Norlignans and Phenylpropanoids from *Metasequoia glyptostroboides* HU et CHENG

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Five new compounds, *i.e.*, the three new norlignans metasequirins G–I (**1**–**3**) and the two new phenylpropanoids 7-(3-ethoxy-5-methoxyphenyl)propane-7,8,9-triol (=1-(3-ethoxy-5-methoxyphenyl)-propane-1,2,3-triol; **4**) and 7-(3-hydroxy-5-methoxyphenyl)propane-7,8,9-triol (=1-(3-hydroxy-5-methoxy-phenyl)propane-1,2,3-triol; **5**), were isolated from the branches and stems of *Metasequoia glyptostroboides* HU et CHENG. Their structures were elucidated by physical, chemical, and spectroscopic methods, including 1D- and 2D-NMR and HR-ESI-MS. The cytotoxicites of the five compounds were tested against A549 and Colo 205 cell lines by the MTT method.

Introduction. – *Metasequoia glyptostroboides* HU et CHENG is the solitary species of the Taxodiaceae family, *Metasequoia* genus, which is often considered as a living fossil plant. The leaves and fruits of *M. glyptostroboides* were used to remedy carbuncle and ringworm [1]. In previous studies, flavonoids [2–5], diterpenoids [5–8], norlignans [9–10], and sterols [5][11] were isolated from this plant. As a part of our ongoing screening program for bioactive natural secondary metabolites, our current investigation on the branches and stems of *M. glyptostroboides* led to the isolation of the three new norlignans metasequirins G–I[1]) (**1**–**3**) and the two new phenylpropanoids 7-(3-ethoxy-5-methoxyphenyl)propane-7,8,9-triol (**4**) and 7-(3-hydroxy-5-methoxy-phenyl)propane-7,8,9-triol (**5**) (*Fig. 1*). In addition, all five compounds were evaluated for cytotoxicities against A549 and Colo 205 cell lines.

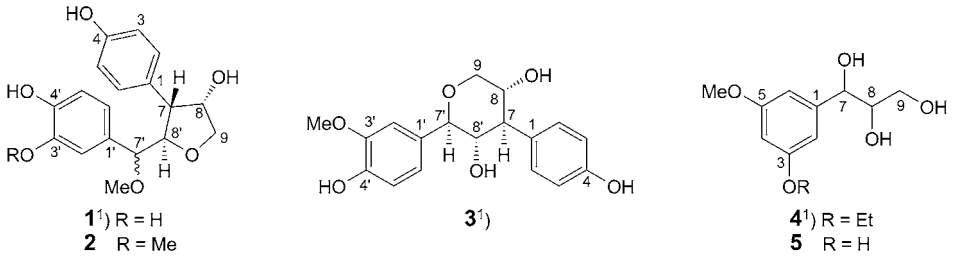

Fig. 1. *New compounds* **1**–**5**, *isolated from* Metasequoia glyptostroboides

[1]) Trivial atom numbering; for systematic names, see *Exper. Part.*

Results and Discussion. – Compound **1** was obtained as a brown gum, and had a molecular formula $C_{18}H_{20}O_6$ as determined by HR-ESI-MS (*m/z* 355.1160 ($[M+Na]^+$). The ^{1}H-NMR spectrum (*Table 1*) showed two pairs of coupled aromatic H-atoms at δ(H) 6.69 (*d*, *J* = 8.5 Hz) and 6.57 (*d*, *J* = 8.5 Hz), suggesting the presence of a 1,4-disubstituted aromatic ring *A*. An obvious *ABX* pattern at δ(H) 6.63 (*d*, *J* = 8.0 Hz), 6.61 (*d*, *J* = 2.0 Hz), and 6.54 (*dd*, *J* = 8.0, 2.0 Hz) was observed which indicated the presence of another, 1′,3′,4′-trisubstituted aromatic ring *C* (*Fig. 2*) The ^{1}H,^{1}H-COSY cross-peaks between H–C(7′)/H–C(8′)/H–C(7)/H–C(8)/CH_2C(9), along with the HMBC cross-peaks between H–C(8′) and C(9), indicated the presence of the six-membered subfragment *B* (*Fig. 2*). Furthermore, the HMBCs H–C(7)/C(1) and H–C(7′)/C(1′) suggested that rings *A* and *C* were linked with *B* by the bonds C(1) – C(7) and C(1′) – C(7′), respectively. A MeO group was assigned to C(7′) by the HMBC cross-peak MeO (δ(H) 3.18)/C(7′). The structure of **1** was similar to that of metasequirin F [12], sharing a similar coupling constant *J*(H–C(7),H–C(8))

