

Two New Sesquiterpenoids from *Helicteres angustifolia*

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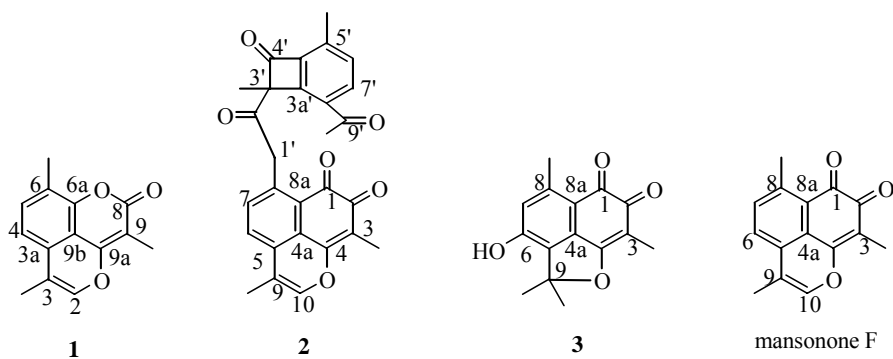
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Abstract: A new sesquiterpenoid lactone, 3,6,9-trimethyl-pyrano[2,3,4-*de*]chromen-2-one (**1**) and a novel sesquiterpenoid quinone, 6-[2-(5-acetyl-2,7-dimethyl-8-oxo-bicyclo[4.2.0]octa-1,3,5-trien-7-yl)-2-oxo-ethyl]-3,9-dimethylnaphtho[1,8-*bc*]pyran-7,8-dione (**2**) together with a known perezone (**3**) were isolated from the roots of *Helicteres angustifolia*. The structures were elucidated as mainly on the basis of 1D and 2D NMR spectroscopic data.

Keywords: *Helicteres angustifolia*, Sterculiaceae, sesquiterpenoid lactone, sesquiterpenoid quinone.

Helicteres angustifolia belongs to the family Sterculiaceae, found throughout eastern and southern China. Its root is used widely in Chinese folk medicine for cough and sore throat, and it also possesses for its anti-inflammatory, antitussive, and expectorant effects¹. From this plant, several triterpenoids², sesquiterpenoid quinones³ and a helicquinone⁴ have been isolated and reported. In the present paper, we describe the isolation and structure elucidation of two new compounds **1** and **2**, as well as a known perezone **3** (Figure 1).

Figure 1 The structure of 1~3 and mansonone F



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Dried powdered root of *H. angustifolia* (10 kg) was extracted with EtOH. And the EtOAc-soluble portion of the extracts was subjected to silica gel column chromatography eluting with petroleum ether containing increasing concentrations of EtOAc. Six fractions were obtained: fraction A (100% petroleum) gave **1** (5.0 mg), fraction C (33% EtOAc) gave compound **2** (6.0 mg), fraction C (33% EtOAc) gave **3** (3.0 mg)

Compound **1** was obtained as orange needles, mp 184-186°C. UV λ_{\max} (MeOH) (log ϵ): 210 (4.36), 247 (4.11), 294 (4.12), 327 (3.94), 345 (3.98), 361 (3.83) nm. IR (KBr) ν : 1693, 1650, 1630, 1596, 1495, 1380, 1267, 1190, 1139, 1041, 855 cm^{-1} . The high resolution EI-MS exhibited the molecular ion peak at m/z 228.0793 [M]⁺ corresponding to the molecular formula C₁₄H₁₂O₃ (calcd. 228.0786 for C₁₄H₁₂O₃). The IR spectrum implied the presence of an unsaturated ester (1693 cm^{-1}) group. The structure of **1** was deduced by detail analysis of the ¹H and ¹³C NMR (**Table 1** and **Table 2**) aided with 2D NMR experiments (¹H-¹H COSY and HMBC). The ¹³C NMR data indicated that the molecule possessed one unsaturated ester carbonyl (C-8 at δ_{C} 164.0 ppm), five olefins, three (δ_{C} 139.4, 150.2, and 158.7 ppm) of them were connected with oxygen, and three methyl groups (δ_{C} 12.8, 15.6, and 8.60 ppm). HMBC correlations (**Figure 2**) of Me-6 (δ_{H} 2.41) to C-5 (δ_{C} 139.4) and C-6a (δ_{C} 127.6), H-5 (δ_{H} 7.37) to C-3a (δ_{C} 158.7) and C-6 (δ_{C} 112.9) revealed that **1** possessed an oxaphenalene skeleton, while three methyl groups were attached to C-3, C-6 and C-9, respectively, that express the methyl signals were located in Me-3 at δ_{C} 12.8, Me-6 at δ_{C} 15.6, and Me-9 at 8.60, respectively. Therefore, compound **1** was elucidated as 3, 6, 9-trimethylnaphtho [1, 8-bc] pyran-7-oxa-8-one.

