Novel Bibenzyl Derivatives from the Tubers of *Bletilla striata*

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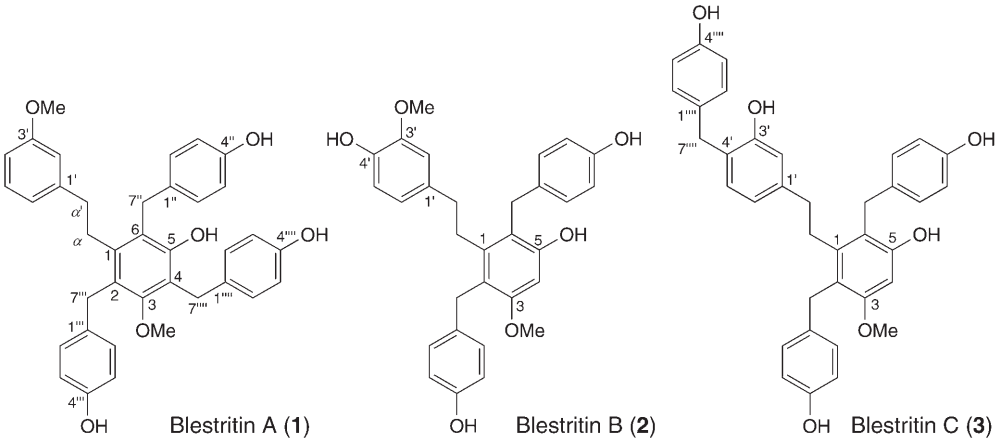
Three novel bibenzyl derivatives, blestritins A–C (**1**–**3**), along with 18 known constituents, were isolated from the tubers of *Bletilla striata* (Orchidaceae), a traditional Chinese medicine used for the treatment of tuberculosis and haemorrhage of the stomach and lungs. Their structures were identified on the basis of spectroscopic analyses.

Introduction. – *Bletilla striata* (THUNB.) REICHB. F. (Orchidaceae) is mainly distributed in East Asia, and its tubers are used as a Chinese traditional medicine for the treatment of tuberculosis and haemorrhage of the stomach or lung [1]. Previous phytochemical studies on *Bletilla* species have led to the isolation of phenanthrene derivatives [2–11], bibenzyls [2][4], flavonoids and phenolic compounds [5], and cyanidin glycosides [12]. As part of our ongoing chemical study on *Bletilla striata*, three novel bibenzyl derivatives, blestritins A–C (**1**–**3**), were isolated from the tubers of *B. striata*, together with 18 known constituents. We report herein the isolation and structural elucidation of these compounds.



Results and Discussion. – Compound **1** was obtained as a white amorphous powder. Its molecular formula was established as $C_{37}H_{36}O_6$ by HR-ESI-MS, giving a quasimolecular ion (*m*/*z* 599.2408 ($[M+Na]^+$)), and by NMR analysis. The IR spectrum showed absorptions at 3405 (OH), 2937 (CH_2), and 1596 and 1511 (aromatic)

cm^{-1}. The UV spectrum with a maximum at 281 nm was in agreement with a bibenzyl (=1,1′-(ethane-1,2-diyl)bis[benzene]) derivative [2]. The structure of **1** was deduced from the ^{1}H- and ^{13}C-NMR (*Table*), ^{1}H,^{1}H-COSY and HMBC (*Figure*), and ROESY data as 2,4,6-tris(4-hydroxybenzyl)-3,3′-dimethoxybibenzyl-5-ol[1]; **1** is a new compound and was assigned the trivial name blestritin A.

