Unusual Poly(phenylacetyloxy)-Substituted 1,1′:4′,1″-Terphenyl Derivatives from Fruiting Bodies of the Basidiomycete *Thelephora ganbajun*

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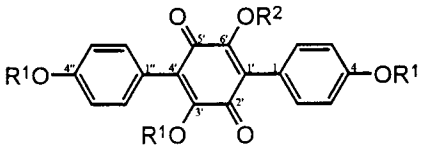
Dedicated to Prof. *Zang Mu* on the occasion of his 70th birthday

Five new poly(phenylacetyloxy)-substituted 1,1′:4′,1″-terphenyl derivatives, ganbajunins A – E (**2** – **6**) were isolated from the fruiting bodies of the Basidiomycete *Thelephora ganbajun* ZANG. Their structures were established by spectroscopic (including 2D-NMR) and chemical means.

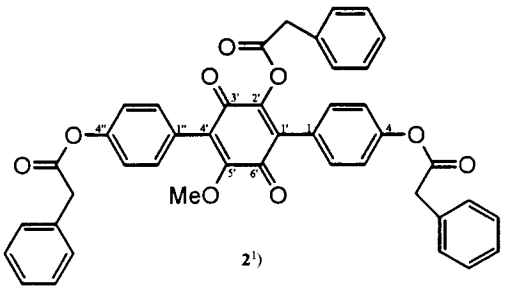
Introduction. – *Thelephora ganbajun* (Basidiomycetes), locally known as 'Gan-Ba-Jun', is a mushroom that grows in symbiosis with pine trees found in Yunnan Province, China [1]. It is one of the most favorite edible mushrooms in Yunnan and has a gastronomic interest due to its unique flavor and taste. Despite its commercial value and special flavor, *T. ganbajun* and the other species of the same genus have been poorly studied with respect to their contents of secondary metabolites. In the course of our search for naturally occurring bioactive metabolites of higher fungi in Yunnan Province [2 – 5], an area that is one of the richest sources of fungi in the world, the chemical constituents of *T. ganbajun* were investigated. Surprisingly, a series of new poly(phenylacetyloxy)-substituted 1,1′:4′,1″-terphenyl derivatives were isolated from this fungus. Natural 1,1′:4′,1″-terphenyl compounds are quite rare and occur often as terphenylquinones [6]; fully aromatic 1,1′:4′,1″-terphenyl compounds are less common and include a number of metabolites with different groups from *Boletopsis lecomelas* [7], *Paxillus atrotomentosus* [8], *Paxillus curtisii* [9], *Aspergillus candidus* [10], *Sarcodon leucopus* [6][11], and *Relicina connivens* (LICHEN) [12]. (Phenylacetyloxy)-substituted 1,1′:4′,1″-terphenyls have not been reported yet in the literature. In this paper, the isolation and structure elucidation of five new poly(phenylacetyloxy)-substituted 1,1′:4′,1″-terphenyl derivatives **2** – **6**, called ganbajunins A – E, and of the analogue **1** are described.

Results and Discussion. – The AcOEt-partitioned MeOH extract of the air-dried powders of fruiting bodies of *T. ganbajun* was subjected to repeated column chromatography to afford compounds **1** – **6**. On the basis of 1D- and 2D-NMR experiments (HMBC, HMQC) and chemical transformation, **1** was identified as 3′,4,4″-trihydroxy-6′-methoxy[1,1′:4′,1″-terphenyl]-2′,5′-dione, and **2** – **6** were deduced to be a series of 1,1′:4′,1″-terphenyl analogues substituted by three or two phenylacetyloxy groups. Their structures were established as tris[benzeneacetic acid] 5′-methoxy-3′,6′-dioxo[1,1′:4′,1″-terphenyl]-2′,4,4″-triyl ester[1]) (**2**), tris[benzeneacetic acid] 7,8-dihydroxy-3-(4-hydroxyphenyl)dibenzofuran-1,2,4-triyl ester (**3**), bis[benzeneacetic acid]

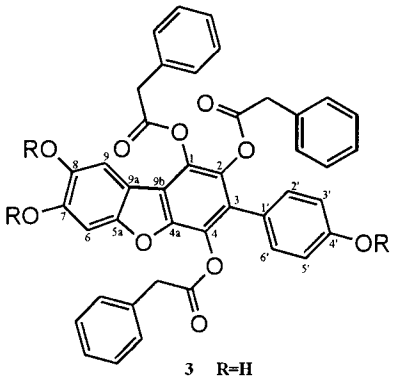
[1]) For convenience, **2** is numbered like **1** for the discussion of the NMR data; see name and formula of **2** for systematic numbering.



