

A New Benzofuran Derivative from the Bark of Mulberry Tree

Sheng Jun DAI, Zhi Bo MA, Shuai LI, Ruo Yun CHEN, De Quan YU*

Institute of Materia Medica, Chinese Academy of Medical Sciences &
Peking Union Medical College, Beijing 100050

Abstract: From the EtOH extract of the barks of *Morus macroura* Miq, a new benzofuran derivative, macrouirin D **1**, together with four known benzofuran derivatives, macrouirin B **2**, 2-(3,5-dihydroxyphenyl)-5,6-dihydroxybenzofuran **3**, moracin M **4**, and mulberroside C **5** were isolated, and their structures were determined on the basis of spectroscopic evidence and chemical correlation with known compounds.

Keywords: *Morus macroura* Miq., macrouirin D.

Morus macroura Miq. belongs to the genus *morus* of the family Moraceae, distributed in the south part of China, especially in Xishuangbanna, Yunnan province. In the previous paper ¹, we reported the isolation and structure determination of a new benzofuran derivative from the barks of the listed plant. Further phytochemical investigation of the EtOH extract of the barks of *Morus macroura* resulted in the isolation of five benzofuran derivatives (**Figure 1**), among which compound **1** is a new one, compounds **3** and **5** were isolated and purified from this plant for the first time. Herein, we report the structure elucidation of the new benzofuran derivative, macrouirin D.

Macrouirin D was isolated as brown powder, $[\alpha]_D^{30} -5.2$ (c 0.12, CH₃COCH₃), exhibiting strong blue fluorescence under UV light at 254 nm. It showed a quasi-molecular [M+H]⁺ ion peak at *m/z* 501.1 in its FABMS, and the HRFAB-MS gave a [M+H]⁺ ion peak at *m/z* 501.1162 (calcd. for C₂₈H₂₁O₉, 501.1186), corresponding to the molecular formula C₂₈H₂₀O₉. The IR spectrum (KBr, cm⁻¹) of macrouirin D showed absorption bands ascribable to hydroxyl (3400) and aromatic groups (1606, 1450). The UV spectrum showed maxima at 232, 333 nm, and was very similar to those of macrouirin C, so it was a 2-phenylbenzofuran derivative probably ².

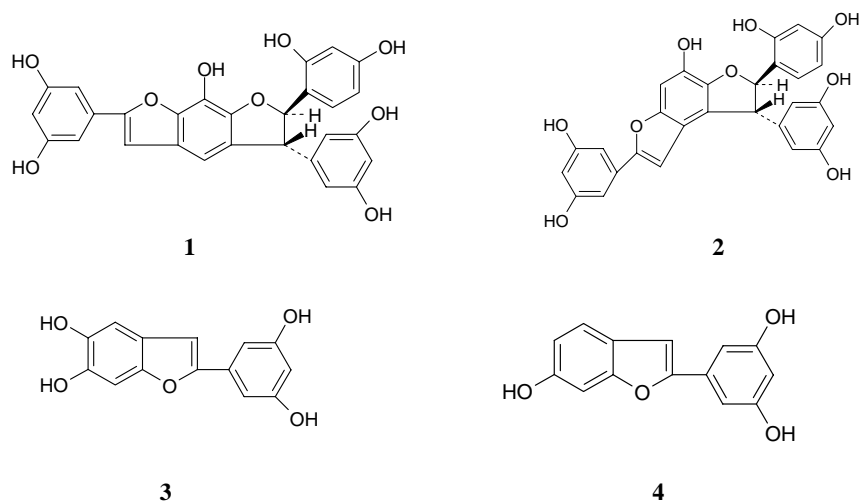
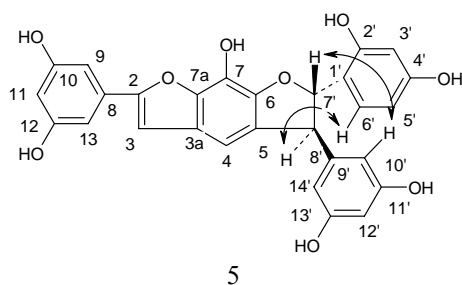
The ¹H-NMR spectrum of macrouirin D (**Table 1**) exhibited two sets of signals for 3,5-dihydroxybenzene moieties at δ6.71 (d, 2H, J=2.0), δ6.28 (t, 1H, J=2.0), δ6.31 (d, 2H, J=2.0) and δ6.22 (t, 1H, J=2.0), one set of signals for 2,4-dihydroxybenzene moiety at δ6.47 (d, 1H, J=2.0), δ 6.30 (dd, 1H, J=2.0,8.5), and δ 7.11 (d, 1H, J=8.5), one aromatic proton signal at δ 6.99 (s, 1H), one proton of furan nucleus signal at δ6.97 (s, 1H) as well as two coupled doublets at δ5.85 (d, 1H, J=7.0) and δ4.86 (d, 1H, J=7.0). In the ¹H-¹H

