

鸡脚参中一个新木脂素

项伟, 黎胜红, 纳智, 张宏杰, 赵勤实,
林中文, 孙汉董*

(中国科学院昆明植物研究所植物化学与西部植物资源持续利用国家重点实验室, 云南 昆明 650204)

摘要: 从鸡脚参 [*Orthosiphon wulfenioides* (Diels) Hand.-Mazz.] 根中提取分离了一个新的木脂素, 命名为鸡脚参木脂素。其结构由 NMR、MS 等波谱分析确定。初步活性实验显示该化合物不具备抗真菌和抗肿瘤活性。

关键词: 鸡脚参; 木脂素; 鸡脚参木脂素。

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A New Lignan from *Orthosiphon wulfenioides*XIANG Wei, LI Sheng-Hong, NA Zhi, ZHANG Hong-Jie, ZHAO Qin-Shi,
LIN Zhong-Wen, SUN Han-Dong*(State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany,
Chinese Academy of Sciences, Kunming 650204, China)

Abstract: A new lignan, named orthosilignin, was isolated from the ethyl acetate extract of the roots of *Orthosiphon wulfenioides* (Diels) Hand.-Mazz. Its structure was elucidated by spectral methods. It did not display antifungal and anticancer activity in the bioassay experiments.

Key words: *Orthosiphon wulfenioides*; lignan; orthosilignin

Orthosiphon wulfenioides (Diels) Hand.-Mazz, a folk medicinal plant growing in Southwest of China, has been used for treating fracture, dyspepsy, arthritic, vascular inflammation, edema, and biliary lithiasis (Jiangsu New Medical College, 1985; Matsubara *et al*, 1999; Ohashi *et al*, 2000). In the investigation of biologically active substances from this plant, a new lignan, named orthosilignin (1) was isolated. Its structure was elucidated by spectral methods.

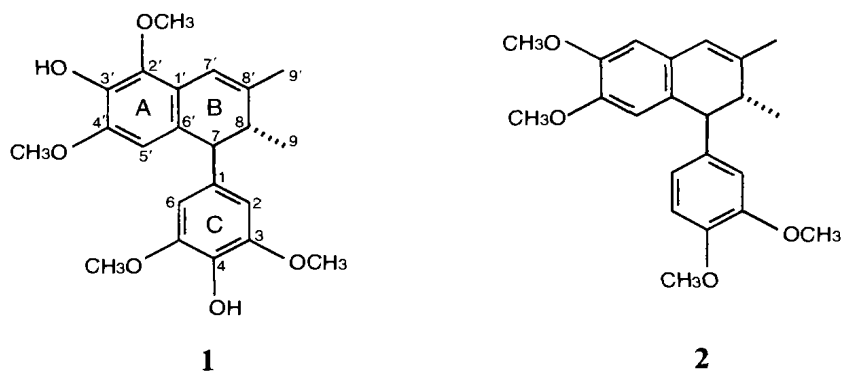
1 Results and discussion

Compound 1 was obtained as a colorless cubic crystal (CHCl_3), possessed a molecular formula of $\text{C}_{22}\text{H}_{26}\text{O}_6$ on the basis of EIMS (m/z 386, base peak, $[\text{M}]^+$) and HREIMS (found: m/z 386.1721,

* 通讯联系人: Corresponding author

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作者简介: 项伟 (1964 -) 男, 在读博士研究生, 主要从事植物化学研究。



calcd: 386.1729), which was supported by its ^{13}C NMR (including DEPT) spectra. The IR spectrum showed a broad absorption at 3487 cm^{-1} indicating the existence of hydroxyl groups. Further, IR bonds at 1615, 1516, 1460 cm^{-1} suggested the occurrence of phenyl groups. The UV spectrum showed absorption at 295 and 250 nm consistent with phenylethenyl functionality. Analysis of the ^1H and ^{13}C NMR showed that compound **1** contained two methyls, four aromatic/olefinic methines and ten aromatic/olefinic quaternary carbons (including six oxygenated ones), along with four methoxyl groups. From the amounts and chemical shifts of the carbon signals, two $\text{C}_6 - \text{C}_3$ units could be easily recognized and thus an aryldihydronaphthalene type lignan skeleton was evident. All methoxyl groups in **1**, unlike in magnoliadiol (Miyazawa *et al*, 1996), were in the range of δ_{H} 3.73 – 3.84, which implied that C – 5' of **1** was non-substituted. The tri-substituted double bond could be formed exclusively between C – 7' and C – 8', which was confirmed by the downfield $\text{CH}_3 - 9'$ signal (δ_{H} 1.79) and HMBC correlation of the olefinic proton at δ_{H} 6.42 (H – 7') with C – 9' (δ_{C} 22.3). Signals at δ_{H} 3.84 (3H, s) and H – 7' correlated with the same quaternary carbon at δ_{C} 142.3, indicating that a methoxyl group was attached to C – 2'. Signal at δ_{H} 3.73 (9H, s) showed ROESY cross-peaks with H – 5' [δ_{H} 6.33 (1H, s)], H – 2 and H – 6 [δ_{H} 6.28 (2H, s)], resulting the assignments of the other three methoxyl groups to be at C – 3, C – 5 and C – 4' respectively. C – 3' and C – 4 of **1** were hydroxylated therefore. The above results were further supported by fragmental ion peaks at m/z 232 and 154 (Fig.1) in the EIMS spectrum.

