Chinese Chemical Letters Vol. 11, No. 10, pp. 905–908, 2000

Sesquiterpene Lactones from Notoseris Porphyrolepis

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Abstract: Two new sesquiterpene lactones, notoserolides A and B, along with 12 known compounds were isolated from the aerial parts of *Notoseris porphyrolepis*. By means of spectral methods including MS, NMR (^{1}H NMR, ^{13}C NMR, DEPT, HMQC, HMBC) and X-ray diffraction, as well as chemical reactions, the structures of notoserolides A and B were established as austricin 8-*O*-β-D-glucopyranoside and 8-*O*-senecioylaustricin, respectively.

Keywords: *Notoseris porphyrolepis*, Asteraceae, sesquiterpene lactones, guaianolides, noto-serolides A and B.

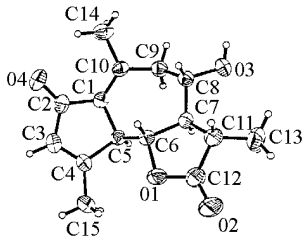
The genus *Notoseris* comprising of 14 species is native to China, and *Notoseris porphyrolepis* Shin is mainly distributed in southwestern China[1]. So far there are many reports on sesquiterpenes isolated from Asteraceae[2], but nothing is known about secondary metabolites of *Notoseris*. From the aerial parts of *N. porphyrolepis*, two new guaianolides A and B, named notoserolides A (**2**) and B (**3**), along with 12 known compounds, austricin (**1**), artesin[3], magnolialide[4], deoxylactucin[5], jacquinelin[5], crepidiaside B[6], stigmasterol, stigmasterol glucoside, oleanolic acid, betulinic acid, luteolin and luteolin 7-*O*-glucoside, were isolated and identified.

Compound **1**, $C_{15}H_{18}O_4$, was obtained as colorless prisms (m.p. 124-6℃). The IR spectrum of **1** showed the presence of a hydroxyl (3502 cm^{-1}), a γ-lactone carbonyl (1768, 1674 cm^{-1}) and an α,β-unsaturated ketone (1640, 1616 cm^{-1}) groups. Its DEPT spectrum indicated that **1** was characteristic of a guaianolide[7]. Austricin[8] and grossmisin[9] are a pair of epimers of C-11. ^{1}H and ^{13}C NMR data showed that **1** should be one of them. To unambiguously determine the structure of **1**, we carried out its X-ray diffraction (**Figure 1)**, and confirmed it to be austricin.

Compound **2** was obtained as an amorphous powder (m.p. 247-8℃). Its molecular formula was assigned as $C_{21}H_{28}O_9$ by HREIMS (M^+ *m*/*z* 424.1721, Calcd. 424.1733). The IR spectrum of **2** exhibited similar absorptions (3413, 1752, 1670, 1616 cm^{-1}) to those of **1**. Its UV spectrum in ethanol gave absorption peak at 260 nm, indicating the presence of an α,β-unsaturated ketone. In the EIMS spectrum of **2**, besides a molecular ion peak at *m*/*z* 424, the fragment ion peaks at *m*/*z* 262 [M-hexose]$^+$, 246 [M-hexose-O]$^+$ and 136 (base peak) were observed. On acid hydrolysis, **2** gave **1** and D-glucose,

identified by direct comparison with authentic samples. Since the signal of an anomeric proton of glucose appeared at δ 4.47 with coupling constant J = 7.9 Hz, the anomeric center has α ,β configuration. The ^{13}C NMR data of sugar moiety (**Table 1**) indicated that it is a β-D-glucopyranoside unit[10]. By comparison of ^{13}C NMR spectral data of **2** with those of **1**, the C-8 shifted from δ 70.0 to 79.2, and C-7 and C-9 shifted from δ 62.5 and δ 49.6 to 61.6 and 47.5, respectively. In addition, the HMBC experiment showed the key long-range heteronuclear correlations from H-8 to C-1' and from H-1' (the anomeric proton of glucose) to C-8. Careful examination of the ^{1}H-^{1}H COSY, HMQC and HMBC spectra allowed all proton and carbon signals of **2** to be assigned (**Table 1)**. Based on all these evidence, compound **2** was elucidated to be austricin 8-*O*-β-D-glucopyranoside.