Table 1. *^{1}H- and ^{13}C-NMR Data* (CD_3OD, 400 and 100 MHz, resp.) *of Compounds* **1** *and* **2**[1])[a]). δ in ppm, *J* in Hz.

	1				**2**	
	δ(H)	δ(C)	^{1}H,^{1}H-COSY	HMBC	δ(H)	δ(C)
C(1)		133.4 (*s*)				133.1 (*s*)
H–C(2)	6.69 (*d*, *J* = 8.5)	129.9 (*d*)	H–C(3)	C(1), C(3), C(4), C(5), C(6), C(7)	6.63 (*d*, *J* = 6.8)	129.8 (*d*)
H–C(3)	6.57 (*d*, *J* = 8.5)	116.5 (*d*)	H–C(2)	C(1), C(2), C(5), C(6)	6.55 (*d*, *J* = 6.8)	116.2 (*d*)
C(4)		157.3 (*s*)				157.0 (*s*)
H–C(5)	6.57 (*d*, *J* = 8.5)	116.5 (*d*)	H–C(6)	C(1), C(2), C(3), C(6)	6.55 (*d*, *J* = 6.8)	116.2 (*d*)
H–C(6)	6.69 (*d*, *J* = 8.5)	129.9 (*d*)	H–C(5)	C(1), C(2), C(3), C(4), C(5), C(7)	6.63 (*d*, *J* = 6.8)	129.8 (*d*)
H–C(7)	2.87 (*dd*, *J* = 7.0, 4.8)	57.4 (*d*)	H–C(8), H–C(8′)	C(1), C(2), C(6), C(8), C(8′)	2.79 (*dd*, *J* = 7.0, 4.0)	57.6 (*d*)
H–C(8)	4.22 (*dd*, *J* = 9.5, 4.8)	80.8 (*d*)	H–C(7), CH_2(9)		4.08 – 4.10 (*m*)	90.9 (*d*)
CH_2(9)	4.09, 3.83 (2*dd*, each *J* = 9.5, 4.5)	75.5 (*t*)	H–C(8)		4.08 – 4.10 (*m*)	75.3 (*t*)
C(1′)		130.9 (*s*)				130.4 (*s*)
H–C(2′)	6.61 (*d*, *J* = 2.0)	116.4 (*d*)		C(1′), C(3′), C(4′), C(5′), C(7′)	6.54 (*s*)	112.3 (*d*)
C(3′)		146.6 (*s*)				149.2 (*s*)
C(4′)		146.7 (*s*)				148.0 (*s*)
H–C(5′)	6.63 (*d*, *J* = 8.0)	116.03d	H–C(6′)	C(1′), C(2′), C(3′), C(4′)	6.67 – 6.68 (*m*)	115.7 (*d*)
H–C(6′)	6.54 (*dd*, *J* = 8.0, 2.0)	121.4 (*d*)	H–C(5′)	C(2′), C(3′), C(4′), C(7′)	6.67 – 6.68 (*m*)	122.9 (*d*)
H–C(7′)	4.11 (*d*, *J* = 7.0)	87.2 (*d*)	H–C(8′)	C(1′), C(2′), C(6′), C(8′)	4.16 (*d*, *J* = 7.0)	87.5 (*d*)
H–C(8′)	4.03 (*dd*, *J* = 7.0)	91.0 (*d*)	H–C(7), H–C(7′)	C(1), C(7), C(7′), C(9)	4.23 (*dd*, *J* = 7.0, 4.0)	80.8 (*d*)
*Me*O–C(3′)					3.62 (*s*)	56.3 (*q*)
*Me*O–C(7′)	3.18 (*s*)	56.8 (*q*)		C(7′)	3.18 (*s*)	56.6 (*q*)

[a]) Assignments were confirmed by HSQC, ^{1}H,^{1}H-COSY, and HMBC experiments.

