A New *p*-Terphenyl Derivative from the Mushroom *Thelephora vialis*

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One novel *p*-terphenyl compound, named vialisyl A (**1**), was isolated from the fruiting bodies of *Thelephora vialis*, together with six known compounds, ganbajunin B (**2**), phenylacetic acid (**3**), a mixture of ganbajunins D (**4**) and E (**5**), and vialinins A (**6**) and B (**7**). Their structures were established by extensive analysis of spectroscopic data (including ^{1}H- and ^{13}C-NMR, HSQC, HMBC, 2D-INADEQUATE) as well as by comparison with literature reports.

Introduction. – *Thelephora vialis*, belonging to the family Thelephoraceae, is mainly distributed in Yunnan Province, P. R. China. It is a favorite edible mushroom and has been used as folk medicine for treating rheumatism, arthralgia, and spasm. Some compounds isolated from this basidiomycete have significant activity. For example, vialinins A and B strongly inhibit TNF-α production, which may be promising candidates for a new type of anti-allergic agent [1][2]. In order to search for other bioactive ingredients from this mushroom, the EtOH extract of the fruiting bodies of *Thelephora vialis* was studied. Seven compounds were isolated from the AcOEt fraction, including one novel *p*-terphenyl, named vialisyl A (**1**), together with six known compounds, ganbajunin B (**2**), phenylacetic acid (**3**), a mixture of ganbajunins D (**4**) and E (**5**), and vialinins A (**6**) and B (**7**) (*Fig.*) [3]. Herein, we describe the isolation and structure elucidation of compound **1**.

Results and Discussion. – Vialisyl A (**1**) was obtained as greenish powder. The molecular formula was determined to be $C_{34}H_{22}O_{10}$ by HR-ESI-MS (*m*/*z* 589.1147 ([*M* – H]$^-$, calc. 589.1140)). The ^{1}H- and ^{13}C-NMR spectra seemed to just have eleven H-atom and 17 C-atom signals, which implied the stucture of compound **1** was completely symmetrical. The ESI-MS data (*m*/*z* 589 ([*M* – H]$^-$), 353 ([*M* – H – 2 PhCH=CO]$^-$)) suggested the presence of two phenylacetyl moieties, which was consistent with a set of characteristic C-atom resonances at δ(C) 169.0, 133.2, 2 × 129.7, 2 × 128.6, 127.3, 39.4. In the ^{1}H-NMR data, except for seven H-atoms assigned to the phenylacetyl moiety, there were only four single H-atoms (δ(H) 9.76, 9.19, 7.17, 7.15). When one drop of D_2O was added, the signals at δ(H) 9.76 and 9.19 disappeared, indicating the existence of two phenolic OH groups. Their chemical shifts and spin-spin splitting patterns established partial structure of a 1,2,4,5-tetrasubstituted aromatic ring, which was