Figure 1. X-ray structure of austricin (**1**)



Compound **3**, colorless needles, m.p. 214-5℃, analyzed for $C_{20}H_{24}O_5$ on the basis of its HREIMS (M^+ *m*/*z* 344.1621, Calcd. 344.1624) and ^{13}C NMR spectral data (**Table 1**). The IR spectrum of **3** showed an α,β-unsaturated ester (1724 cm^{-1}) in addition to a hydroxyl (3426 cm^{-1}), a γ-lactone carbonyl (1789, 1680 cm^{-1}), and an α,β-unsaturated ketone (1637, 1608 cm^{-1}) groups similar to those of **1**. Its UV spectrum in ethanol gave absorption peaks at 220 nm (α,β-unsaturated ester) and 255 nm (α,β-unsaturated ketone). The EIMS spectrum of **3** exhibited a molecular ion peak at *m*/*z* 344 and fragment ion peaks at *m*/*z* 261 $[M\text{-acyl-H}]^+$, 246 $[M\text{-acyl-H}_2O]^+$ and 83 (base peak). On mild alkali hydrolysis, **3** afforded **1**. A direct comparison of ^{13}C NMR spectral data of **3** with those of **1** suggested that **3** should have an additional acyl moiety, which was identified as senecioyl group[11]. In **3**, the esterification site was inferred at C-8, since the ^{1}H NMR signal of H-8 was downfield shifted $\Delta\delta$ 1.17 ppm, when compared with that of **1**. This result was further confirmed by HMBC experiment of **3**. The key HMBC correlations from H-8 to C-1' and from H-2' to C-8, were observed. Analysis of DEPT, HMQC and HMBC spectra allowed all proton and carbon signals of **3** to be assigned (**Table 1)**. Therefore, compound **3** was elucidated as 8-*O*-senecioylaustricin.

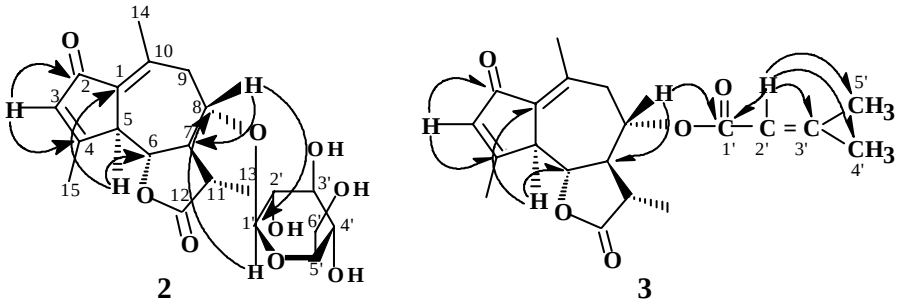
Table 1. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectral data for **2** and **3**

	2[a]		**3**[b]	
Position	δ_H, mult. J (Hz), int.	δ_C	δ_H, mult. J (Hz), int.	δ_C
1		134.3		134.3

2		197.9		195.6
3	6.14 , t, 1.3, 1H	136.0	6.15 , t, 1.6, 1H	135.9
4		173.5		171.1
5	3.59, d, 10.0, 1H	52.5	3.68, d, 10.4, 1H	51.8
6	3.70, t, 10.4, 1H	83.2	3.90, t, 10.4, 1H	81.9
7	2.36, dd, 10.8, 10.4, 1H	61.6	2.58, dd, 10.8, 10.4, 1H	59.2
8	3.75, br t, 10.8, 1H	79.2	4.89, br t, 10.8, 1H	70.3
9	2.95, dd, 12.0, 1.8, 1H	47.5	2.86, dd, 12.0, 2.0, 1H	45.0
	2.71, dd, 13.6, 12.0, 1H		2.38, dd, 13.6, 12.0, 1H	
10		149.7		145.5
11	2.70, q, 6.9, 1H	41.8	2.66, q, 6.8, 1H	40.9
12		180.5		177.5
13	1.46, d, 6.9, 3H	16.1	1.26, d, 6.8, 3H	15.3
14	2.41, s, 3H	21.7	2.27, s, 3H	22.5
15	2.29, s, 3H	20.0	2.19, s, 3H	19.8
1’	4.47, d, 7.9, 1H	105.5		165.6
2’	3.21, t, 7.9, 1H	75.4	5.73, m, 1.2, 1H	115.9
3’	*	78.7		159.6
4’	*	71.5	1.94, br s, 3H	27.4
5’	*	78.1	2.40, br s, 3H	21.0
6’	3.89, dd, 11.8, 1.5, 1H	62.7		
	3.70, dd, 11.8, 6.9, 1H			

a: CD_3OD b: CD_3COCD_3; * overlapped with H_2O or other peaks

Figure 2. The important HMBC correlations for **2** and **3**



Acknowledgments

This work was financially supported by the Special Project of Biological Science and Technology of the Chinese Academy of Sciences (STZ-97-3-08). We are grateful to Prof. De Zhu WANG and Prof. Hui Ling LIANG (Kunming Institute of Biology, the Chinese Academy of Sciences) for their help in determining NMR and MS spectra.

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Received 14 April 2000