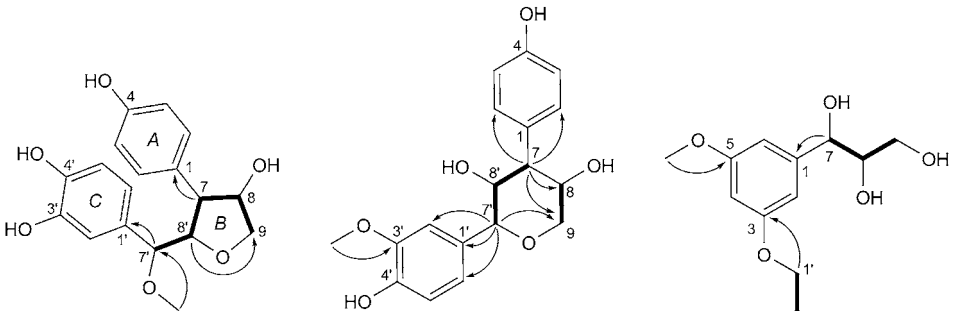

Fig. 2. *Key* $^1H,^1H$*-COSY* (—) *and HMBC* (H → C) *features of* **1**, **3**, *and* **4**

(= 4.8 Hz) but having different coupling constants of J(H–C(7),H–C(8′)) (= 7.0 Hz) and J(H–C(7′),H–C(8′)) (= 7.0 Hz) (metasequirin F: $J(7,8) = 3.0$ Hz, $J(7,8') = 4.8$ Hz, and $J(7',8') = 3.6$ Hz). By comparing the NMR data with those of metasequirin F, the relative configuration of H–C(8) was established as β. The coupling constants of **1** suggested that H–C(7) was on the same β side as H–C(8), and H–C(8′) was on the opposite α side. Although the NOESY correlations H–C(7)/H–C(7′) and a large coupling constant J(H–C(7′),H–C(8′)) were observed, the orientation of H–C(7′) could not be deduced. Thus, the structure given in *Fig. 1* was deduced for **1**, which was named metasequirin G[1]).

Compound **2** was obtained as a brown gum. The molecular formula was $C_{19}H_{22}O_6$ as determined by the $[M + Na]^+$ ion peak at m/z 369.1311 in the HR-ESI-MS, appearing 14 mass units higher than that of **1**. The data of the NMR spectra (*Table 1*) demonstrated that **2** was an analogue of **1**, carrying an extra MeO group at C(3′). Furthermore, the 2D-NMR data demonstrated that the other parts of **2** were the same as those of **1**. Thus, the structure of **2** was elucidated, which was named metasequirin H[1]) (*Fig. 1*).

Compound **3** was obtained as a brown gum. The molecular formula was $C_{18}H_{20}O_6$, as established by HR-ESI-MS (m/z 355.1149 ($[M + Na]^+$)). The ^{1}H- and ^{13}C-NMR spectra (*Table 2*) of **3** showed a quite similar pattern to those of (2*R*,3*R*,4*S*,5*S*)-2,4-bis(4-hydroxyphenyl)tetrahydro-2*H*-pyran-3,5-diol [13], suggesting that **3** possessed a similar framework, except for an extra MeO group (and the relative configuration). The key HMBCs between MeO (δ(H) 3.81) and C(3′) indicated that the extra MeO was attached to C(3′) (*Fig. 2*). In accord to the former report [13], H–C(8) was assigned as β-oriented. In the NOESY plot, the key correlation H–C(8)/H–C(8′) suggested that H–C(8′) was β-oriented as well, and correlations H–C(8′)/H–C(2) and H–C(6) indicated that H–C(7) was α-oriented. The α-orientation of H–C(7′) was demonstrated by the NOESY cross-peak H–C(7)/H–C(7′) (*Fig. 3*). Thus, the relative configuration of **3** was as shown in *Fig. 1*, and the compound was named metasequirin I[1]).