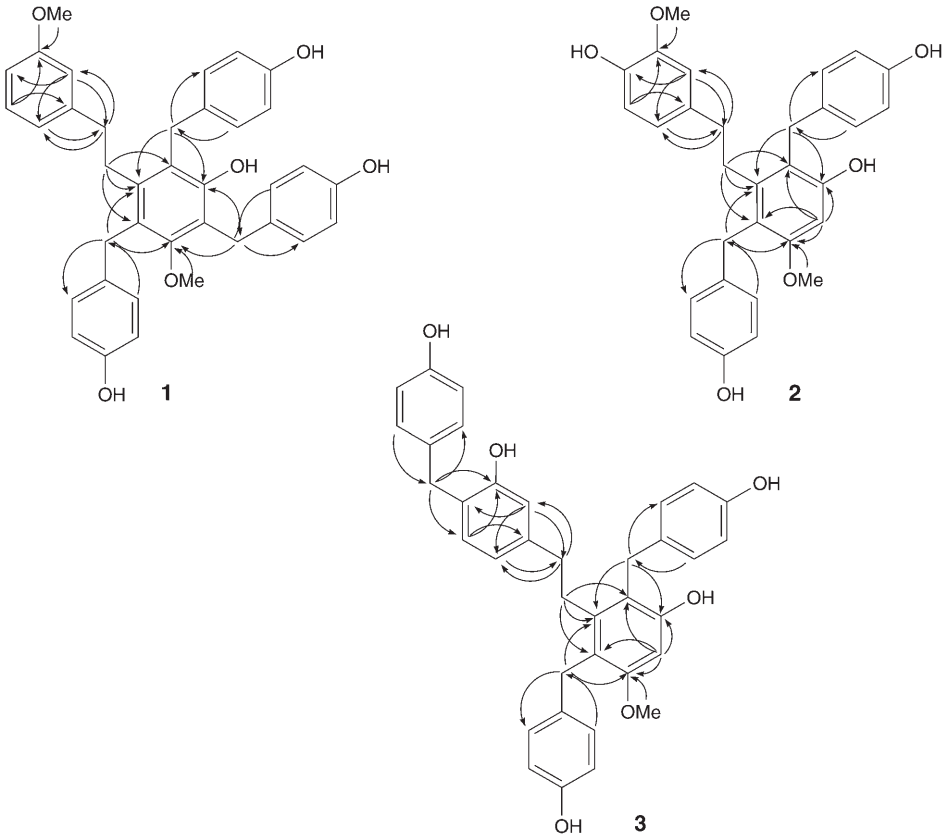


Figure. *Key ^{1}H,^{13}C long-range correlation signals* (^{1}H → ^{13}C) *in the HMBC spectra of* **1**–**3**

The ^{1}H-NMR displayed six *d* or *m* at δ(H) 6.89 (*d*, *J* = 8.6 Hz, 2 H), 6.60–6.64 (*m*, 2 H), 6.83 (*d*, *J* = 8.4 Hz, 2 H), 6.59–6.63 (*m*, 2 H), 7.02 (*d*, *J* = 8.5 Hz, 2 H), and 6.63–6.66 (*m*, 2 H) due to three *AABB* systems characteristic of 4-substituted benzyl groups, and three *s* at δ(H) 4.02 (2 H), 3.93 (2 H), and 4.04 (2 H) due to three benzyl CH_2 groups. Four aliphatic protons due to bibenzyl CH_2 groups appeared as a pair of *m* at δ(H) 2.30–2.40 (2 H) and 2.61–2.71 (2 H), and two MeO at δ(H) 3.45 (*s*) and 3.67 (*s*) and four aromatic protons at δ(H) 6.40 (br. *s*, 1 H), 6.63–6.67 (*m*, 1 H), 7.08 (*t*, *J* = 7.6 Hz, 1 H), and 6.57 (*d*, *J* = 7.6 Hz, 1 H), assigned to H–C(2′), H–C(4′), H–C(5′), and H–C(6′) by the ^{1}H,^{1}H-COSY cross-peaks and coupling patterns, were also observed in the ^{1}H-NMR spectrum. The ^{13}C-NMR spectrum showed 37 C-signals assigned by DEPT experiments to two Me, five CH_2, and sixteen CH groups, and

