p-Terphenyls from the Basidiomycete *Thelephora aurantiotincta*

Lin Hu and Ji-Kai Liu*

Kunming Institute of Botany, the Chinese Academy of Sciences, Kunming 650204, P.R. China. Fax: +86871 5150227. E-mail: jkliu@mail.kib.ac.cn

* Author for correspondence and reprint requests

Z. Naturforsch. **58c**, 452–454 (2003); received January 9/February 27, 2003

A new *p*-terphenyl, named aurantiotinin A (1), together with ganbajunin C (2) and atromentin (3) were isolated from the fruiting bodies of the basidiomycete *Thelephora aurantiotincta* Corner. Their structures were established by spectral (MS, IR, UV, NMR, H-H COSY, HMQC, HMBC measurement) and chemical methods.

Key words: Thelephora aurantiotincta, p-Terphenyls, Aurantiotinin A

Introduction

The basidiomycete Thelephora aurantiotincta Corner belongs to the family Thelephoraceae. It grows in symbiosis with pine trees (Mao, 1998) and is sold in mixture with T. ganbajun Zang as delicious mushrooms with unique flavor and taste in Yunnan province, P.R. China. Up to date there have been no reports on the chemical constituents of T. aurantiotincta. However, the isolation of a series unusual poly (phenylacetyloxy)-substituted p-terphenyls (Hu et al., 2001; Hu and Liu, 2001) from the fruiting bodies of T. ganbanjun prompted us to start a chemical investigation on T. aurantio*tincta*. As a result, a new *p*-terphenyl derivative, named aurantiotinin A (1), together with ganbajunin C (2) (Hu et al., 2001) and atromentin (3) (Kögl and Pstowsky, 1924) were isolated from the fruiting bodies of T. aurantiotincta. This paper deals with their isolation and structural elucidation based on spectral and chemical methods.

Results and Discussion

Compound **1** was isolated as a white powder. Its molecular formula was assigned to be $C_{33}H_{24}O_9$ based on HR-EI-MS ([M]⁺: 564.1422, calc. 564.1420). The IR spectrum showed the wide absorption band of a hydroxyl group near 3437 cm⁻¹, and strong bands at 1739, 1716 cm⁻¹, indicative of an ester grouping and a carbonyl group, respec-

tively. ¹H NMR displayed three groups of signals of AA'BB' system arising from protons of 1,4-disubstitued aromatic rings [δ 7.17 (2H, d, J = 8.5 Hz, H-3, 5), 6.80 (2H, d, J = 8.5 Hz, H-2, 6); 7.20 (2H, d, J = 8.5 Hz, H-3", 5"), 6.71 (2H, d, J = 8.5 Hz, H-2", 6"); 7.69 (2H, d, H-3"", 5""), 6.77 (2H, d, J =8.7 Hz, H-2", 6")], mutiplets of mono-substituted benzene (δ 7.00 ~ 7.05, *m*, H-C_{*m*,*p*}; 6.80, *m*, H-C_o) and singlet of a methylene (δ 3.32, s, CH₂). Apart from signals of mono-substituted benzene and a methylene (see Table I), ¹³C NMR exhibited signals of two carboxyl groups (& 171.4, C=O; 164.1, C-1"), two 1, 4-disubstitued aromatic rings (8 123.9, C-1; 116.1, C-2, 6; 132.6, C-3, 5; 158.1, C-4 and 8 124.1, C-1"; 115.9, C-2", 6"; 132.6, C-3", 5"; 158.0, C-4"), a hexa-substituted aromatic ring (8 125.0, C-1', 4'; 142.5, C-2', 3', 5', 6'), remaining two sp² methine groups (δ 135.1, C-3''', 5'''; 116.3, C-2"', 6"') and two sp² quaternary carbons (δ 166.2, C-7", 120.9, H-4"). HMBC displayed the long distance correlations between C-1' and H-2, 6; C-4' and H-2", 6", indicated the existence of p-terphenyls carbon skeleton, which was also confirmed by

Table I. ¹H and ¹³C NMR Data for **1** (δ in ppm, *J* in Hz, in CD₃OD).