Compound **4** was obtained as a yellowish gum with a molecular formula of $C_{12}H_{18}O_5$ as deduced from the HR-ESI-MS (m/z 265.1058 ($[M + Na]^+$). The ^{1}H-NMR spectrum (*Table 3*) showed three low-field *s* at δ(H) 6.92 (*s*), 6.77, and 6.77, indicating the presence of a 1,3,5-trisubstituted aromatic ring. In the ^{1}H,^{1}H-COSY plot, the

Table 2. *^{1}H- and ^{13}C-NMR Data* (CD_3OD, 400 and 100 MHz, resp.) *of Compound* **3**[1])[a]). δ in ppm, J in Hz.

	δ(H)	δ(C)	^{1}H,^{1}H-COSY	HMBC
C(1)		131.0 (*s*)		
H–C(2)	6.78 (*d*, J = 8.6)	131.5 (*d*)	H–C(3)	C(4), C(6), C(7)
H–C(3)	6.68 (*d*, J = 8.6)	116.3 (*d*)	H–C(2)	C(1), C(4)
C(4)		157.6 (*s*)		
H–C(5)	6.68 (*d*, J = 8.6)	116.3 (*d*)	H–C(6)	C(1), C(4)
H–C(6)	6.78 (*d*, J = 8.6)	131.5 (*d*)	H–C(5)	C(2), C(4), C(7)
H–C(7)	2.66 (*d*, J = 5.1)	57.7 (*d*)	H–C(8′)	C(2), C(6), C(8), C(9)
H–C(8)	4.20–4.23 (*m*)	80.5 (*d*)	CH_2(9)	C(8′), C(9)
CH_2(9)	3.99–4.42, 3.77–3.78 (2*m*)	76.3 (*t*)	H–C(8)	C(8′)
C(1′)		135.2 (*s*)		
H–C(2′)	6.50 (*d*, J = 2.0)	115.9 (*d*)		C(3′), C(4′), C(6′), C(7′)
C(3′)		149.1 (*s*)		
C(4′)		147.5 (*s*)		
H–C(5′)	6.74 (*d*, J = 8.3)	112.4 (*d*)		C(1′), C(3′), C(4′)
H–C(6′)	6.30 (*dd*, J = 8.3, 2.1)	120.5 (*d*)		C(2′), C(3′), C(7′)
H–C(7′)	4.22 (*d*, J = 8.8)	75.4 (*d*)	H–C(8′)	C(1′), C(2′), C(6′), C(9)
H–C(8′)	4.43–4.45 (*m*)	86.7 (*d*)	H–C(7), H–C(7′)	C(1′), C(7), C(7′)
*Me*O–C(3′)	3.81 (*s*)	56.7 (*q*)		C(3′)

[a]) Assignments were confirmed by HSQC, ^{1}H,^{1}H-COSY, and HMBC experiments.

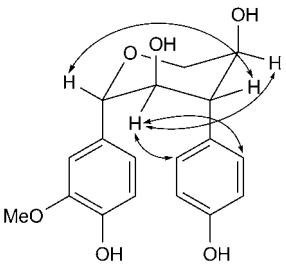

Fig. 3. *Selected NOESY* (H ↔ H) *correlations of* **3**

correlations H–C(7)/H–C(8)/CH_2(9) and CH_2(1′)/Me(2′) were observed. Furthermore, the HMBC cross-peaks H–C(7)/C(1) and CH_2(1′)/C(3) revealed that the C_3 unit was connected with the aromatic ring *via* the C(1)–C(7) bond, and the EtO group was positioned at C(3) (*Fig. 2*). Likewise, a MeO group was located at C(5). Thus, **4** was elucidated to be 7-(3-ethoxy-5-methoxyphenyl)propane-7,8,9-triol. Its relative configuration cannot be assumed on the basis of the coupling constant between H–C(7) and H–C(8) (J = 6.7 Hz) [14].