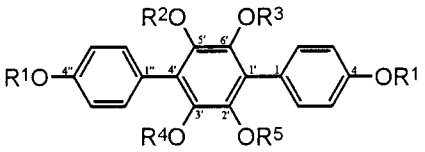
1 R^1=H, R^2=Me
1a R^1=R^2=H
1b R^1=Ac, R^2=Me



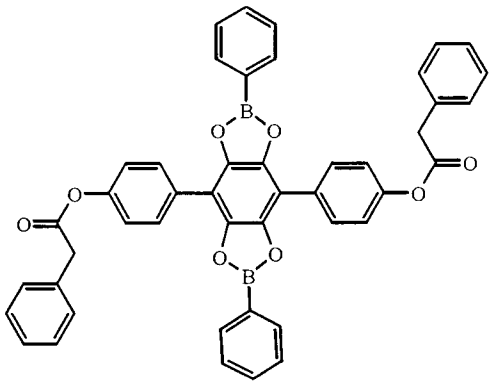
2[1])



3 R=H
3a R=MeO



4 R^1=$COPhCH_2$, R^2=R^3=R^4=R^5=H
4a R^1=$COPhCH_2$, R^2=R^3=R^4=R^5=Ac
5 R^1=R^3=R^5=H, R^2=R^4=CH_2COPh
6 R^1=R^3=R^4=H, R^2=R^5=CH_2COPh
7 R^1=R^4=R^5=H, R^2=R^3=CH_2COPh



4b

2′,3′,5′,6′-tetrahydroxy[1,1′:4′,1″-terphenyl]-4,4″-diyl ester (**4**), bis[benzeneacetic acid] 3′,4,4″,5′-tetrahydroxy[1,1′:4′,1″-terphenyl]-2′,6′-diyl ester (**5**), bis[benzeneacetic acid] 3′,4,4″,6′-tetrahydroxy[1,1′:4′,1″-terphenyl]-2′,5′-diyl ester (**6**).

Compounds **1** and **2** were obtained as orange needles. High-resolution EI-MS of **1** indicated a molecular formula of $C_{19}H_{14}O_6$ (M^+ at m/z 338.0807, calc. 338.0790) with 13 degrees of unsaturation and showed a significant ion peak at m/z 323 (loss of Me). The presence of one MeO group was implied by the NMR data (*Table 1*; δ (H) 3.96 (*s*), δ (C) 61.7). The ^{1}H-NMR spectrum of the triacetate **1b** of **1** confirmed the structure proposed for **1**, as well as the formation of atromentin (**1a**), one of the important coloring components found in fungi [14], on treatment of **1** with HBr and AcOH. Compound **2** was found to be spectroscopically similar to **1** (see *Table 1*). Compound **1** was reported previously as an artificial product [13].

Table 1. *^{1}H and ^{13}C-NMR Data* (500 and 125 MHz, resp.) *for* **1** *and* **2**[1]) *in CD_3OD.* δ in ppm, J in Hz

	δ (C)		HMBC (selected)	δ (H)	
	1	**2**[1])		**1**	**2**[1])
C(5′)	185.2	184.3			
C(6′)	156.2	148.1			
C(1′)	121.9	129.2	H–C(2,6)		
C(2′)	183.9	182.2			
C(3′)	154.5	156.3			
C(4′)	126.5	134.8	H–C(2″,6″)		
C(1″)	121.1	122.1	H–C(3″,5″)		
H–C(2″,6″)	133.0	133.2		7.36 (‘*d*’, J = 8.5)	7.17 (‘*d*’, J = 8.7)
H–C(3″,5″)	115.9	115.8		6.88 (‘*d*’, J = 8.5)	6.82 (‘*d*’, J = 8.7)
C(4″)	159.4	159.2	H–C(2″,6″)		
C(1)	123.0	120.7	H–C(3,5)		
H–C(2,6)	133.3	132.7		7.28 (‘*d*’, J = 8.5)	7.07 (‘*d*’, J = 8.7)
H–C(3,5)	115.8	116.0		6.87 (‘*d*’, J = 8.5)	6.73 (‘*d*’, J = 8.7)
C(4)	158.8	159.6	H–C(2,6)		
CO		170.8			
CH_2		41.2	H–C_o		3.78, 3.76, 3.76 (*s*)
C_{ipso}		134.3	CH_2, H–C_o		
H–C_o		115.7			7.18 (*m*)
H–C_m		130.5			7.27 (*dd*, J = 7.6, 7.5)
H–C_p		129.6	H–C_o		7.24 (*m*)
MeO	61.7	61.7	C(6′)[a])[b])	3.96 (*s*)	3.78 (*s*)

[a]) HMBC for **1**. [b]) HMBC for **2**[1]).

