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A NEW COMPOUND: XYLOKETAL H FROM MANGROVE FUNGUS *Xylaria* SP. FROM THE SOUTH CHINA SEA COAST

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*A new metabolite xyloketal H (**1**), was isolated from mangrove fungus* Xylaria *sp. (No.2508) obtained from the South China Sea. By spectroscopic analyses, primarily 2D NMR methods and X-ray diffraction experiments, its structure was elucidated.*

Key words: mangrove fungus, *Xylaria* sp., xyloketal, X-ray structure analysis.

In recent years, many new bioactive compounds have been isolated from different sources of marine organisms, especially marine fungi [1]. The mangrove fungus strain No. 2508, which was collected from seeds of an angiosperm tree and identified as *Xylaria* species (*Ascomycota*), was found to produce rich secondary metabolites. We have previous reported seven ketal compounds, xyloketals A~G, and a novel *N*-cinnamoylcyclopeptide isolated from the fermentation broth of this fungus [2–5]. Recently, we have embarked on a study of the metabolites of No. 2508 and have again isolated a new ketal compound, xyloketal H (**1**). Its structure was elucidated by analysis of spectroscopic data and X-ray diffraction analysis.

A 200 L culture filtrate was concentrated and extracted with ethyl acetate. The extract was repeatedly chromatographed on silica gel columns. Xyloketal H (**1**) was obtained from the 3% chloroform/petroleum ether fraction as a colorless block crystals (18 mg). It had the molecular formula $C_{20}H_{26}O_5$, as established by FABMS at *m/z* 347 $[M+H]^+$ and elemental analysis (Found: C, 68.98; H, 7.238. $C_{20}H_{26}O_5$ requires C, 69.34; H, 7.514%).

In the ^1H and ^{13}C NMR spectra (Table 1), two methylene groups at δ_H 3.50, 4.16; δ_C 74.5 and δ_H 3.54, 4.18; δ_C 74.1 indicate that they are located at the *ortho*-position of the oxygen atom, and the other two methylene groups at δ_H 2.81, 2.84; δ_C 18.5 and δ_H 2.16, 2.67; δ_C 18.7 should link up with the olefinic carbon. ^{13}C NMR and DEPT spectra also showed four sets of signals of quaternary carbon at different chemical shifts (186.7, 152.2 and 152.1, 107.7 and 104.4, 99.6 and 95.9), which suggested the presence of ketal. In the HMBC spectrum (Fig. 1), correlations between C-2 and H-4, H-6, H-7, H-10, C-6 and H-4, H-7, H-10, H-11, C-5 and H-4, H-6, H-7, H-11, C-8 and H-6, H-7, H-13 provide some important structure information. The molecular structure of **1** was finally confirmed by X-ray diffraction analysis (Fig. 2).

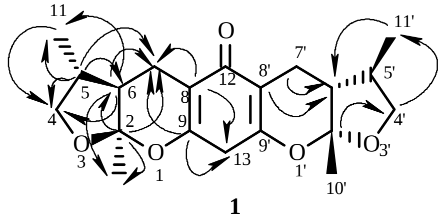

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Fig. 1. The correlations of HMBC of **1**.

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TABLE 1. NMR Data of **1** ($CDCl_3$, δ, ppm, J/Hz)

C atom	δ_C (DEPT)	δ_H	C atom	δ_C (DEPT)	δ_H
2	107.7 (C)		8	99.6 (C)	
2′	104.4 (C)		8′	95.9 (C)	
4	74.5 (CH_2)	3.50 (dd, J = 8.5, 2.0)	9	152.2 (C)	
		4.16 (dd, J = 8.5, 2.0)	9′	152.1 (C)	
4′	74.1 (CH_2)	3.54 (dd, J = 8.5, 2.5)	10	23.1 (CH_3)	1.49 (s)
		4.18 (dd, J = 8.5, 2.5)	10′	22.7 (CH_3)	1.52 (s)
5	35.5 (CH)	2.13 (m)	11	16.1 (CH_3)	1.05 (d, J = 6.5)
5′	35.4 (CH)	2.14 (m)	11′	15.9 (CH_3)	1.07 (d, J = 6.5)
6	47.8 (CH)	1.88 (ddd, J = 6.5, 4,5, 1.0)	12	186.7 (C)	
6′	47.6 (CH)	1.92 (ddd, J = 5.5, 4.0, 1.0)	13	18.5 (CH_2)	2.81 (d, J = 1.5)
7	18.7 (CH_2)	2.16 (d, J = 7.0)			2.84 (d, J = 1.5)
		2.67 (d, J = 6.5)			
7′	18.6 (CH_2)	2.64 (d, J = 7.0)			
		2.70 (d, J = 6.5)			

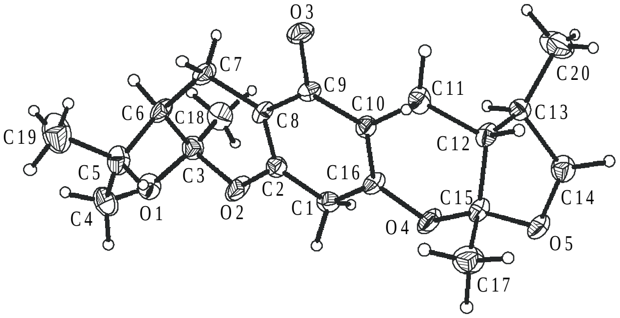

Fig. 2. The structure of **1**.

EXPERIMENTAL

General Methods. ^1H, ^{13}C, DEPT, NMR spectroscopic data were recorded on a Varian Inova 500NB NMR spectrometer with tetramethylsilane as internal standard. Mass spectra were measured with a VG-ZAB-HS mass spectrometer. The X-ray data were generated on a Bruker Smart 1000 CCD system diffractometer.

Fungus Strain and Purification. A strain of the fungus *Xylaria* sp. (No. 2508) was isolated from a seed of an angiosperm tree in Mai Po, Hong Kong, and was stored in the Department of Applied Chemistry, Zhongshan University, PR China. Starter cultures (from Professor E. B. Gareth Jones and Dr. L. L. P. Vrijmoed) were maintained on cornmeal seawater agar. Plugs of agar supporting mycelial growth were cut and transferred aseptically to a 250 mL Erlenmeyer flask containing 100 mL of liquid medium GYT (glucose 10 g/L, peptone 2g/L, yeast extract 1 g/L, NaCl 30g/L). The flask was incubated at 30°C on a rotary shaker for 5–7 days. The mycelium was aseptically transferred to a 300 L fermenter containing 200 L of GYT medium and was incubated at 30°C for 86 h. The culture (200 L) was filtered through cheesecloth. The filtrate was concentrated to 3.5 L below 60°C and extracted six times by shaking with an equal volume of ethyl acetate. The combined extracts were chromatographed on silica gel using gradient elution from petroleum ether to chloroform to obtain **1** from elution with 3% chloroform/petroleum ether as a colorless block crystals.

X-Ray Structure Analysis. A transparent single crystal obtained from ethanol solution was measured on a Bruker Smart 1000 CCD diffractometer (Mo Kα-radiation, graphite monochromator). Crystal data for **1**: $C_{20}H_{26}O_5$ orthorhombic, $P2_12_12_1$, $a = 8.7702(12)$ Å, $b = 9.4137(13)$ Å, $c = 21.946(3)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 1811.9(4)$ Å^3, $Z = 4 D_{calcd} = 1.270$ Mg/m^3, $\mu = 0.090$ mm^{-1}, F(000) = 744.

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