Compound **5** was obtained as a yellowish gum. The molecular formula was $C_{10}H_{14}O_5$ as shown by the HR-ESI-MS (*m*/*z* 237.0740 ($[M + Na]^+$)). The ^{1}H- and ^{13}C-NMR data (*Table 3*) were similar to those of compound **4**, except that the EtO group at C(3) was replaced by an OH group. Thus, the structure of **5** was elucidated to be 7-(3-hydroxy-5-methoxyphenyl)propane-7,8,9-triol.

Table 3. *^{1}H- and ^{13}C-NMR Data* (CD_3OD, 400 and 100 MHz, resp.) *of Compounds* **4** *and* **5**[a]). δ in ppm, J in Hz.

	4				**5**	
	δ(H)	δ(C)	^{1}H,^{1}H-COSY	HMBC	δ(H)	δ(C)
C(1)		132.2 (*s*)				134.4 (*s*)
H–C(2)	6.92 (*s*)	111.8 (*d*)		C(1), C(3), C(5), C(6), C(7)	6.92 (*s*)	110.9 (*d*)
C(3)		147.4 (*s*)				145.3 (*s*)
H–C(4)	6.77 (*s*)	116.0 (*d*)		C(1), C(2), C(3), C(5)	6.77 (*s*)	114.7 (*d*)
C(5)		149.1 (*s*)				147.0 (*s*)
H–C(6)	6.77 (*s*)	121.4 (*d*)		C(1), C(2), C(3), C(5), C(7)	6.77 (*s*)	119.1 (*d*)
H–C(7)	4.20 (*d*, J = 6.7)	83.6 (*d*)	H–C(8)	C(1), C(1′), C(2), C(6), C(9)	4.20 (*d*, J = 6.7)	75.9 (*d*)
H–C(8)	3.64 – 3.66 (*m*)	77.1 (*d*)	H–C(7), CH_2(9)	C(7)	3.65 – 3.66 (*m*)	72.8 (*d*)
CH_2(9)	3.44 (*dd*, J = 11.5, 3.9), 3.30 (overlapped)	64.0 (*t*)	H–C(8)	C(7), C(8)	3.37 – 3.39 (*m*)	62.6 (*t*)
CH_2(1′)	3.36 – 3.38 (*m*)	65.2 (*t*)	H–C(2′)	C(2′), C(3)		
Me(2′)	1.17 (*t*, J = 7.0)	15.6 (*q*)	H–C(1′)	C(1′)		
MeO	3.85 (*s*)	56.4 (*q*)		C(5)	3.85 (*s*)	55.5 (*q*)

[a]) Assignments were confirmed by HSQC, ^{1}H,^{1}H-COSY, and HMBC experiments.

Compounds **1** – **5** were tested for cytotoxicities against A549 and and Colo 205 cell lines [15]. AMD (aminoguanidine) was used as a positive control. However, all the compounds showed mild activities with IC_{50} values in the range of 50 – 100 μM.

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Experimental Part

General. TLC: *$HSGF_{254}$* Silica-gel plates (SiO_2; 10 – 40 μm; *Yantai Huiyou*, China); detection by spraying with 10% H_2SO_4 reagent. Column chromatography (CC): SiO_2 (100 – 200 or 200 – 300 mesh; *Yantai Huiyou*, China) and *Sephadex LH-20* (*GE Healthcare Bio-Sciences AB*, Sweden). Prep. HPLC: *Shimadzu-PRC-ODS-EV0233* column and *Shimadzu-LC-6AD* system; t_R in min. Optical rotations: *Jasco-P-2000* polarimeter. UV Spectra: *Shimadzu-UV-2550* spectrophotometer; in MeOH; λ_{max} (log ε) in nm. IR Spectra: *Bruker-FT-IR-Vector*-22 spectrometer; KBr pellets; $\tilde{\nu}$ in cm^{-1}. ^{1}H- and ^{13}C-NMR Spectra: *Bruker-Avance-400* spectrometers; at 400 (^{1}H) and 100 (^{13}C) MHz; δ in ppm rel. to Me_4Si as internal standard, J in Hz. ESI-MS: *Agilent-1100* mass spectrometer and *Autospec-Ultima-ETOF* apparatus; in *m*/*z*. HR-ESI-MS: *Q-TOF* micro mass spectrometer (*Waters*, USA); in *m*/*z*.