The ^{1}H-NMR of triacetate **1b** exhibited *s* at δ 2.21, 2.30, 2.31 for the acetate groups, and peaks at m/z 464 (M^+), 422 ([M – Ac]$^+$), 380 ([M – 2 Ac]$^+$), 338 ([M – 3 Ac]$^+$) in its EI-MS suggested the presence of three OH groups in **1**. The signals of **1** at δ (H) 7.28 and 6.87 (2‘*d*’, each J = 8.5 Hz) and 7.36 and 6.88 (2‘*d*’, each J = 8.5 Hz) formed two *AA′BB′* systems arising from the protons of two 1,4-disubstituted benzene rings [15]. Taking the molecular formula and the remaining five degrees of unsaturation into consideration, the remaining six quaternary sp^2 C-signals in the ^{13}C-NMR of **1** (*Table 1*) represented a tetrasubstituted benzoquinone moiety. The data of **1a** allowed us to assign a 3,6-diaryl-1,4-benzoquinone moiety as the connection pattern between the two 1,4-disubstituted benzene rings and established substitution at C(3′), C(4), C(4″), and C(6′) of **1**. The MeO group of **1** was assigned to be at C(6′) of the central ring by the observed HMBC correlation of the MeO protons with C(6′).

The NMR data of **2**[1]) (*Table 1*) and its MS data (m/z at 693 ([M + 2 – H]$^+$), 575 ([M + 2 – H – PhCH=CO]$^+$), 457 ([M + 2 – H – 2PhCH=CO]$^+$), and 339 ([M + 2 – H – 3 PhCH=CO]$^+$)) suggested the presence of three benzeneacetate moieties. Close comparison of the ^{1}H- and ^{13}C-NMR spectra of **1** and **2** clearly revealed the phenylacetyloxy groups at C(3′)[1]), C(4), and C(4″) of **2** replacing OH groups of **1**. Confirmation was obtained from the alkaline hydrolysis of **2**, which yielded benzeneacetic acid and compound **1**.

The NMR (*Table 2*), UV, and IR data of **3** are in good agreement with those of a series of cycloleucomelone leucoacetates that have the same C-skeleton, isolated from the basidiomycete *Boletopsis leucomelas* [7a]. The position of three OH groups was identified by means of its trimethoxy derivative **3a** by the HMBC correlations between the MeO protons with C(7), C(8), and C(4′). The high-resolution FAB-MS (neg.) of **3** indicated a molecular formula of $C_{42}H_{30}O_{10}$ ($[M-H]^+$ at m/z 693.1764, calc. 693.1761) with 28 degrees of unsaturation. The presence of three phenylacetyloxy groups was suggested by the successive loss of three PhCH=C=O moieties in the FAB-MS (neg.).

Table 2. *^{1}H- and ^{13}C-NMR Data* (500 and 125 MHz, resp.) *for* **3** *and* ***3a*** *in CD_3COCD_3*. δ in ppm, J in Hz

