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GUAIANOLIDES FROM *PICRIS RADICATA**

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Key Word Index—*Picris radicata*; Asteraceae; sesquiterpene lactone.

Abstract—The methylene chloride–methanol (1 : 1) extract of the aerial parts of *Picris radicata* Forssk afforded two new guaianolides. The structures were established from spectral data. Copyright © 1996 Published by Elsevier Science Ltd

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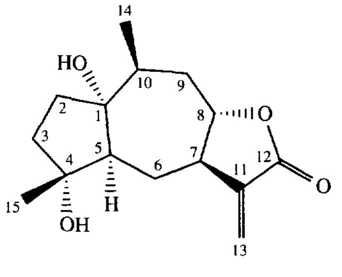
INTRODUCTION

A few species of the old genus *Picris* have been chemically studied and have furnished guaianolides, guaianolide glycosides, eudesmanolides and ionone glycosides [1–4]. Some members of the genus have been used as a galactogague, diuretic and refrigerant, while *P. divaricata* is prescribed to treat abscesses or boils in the breast and leucorrhea [5]. The ionone glycosides, isolated from the genus, were reported to have hypnotic and sedative activities [6].

RESULTS AND DISCUSSION

Silica gel chromatography of the CH_2Cl_2–MeOH (1 : 1) extract of the aerial parts of *P. radicata* afforded two new sesquiterpene lactones (**1**) and (**2**). The EI-mass spectrum of **1** showed a molecular peak at m/z 266 consistent with $C_{15}H_{22}O_4$, followed by the consecutive loss of two molecules of water as indicated by peaks at m/z 248 and 230. The spectral data showed the partial structure of a γ-lactone (IR, 1770 cm^{-1}, ^{13}C NMR, δ 169.20). The ^1H and ^{13}C NMR spectral data suggested that **1** has a guaianolide skeleton, the multiplicity of the carbons was determined from DEPT experiments and proved the presence of two tertiary oxygen bearing carbons at δ 69.90 and 69.70, and a secondary one at δ 82.53. On the other hand, the ^1H NMR spectrum showed two narrow doublets at δ 6.20 and 5.55 typical for H-13, while the *ddd* at δ 4.02 was assigned to H-8. Furthermore, the H-7 multiplet was found at δ 3.00, H-14 as a doublet at δ 0.92 and H-15 as a sharp singlet at δ 1.35. The downfield shift of H-15 located one of the hydroxyl groups at C-4. The location of the other protons could be easily deduced from ^1H–^1H COSY. Starting from the well known signals, H-8 and H-7, the two protons of H-6 were detected at δ 2.02 and 1.90, and showed further correlation with a broad doublet at δ 2.55 (H-5) and led to the following sequence: C(5)H–C(6)H_2–C(7)H–C(8)H. Thus, the second hydroxyl group must be placed at C-1.

The stereochemistry of compound **1** was established from chemical shifts as well as NOESY experiments. The chemical shift of H-8 at δ 4.02 confirmed the β-configuration of the proton [7, 8]. Additionally, ^1H–^1H NOESY correlated H-8_β with H-14, H-7_α with H-5, which itself showed correlation with H-6_α at 1.90, while H-6_β at δ 2.02 correlated with H-15 at δ 1.35.



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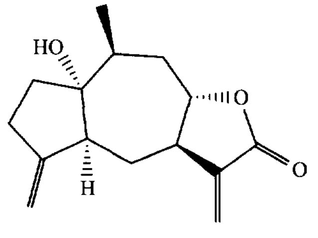

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*Part 27 in the series 'Constituents of Plants Growing in Qatar'.

The presence of H-5 at lower field suggested that the 1-hydroxyl group was in the α-orientation [9].

From comparison of the spectral data of **2** with those of **1**, it was obvious that **2** had a $\Delta^{4,15}$ double bond. This was clear from the replacement of the methyl signal, H-15, at δ 1.35 by two broad singlets at δ 5.02 and 4.78. The other signals were observed at their expected chemical shifts, H-13 at δ 6.15 and 5.45, H-8 at δ 4.13, H-7 at δ 3.07 and H-14 at δ 0.98. The mass spectrum showed the molecular ion peak at *m/z* 248, $C_{15}H_{20}O_3$, followed by elimination of water at *m/z* 230.

EXPERIMENTAL

Plant material. Aerial parts of *P. radicata* were collected from Qatar in March 1993. A voucher specimen is deposited in the Department of Botany, University of Qator.

Extraction and isolation. The ground air-dried aerial parts (100 g) of *P. radicata* were extracted with CH_2Cl_2–MeOH (1:1) for 24 hr. The solvent was removed and the lipid partioned between $CHCl_3$–H_2O (1:1). The organic layer was evapd and defatted to yield 0.46 g of crude sesquiterpene lactones which were sepd by Sephadex LH-20 to give 12 mg of **1** and 1.5 mg of **2**.

1α,4α-*Dihydroxy-guaia*-11(13)-*ene*-8α,12-*olide* (**1**). Gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3550, 3500, 1760. EI-MS *m/z*: 266 $[M]^+$ (4.2), 248 $[M-H_2O]^+$ (30), 230 $[M-2H_2O]^+$ (52). ^{1}H NMR (400 MHz $CDCl_3$): δ 6.20 (1H, *d*, $J = 3.2$ Hz, H-13), 5.55 (1H, *d*, $J = 3$ Hz, H-13′), 4.02 (1H, *ddd*, $J = 3.5$, 10, 12 Hz, H-8), 3.00 (1H, *m*, H-7), 2.55 (1H, *br d*, $J = 8.70$, H-5), 2.08 (1H, *ddd*, $J = 3.6$, 3.7 and 12.7 Hz, H-9), 2.02 (2H, *m*, H-6 and H-10), 1.90–1.80 (4H, *m*, H-6′, H-3, H-2) 1.35 (3H, *s*, H-15), 1.25 (1H, *m*, H-2), 0.92 (3H, *d*, $J = 7.5$ Hz, H-14). ^{13}C NMR (100 MHz, $CDCl_3$) (assigned by ^{1}H–^{13}C hetero-COSY): C-1 to C-15: δ 9.90 (*s*), 28.91 (*t*), 32.72 (*t*), 69.70 (*s*), 47.74 (*d*), 30.60 (*t*), 44.40 (*d*), 82.53 (*d*), 40.43 (*t*), 34.60 (*d*), 139.08 (*s*), 169.32 (*s*), 119.77 (*t*), 14.62 (*q*), 15.51 (*q*) (C-1/C-4 and C-2/C-3 may be interchangeable).

1α-*Hydroxy-guaia*-4(15), 11(13)-*diene*-8α, 12-*olide* (**2**). Gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500, 1765. *EI-MS m/z*: 248 $[M]^+$ (37), 230 $[M-H_2O]^+$ (43), 215 $[230-CH_3]^+$ (20). ^{1}H NMR (400 MHz; $CDCl_3$): δ 6.15 (1H, *d*, $J = 3.3$ Hz, H-13), 4.45 (1H, *d*, $J = 3.0$ Hz, H-13′), 4.12 (1H, *ddd*, $J = 3.5$, 10, 12 Hz, H-8) 3.07 (1H, *m*, H-7), 0.98 (3H, *d*, $J = 7.5$ Hz, H-14).

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