Plant Material. The branches and stems of *M. glyptostroboides* were collected in Jiangxi Province, P. R. China, in August 2009, and were authenticated by Prof. *Hanmin Zhang*, Department of Pharmacognosy, School of Pharmacy, Second Military Medical University. A voucher specimen (No. 2009MGH) is deposited with the School of Pharmacy, Shanghai Jiao Tong University.

Extraction and Isolation. The branches and stems of *M. glyptostroboides* (9.5 kg) were successively extracted with 95% EtOH (10 × 6 l, each for 24 h). The 95% EtOH extract (167.6 g) was suspended in H_2O (5 l) and extracted with petroleum ether (3 × 5 l succesively, each for 24 h; 30.0 g), CH_2Cl_2 (6 × 5 l successively, each for 24 h; 20.0 g), AcOEt (6 × 5 l succesively, each for 24 h; 12.0 g), and BuOH (3 × 5 l succesively, each for 24 h; 20.0 g). The CH_2Cl_2 extract *A* (20.0 g) was subjected to CC (SiO_2 (200–300 mesh, 250.0 g), 6 × 70 cm, CH_2Cl_2/MeOH 100:1 → 1:1 (each 4.0 l)): *Fractions A1–A11. Fr. A4* (1.2 g) was subjected to CC (SiO_2 (200–300 mesh, 12.0 g), 4 × 52 cm, petroleum ether/acetone 10:1 → 1:1 (each 2.0 l)): *Frs. A4.1–A4.8. Fr. A4.5* (90.0 mg) was separated by prep. HPLC (MeOH/H_2O 3:7, flow rate 8 ml/min): **4** (2.0 mg; t_R 32.9). *Fr. A5* (1.5 g) was subjected to CC (SiO_2 (200–300 mesh, 10.0 g), 4 × 52 cm, CH_2Cl_2/MeOH 100:1 → 20:1 (each 2.0 l)): *Frs. A5.1–A5.7. Fr. A5.3* (138.6 mg) was separated by prep. HPLC (MeOH/H_2O 3:7, flow rate 8 ml/min): **2** (2.0 mg, t_R 25). The AcOEt extract *B* (12.0 g) was subjected to CC (SiO_2 (200–300 mesh, 150.0 g), 6 × 70 cm, CH_2Cl_2/MeOH 100:1 → 1:1 (each 4 l)): *Frs. B1–B10. Fr. B9* (3.0 g) was further subjected to CC (*Sephadex LH-20* (300.0 g), 4 × 120 cm, MeOH): *Frs. B9.1–B9.3. Fr. B9.1* (452.1 mg) was separated by prep. HPLC (MeOH/H_2O 1:4, flow rate 8 ml/min): **5** (3.0 mg; t_R 9.3). *Fr. B9.2* (212.3 mg) was separated by prep. HPLC (MeOH/H_2O 1:4, flow rate 8 ml/min): **3** (3.0 mg; t_R 30). *Fr. B10* (3.0 g) was further subjected to CC (SiO_2 (200–300 mesh, 30.0 g), 4 × 52 cm, CH_2Cl_2/MeOH 15:1 → 2:1 (each 2 l)): *Frs. B10.1–B10.8. Fr. B10.4* (195.0 mg) was separated by prep. HPLC (MeOH/H_2O 1:3, flow rate 8 ml/min): **1** (3.0 mg, t_R 35.2).

Assay for Cytotoxic Activities. A cytotoxicity assay was carried out according to *Denizot* and *Lang* [14]. The cells (concentration $4–6 \cdot 10^4$ cells/ml) were seeded in each well containing *Dulbecco*'s modified *Eagle*'s medium (DMEM, 100 µl) and incubated for 24 h at 37° in an atmosphere containing 5% CO_2. Then, various concentrations of samples were added (10 µl in each well) and left for 72 h at 37° in an atmosphere containing 5% CO_2. Subsequently, 20 µl of FBS-free medium containing 5 mg/ml of MTT (= 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-2*H*-tetrazolium bromide) soln. were added to the wells. After 4 h of incubation at 37°, the medium was discarded, and the formazan blue formed in the cells was dissolved by adding DMSO (100 µl). The optical density was measured at 570 nm with a microplate reader (*WellscanMK-2*, *Labsystems*, Finland). AMD (aminoguanidine) was used as a positive control.

