Tremellin, a Novel Symmetrical Compound, from the Basidiomycete *Tremella aurantialba*

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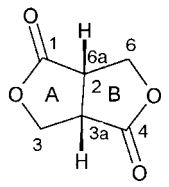
A novel, highly symmetrical compound, named tremellin (**1**), was isolated from the fruiting bodies of the basidiomycete *Tremella aurantilba*. Its structure was established by spectroscopic means and X-ray analysis.

Introduction. – *Tremella aurantialba* is one of the edible mushrooms that has been used as antihepatitis agent and immunostimulant [1]. The fungus is distributed in Yunnan, Sichuan, Xizang, Gansu, and Jiangxi provinces of China [2]. As part of our studies on the active metabolites from higher fungi [3–9], the chemical constituents of *Tremella aurantialba* were investigated. The present report deals with the structure elucidation of a new compound **1**, named tremellin, which was isolated from the fruiting bodies of this fungus. Tremellin (**1**) has a simple, highly symmetric structure.



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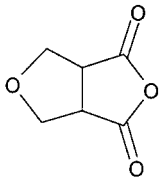

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Results and Discussion. – *T. aurantialba* (dry weight 3.5 kg) was extracted with $CHCl_3$/MeOH 1:1. Repeated chromatography afforded tremellin (**1**; 10 mg) as colorless needles with a molecular formula of $C_6H_6O_4$ (HR-MS: *m*/*z* 142.0264 (M^+, $C_6H_6O_4^+$; calc. 142.0266). The ^{1}H- and ^{13}C-NMR and IR data established its structure as tetrahydro-1*H*,4*H*-furo[3,4-*c*]furan-1,4-dione (**1**).

Three signals in the ^{13}C-NMR (DEPT) spectrum of **1** were recognized (1 C, 1 CH_2, 1 CH), which were assigned to a carbonyl (δ 175.5), an oxymethylene (δ 68.9), and a methine group (δ 40.7). The three signals in the ^{1}H-NMR spectrum at δ (H) 4.67 (*d*, $J = 9.7$ Hz, H_a–C(3), H_a–C(6)), 4.07 (*m*, H_b–C(3), H_b–C(6)), and 3.51 (*m*, H–C(3a), H–C(6a)) revealed a highly symmetrical structure and led to the deduction of two possible structures **1** and **2**. In the IR spectrum of tremellin, the carbonyl absorption at 1765 cm^{-1} indicated the presence of a γ-lactone moiety, and the fragment ion *m*/*z* 98 ($[M - CO_2]^+$) in the EI-MS confirmed the presence of this γ-lactone unit.

The relative configuration of tremellin (**1**) was established by a single-crystal X-ray-analysis (*Figs. 1* and *2*).

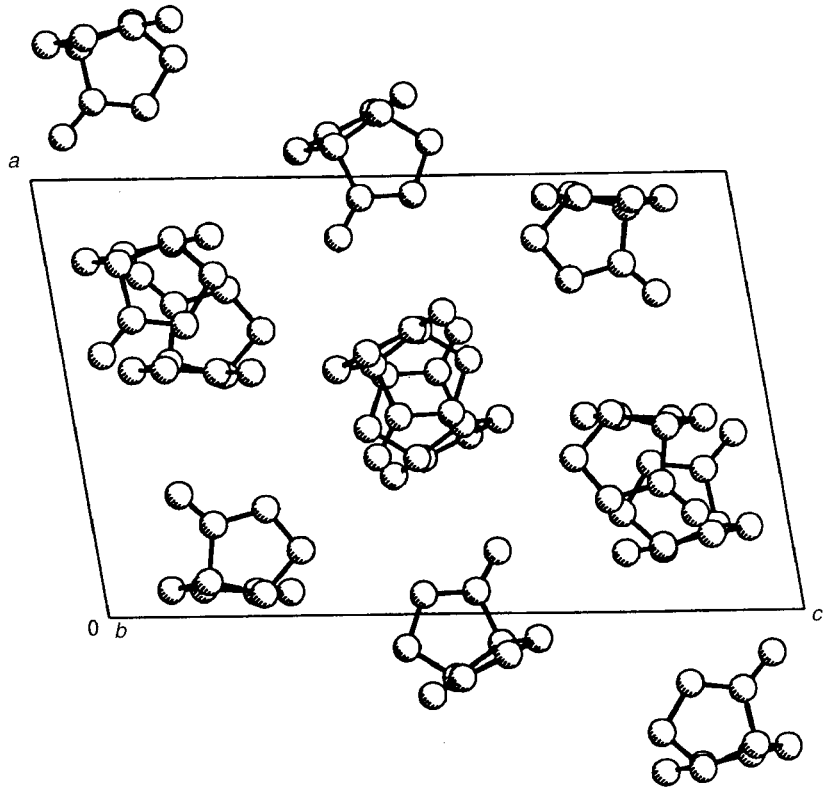

Fig. 1. *Perspective views of the molecules in the unit cell along the b axis*

Experimental Part

General. M.p.: uncorrected. IR: KBr pellets; in cm^{-1}. ^1H- and ^{13}C-NMR: *Bruker DRX-500* spectrometers, δ in ppm, J in Hz. MS. *VG Autospect-3000* spectrometer; m/z (rel. int).