Table 1 ¹H NMR spectra data of compound **1**~**3** and mansonone F^{a1}(CDCl₃, δ ppm)

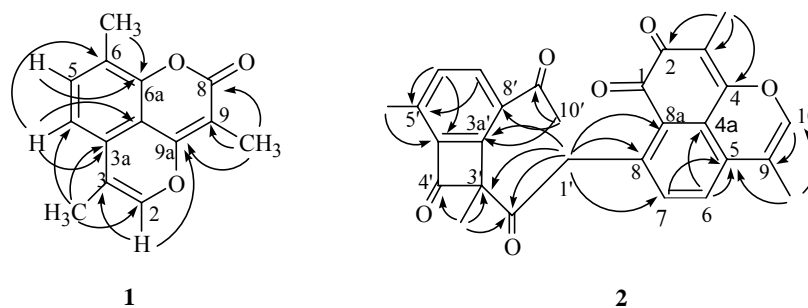
C	1	2	3	Mansonone F
2	6.85 (d, 1.0 Hz)			
4	6.92 (d, 8.0 Hz)			
5	7.37 (d, 8.0 Hz)			
6		7.57 (d, 8.0 Hz)		7.69 (d, 8.0 Hz)
7		7.48 (d, 8.0 Hz)	6.84 (s)	7.59 (d, 8.0 Hz)
10		7.12 (s)		7.50 (d, 1.5)
1'		3.50 (s)		
6'		7.61 (d, 8.0 Hz)		
7'		7.63 (d, 8.0 Hz)		
10'		2.55 (s)		
3-Me	2.01 (d, 1.0 Hz)	1.95 (s)	2.09 (s)	1.85 (s)
6-Me	2.41 (s)			
8-Me			2.65 (s)	2.62 (s)
9-Me	2.03 (s)	2.15 (s)	2 × 1.91 (s)	2.09 (d, 1.5 Hz)
3'-Me		1.28 (s)		
5'-Me		2.70 (s)		

^{a1} ¹H NMR spectra were obtained at 500 MHz, and recorded in CDCl₃ at room temperature using TMS as internal standard.

Table 2 ^{13}C NMR spectra data of compound **1**–**3** and mansonone F^a (CDCl₃, δ ppm)

C	1	2	3	Mansonone F
1		182.2	181.1	181.2 (s)
2	139.4	177.6	178.1	177.0 (s)
3	112.9	113.7	108.6	111.6 (s)
3a	127.6			
4	115.0	161.8	168.0	160.9 (s)
4a		124.6	136.8	125.9 (s)
5	133.6	130.9	131.2	122.9 (s)
6	125.0	128.3	158.3	128.9 (s)
6a	150.2			
7		137.1	120.3	136.5 (d)
8	164.0	143.7	146.6	145.2 (s)
8a		127.2	117.4	129.0 (d)
9	98.3	112.1	96.4	112.1 (s)
9a	158.7			
9b	110.7			
10		140.9		140.9 (d)
1'		39.7		
2'		201.9		
3'		53.1		
3a'		137.9		
4'		202.8		
4a'		141.6		
5'		137.9		
6'		133.0		
7'		138.1		
8'		137.1		
9'		203.0		
10'		30.5		
3-Me	12.8	7.70	8.29	7.50 (q)
6-Me	15.6			
8-Me			20.5	22.4 (q)
9-Me	8.60	12.9	2 × 25.9	12.1 (q)
3' - Me		18.3		
5' - Me		19.1		

^a ^1H NMR spectra were obtained at 125MHz, and recorded in CDCl₃ at room temperature using TMS as internal standard.

Figure 2 HMBC (H \rightarrow C) correlations observed in compound **1** and **2**

Compound **2** was isolated as a deep violet crystal, mp 218-220°C. UV λ_{\max} (MeOH) (log ϵ): 244 (4.82), 290 (4.00), 331 (4.02), 567 (3.86) nm. IR(KBr) ν : 3073, 2921, 1739, 1703, 1636, 1598, 1579, 1482, 1451, 1377, 1355, 1331, 1256, 1189, 1116, 1056, 1018, 992, 910, 860 cm^{-1} . The molecular formula, $\text{C}_{28}\text{H}_{22}\text{O}_6$, was established by high resolution EI-MS. The molecular ion peak was at m/z 455.1502 $[\text{M}+\text{H}]^+$ (Calcd. 455.1494 for $\text{C}_{28}\text{H}_{23}\text{O}_6$). Combining with ^{13}C NMR data, it implied that eighteen unsaturation degrees exist in the molecular. The UV absorption maximum in MeOH at λ_{\max} 244, 290, 331 and 567 nm suggested the presence of mansonone F^3 . Its IR spectrum showed a strong absorption band at 1739 cm^{-1} , indicating the presence of a five or four membered ketone carbonyl.

^1H and ^{13}C NMR spectral data also showed the common structural part as mansonone F^3 , except for compound **2** having a methene group (δ_{H} 3.50 ppm and δ_{C} 164.0 ppm) replacing the Me-6 of mansonone F. In addition, one more part of **2** contained three carbonyl carbon (δ_{C} 203.0, 202.8 and 201.9 ppm), and a phenyl group [δ_{H} 7.61 (d, $J=8.0$ Hz, H-6'), 7.63 (d, $J=8.0$ Hz, H-7') ppm, and δ_{C} 137.9, 141.6, 137.9, 133.0, 138.1, 137.1 ppm]. The complete assignments of these sections were established from analysis of the HMBC spectral data (**Figure 2**). The carbonyl carbon at δ_{C} 201.9 (C-2') showed correlations with H-1', the phenyl carbon δ_{C} 137.9 (C-3a') showed correlations with H-1' and Me-10'. And the correlations of H-3' to C-4' (δ_{C} 202.8) and C-2' (δ_{C} 201.9), and H-1' to C-3' (δ_{C} 53.1) confirmed the presence of a four member ketone. Therefore, compound **2**, was determined as 6-[2-(5-acetyl-2, 7-dimethyl-8-oxo-bicyclo-[4.2.0]octa-1, 3, 5-trien-7-yl)-2-oxo-ethyl]-3, 9-dimethyl-naphtho[1, 8-*bc*]pyran-7, 8-dione mainly.

Compound **3** was identified as 3-hydroxy-2, 2, 5, 8-tetramethyl-2H-naphtho[1, 8-*bc*]furan-6, 7-dione by comparing its physical and spectral data with literature values⁵.

Acknowledgments

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