By comparing the coupling constants of H – 7 [δ_{H} 3.59 (1H, d, $J = 3.4\text{ Hz}$)] and H – 8 [δ_{H} 2.34 (1H, dq, $J = 3.4, 7.1\text{ Hz}$)], and the chemical shifts of C – 7 [δ_{C} 51.5 (d)], C – 8 [δ_{C} 41.7 (d)] and their neighboring carbons with those corresponding values of cyclogalgravin (**2**) (Fonseca *et al*, 1979), compound **1** should possess the same relative stereochemistry as **2** at C – 7 and C – 8. In the structure of **1**, ring B preferred the flattening rather than a half-chair conformation, because of the existence of a double bond between C – 7' and C – 8'. The signal at δ_{H} 3.59, owing to H – 7, appeared as a doublet with $J = 3.40\text{ Hz}$, compatible with a dihedral angle of *ca* 70° between the H – 7 and H – 8. Accordingly, $\text{CH}_3 - 9$ and ring C were established at pseudoaxial positions. Furthermore, this postulation was confirmed by ROESY correlations of H – 7 with H – 5', H – 2 and H – 6,

as well as correlation of H - 8 with H - 2 and H - 6 respectively.

Compound **1** was subjected to bioassay evaluations, including antifungal (toward *penicillium avel-lanceum* UC - 4376), anti - inflammatory and cytotoxic (toward K562 cell) tests. Unfortunately, there was not significant activity being observed in the above experiments.

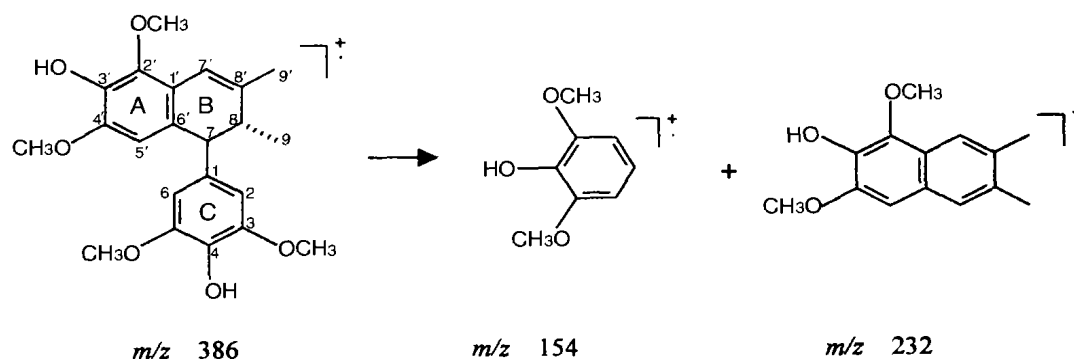


Fig. 1 The selected MS fractions of **1**

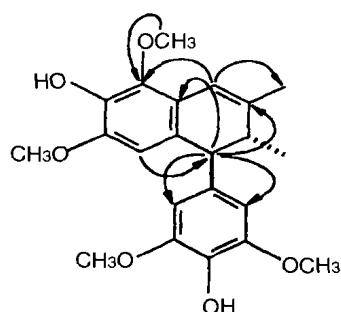


Fig. 2 Selected HMBC correlations of **1** (500 MHz, in $CDCl_3$)

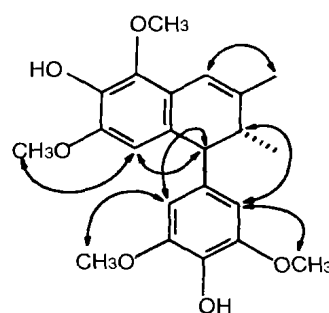


Fig. 3 Selected ROESY correlations of **1** (500 MHz, in $CDCl_3$)

2 Experimental

2.1 General experimental procedures

Melting point was determined on an XRC - 1 micro-melting point apparatus and was uncorrected. Optical rotation was taken on JASCO DIP - 370 digital polarimeter. UV spectra was obtained on UV - 210A spectrometer. IR spectra was obtained on Bio-Rad FTS - 35 spectrometer with KBr pellets. MS and HRMS spectra were measured on VG Auto Spec - 3000 spectrometer at 70 eV. 1D and 2D NMR experiment was conducted on Bruker DRX - 500 instrument with TMS as internal standard, respectively. Isolation and purification were performed by column chromatography and TLC on silica gel.