	3		HMBC (selected)	**3a**		HMBC (selected)
	δ (C)	δ (H)		δ (C)	δ (H)	
C(1)	124.9			127.1		
C(2)	137.2			137.8		
C(3)	128.3		H–C(2′,6′)	123.5		H–C(2′,6′)
C(4)	139.0			139.0		
C(4a)	146.9			145.8		
C(5a)	152.2		H–C(9)	152.3		H–C(9)
H–C(6)	99.3	7.11 (*s*)		99.2	7.12 (*s*)	
C(7)	148.1		H–C(6,9)	148.2		H–C(6,9), MeO–C(7)
C(8)	143.7		H–C(6,9)	143.8		H–C(6,9), MeO–C(8)
H–C(9)	107.7	7.22 (*s*)		107.4	7.19 (*s*)	
C(9a)	114.2		H–C(6,9)	116.3		H–C(6,9)
C(9b)	120.0		H–C(9)	119.6		H–C(9)
C(1′)	123.5		H–C(3′,5′)	125.3		H–C(3′,5′)
H–C(2′,6′)	137.1	7.01 (‘*d*’, $J=8.5$)		133.4	7.04 (‘*d*’, $J=8.5$)	
H–C(3′,5′)	116.1	6.83 (‘*d*’, $J=8.5$)		116.2	6.80 (‘*d*’, $J=8.5$)	
C(4′)	158.3		H–C(2′,6′)	158.1		H–C(2′,6′), MeO–C(4′)
CO	169.1 (×2), 169.6			169.2 (×2), 169.6		
CH_2	41.0	3.78, 3.72, 3.62		41.2		
C_{ipso}	134.3 (×2), 134.4			134.3 (×3)		
H–C_o	130.2 (×2), 130.6	7.28, 7.44 (*m*)		130.1 (×2), 130.5	7.28, 7.44 (*m*)	
H–C_m	129.3 (×2), 129.7	7.26–7.35 (*m*)		129.4 (×2), 129.9	7.26–7.35 (*m*)	
H–C_p	127.8 (×2), 128.3	7.26–7.35 (*m*)		127.7 (×2), 128.4	7.26–7.35 (*m*)	
MeO–C(4′)				61.2	3.70 (*s*)	
MeO–C(7)				61.5	3.75 (*s*)	
MeO–C(8)				61.5	3.72 (*s*)	

Three exchangeable ^{1}H-NMR signals recorded for **3** in D_2O at δ 8.79, 8.59, and 8.17 implied the existence of three phenolic OH groups. A 1,4-disubstituted and a 1,2,4,5-tetrasubstituted aromatic ring were established by ^{1}H,^{1}H coupling constants and corresponding ^{1}H- and ^{13}C-NMR chemical shifts, which were assigned by HMQC

and HMBC (*Table 2*). Considering the molecular formula and ^{13}C-NMR (DEPT) data, the remaining five degrees of unsaturation could be attributed to a third hexasubstituted aromatic ring and an ether bridge connecting two of the aromatic rings of **3** to form a dibenzofuran unit. The HMBC correlations of H–C(9) with C(9a) and C(9b), and of H–C(2′) and H–C(6′) with C(3) established that the three aromatic rings belong to a 3-phenyldibenzofuran unit with six functional groups located at C(1), C(2), C(4), C(7), C(8), and C(4′) (also assigned by HMBC, see *Table 2*).

Compounds **4**–**6** were isomers containing a 1,1′: 4′,4″-terphenyl core structure with two phenylacetyloxy groups, as established by spectroscopic-data analysis. The molecular formula of **4** was assigned to be $C_{34}H_{26}O_8$ with 22 degrees of unsaturation by high-resolution FAB-MS ($[M-H]^+$ at *m*/*z* 561.1512, calc. 561.1549) and NMR data (see *Table 3*). The presence of two phenylacetyloxy groups and four OH groups in **4** was suggested by its FAB-MS (neg.) (loss of two PhCH=C=O moieties from $[M-H]^+$ and by the EI-MS (*m*/*z* 688, *M* and ^{1}H-NMR data (δ 1.96 (*s*)) of its tetraacetate **4a**. When **4** was treated with phenylboronic acid, and the reaction mixture was examined directly by FAB-MS (neg.) [6], an ion observed at *m*/*z* 733 ($[M-H]^+$) indicated the formation of a bis-phenylboronate **4b**, which implied the presence of two pairs of vicinal OH groups.

Table 3. *^{1}H- and ^{13}C-NMR Data* (500 and 125 MHz, resp.) *for* **4**–**6** *in CD_3COCD_3*. δ in ppm, *J* in Hz