Metasequirin G (= rel-*(3*R*,4*S*,5*S*)-5-[(3,4-Dihydroxyphenyl)methoxymethyl]tetrahydro-4-(4-hydroxyphenyl)furan-3-ol*; **1**): Brown gum. $[\alpha]_D^{25} = +32.0$ ($c = 0.05$, MeOH). UV (MeOH): 310 (sh, 2.29), 275 (1.03), 235 (0.48), 215 (0.94), 200 (1.05). IR: 3430, 2925, 1620, 1516, 1384, 1048, 749, 604. ^{1}H- and ^{13}C-NMR: *Table 1*. HR-ESI-MS: 355.1160 ($[M+Na]^+$, $C_{18}H_{20}NaO_6^+$; calc. 355.1152).

Metasequirin H (= rel-*(3*R*,4*S*,5*S*)-Tetrahydro-5-[(4-hydroxy-3-methoxyphenyl)methoxymethyl]-4-(4-hydroxyphenyl)furan-3-ol*; **2**): Brown gum. $[\alpha]_D^{25} = +46.7$ ($c = 0.05$, MeOH). UV (MeOH): 305 (sh, 2.40), 275 (0.94), 200 (0.43). IR: 3424, 2924, 2855, 1615, 1516, 1457, 1384, 1263, 1156, 1084, 827, 747, 556. ^{1}H- and ^{13}C-NMR: *Table 1*. HR-ESI-MS: 369.1311 ($[M+Na]^+$, $C_{19}H_{22}NaO_6^+$; calc. 369.1309).

Metasequirin I (= rel-*(2*R*,3*S*,4*R*,5*R*)-Tetrahydro-2-(4-hydroxy-3-methoxyphenyl)-4-(4-hydroxyphenyl)-2*H*-pyran-3,5-diol*; **3**): Brown gum. $[\alpha]_D^{25} = +66.2$ ($c = 0.06$, MeOH). UV (MeOH): 305 (sh, 1.83), 280 (0.89), 270 (0.96), 250 (1.04), 220 (0.48), 200 (0.63). IR: 3432, 2925, 1633, 1386, 1242, 1158, 747, 633, 558, 507. ^{1}H- and ^{13}C-NMR: *Table 2*. HR-ESI-MS: 355.1149 ($[M+Na]^+$, $C_{18}H_{20}NaO_6^+$; calc. 355.1152).

7-(3-Ethoxy-5-methoxyphenyl)propane-7,8,9-triol (= *1-(3-Ethoxy-5-methoxyphenyl)propane-1,2,3-triol*; **4**): Yellowish gum. $[\alpha]_D^{25} = +40.4$ ($c = 0.05$, MeOH). UV (MeOH): 310 (1.52), 245 (0.62), 200 (0.55). IR: 3427, 2924, 2855, 1068, 1517, 1459, 1386, 1268, 1157, 1096, 1038, 596. ^{1}H- and ^{13}C-NMR: *Table 3*. HR-ESI-MS: 265.1058 ($[M+Na]^+$, $C_{12}H_{18}NaO_5^+$; calc. 265.1046).

7-(3-Hydroxy-5-methoxyphenyl)propane-7,8,9-triol (= *1-(3-Hydroxy-5-methoxyphenyl)propane-1,2,3-triol*; **5**): Yellowish gum. $[\alpha]_D^{25} = +106.7$ ($c = 0.08$, MeOH). UV (MeOH): 300 (sh, 1.52). IR: 3412, 2972, 2925, 1610, 1517, 1456, 1385, 1228, 1157, 1087, 1046, 880, 747, 561. ^{1}H- and ^{13}C-NMR: *Table 3*. HR-ESI-MS: 237.0740 ($[M+Na]^+$, $C_{10}H_{14}NaO_5^+$; calc. 237.0733).

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