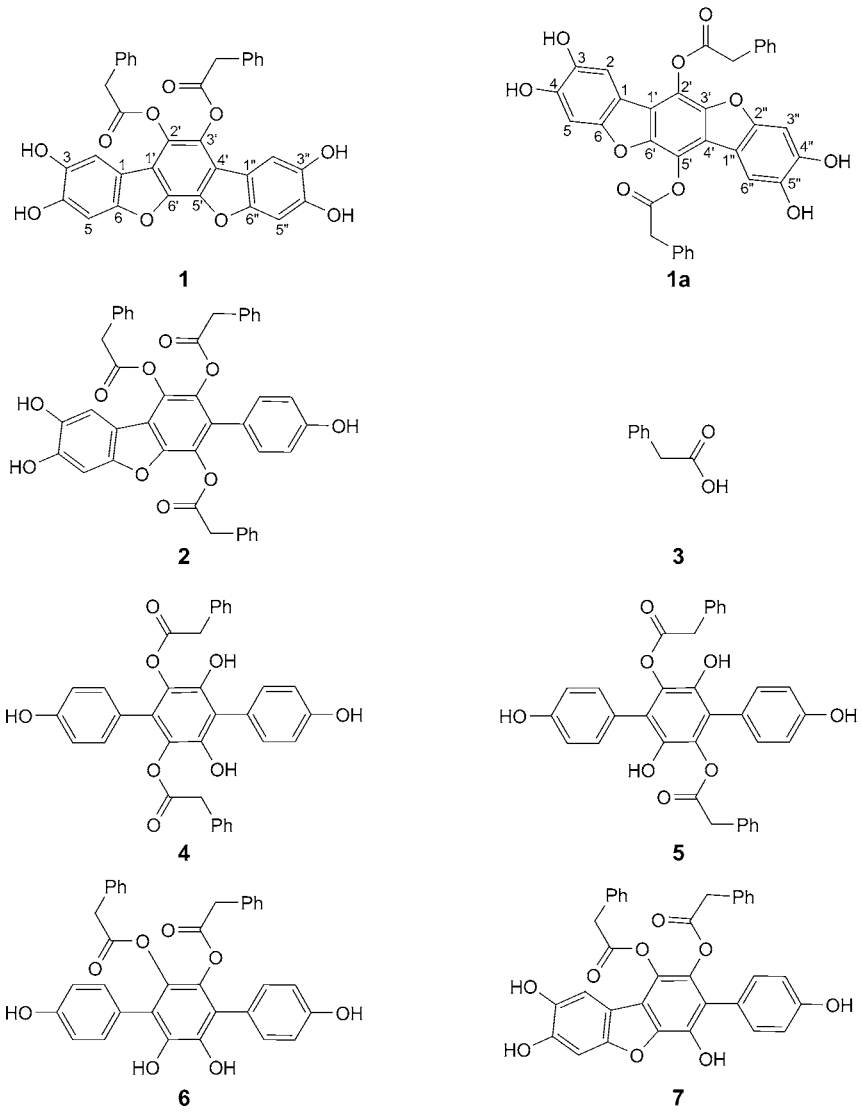

Figure. *Structures of compounds* **1**–**7**

confirmed by further analysis of HSQC and HMBC spectra, with the corresponding ^{13}C-NMR chemical shifts at δ(C) 150.3, 147.0, 143.3, 112.7, 106.0, 98.8. Due to the completely symmetrical structure, the remaining three quaternary C-atom signals (δ(C) 137.0, 130.6, 116.6) were attributed to a hexasubstituted aromatic ring, that finally formed a *p*-terphenyl skeleton. Considering total 24 degrees of unsaturation of the molecule, the remaining two degrees of unsaturation indicated an ether bridge connecting two of the aromatic rings. As a result, two possible structures, **1** and

1a (*Fig.*), containing a *p*-terphenyl skeleton with *ortho*- and *para*-positioned phenylacetyloxy groups, respectively, were consistent with the spectroscopic data. HMBCs from H–C(2,2″) to C(3,3″), C(4,4″), C(6,6″), and C(1′,4′) showed that the chemical shift of C(1′,4′) was δ(C) 116.6. Because there were no correlation signals with the two quaternary C-atoms (δ(C) 137.0, 130.6), it was difficult to assign them. Comparison of the ^{13}C-NMR signals of **1** with those of a reference compound polyozellin [4] suggested that the chemical shift of C-atom which linked to ether bond was δ(C) 137.0, and acetyl linked C-atom was δ(C) 130.6.

As the HMBC experiment could not distinguish **1** from **1a**, a 2D-INADEQUATE experiment was applied for the elucidation of the substitutent positions. If the structure was **1a**, a correlation between δ(C) 130.6 (C(2′,5′)) and 137.0 (C(3′,6′)) would be expected. In fact, there was no cross-peak at all, so the structure of **1a** was excluded. The correlations between δ(C) 116.6 (C(1′,4′)) and 130.6 (C(2′,3′)), between δ(C) 116.6 (C(1′,4′)) and 137.0 (C(6′,5′)), between δ(C) 116.6 (C(1′,4′)) and 112.7 (C(1′,1″)), and no correlations between δ(C) 137.0 and 130.6 confirmed that the correct structure must be **1**.