C	δ (C)			HMBC (selected)	δ (H)		
	4	**5**[2])	**6**		**4**	**5**[2])	**6**
C(4″)	158.1	157.9	157.8	H–C(2″,6″)			
H–C(3″,5″)	116.14	115.9	115.8		7.09 (‘*d*’, *J* = 8.4)	7.00 (‘*d*’, *J* = 8.5)	7.11 (‘*d*’, *J* = 8.4)
H–C(2″,6″)	132.6	131.6	132.4		6.76 (‘*d*’, *J* = 8.4)	6.78 (‘*d*’, *J* = 8.5)	6.82 (‘*d*’, *J* = 8.4)
C(1″)	124.8	124.7	124.5	H–C(3″,5″)			
C(4′)	124.0	130.3	124.3	H–C(2″,6″)			
C(5′)	142.6	133.0	143.1				
C(6′)	142.6	145.7	145.6				
C(1′)	124.0	118.1	124.2	H–C(2,6)			
C(2′)	142.6	145.7	143.1				
C(3′)	142.6	133.0	145.6				
C(1)	124.8	124.5	124.3	H–C(3,5)			
H–C(2,6)	132.6	133.1	132.4		7.09 (‘*d*’, *J* = 8.4)	7.26 (‘*d*’, *J* = 7.6)	7.11 (‘*d*’, *J* = 8.4)
H–C(3,5)	116.1	115.9	115.8		6.76 (‘*d*’, *J* = 8.4)	6.88 (‘*d*’, *J* = 7.6)	6.82 (‘*d*’, *J* = 8.4)
C(4)	158.1	157.7	157.8	H–C(2,6)			
CO	171.2	170.8	170.7				
CH_2	41.2	41.5	41.5		3.62 (*s*)	3.24 (*s*)	3.25 (*s*)
C_{ipso}	134.7	134.8	134.8				
H–C_o	129.5	129.0	129.0		6.98 (*m*)	6.97 (*m*)	6.97 (*m*)
H–C_m	130.4	130.6	130.3		7.20–7.25 (*m*)	7.19–7.20 (*m*)	7.19–7.20 (*m*)
H–C_p	128.1	127.5	127.5		7.20–7.25 (*m*)	7.19–7.20 (*m*)	7.19–7.20 (*m*)

In addition to the signals of the phenylacetyloxy groups, the ^{1}H-NMR spectrum of **4** displays resonances at δ 7.09 and 6.76 (‘*d*’, *J* = 8.4 Hz), arising from an *AA′BB′* system which was attributed to 1,4-disubstituted aromatic rings. The ^{13}C-NMR of **4** showed not only signals of two symmetric 1,4-disubstituted aromatic rings, but also two signals (δ 124.0 and 142.6) for the last six aromatic quaternary C-atoms of a highly symmetric hexasubstituted aromatic ring.

Compounds **5**[2]) and **6** were isolated as a 4:1 mixture. Their ^{1}H- and ^{13}C-NMR (*Table 3*) and FAB-MS data unambiguously settled the molecular formula as $C_{34}H_{26}O_8$, and established the presence of 1,1′:4′,1″-terphenyl moiety and partial structures that include two phenylacetyloxy and four OH groups. The location of these substituents at the terphenyl skeleton were assigned by comparison of the ^{1}H-NMR spectra with that of **4**.

In the case of **4**, the ^{1}H-NMR signals of the CH_2 protons of the phenylacetyloxy groups at C(4) and C(4″) of the terminal rings at δ 3.62 were shifted upfield by *ca*. 0.4 ppm in the case of **5** and **6** (see *Table 3*), suggesting positions at the central ring for these groups (anisotropic effect); both of the CH_2 protons of **5** and **6** were shifted upfield. Compound **5**[2]) displayed two groups of ^{1}H-NMR resonances at δ 7.26 ('*d*', J = 7.6 Hz) and 6.88 ('*d*', J = 7.6 Hz) and at 7.00 ('*d*', J = 8.5 Hz) and 6.78 ('*d*', J = 8.5 Hz), which were assigned to H–C(2,6) and H–C(3,5) and to H–C(3″,5″) and H–C(2″,6″), respectively, of two unsymmetric 1,4-disubstituted aromatic rings, while compound **6** exhibited only one group of signals at δ 7.11 ('*d*', J = 8.4 Hz) and 6.82 ('*d*', J = 8.4 Hz), which were assigned to H–C(3″,5″) and H–C(2,6) and to H–C(2″,6″) and H–C(3,5), respectively, of two symmetric 1,4-disubstituted aromatic rings. Considering three possible substitution patterns, the structure with two *m*-positioned phenylacetyloxy groups was consistent with the spectroscopic data for **5**.

Two possible structures, **6** and **7** with *p*- and *o*-positioned phenylacetyloxy groups, respectively, were consistent with the spectroscopic data of compound **6**. When **6** was treated with phenylboric acid as described previously, no derivative was detected, which excluded the existence of the possible structure **7** with vicinal OH groups. Moreover, the mixture **5**/**6** is unstable, and its color converts to orange easily. The FAB-MS of the minor coloring constituent isolated from the orange mixture showed peaks at *m*/*z* 561 ($[M+2-H]^+$) and 559 ($[M-H]^+$), indicating the formation of a 1,4-quinone by oxidation of compound **6**. Since fully 1,1′:4′,1″-terphenyls with two *p*-positioned OH groups at the central ring show a great tendency to convert to pigments with a 1,4-quinone function at the terphenyl skeleton by aerial oxidation [8a], the structure of compound **6** was deduced to contain two *p*-positioned phenylacetyloxy groups.

