A new diarylheptanoid from the bark of *Myrica nana*

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A new diarylheptanoid, 3,5-dimethoxyl-17-hydroxyl-4,19-diketo-11-ene-[7,0]metacyclophane, named as nanaone, was isolated from the bark of *Myrica nana* along with six known compounds. Their structures were elucidated by various spectroscopic methods including 2D-NMR techniques or comparison with authentic samples.

Keywords: myrica nana, nanaone, metacyclophane, benzoquinone

The Myricaceae plant *Myrica nana* Cheval is widely distributed in the southwest of China. The bark of *M. nana* has been used for treatment of dysentery, diarrhoea, stomach ache and rheumatism.[1] Several phenolic compounds have been isolated previously from the fresh leaves of *M. nana*.[2] Very little is known about the chemical constituents of the bark of this plant. In a search for the active constituents of *M. nana*, we have made a detailed investigation of its bark, and isolated a new diarylheptanoid along with six known compounds.

The known compounds were identified by comparing their spectral data with those of authentic samples or with those reported in literature as myricanol **2**,[3] myricanone **3**,[3] taraxerol **4**,[4] myricadiol **5**,[4] myricetin **6**[5] and myricetrin **7**.[5]

Compound **1** was obtained as red crystals. The molecular formula, $C_{21}H_{22}O_5$, was obtained from the quasimolecular ion at *m/z* 377.1367 $[M + Na]^+$ in the HRESI-MS spectrum, which was further confirmed by ^1H, ^{13}C NMR data (Table 1). The UV spectrum of **1** showed absorption maxima at 284 nm (logε = 4.45) and the IR spectrum showed the presence of hydroxyl group (ν_{max} 3435 cm^{-1}), olefin (ν_{max} 1625 cm^{-1}) and a conjugated carbonyl group (ν_{max} 1668 cm^{-1}). The ^1H NMR spectrum showed signals for two methoxyl groups (δ 4.00, 3.97), three aromatic protons (ABX pattern): δ 6.78 (d, J = 2.0 Hz, H-18), 6.88 (d, J = 8.0 Hz, H-16) and 7.10 (dd, J = 2.0, 8.0 Hz, H-15) suggesting the presence of 1, 2, 4-trisubstituted phenyl group, and an *E*-alkene: δ 5.68 (dt, J = 15.5, 7.0 Hz, H-12), 5.88 (dt, J = 15.5, 7.0 Hz, H-11). A $-CH_2CH{=}CH(CH_2)_4-$ moiety was identified from the ^1H–^1H COSY cross signals (Fig.2) together with the HMQC experiment. Cross peaks between H-15 and H-16 were also observed in the ^1H–^1H COSY spectrum (Fig. 2). The ^{13}C NMR spectrum showed the presence of a *p*-benzoquinone (δ 183.8, 184.1), which was further confirmed by HMBC correlations (Fig. 2). The connections of C-6 to C-7, C-13 to C-14 and C-1 to C-2 were determined by the HMBC correlations of H-7 with C-5, C-6 and C-19, H-13 with C-14, C-15 and C-18, H-18 with C-2, C-17 and C-15. The phenolic hydroxy group (δ 5.90) was assigned as 17-OH from the HMBC cross signals of the 17-OH (δ 5.90) with C-1 and C-16. Two methoxyl groups were located at C-3 and C-5 on the basis of the HMBC cross signals between δ 4.00 (3H, s) and C-5, δ 3.97 (3H, s) and C-3. No NOESY correlation was found between these two methoxyl groups. In the light of these observations, the structure of **1** was assigned as 3, 5-dimethoxy-17-hydroxy-4, 19- diketo-11-ene-[7,0] metacyclophane, named as nanaone (Fig. 1).

Table 1 ^1H (600 MHz) and ^{13}C NMR (125 MHz) data of **1** in $CDCl_3$ (TMS, δ ppm)

No.	δ_H	δ_C
1		121.3
2		140.2
3		145.0
4		183.8
5		144.5
6		146.2
7	2.31 (m), 1.66 (m)	25.6
8	1.90 (m), 1.37 (m)	27.1
9	1.95 (m), 1.24 (m)	21.3
10	2.21 (m), 2.13 (m)	42.0
11	5.88 (dt, J = 15.5, 7.0 Hz)	135.8
12	5.68 (dt, J = 15.5, 7.0 Hz)	130.2
13α	2.73 (dt, J = 4.2, 13.2 Hz)	38.9
13β	3.02 (dt, J = 3.0, 13.2 Hz)	
14		132.4
15	7.10 (dd, J = 2.0, 8.0 Hz)	130.2
16	6.88 (d, J = 8.0 Hz)	117.5
17		152.5
18	6.78 (d, J = 2.0 Hz)	134.2
19		184.1
CH_3O-3	3.97 (s)	61.0
CH_3O-5	4.00 (s)	61.1
17-OH	5.90 (brs)	

Experimental

Melting points were determined on an XRC-1 micromelting point apparatus and were uncorrected. UV and IR spectra were recorded on a Lambda 35 spectrometer and a Perkin Elmer spectrum one FT-IR spectrometer, respectively. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-600 spectrometer with TMS as the internal standard. Mass spectra were obtained on Finnigen-LCQ^{DECA} (ESI-MS) or a Bio-TOF IIIQ mass spectrometer (HR-ESI-MS). Optical rotations were measured on a Perkin Elmer 341 automatic polarimeter. Separation and purification were performed by column chromatography on silica gel (200–300 mesh, Qingdao Haiyang Chemical Co. Ltd.).