Mushroom Material. The fruiting bodies of the basidiomycete *Tremella aurantialba* were provided by the Kunming Institute of Edible Mushroom.

Extraction and Isolation. The entire fruiting bodies of *Tremella aurantialba* (dry weight 3.5 kg) were extracted with $CHCl_3$/MeOH 1:1 at r.t. (4 times). The residue was first extracted with petroleum ether and then with AcOEt. The AcOEt extract (36.5 g) was submitted to column chromatography (silica gel, gradient $CHCl_3$/AcOEt 10:0, 9:1, 8:2). The combined fractions ($CHCl_3$/AcOEt 9:1) were purified by recrystallization from petroleum ether/Et_2O to give pure tremellin (**1**, 10 mg).

Tremellin (= rel-*(3a*R,*6a*R*)-Tetrahydro-1*H,*4*H-*furo[3,4-*c*]furan-1,4-dione*; **1**). Colorless crystals. M.p. 130–133° (petroleum ether/Et_2O). IR (Kbr): 3514, 2985, 1765, 1477, 1370, 1299, 1176. ^1H-NMR ($CDCl_3$): 3.51 (*m*, 2 H); 4.54 (*m*, 2 H); 4.67 (*d*, $J = 9.7$, 2 H). ^{13}C-NMR ($CDCl_3$): 40.7 (CH_2); 68.9 (CH); 175.5 (C=O). HR-EI-MS: 142.0264 ($C_6H_6O_4^+$, M^+; calc. 142.0266). EI-MS: 142 (48), 98 (23), 84 (34), 69 (100), 55 (72), 54 (76).

X-Ray Analysis. Crystal data: $C_6H_6O_4$, M 142, monoclinic, space group $P2_1/a$; $a = 11.3010(11)$, $b = 9.1700(10)$, $c = 17.6090(21)$ Å, $\beta = 99.785(7)°$, $V = 1798.3(3)$ Å^3, $Z = 12$. Final R_f and R_w values were 0.064 and 0.052, resp. A total of 2557 reflections were recorded in the ω scanning mode with a *MAC-DIP-2030K*

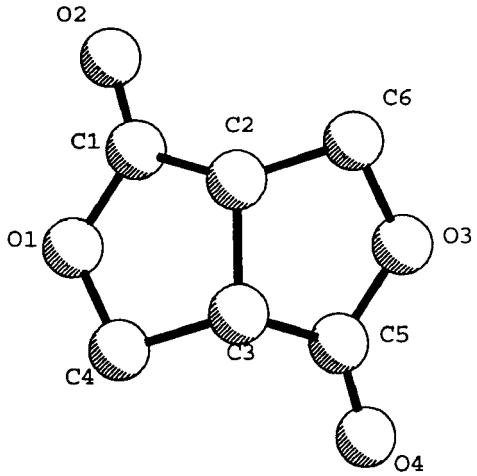

Fig. 2. *Perspective view of tremellin* (**1**) *from the X-ray analysis.* Arbitrary numbering.

diffractometer with graphite-monochromated Mo-$K\alpha$ scanning radiation. The structure was solved by the direct method (SHELXS-86).

Crystallographic data (excluding structure factors) have been deposited with the *Cambridge Crystallographic Data Centre*. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ UK (fax: +44(1223) 336033; e-mail: deposit@cdc.ac.uk).

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REFERENCES

[1] S. Y. Chen, H. Y. Chen, 'Collection of Mushroom Prescriptions', Shanghai Scientific and Technological Literature Press, Shanghai, 2000, p. 68.
[2] X. L. Mao, 'Economic Fungi of China', Academic Press, Beijing, 1998, p. 458.
[3] Z. H. Ding, Z. J. Dong, J. K. Liu, *Helv. Chim. Acta* **2001**, *84*, 259.
[4] J. M. Gao, Z. J. Dong, J. K. Liu, *Lipids* **2001**, *36*, 175.
[5] J. M. Gao, L. Hu, Z. J. Dong, J. K. Liu, *Lipids* **2001**, *36*, 521.
[6] L. Hu, J. M. Gao, J. K. Liu, *Helv. Chim. Acta* **2001**, *84*, 3342.
[7] J. W. Tan, Z. J. Dong, J. K. Liu, *Helv. Chim. Acta* **2000**, *83*, 3191.
[8] S. H. Wu, X. D. Luo, Y. B. Ma, J. K. Liu, *J. Nat. Prod.* **2000**, *63*, 534.
[9] J. M. Gao, L. Hu, J. K. Liu, *Steroids* **2001**, *66*, 771.

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