Experimental Part

General. TLC: GF_{254} plates (*Qingdao Marine Chemical Factory*). Column chromatograph (CC): silica gel (SiO_2, 200–300 mesh; *Qingdao Marine Chemical Factory*), *Sephadex LH-20* (*GE Healthcare Bio-Sciences AB*), *ODS* (45–70 μm; *Merck*). UV Spectra: *UV-1800* spectrophotometer (*Shimadzu*); λ_{max} (log ε) in nm. IR Spectra: *WQF-310* FT-IR spectrometer (*Beijing Second Optical Instruments Factory*) in KBr pellets; $\tilde{\nu}$ in cm^{-1}. ^{1}H- and ^{13}C-NMR spectra: *AV-400* spectrometer (*Bruker*), in (D_6)DMSO; δ in ppm with solvent peaks used as reference; *J* in Hz. 2D-INADEQUATE Spectra: *AVANCE III HD 600* MHz (*Bruker*), equipped with 5 mm ^{13}C observe *CryoProbe*. The INADEQUATE NMR spectrum was acquired with pulse sequence inadgpqfsp, relaxation delay (D1) of 5 s, spectrometer frequency (SF) 150.95 MHz, acquisition time (AQ) 0.014 s, number of scans (NS) 512, TD (F1) 128, *J*(C,C) value of 50 Hz in the pulse sequence, and temp. 298.2 K. The total runtime of INADEQUATE experiment was about 90 h. ESI-MS: *Quattro micro™ API* (*Waters*). HR-ESI-MS: *micrOTOF-QII* mass spectrometer (*Bruker Daltonik GmbH*); in *m*/*z*.

Plant Material. The fruiting bodies of *thelephora vialis* was collected in August 2010, at Kunming, Yunnan Province, P. R. China, and identified by *Ying-Qun Yuan* (Senior Engineer of Tianjin Zhongxin Pharmaceuticals). A voucher specimen (No. 201015) was deposited with the Herbarium of the Department of Medicinal Plants, Tianjin Zhongxin Pharmaceuticals R&D Center.

Extraction and Isolation. The air-dried fruiting bodies of *Thelephora vialis* (2.0 kg) were refluxed with 95% EtOH (2 × 20 l, 2 h each), then the residue was refluxed with 70% EtOH (1 × 16 l, 2 h). The combined filtrate was concentrated under reduced pressure to yield a dark brown syrup (200 g). The EtOH extract was suspended in H_2O and partitioned successively with petroleum ether, AcOEt. The AcOEt extract (120 g) was subjected to CC (SiO_2; CH_2Cl_2/acetone 20 : 1, 15 : 1, 10 : 1, 8 : 1, 5 : 1, 2 : 1) to give nine fractions (*Frs. 1–9*). *Fr. 6* (5.0 g) was separated by CC (*ODS*, 50%, 60%, 70% MeOH/H_2O) to afford four compounds **1** (100 mg), **3** (245 mg), a mixture of **4** and **5** (960 mg). *Fr. 7* (5.8 g) was subjected to CC (*ODS*; 60–70% MeOH/H_2O), then separated by prep. HPLC (40% MeCN/H_2O) to yield two compounds **6** (650 mg), **7** (82 mg). *Fr. 3* (1.1 g) was separated by CC (*Sephadex LH-20*; acetone) to give compound **2** (532 mg).

Vialisyl A (*=2,3,8,9-Tetrahydroxydibenzo[*d,d′*]benzo[1,2-*b*:6,5-*b′*]difuran-5,6-diyl Bis(phenylacetate)*; **1**). Greenish powder. UV (MeOH): 346 (4.76), 330 (4.59), 278 (4.09), 246 (4.50). IR (KBr): 3552, 3392, 1745, 1609, 1305, 1121, 849, 745. ^{1}H- and ^{13}C-NMR: see *Table*. HR-ESI-MS (neg.): 589.1147 ([*M* – H]$^-$, $C_{34}H_{21}O_{10}^-$; calc. 589.1140).

Table. *^{1}H- and ^{13}C-NMR Spectroscopic Data* ((D_6)DMSO) *of Compound* **1**. δ in ppm.

Position	δ(H)	δ(C)	2D-INADEQUATE
1, 1″		112.7	106.0, 116.6, 150.3
2, 2″	7.15 (*s*)	106.0	112.7, 143.3
3, 3″		143.3	106.0, 147.0
4, 4″		147.0	98.8, 143.3
5, 5″	7.17 (*s*)	98.8	147.0, 150.3
6, 6″		150.3	98.8, 112.7
1′, 4′		116.6	112.7, 130.6, 137.0
2′, 3′		130.6	116.6
6′, 5′		137.0	116.6
CO		169.0	39.4
CH_2	4.06 (*s*)	39.4	133.2, 169.0
C_{ipso}		133.2	39.4, 129.7
C_o	7.41 – 7.44 (*m*)	129.7	128.6, 133.2
C_m	7.41 – 7.44 (*m*)	128.6	127.3, 129.7
C_p	7.33 – 7.38 (*m*)	127.3	128.6
3, 3″-OH	9.19 (*s*)		
4, 4″-OH	9.76 (*s*)		

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