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

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

	1		**2**		**3**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
C(1)		141.2 (*s*)		143.2 (*s*)		143.2 (*s*)
C(2)		126.2 (*s*)		121.8 (*s*)		120.7 (*s*)
C(3)		158.3 (*s*)		158.7 (*s*)		158.8 (*s*)
C(4) or H–C(4)		121.7 (*s*)	6.48 (*s*)	98.4 (*d*)	6.47 (*s*)	98.4 (*d*)
C(5)		154.6 (*s*)		156.2 (*s*)		156.4 (*s*)
C(6)		125.5 (s)		120.7 (*s*)		120.0 (*s*)
$CH_2(\alpha)$	2.61–2.71 (*m*)	33.9 (*t*)	2.60–2.70 (*m*)	34.0 (*t*)	2.62–2.71 (*m*)	33.8 (*t*)
C(1′)		145.5 (*s*)		135.6 (*s*)		143.2 (*s*)
H–C(2′)	6.40 (br. *s*)	115.0 (*d*)	6.38 (*d*, J = 1.8)	113.3 (*d*)	6.52 (*d*, J = 1.6)	116.1 (*d*)
C(3′)		161.5 (*s*)		149.0 (*s*)		156.4 (*s*)
H–C(4′) or C(4′)	6.63–6.67 (*m*)	113.2 (*d*)		145.8 (*s*)		127.6 (*s*)
H–C(5′)	7.08 (*t*, J = 7.6)	130.7 (*d*)	6.60–6.65 (*m*)	116.3 (*d*)	6.79 (*d*, J = 7.6)	131.7 (*d*)
H–C(6′)	6.57 (*d*, J = 7.6)	122.1 (*d*)	6.44 (*dd*, J = 8.0, 1.8)	121.8 (*d*)	6.38 (*dd*, J = 7.6, 1.6)	120.9 (*d*)
$CH_2(\alpha')$	2.30–2.40 (*m*)	38.2 (*t*)	2.16–2.26 (*m*)	37.5 (*t*)	2.16–2.26 (*m*)	37.9 (*t*)
C(1″)		133.9 (*s*)		134.7 (*s*)		134.9 (*s*)
H–C(2″,6″)	6.89 (*d*, J = 8.6)	130.5 (*d*)	6.94 (*d*, J = 8.4)	130.4 (*d*)	6.92 (*d*, J = 8.6)	130.6 (*d*)
H–(3″,5″)	6.60–6.64 (*m*)	116.5 (*d*)	6.60–6.64 (*m*)	116.2 (*d*)	6.59–6.63 (*m*)	116.4 (*d*)
C(4″)		156.8 (*s*)		156.3 (*s*)		156.4 (*s*)
CH_2(7″)	4.02 (*s*)	32.5 (*t*)	3.91 (*s*)	31.5 (*t*)	3.90 (*s*)	31.7 (*t*)
C(1‴)		134.7 (*s*)		134.8 (*s*)		134.9 (*s*)
H–(2‴,6‴)	6.83 (*d*, J = 8.4)	130.4 (*d*)	6.85 (*d*, J = 8.8)	130.2 (*d*)	6.84 (*d*, J = 8.7)	130.4 (*d*)
H–(3‴,5‴)	6.59–6.63 (*m*)	116.5 (*d*)	6.58–6.62 (*m*)	116.2 (*d*)	6.56–6.59 (*m*)	116.4 (*d*)
C(4‴)		156.8 (*s*)		156.3 (*s*)		156.4 (*s*)
CH_2(7‴)	3.93 (*s*)	32.4 (*t*)	3.89 (*s*)	31.4 (*t*)	3.89 (*s*)	31.5 (*t*)
C(1⁗)		133.9 (*s*)				134.2 (*s*)
H–C(2⁗,6⁗)	7.02 (*d*, J = 8.5)	130.7 (*d*)			6.97 (*d*, J = 8.3)	131.3 (*d*)
H–C(3⁗,5⁗)	6.63–6.66 (*m*)	116.5 (*d*)			6.63–6.66 (*m*)	116.4 (*d*)
C(4⁗)		156.8 (*s*)				156.7 (*s*)
CH_2(7⁗)	4.04 (*s*)	30.6 (*t*)			3.79 (*s*)	35.9 (*t*)
*Me*O–C(3)	3.45 (*s*)	62.7 (*q*)	3.76 (*s*)	56.3 (*q*)	3.78 (*s*)	56.4 (*q*)
*Me*O–C(3′)	3.67 (*s*)	56.1 (*q*)	3.78 (*s*)	56.7 (*q*)		

fourteen quaternary C-atoms. According to the ^{1}H- and ^{13}C-NMR data and the molecular formula, the basic structure of **1** was characterized as a bibenzyl derivative with three 4-substituted benzyl, one OH and two MeO groups. In the ROESY plot, the NOE correlations H–C(α)/H–C(7″) and H–C(7‴), MeO (δ(H) 3.67)/H–C(2′) and H–C(4′), and MeO (δ(H) 3.45)/H–C(7‴) and H–C(7⁗) were observed, indicating the location of three 4-substituted benzyl groups at C(2), C(4), and C(6), and of the MeO groups at C(3′) and C(3), which were further supported by ^{13}C,^{1}H long-range correlation signals in its HMBC plot (*Figure*).