* E-mail: dqyu@imm.ac.cn

COSY experiment, the above all proton correlations were observed. In the HMBC spectrum, the long-range correlations between H-7' and C-1', C-2', C-6', C-9', C-6; H-8' and C-1', C-7', C-9', C-10' (or C-14'), C-5, C-6; H-3 and C-2, C-3a, C-4, C-7a, C-8; H-4 and C-3, C-5, C-6, C-7a, H-9 (or H-13) and C-2; H-10' (or H-14') and C-8'; as well as H-6' and C-7' allowed the skeleton connection of macrouirin D as indicated (**Figure 1**). A pair of *trans* protons at δ 5.85 (d, 1H, $J=7.0$) and δ 4.86 (d, 1H, $J=7.0$) were similar to those of gnetuhainin A³. In the elected NOE spectrum of macrouirin D (**Figure 2**), the obvious NOEs between H-7' and H-10' (or H-14'), as well as between H-8' and H-6' suggested a *trans* orientation of H-7' and H-8'. If it was a *cis* orientation, the NOEs between H-7' and H-8' would be obvious, furthermore, the chemical shifts of H-10' and H-14' would be further upfield due to the shielding of 7'-phenyl⁴. Thus, the structure of macrouirin D (**1**) was determined as shown (**Figure 1**).

Table 1 ¹H(500MHz) and ¹³C (125MHz) NMR spectral data for macrouirin D in CD₃COCD₃

Position	1		2		1 HMBC
	δ_{H} (J, Hz)	δ_{C}	H (J, Hz)	δ_{C}	
2		155.5		155.7	
3	6.97(1H, s)	102.7	6.56(1H, s)	98.4	C ₂ , C _{3a} , C ₄ , C _{7a} , C ₈
3		124.3		119.0	
4	6.99(1H, s)	106.9		118.8	C ₃ , C ₅ , C ₆ , C _{7a}
5		113.3		133.2	
6		148.3		141.0	
7		133.4	6.96(1H, s)	100.5	
7		139.8		151.8	
8		146.2		145.6	
9	6.71(1H, s)	103.6	6.74, d, (2.5)	107.1	C ₂ , C ₁₁
10		159.6		159.7	
11	6.28, t, (2.0)	103.2	6.46, t, (2.5)	103.3	C ₉ , C ₁₀ , C ₁₂ , C ₁₃
12		159.6		159.7	
13	6.71, d, (2.0)	103.6	6.74, d, (2.5)	103.5	C ₂ , C ₁₁
1		119.3		121.4	
2		156.5		156.8	
3	6.47, d, (2.0)	103.5	6.30, d, (2.5)	103.5	
4		159.2		159.2	
5	6.30, dd, (2.0, 8.0)	107.4	6.29, dd, (2.5, 8.5)	107.3	
6	7.11, d, (8.0)	128.6	7.14, d, (8.5)	129.0	C ₄ , C ₇
7	5.85, d, (7.0)	90.1	5.81, d, (7.0)	89.6	C ₂ , C ₆ , C ₈
8	4.86, d, (7.0)	54.9	4.78, d, (7.0)	56.3	C ₁ , C ₇ , C ₉
9		145.6		145.6	
10	6.31, d, (2.0)	106.8	6.33, d, (2.0)	103.5	C ₈ , C ₁₁ , C ₁₂
11		159.4		159.4	
12	6.22, t, (2.0)	102.1	6.22, t, (2.0)	102.0	C ₁₀ , C ₁₄ , C ₁₁ , C ₁₃
13		159.4		159.4	
14	6.31, d, (2.0)	106.8	6.74, t, (2.0)	107.1	C ₈ , C ₁₁ , C ₁₂

Figure 1 Chemical structures of compounds 1-5**Figure 2** Key NOE correlations for macourin D**References**

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