2.2 Plant materials

The root of *Orthosiphon wulfenoides* was collected in September 1999 from Eryun county, Yunnan Province and air-dried. The identity of the plant material was verified by Prof. Lin Zhong-Wen. A voucher specimen was deposited in the state key laboratory of phytochemistry and plant resources in west China, Kunming Institute of Botany, Chinese Academy of Sciences.

Table 1 The ^1H , ^{13}C NMR data of orthosilignin (δ in ppm, J in Hz)

Position	$^1\text{H}^a$	$^{13}\text{C}^b$	DEPT
1		137.0	C
2	6.28 (1H, s)	104.4	CH
3		146.6	C
4		133.1	C
5		146.6	C
6	6.28 (1H, s)	104.4	CH
7	3.59 (1H, d, $J = 3.4$)	51.5	CH
8	2.34 (1H, dq, $J = 3.4, 7.1$)	41.7	CH
9	1.03 (3H, d, $J = 7.1$)	18.5	CH_3
1'		120.7	C
2'		142.3	C
3'		136.4	C
4'		145.8	C
5'	6.33 (1H, s)	108.1	CH
6'		126.6	C
7'	6.42 (1H, s)	114.9	CH
8'		138.8	C
9'	1.79 (3H, s)	22.3	CH_3
3-OCH ₃	3.73 (3H, s) s	56.0	CH_3
5-OCH ₃	3.73 (3H, s)	56.0	CH_3
2'-OCH ₃	3.84 (3H, s)	60.9	CH_3
4'-OCH ₃	3.73 (3H, s)	56.0	CH_3

^aRecorded at 500 MHz in CDCl_3 ;^bRecorded at 125 MHz in CDCl_3 ;

2.3 Extraction and isolation

The air dried and powdered root (3.0 kg) of *Orthosiphon wulferioides* was extracted with 70% aqueous acetone for four times at room temperature to give an extract (600 g), which was partitioned between EtOAc and H_2O . The EtOAc extract (60 g) was chromatographed on a silica gel column, eluting with gradient mixtures of petroleum ether and chloroform (from 100% petroleum ether to 100% chloroform). According to the differences in composition monitored by TLC (Si gel), 3 fractions were obtained. The third fraction was purified by recrystallization from chloroform to afford orthosilignin (500 mg).

2.4 Identification

Compound 1, $\text{C}_{22}\text{H}_{26}\text{O}_6$, colorless cubic crystals (CHCl_3), mp 117–118°C, $[\alpha]_D^{25} - 3.1^\circ$ (c 1.15, CHCl_3); $\text{UV}^{\text{MeOH}}_{\text{max}}$: 295, 250 nm; $\text{IR}^{\text{KBr}}_{\text{max}}$: 1117, 1216, 1320, 1460, 1497, 1516, 1616, 2954, 3487 cm^{-1} ; EIMS: 386 $[\text{M}]^+$ (100%), 371 (25%), 339 (20%), 311 (19%), 279 (15%), 232 (70%), 217 (45%), 181 (47%), 167 (37%), 154 (35%), 139 (30%), 115 (33%); ^1H and ^{13}C NMR data see table 1.

References:

- Fonseca SF, Nielsen LT, Ruveda EA, 1979. Lignans of *Araucaria angustifolia* and ^{13}C NMR analysis of some phenyltetralin lignans [J]. *Phytochemistry*, **18**: 1703–1708
- Jiansu New Medical College, 1985. The Dictionary of Chinese Traditional Medicine [M]. Shanghai: Shanghai Science Press, 202
- Matsubara T, Bohgaki T, Watarai M, et al, 1999. Antihypertensive actions of methylpariiochromene A from *Orthosiphon aristatus*, an Indonesian traditional medicinal plant [J]. *Biological and Pharmaceutical Bulletin*, **22**: 1083–1088
- Miyazawa M, Kasahara H, Kameoka H, 1996. (-)-Magnofargesin and (+)-Magnoliadiol, two lignans from *Magnolia fargesii* [J]. *Phytochemistry*, **42**: 531–533
- Ohashi K, Bohgaki T, Shibuya H, 2000. Antihypertensive substance in the leaves of *Orthosiphon aristatus* in Java Island [J]. *Journal of the Pharmaceutical Society of Japan*, **120**: 474–482