Plant material. The bark of *M. nana* was collected from Baise District of Guangxi Province of China in September 2007 and identified by Prof. Dingyong Wang (College of Pharmacy, Guangdong Pharmaceutical University). A voucher specimen of the sample (No.20070910) was deposited at the Herbarium of Guangdong Pharmaceutical University.

Extraction and isolation. Air-dried and powdered barks of *M. nana* (4.5 kg, 20–30 mesh) were soaked with MeOH (20.0 L × 3, 7 days each) at room temperature. The MeOH was evaporated under reduced pressure to afford 785.0 g residue, which was suspended in water (1.5 L) and extracted with petroleum ether (2.0 L × 4), $CHCl_3$ (2.0 L × 5), EtOAc (2.0 L × 3) and n-BuOH saturated with water (2.0 L × 4) to give corresponding fractions A (58.5 g), B (29.0 g), C (73.5 g) and D (115.0 g). Fraction B was subjected to chromatography on 200–300 mesh silica gel (800 g, 90 mm × *L*550 mm) to produce **4** (83 mg) [petroleum ether–EtOAc (10 : 1, V/V) as eluant], **5** (37 mg) [petroleum ether–EtOAc (8 : 1, V/V) as eluant], **1** (56 mg) [petroleum ether–EtOAc (5 : 1, V/V) as eluant], **3** (55 mg) [petroleum ether–CH_3COCH_3 (6 : 1, V/V) as eluant], **2** (45 mg) [petroleum ether–CH_3COCH_3 (4 : 1, V/V) as eluant], respectively. Fraction C was subjected to chromatography on 200–300 mesh silica gel (1000 g, 100 mm × *L*750 mm) to give **4** (65 mg) [$CHCl_3$–MeOH (6:1, V/V) as eluant], **5** (203 mg) [$CHCl_3$-MeOH (3:1, V/V) as eluant].

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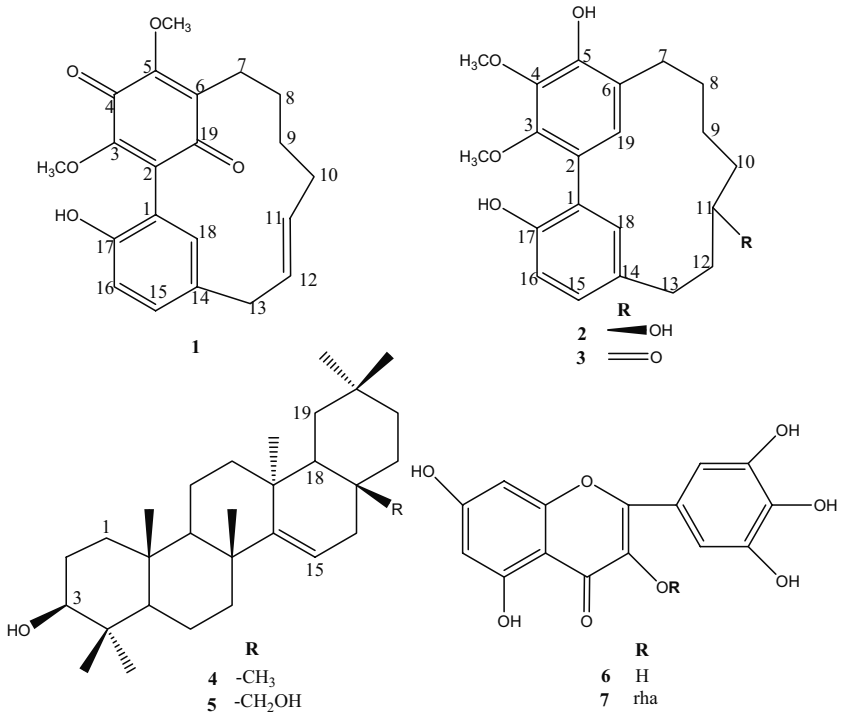

Fig. 1 Structure of compounds **1–7**.

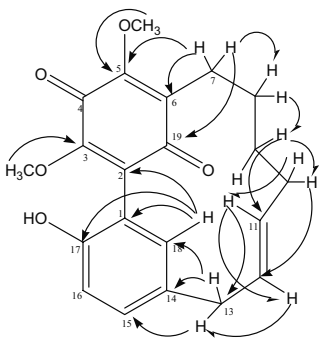

Fig. 2 Key HMBC or ^{1}H–^{1}H correlations in **1** (↗ ^{1}H–^{1}H COSY; ↗ HMBC).

Nanaone **1**: $C_{21}H_{22}O_5$, red crystal; $[\alpha]_{23}^{D}$ + 10.5°(c 0.20, MeOH); UV (MeOH):λ_{max} (logε) 2.25 (3.45), 284 (4.45), 380 (1.35) nm; IRν_{max} (KBr): 3435, 3012, 2930, 2855, 1668, 1625, 1600, 1568, 1507, 1278, 1200, 1145, 1105, 980, 820 and 755 cm^{-1}; HRESI-MS (positive mode) *m/z*: 377.1367 $[M + Na]^+$ (Calcd for $C_{21}H_{22}O_5Na$: 377.1374); ESI-MS (negative mode) *m/z*: 353.1 $[M–H]^-$; ^{13}C NMR and ^{1}H NMR data are shown in Table 1.

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