Position	$\boldsymbol{\delta}_{C}$	$\delta_{\rm H}$	HMBC (selected)
C (1)	123.9		H-C (3, 5)
H-C (2, 6)	116.1	6.80 (d, J = 8.5)	- (-)-)
H-C (3, 5)	132.6	7.17(d, J = 8.5)	
C (4)	158.1		H-C (2, 6)
C(1')	125.0		H-C (2, 6)
C(2', 6')	142.5		- () -)
C(3',5')	142.5		
C (4')	125.0		H-C (2", 6")
C (1")	124.1		H-C (3", 5")
C (2", 6")	115.9	6.71 (d, J = 8.5)	
C (3", 5")	132.6	7.20(d, J = 8.5)	
C (4")	158.0		H-C (2", 6")
cò í	171.4		
CH ₂	41.3	3.32, s	H-C _o
Cipso	135.1	,	H-C _m
H-C	130.1	6.80, <i>m</i>	H-C _n
H-C _m	129.3	7.00-7.05, m	P
H-C	127.9	7.00-7.05, m	H-C _o
$C(1^{F''})$	164.1	,	H-C (3", 5")
H-C (2", 6")	116.3	6.77 (d, J = 8.7)	
C (4"")	120.9		
H-C (3‴, 5‴)	135.1	7.69 (d, J = 8.7)	H-C (2", 6")
C (7‴)	166.2		H-C (3‴, 5‴)

0939-5075/2003/0500-0452 \$ 06.00 © 2003 Verlag der Zeitschrift für Naturforschung, Tübingen · www.znaturforsch.com · D

the characteristic peak at m/z 324 appeared in EI-MS. Despite of this peak which was formed by the lost of two fragments of 118 amu and 122 amu from molecular ion peak (m/z 564), EI-MS also displayed a characteristic ion peak (m/z 446)formed by the loss of a segment of 118 amu, which was attributed to be PhCH₂CO by considering and comparing NMR data with those of (phenylacetyloxy)-substituted *p*-terphenyls isolated from the fruiting bodies of T. ganbanjun (Hu et al., 2001; Hu and Liu, 2001). Another one of 122 amu was attributed to a fragment of C₇H₆O₂ based on the analysis of NMR data (see Table I), the molecular formula of 1, and on the base ion peak at m/z 121 $([C_7H_5O_2]^+)$ shown in EI-MS. HMBC exhibited the correlation peaks between C(1''') and H-3''', 5''', C (4"') and H-2"', 6"', C (7"') and H- 3"', 5"', indicative of a partial structure as shown in Fig. 1.



Fig. 1.

According to the above analysis, structure of 1 was assigned as a *p*-terphenyl containing a phenylacetyloxyl group, four hydroxyl groups and a group as shown in Fig. 2. When 1 was treated with phenylboronic acid as previously described (Tringali *et al.*, 1987) and the mixture was detected directly by negative FAB-MS. The quasi-molecular ion peak observed at m/z 735, indicated the formation of bis-phenylboronate, which implied the presence of two pairs of vicinal hydroxyl groups. Then, the structure of **1** was determined as [2,5cyclohexadien-1-one,4-carbonyl]4-phenylacetyloxy-[1,1',4',1"-terphenyl]-4"-yl semialdehyde, as shown in Fig. 2.

Experimental

General

M.p.: uncorrected. UV spectral: *UV-210* spectrometer, λ_{max} (log ε). IR: *Perkin-Elmer 577* spectrometer, KBr pellets, in cm⁻¹. ¹H and ¹³C NMR: *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 aurantiotincta* Corner were collected at Simao in Yunnan province, P.R. China, in August of 2002. This fungus was identified by Prof. Mu Zang at Kunming Institute of Botany, the Chinese Academy of Sciences, where a voucher specimen was deposited (HKAS 41001).

Extraction and Isolation

The fresh fruiting bodies of *T. aurantiotincta* were dried at 45 °C. The crushed powders (65 g) were defatted with petroleum (G.p. 40 °C) and exhaustively extracted with methanol (100 ml \times 7) at room temperature. The extracts were evaporated under reduced pressure and afforded a brown gum, which was suspended in water and extracted



Fig. 2. The structures of new compound (1, aurantiotinin A), ganbajunin C (2, Hu et al., 2001) and atromentin (3, Kögl) and Pstowsky, 1924).

with EtOAc (15 ml × 5). The EtOAc layer (E) afforded 2.8 g gums and aqueous layer (W) afforded 4 g of gums after evap. *in vacuo*. (E) was subjected to RP-18 column chromatography eluted with 75% MeOH/H₂O to give compound **1** (8 mg) and **2** (22 mg). (W) was subjected to RP-18 column chromatography eluted with 25% MeOH/H₂O to give compound **3** (9 mg).

