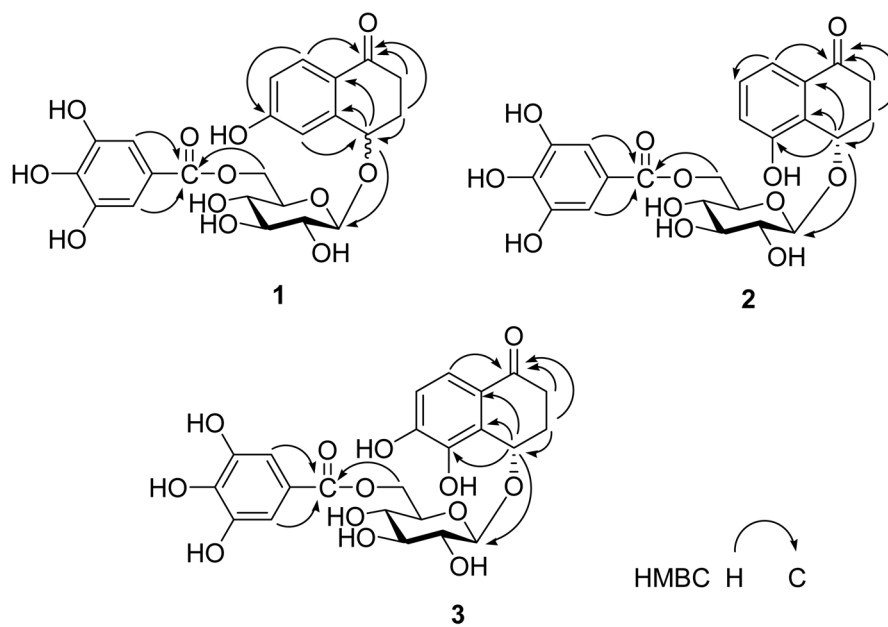
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**Figure 1.**  
-Tetralone Derivatives from the Fresh Pericarps of *Juglans sigillata*





**Figure 2.**  
Key HMBC Correlations of Compounds 1–3



$^{13}\text{C}$ - and  $^1\text{H}$ -NMR Data of **1-3** (in  $\text{CD}_3\text{COCD}_3$ , 500 MHz and 125 MHz for  $^1\text{H}$  and  $^{13}\text{C}$  NMR, respectively, in ppm,  $J$  values in Hz)

Table 1

No.	1		2		3	
	(C)	(H)	(C)	(H)	(C)	(H)
1	197.8		199.7		199.0	
2	35.0	2.65 ( <i>ddd</i> , $J = 4.5, 7.0, 17.0$ )	33.4	2.88 ( <i>dt</i> , $J = 19.0, 6.0$ )	33.1	2.78 ( <i>ddd</i> , $J = 4.5, 9.5, 18.5$ )
		2.28-2.37 ( <i>m</i> )		2.36-2.44 ( <i>m</i> )		2.34 ( <i>ddd</i> , $J = 4.5, 8.5, 18.5$ )
3	31.2	2.28 ( <i>dt</i> , $J = 17.0, 5.0$ )	29.0	2.33 ( <i>dt</i> , $J = 21.0, 4.7$ )	29.2	2.28 ( <i>dt</i> , $J = 17.5, 4.5$ )
		2.08-2.13 ( <i>m</i> )		2.11 ( <i>dt</i> , $J = 16.0, 4.7$ )		2.05-2.09 ( <i>m</i> )
4	74.4	4.82 ( <i>dd</i> , $J = 10.0, 4.3$ )	71.0	5.24 ( <i>t</i> , $J = 4.0$ )	71.0	5.25 ( <i>t</i> , $J = 4.0$ )
5	114.5	7.08 ( <i>d</i> , $J = 2.4$ )	156.0		143.0	
6	163.1		121.8	7.14 ( <i>d</i> , $J = 7.0$ )	151.6	
7	116.3	6.81 ( <i>dd</i> , $J = 8.6, 2.4$ )	130.2	7.26 ( <i>t</i> , $J = 7.8$ )	115.8	6.89 ( <i>d</i> , $J = 8.4$ )
8	130.0	7.74 ( <i>d</i> , $J = 8.6$ )	118.2	7.37 ( <i>d</i> , $J = 7.8$ )	120.6	7.35 ( <i>d</i> , $J = 8.4$ )
9	124.3		133.5		124.9	
10	147.0		128.7		129.3	
1	103.7	4.60 ( <i>d</i> , $J = 7.9$ )	103.5	4.64 ( <i>d</i> , $J = 8.0$ )	103.2	4.64 ( <i>d</i> , $J = 7.9$ )
2	74.3	3.31 ( <i>dd</i> , $J = 8.9, 7.9$ )	74.4	3.22 ( <i>dd</i> , $J = 8.0, 9.0$ )	74.2	3.22 ( <i>t</i> , $J = 8.5, 7.9$ )
3	77.1	3.48 ( <i>t</i> , $J = 8.9$ )	76.9	3.48 ( <i>t</i> , $J = 8.9$ )	76.8	3.47 ( <i>t</i> , $J = 8.9$ )
4	71.1	3.42 ( <i>t</i> , $J = 9.4$ )	70.7	3.41 ( <i>t</i> , $J = 9.4$ )	71.3	3.43 ( <i>t</i> , $J = 9.4$ )
5	76.5	3.67-3.71 ( <i>m</i> )	74.7	3.68-3.70 ( <i>m</i> )	74.6	3.65-3.69 ( <i>m</i> )
6	63.4	4.57 ( <i>dd</i> , $J = 11.8, 2.5$ )	64.4	4.57 ( <i>dd</i> , $J = 12.0, 2.5$ )	64.4	4.55 ( <i>dd</i> , $J = 11.8, 2.0$ )
		4.36 ( <i>dd</i> , $J = 11.8, 7.2$ )		4.35 ( <i>dd</i> , $J = 12.0, 8.5$ )		4.34 ( <i>dd</i> , $J = 11.8, 7.1$ )
1	121.0		120.8		120.8	
2	109.7	7.11 ( <i>s</i> )	109.7	7.12 ( <i>s</i> )	109.7	7.10 ( <i>s</i> )
3	145.8		145.8		145.6	
4	139.0		139.1		138.9	
5	145.8		145.8		145.6	
6	109.7	7.11 ( <i>s</i> )	109.7	7.12 ( <i>s</i> )	109.7	7.10 ( <i>s</i> )
7	167.3		167.3		167.4	