Compound **2** was isolated as a white, amorphous powder with the molecular formula $C_{30}H_{30}O_6$ as established by HR-ESI-MS. The IR and UV spectra of **2** were similar to those of **1**. The structure of **2** was deduced as 2,6-bis(4-hydroxybenzyl)-3,3′-

dimethoxybibenzyl-4′,5-diol[1]), called blestritin B, from ^{1}H- and ^{13}C-NMR (*Table*), ^{1}H,^{1}H-COSY and HMBC (*Figure*), and ROESY data.

The ^{1}H-NMR of **2** exhibited the resonances of two pairs of 4-substituted benzyl groups at δ(H) 6.94 (*d*, *J* = 8.4 Hz, 2 H), 6.60–6.64 (*m*, 2 H), 6.85 (*d*, *J* = 8.8 Hz, 2 H), and 6.58–6.62 (*m*, 2 H), two benzyl CH_2 groups at δ(H) 3.91 (*s*, 2 H) and 3.89 (*s*, 2 H), four aliphatic protons due to bibenzyl CH_2 groups at δ(H) 2.16–2.26 (*m*, 2 H) and 2.60–2.70 (*m*, 2 H), two MeO groups at δ (H) 3.76 (*s*) and 3.78 (*s*), an *ABX* system at δ(H) 6.38 (*d*, *J* = 1.8 Hz, 1 H), 6.44 (*dd*, *J* = 8.0, 1.8 Hz, 1 H), 6.60–6.65 (*m*, 1 H), and one *s* at 6.48 (*s*, 1 H). In the ^{13}C-NMR and DEPT spectra, 30 C-signals belonging to two Me, four CH_2, and twelve CH groups, and twelve C-atoms were observed. These data revealed a bibenzyl skeleton with two 4-substituted benzyl, two OH, and two MeO groups. The aromatic protons appearing as an *ABX* system at δ(H) 6.38, 6.60–6.65, and 6.44 were assigned to H–C(2′), H–C(5′), and H–C(6′), and the *s* at δ(H) 6.48 to H–C(4), respectively, according to the ^{13}C,^{1}H long-range correlation signals observed for H–C(α′)/C(1′), C(2′), and C(6′), H–C(2′)/C(4′) and C(6′), H–C(5′)/C(1′) and C(3′), and H–C(4)/C(2), C(3), C(5), and C(6) in the HMBC plot (*Fig.*). In the ROESY plot of **2**, NOE correlations MeO (δ(H) 3.76)/H–C(4) and H–C(7‴) and MeO (δ(H) 3.78)/H–C(2′) were found, indicating the location of two MeO groups at C(3) and C(3′).

To compound **3**, obtained as a white amorphous powder, the elemental formula $C_{36}H_{34}O_6$ was assigned as deduced from HR-ESI-MS and NMR data. The ^{1}H- and ^{13}C-NMR spectra and molecular formula suggested that the structure of **3** was very similar to that of **2**, except for the appearance of another 4-substituted benzyl group and the absence of a MeO group in **3**. The additional benzyl group was located at C(4′) according to the ^{13}C,^{1}H long-range correlation signals at H–C(7⁗)/C(3′), C(4′), and C(5′) (*Fig.*), and also the NOE correlation H–C(7⁗)/H–C(5′). The NOE correlations MeO/H–C(4) and H–C(7‴) suggested the location of the MeO group at C(3). Thus, compound **3** was determined as 2,4′,6-tris(4-hydroxybenzyl)-3-methoxybibenzyl-3′,5-diol[1]), which has been given the trivial name blestritin C.