In recent years, it has been reported that several 1,1′:4′,1″-terphenyl compounds exhibit considerable bioactivities; *e.g.*, they are active toward HeLa [10b] and KB cells [11], are potent IgE-antibody suppressants [16], and have antiinsect and antibacterial [17], and specific 5-lipoxygenase inhibitory [7a] activities. Because of their promising biological activities, they have generated strongly increasing research interest. Unfortunately, no significant biological activity of the above-described poly(phenylacetyloxy)-substituted 1,1′:4′,1″-terphenyl derivatives ganbajunins A–E (**2**–**6**) was observed until now, and further investigations are still planned.

Experimental Part

General. M.p.: uncorrected. UV Spectra: *UV-210* spectrometer; λ_{max} (log ε) in nm. IR Spectra: *Perkin-Elmer 577* spectrometer; KBr pellets; in cm^{-1}. ^{1}H- and ^{13}C-NMR Spectra: *Bruker DRX-500* spectrometer; δ in ppm, J in Hz. MS: *VG Autospec-3000* spectrometer; *m*/*z* (rel. %).

Mushroom Material. The fresh fruiting bodies of *Thelephora ganbajun* were collected at Wudin country in Yunnan province, P.R. China, in June, 2000. The voucher specimen (HMAS 52851) was deposited at the herbarium of the Kunming Institute of Botany, the Chinese Academy of Sciences.

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[2]) For convenience, **5** and **7** are numbered like **4** for the discussion of the NMR data; see names for systematic numbering.

Extraction and Isolation. Air-dried and powdered *T. ganbajun* (585 g) were defatted with petroleum ether (40–60°) at r.t. The solvent-free powder was exhaustively extracted with MeOH to afford a brown gum (50 g), which was taken up in H_2O and extracted with AcOEt. After evaporation of the extract, the residue (32 g) was subjected to *Sephadex LH-20* chromatography (gradient AcOEt/MeOH): six fractions. *Fr. 2–4* were further purified by repeated reversed-phase column chromatography (CC) (*RP18*, MeOH/H_2O) or by recrystallization to give the pure compounds **1** (80 mg), **2** (160 mg), **3** (250 mg), and **4** (45 mg), and the mixture **5**/**6** (12 mg).

Atromentin (= 3′,4,4″,6′-Tetrahydroxy[1,1′:4′,1″-terphenyl]-2′,5′-dione = 2,5-Dihydroxy-3,6-bis(4-hydroxyphenyl)cyclohexa-2,5-diene-1,4-dione; **1a**). A soln. of **1** (20 mg) in acetone (1 ml) 48% HBr soln. (10 ml), and AcOH (5 ml) were refluxed at 50° for 2 h. The mixture was neutralized to pH 6.5–7.0 with 0.5N NaOH and subjected to CC (*RP8*, 5% MeOH/H_2O): 8 mg of **1a**. Purple microcrystals (MeOH/H_2O). M.p. >300°. UV (MeOH): 355 (3.71), 263 (4.42), 205 (4.69). IR: 3310, 1630, 1615, 1515, 1440, 1315, 1250, 1190, 1000, 855, 810, 780, 725. ^{1}H-NMR (CD_3OD): 7.55 (*d*, *J* = 8.6, 2 H); 6.88 (*d*, *J* = 8.6, 2 H). EI-MS (70 eV): 326 (12, $[M+2]^+$), 325 (18, $[M+1]^+$), 324 (100, M^+), 316 (7), 296 (21), 270 (10). UV and MS: in agreement with [8a][18].

2-O-Methylatromentin (= 3′,4,4″-trihydroxy-6′-methoxy[1,1′:4′,1″-terphenyl]-2′,5′-dione = 2-Hydroxy-3,6-bis(4-hydroxyphenyl)-5-methoxycyclohexa-2,5-diene-1,4-dione; **1**). Orange needles (from MeOH/H_2O). M.p. 247–248°. UV (MeOH): 367 (3.61), 273 (4.33), 203 (4.45). IR: 3700–2800, 1641, 1610, 1512, 1440, 1291, 1314, 1216, 1025. ^{1}H- and ^{13}C-NMR: see *Table 1*. HR-EI-MS: 338.0807 ($C_{19}H_{14}O_6^+$, M^+; calc. 338.0790). EI-MS (70 eV): 338 (100, M^+), 323 (14, $[M-Me]^+$), 310 (52, $[M-CO]^+$), 295 (71, $[M-CO-Me]^+$), 267 (50, $[M-2\,CO-Me]^+$), 239 (85, $[M-3\,CO-Me]^+$), 165 (30), 145 (44), 133 (52), 121 (30), 105 (84), 91 (23), 77 (57).