Aurantiotinin A (= [2,5-cyclohexadien-1-one,4carbonyl]4-phenylacetyloxy-[1,1',4',1"-terphenyl]-4"-yl semialdehyde, **1**), white powder. UV (MeOH) λ_{max} (log ε): 261 (3.61), 205 (4.45) nm. IR^{KBr}_{max} v cm⁻¹: 3437 (brd.), 2929, 2063, 1739, 1716, 1610, 1525, 1457, 1339, 1264, 1025, 835. HR-EI-MS: 564.1422 ([C₃₃H₂₄O₉]⁺, Calc. 564.1420), EI-MS 70 eV (rel. int.) *m/z*: 564 (5, M⁺), 446 (15, [M–PhCH₂CO]⁺), 430 (13, [M–H₂O–PhCH₂CO]), 324 (65, [M–PhCH₂CO– C₇H₅O₂]⁺), 310 (90, [M–PhCH₂CO–C₇H₅O₂– CH₂]⁺), 121 (100, [C₇H₅O₂]⁺). FAB-MS (neg.): 717 (20, [M–H+Gly]⁺), 563 (100, [M–H]⁺). ¹H, ¹³C NMR see Table I.

Ganbajunin C (= bis[benzeneacetic acid]2',3',5',6'tetrahydroxy[1,1':4',1"-terphenyl]-4,4"-diyl ester, **2**), colorless crystals. M.p. 211.5-212.0 °C; UV (MeOH) λ_{max} (log ε): 372 (3.71), 271 (4.31), 203 (4.58) nm. IR^{KBr}_{max} λ cm⁻¹: 2800–3700, 1745, 1611, 1524, 1494, 1454, 1250, 1136, 1129, 985, 828, 724. FAB-MS (neg.): 561 (100, [M–H]⁺), 443 (22, [M– H–PhCH=CO]⁺), 325(47, [M–H–2PhCH=CO]⁺), 324 (43). NMR data were in consistent with the report (Hu *et al.*, 2001).

Atromentin (= 2,5-dihydroxy-3,6-bis *p*-hydroxyphenyl)-1,4-benzoquinone, **3**), purple crystals (MeOH). M.p. >300 °C. EIMS (70 eV): 326 (12, $[M+2]^+$), 325 (18, $[M+1]^+$), 324 (100, $[M]^+$), 316 (7), 296 (21), 279 (10). FAB-MS (neg.): 417 (4, [M+2-H+Gly]⁺), 325 (60, $[M+2-H]^+$), 309 (45, [M+2-H-O]⁺), 229 (38, $[M-2H-C_6H_5O]^+$), 137 (100, [M- $2H-2C_6H_5O]^+$). ¹H NMR (CD₃OD): 7.86 (*d*, 2H, *J* = 8.4 Hz, H-3, 5, 3", 5"), 6.79 (*d*, 2H, *J* = 8.4 Hz, H-2, 6, 2", 6"). ¹C NMR (CD₃OD): 163.0 (C-2', 3', 4', 5'), 158.2 (C-4, 4"), 132.9 (C-3, 5, 3", 5"), 123.9 (C-1, 4), 121.2 (C-1', 4"), 116.0 (C-2, 6, 2", 6").

Acknowledgements

We wish to acknowledge the financial support from the National Natural Science Foundation of China (30225048).

- Hu L., Gao J. M., and Liu J. K. (2001), Unusual poly(phenylacetyloxy)-substituted 1,1':4',1"-terphenyl derivatives from fruiting bodies of the basidiomycete *Thelephora ganbajun*. Helv. Chim. Acta **84** (11), 3342– 3349.
- Hu L. and Liu J. K. (2001), Two novel phenylacetoxylated *p*-terphenyls from *Thelephora ganbajun* Zang. Z. Naturforsch. 56c, 983–987.
- Kögl F. and Pstowsky J. J. (1924), Fungi dye stuffs. I. Atromentin. Ann. **440**, 19–35.
- Mao X. L. (1998), Economic Fungi of China, 1st edn. Sciences Press, Beijing, p. 458.
- Tringali C., Piattell M., Geraci C., Nicolosi G., and Rocco C. (1987), Previously unreported *p*-terphenyl derivatives with antibiotic properties from the fruiting bodies of *Sarcodon leucompus* (Basidiomycetes), a two dimensional nuclear magnetic resonance study. Can. J. Chem. **65** (7), 2369–2372.

Nachdruck – auch auszugsweise – nur mit schriftlicher Genehmigung des Verlages gestattet Satz und Druck: AZ Druck und Datentechnik GmbH, Kempten