In addition to the three new compounds, 18 known ones were also isolated and characterized as 3′-*O*-methylbatatasin III (= 5-methoxy-3-[2-(3-methoxyphenyl)-ethyl]phenol) [13], batatasin III (= 3-[2-(3-hydroxyphenyl)ethyl]-5-methoxyphenol) [13], 5,4′-dimethoxybibenzyl-3,3′-diol [14], bulbocol (= 4-[(4-hydroxyphenyl)methyl]-3-methoxy-5-[2-(3-methoxyphenyl)ethyl]phenol) [15], gymconopin D (= 2-[(4-hydroxyphenyl)methyl]-5-methoxy-3-[2-(3-methoxyphenyl)ethyl]phenol) [16], 2-(4-hydroxybenzyl)-3-methoxybibenzyl-3′,5-diol [4], 2-(4-hydroxybenzyl)-5-methoxybibenzyl-3,3′-diol [4], bulbocodin (= 3-{2-{2-hydroxy-5-[4-hydroxyphenyl)methyl]phenyl}-ethyl}-2,4-bis[(4-hydroxyphenyl)methyl]-5-methoxyphenol) [15], bulbocodin D (= 3-[2-(3-hydroxyphenyl)ethyl]-2,6-bis[(4-hydroxyphenyl)methyl]-5-methoxyphenol) [17], 2,6-bis(4-hydroxybenzyl)-5,3′-dimethoxybibenzyl-3-ol [2], 2′,6′-bis(4-hydroxybenzyl)-5-methoxybibenzyl-3,3′-diol [2], 4-methoxyphenanthrene-2,7-diol [18], 3,4-dimethoxyphenanthrene-2,7-diol [18], 2,4-dimethoxyphenanthrene-3,7-diol [18], dactylorhin A (= [(2*R*)-2-(β-D-glucopyranosyloxy)-2-(2-methylpropyl)-1,4-dioxobutane-1,4-diyl]) bis-(oxymethylene-4,1-phenylene) bis[β-D-glucopyranoside) [19], dactylorhin E (= 4-{{[(2*R*)-2-(carboxymethyl)-2-(β-D-glucopyranosyloxy)-4-methyl-1-oxopentyl]oxy}methyl}phenyl β-D-glucopyranoside) [19], gymnoside I (= 4-{{[(2*R*)-2-(carboxymethyl)-2-hydroxy-4-methyl-1-oxopentyl]oxy}methyl}phenyl β-D-glucopyranoside) [20], and gymnoside II (= 4-{{[(3*R*)-3-carboxy-3-hydroxy-5-methyl-1-oxohexyl]oxy}methyl}-phenyl β-D-glucopyranoside) [20]. Among them, 3′-*O*-methylbatatasin III, batatasin

III, 5,4′-dimethoxybibenzyl-3,3′-diol, gymconopin D, bulbocodin, bulbocodin D, 4-methoxyphenanthrene-2,7-diol, 3,4-dimethoxyphenanthrene-2,7-diol, 2,4-dimethoxyphenanthrene-3,7-diol, dactylorhin A, dactylorhin E, gymnoside I, and gymnoside II were found for the first time in this plant.

Experimental Part

General. Column chromatography (CC): silica gel *H60* (*Qingdao Haiyang Chemical Group Corporation,* Qingdao, P. R. China), *Sephadex LH-20* (*Pharmacia Biotech AB*, Uppsala, Sweden). Prep. HPLC: *Varian SD-1* instrument equipped with a *RP-C_{18}* column (*Merck NW25*, 20 mm × 250 mm; 10 ml/min) and *ProStar 320-UV-Vis* detector (254 nm). TLC: *HSG_{254}* silica gel plates (*Yantai Chemical Industrial Institute*, Yantai, P. R. China). UV Spectra: *Beckman DU-7* spectrometer; λ (log ε) in nm. IR Spectra: *Perkin-Elmer 577* spectrometer; $\tilde{\nu}$ in cm^{-1}. NMR Spectra: *Bruker AM-400* spectrometer; δ in ppm rel. to $SiMe_4$ as internal standard, *J* in Hz. HR-ESI-MS: *Mariner* spectrometer; in *m/z*.

Plant Material. The tubers of *Bletilla striata* were purchased from the *Shanghai Yanghetang Herb Medicine Company* in September, 2006, and identified by Prof. *Jin-Gui Shen* of the Shanghai Institute of Materia Medica, Chinese Academy of Sciences. A voucher specimen was deposited in the Herbarium of the Shanghai Institute of Materia Medica (No. 20070330).