2-O-Methylatromentin Triacetate (= 3′,4,4″-Triacetoxy-6′-methoxy[1,1′:4′,1″-terphenyl]-2′,5′-dione = 2-(acetyloxy)-3,6-bis[(4-acetyloxy)phenyl]-5-methoxycyclohexa-2,5-diene-1,4-dione; **1b**). To the soln. of **1** (15 mg) in acetone (0.5 ml) and Ac_2O (1 ml), pyridine (1 ml) was added. After standing overnight, a precipitate was formed as soon as the mixture was poured into cold H_2O (20 ml). The precipitate was filtered off and 22 mg of **1b** were obtained after recrystallization from MeOH/H_2O. Orange needles. M.p. 193–195°. ^{1}H-NMR ($CDCl_3$): 2.21 (MeCO); 2.30, 2.31 (MeCO); 3.93 (MeO); 7.51, 7.33 ('*d*', *AA′,BB′*, *J* = 8.6); 7.35, 7.15 ('*d*', *AA′,BB′*, *J* = 8.5). EI-MS: 466 (4, $[M+2]^+$), 464 (2, M^+), 422 (62, $[M-Ac]^+$), 380 (64, $[M-2\,Ac]^+$), 338 (100, $[M-3\,Ac]^+$), 323 (6, $[M-Ac-Me]^+$), 310 (32), 295 (25), 279 (14), 239 (25).

Ganbajunin A (= *Tris[benzeneacetic Acid] 5′-Methoxy-3′,6′-dioxo[1,1′:4′,1″-terphenyl]-2′,4,4″-triyl Ester*; **2**). Orange needles (from MeOH/H_2O). M.p. 150–151°. UV (MeOH): 374 (3.84), 233 (4.49), 205 (4.73). IR: 1754, 1658, 1591, 1513, 1440, 1283, 1230, 1176, 1076, 1097, 1027, 834. ^{1}H- and ^{13}C-NMR: see *Table 1*. EI-MS: 340 (32, $[M+2-3\,PhCH{=}CO]^+$), 338 (100, $[M-3\,PhCH{=}CO]^+$), 323 (6, $[M-3\,PhCH{=}CO-Me]^+$), 310 (27), 295 (44), 267 (17), 239 (47), 165 (10), 145 (15), 133 (17), 118 (63), 105 (38), 91 (74). FAB-MS (neg.): 693 (20, $[M+2-H]^+$), 575 (19, $[M+2-H-PhCH{=}CO]^+$), 457 (54, $[M+2-H-2\,PhCH{=}CO]^+$), 339 (100, $[M+2-H-3\,PhCH{=}CO]^+$), 323 (46, $[M+2-3\,PhCH{=}CO-Me]^+$). Note: Quinones frequently give $[M+2]^+$ ions due to partial hydrogenation in the ion source [12].

Ganbajunin B (= *Tris[benzeneacetic Acid] 7,8-Dihydroxy-3-(4-hydroxyphenyl)dibenzofuran-1,2,4-triyl Ester;* **3**). Colorless needles (from MeOH/H_2O). M.p. 197–198°. UV (MeOH): 344 (4.02), 329 (4.28), 303 (4.20), 264 (4.24), 251 (4.25), 220 (4.54), 207 (4.73). IR: 2800–3600, 1753, 1606, 1518, 1470, 1416, 1340, 1299, 1222, 1120, 989, 847, 723. ^{1}H- and ^{13}C-NMR: see *Table 2*. HR-FAB-MS (neg.): 693.1764 ($C_{42}H_{29}O_{10}^+$, $[M-H]^+$; calc. 693.1761). FAB-MS (neg.): 693 (91, $[M-H]^+$), 575 (77, $[M-H-PhCH{=}CO]^+$), 475 (83, $[M-H-2\,PhCH{=}CO]^+$), 338 (100, $[M-H-3CO-Me]^+$).