Extraction and Isolation. Powdered air-dried tubers of *B. striata* (3.0 kg) were percolated with 95% EtOH (20.0 l) at r.t. The extract was concentrated, the residue suspended in H_2O (2.0 l) and then extracted successively with $CHCl_3$ (3 × 2.0 l), and BuOH (3 × 2.0 l), yielding a $CHCl_3$ extract (60.0 g) and a BuOH extract (25.3 g). The $CHCl_3$ extract (60.0 g) was subjected to CC (SiO_2, petroleum ether/acetone 10:1 → 1:1): *Fractions 1–7. Fr. 2* (820 mg) was resubjected to CC (*Sephadex LH-20*, EtOH): *3′-O-methylbatatasin III* (129 mg). *Fr. 4* (4.0 g) was separated by CC (*Sephadex LH-20*, EtOH): *Fr. 4.1* (1.5 g), *Fr. 4.2* (2.0 g), and *Fr. 4.3* (581 mg). *Fr. 4.2* (2.0 g) was separated by prep. HPLC (*RP-18*, MeOH/H_2O 4:6 → 10:0): *batatasin III* (592 mg), *4′,5-dimethoxybibenzyl-3,3′-diol* (9 mg), *bulbocol* (125 mg), *gymconopin D* (122 mg), and *2-(4-hydroxybenzyl)-3-methoxybibenzyl-3′,5-diol* (10 mg). *Fr. 4.3* (581 mg) was subjected to prep. HPLC (*RP-18*, MeOH/H_2O 4:6 → 10:0): *4-methoxyphenanthrene-2,7-diol* (12 mg), *3,4-dimethoxyphenanthrene-2,7-diol* (14 mg), and *2,4-dimethoxyphenanthrene-3,7-diol* (8 mg). *Fr. 6* (4.1 g) was separated by prep. HPLC (*RP-18*, MeOH/H_2O 4:6 → 10:0): **1** (9 mg), **2** (7 mg), *2-(4-hydroxybenzyl)-5-methoxybibenzyl-3′,3-diol* (60 mg), *bulbocodin D* (61 mg), *2,6-bis(4-hydroxybenzyl)-3′,5-dimethoxybibenzyl-3-ol* (63 mg), and *2′,6′-bis(4-hydroxybenzyl)-5-methoxybibenzyl-3,3′-diol* (152 mg). *Fr. 7* (6.1 g) was subjected to prep. HPLC (*RP-18*, MeOH/H_2O 4:6 → 10:0): **3** (5 mg) and *bulbocodin* (41 mg). The BuOH extract (25.3 g) was subjected to CC (SiO_2, $CHCl_3$/MeOH/H_2O 3:1:0.1 → 7:3:0.5): *gymnoside I* (420 mg), *gymnoside II* (165 mg), *dactylorhin E* (85 mg), and *dactylorhin A* (50 mg).

Blestritin A (*=2,4,6-Tris(4-hydroxybenzyl)-3,3′-dimethoxybibenzyl-5-ol = 2,4,6-Tris[(4-hydroxyphenyl)methyl]-3-methoxy-5-[2-(3-methoxyphenyl)ethyl]phenol*; **1**): White amorphous powder. UV (MeOH): 281 (2.14). IR (KBr): 3405, 2937, 1612, 1596, 1511, 1438, 1384, 1236, 1170, 1085, 819. ^{1}H- and ^{13}C-NMR: *Table.* HR-ESI-MS: 599.2408 ($[M+Na]^+$, $C_{37}H_{36}NaO_6^+$; calc. 599.2410).

Blestritin B (*=2,6-Bis(4-hydroxybenzyl)-3,3′-dimethoxybibenzyl-4′,5-diol = 3-[2-(4-Hydroxy-3-methoxyphenyl)ethyl]-2,4-bis[(4-hydroxyphenyl)methyl-5-methoxyphenol*; **2**): White amorphous powder. UV (MeOH): 281 (2.17). IR (KBr): 3413, 2919, 1614, 1511, 1459, 1384, 1236, 1105, 819. ^{1}H- and ^{13}C-NMR: *Table.* HR-ESI-MS: 509.1924 ($[M+Na]^+$, $C_{30}H_{30}NaO_6^+$; calc. 509.1940).

Blestritin C (*=2,4′,6-Tris(4-hydroxybenzyl)-3-methoxybibenzyl-3′,5-diol = 3-{2-{3-hydroxy-4-[(4-hydroxyphenyl)methyl]phenyl}ethyl}-2,4-bis[(4-hydroxyphenyl)methyl]-5-methoxyphenol*; **3**): White amorphous powder. UV (MeOH): 281 (2.27). IR (KBr): 3403, 2917, 1594, 1511, 1444, 1382, 1232, 1170, 1107, 815. ^{1}H- and ^{13}C-NMR: *Table.* HR-ESI-MS: 585.2230 ($[M+Na]^+$, $C_{36}H_{34}NaO_6^+$; calc. 585.2253).

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