Ganbajunin B Trimethyl Ether (= *Tris[benzeneacetic Acid] 7,8-Dimethoxy-3-(4-methoxyphenyl)dibenzofuran-1,2,4-triyl Ester*; **3a**). The mixture of **5** (35 mg) in acetone (0.5 ml), MeI (1 ml) and K_2CO_3 (55 mg) was refluxed at 50° for 25 min. Then the mixture was poured into cold H_2O (20 ml) and extracted with Et_2O. The ether extract was evaporated and the residue subjected to CC (*RP C-8*): 3 mg of **3a**. White powder. ^{1}H- and ^{13}C-NMR: see *Table 2*. FAB-MS (neg.): 737 (5), 723 (6), 707 (10), 695 (15), 603 (92), 589 (46), 485 (100), 471 (40), 352 (26), 337 (29).

Ganbajunin C (= *Bis[benzeneacetic Acid] 2′,3′,5′,6′-Tetrahydroxy[1,1′:4′,1″-terphenyl]-4,4″-diyl Ester;* **4**). Colorless crystals (from $CHCl_3$/MeOH). M.p. 211.5–212.0°. UV (MeOH): 372 (3.71), 271 (4.31), 203 (4.58). IR: 2800–3700, 1745, 1611, 1524, 1494, 1454, 1250, 1136, 1129, 985, 828, 724. HR-FAB-MS (neg.): 561.1512 ($C_{34}H_{25}O_8^+$, $[M-H]^+$; calc. 561.1549). FAB-MS (neg.): 561 (100, $[M-H]^+$), 443 (22, $[M-H-PhCH{=}CO]^+$), 325 (47, $[M-H-2\,PhCH{=}CO]^+$), 324 (43).

Ganbajunin C Tetraacetate (= *Bis[benzeneacetic Acid] 2′,3′,5′,6′-Tetrakis(acetyloxy)[1,1′:4′,1″-terphenyl]-4,4″-diyl Ester*; **4a**). As described for **1b**, with **4** (12 mg): 18 mg of **4a**, after recrystallization from MeOH/H_2O. White needles. M.p. 163.5–165.0°. ^{1}H-NMR ($CDCl_3$): 1.96 (*s*, MeCO); 7.28, 6.88 ('*d*', *AA′BB′*, *J* = 8.5). EI-MS (70 eV): 688 (23, M^+), 646 (46, $[M-Ac]^+$), 604 (56, $[M-2\,Ac]^+$), 562 (100, $[M-3\,Ac]^+$).

Ganbajunin D (= *Bis[benzeneacetic Acid] 3′,4,4″,5′-tetrahydroxy-[1,1′:4′,1″-terphenyl]-2′,6′-diyl Ester*; **5**) *and Ganbajunin E* (= *Bis[benzeneacetic Acid] 3′,4,4″,6′-tetrahydroxy[1,1′:4′,1″-terphenyl]-2′,6′-diyl Ester*; **6**) were obtained as a white powder, which turned slowly orange. FAB-MS (neg.): 561 (38, $[M-H]^+$), 443 (100, $[M-H-PhCH{=}CO]^+$), 325 (32, $[M-H-2\ PhCH{=}CO]^+$), 324 (47).

Alkaline Hydrolysis of **2**. The soln. of **2** (15 mg) in acetone (5 ml) and 2N NaOH (10 ml) was refluxed at 50° for 2.5 h. The brown soln. was acidified to pH 6.5 and extracted with AcOEt. The AcOEt was evaporated, and the residue extracted with a small amount of benzene. The benzene soln. was evaporated: 8 mg of benzeneacetic acid. EI-MS: 136 (25, M^+), 118 (3, $[M-H_2O]^+$), 105 (3), 91 (100, $[M-OH-CO]^+$), 77 (3), 65 (20)).

The benzene-insoluble fraction was subjected to CC (*RP8*, 70% MeOH/H_2O): 5 mg of **1a**, identified by TLC ($CHCl_3$/MeOH, 9:1).

Reaction of **4** *with Phenylboronic Acid: Bis[benzeneacetic Acid] [(2,6-diphenylbenzo[*d,d′*]bis[1,3,2]dioxaborole-4,8-diyl)di(4,1-phenylene)] Ester* (**4b**). The mixture of **4** (1 mg) in acetone (0.5 ml) and phenylboronic acid (1 mg) was refluxed at 50° for 4 h and then evaporated. The residual crude **4b** was not purified further. FAB-MS (neg.): 733 (100, $[M-1]^+$), 615 (30, $[M-H-PhCH{=}CO]^+$), 497 (45, $[M-H-2\ PhCH{=}CO]^+$).

Likewise, the mixture **5**/**6** was treated with phenylboronic acid, but no boron derivative was detected.

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