Chinese Chemical Letters Vol. 13, No. 10, pp 955 – 956, 2002 955
http://www.imm.ac.cn/journal/ccl.html

One New Diterpene Glucoside from the Roots of *Rhododendron molle*

Guan Hu BAO[1], Li Quan WANG[1], Kin Fai CHENG[2], Guo Wei QIN[1]*

[1]Shanghai Institute of Materia Medica, Shanghai Institutes for Biological Sciences, Chinese Academy of Sciences, Shanghai 200031
[2]Deprtment of Chemistry, the University of Hong Kong, Hong Kong

Abstract: One new grayanane diterpene glucoside, rhodomoside A **1** was isolated from the roots of *Rhododendron molle* G. Don (Ericaceae). Its structure was elucidated on the basis of spectral analysis.

Keywords: *Rhododendron molle*, Ericaceae, grayanane diterpene glucoside.

As a part of a continuing investigation on the active principles of Ericaceae plants, one new grayanane diterpene glucoside, rhodomoside A, was isolated from the *n*-BuOH fraction of the ethanol extracts of the roots of *Rhododendron molle* G. Don (Ericaceae). In this paper we describe the isolation and structural elucidation of rhodomoside A **1**.

Rhodomoside A **1**, viscous syrup, has the molecular formula $C_{26}H_{42}O_{10}$ based on HREIMS at *m/z* 514.2802 (calcd. 514.2778). Compound **1** gave positive reaction to α-naphthol test. Acidic hydrolysis of **1** afforded glucose as detected by TLC. Furthermore, the ^{1}H NMR signals (δ 4.00~4.97) and ^{13}C NMR signals at (δ 105.44, 75.57, 78.51, 71.76, 78.44, and 62.52) showed great similarity to those of the glucose part of known diterpene glucosides[1], confirming that **1** possessed a glucose unit. Additionally, the ^{1}H NMR spectrum of **1** showed the signals for three tertiary methyls (δ 1.74, 1.53, 1.18, each 3H, *s*), an olefinic methylene (δ 5.16, 5.06, each 1H, *s*), and three oxygenated methines (4.16, 4.57, 4.44, each 1H). Furthermore, the ^{13}C NMR and DEPT spectrum disclosed the presence of three methyls, six methylenes (one olefinic exocyclic), six methines (three oxygenated), and five quaternary carbons (two oxygenated) for the aglycone. The ^{1}H-^{1}H COSY spectrum of **1** revealed the following fragments: -CH-CH_2-CH(OR)-, -CH_2-CH(OR)- and -CH-CH_2-CH_2-CH-CH(OR)-. The above structural features suggested that **1** was a grayanane diterpene glucoside, whose skeleton possessed a 5/7/6/5 membered ring system [2].

The placement of the exomethylene at C-10/20 was based on the following observations in the HMBC spectrum: the signal at δ 151.92 (C-20) correlated with the signals at δ 3.05 (*t*, 1H, H-1), 2.58, 2.46 (*m*, each 1H, H-2), 2.95 (*br s*, 1H, H-9), 1.59 (*m*, 1H, H-11); and the signals at δ 5.06 and 5.16 (*s*, each 1H, H-20) correlated with the signals at δ 44.87 (C-1) and 52.82 (C-9).

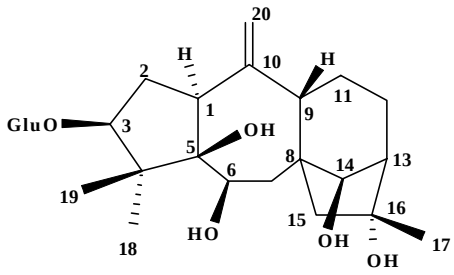
Analysis of the ^{1}H-^{1}H COSY, HSQC and HMBC spectra of **1** allowed its structural

fragments to be determined. In the ^{1}H-^{1}H COSY, the signals at δ 2.58 and 2.46 (CH_2-2) correlated with those at δ 3.05 (H-1) and δ 4.16 (H-3), and the signal at δ 4.57 (H-6) correlated with the signal at δ 2.47 (H-7). In the HMBC spectrum, the correlations of hydrogen at C-18 (δ 1.18) and hydrogen at C-19 (δ 1.74) with C-3 (δ 88.65), C-4 (δ 50.96), and C-5 (δ 83.01) were observed. The above data identified the fragment from C-1 to C-7. In addition, C-3 (δ 88.65) showed a long range correlation with the anomeric proton of glucose at δ 4.97 (*d*, 1H, H-1'), indicating that the hydroxyl group at C-3 is glucosylated. Furthermore, the coupling constant (J = 7.7 Hz) between H-1' and H-2' in the glucose unit suggested a β-orientation of the glucose unit [1].

Generally, in grayanane diterpenoids with H-1α, and C-14β oxygenated group, a strong NOE enhancement was observed between H-1α and H-14α[3]. The NOESY correlation between H-1 (δ 3.05) and H-14 (δ 4.44) suggested a *trans*-fused A/B ring system and an α-orientation of H-1 and H-14. Additionally, the NOESY correlation between H-18 and H-3 and H-6 indicated an α-orientation for H-3 and H-6.

Based on the above spectral analysis, the structure of **1** was established, as the 3-*O*-glucoside of a known grayanotoxin II[4]. Much similarity of the ^{13}C NMR signals between the aglycone of **1** and those of the known grayanotoxin II except for the signals at/around C-3 further confirmed its structure as 10 (20)-grayanotoxene-3β, 5β, 6β, 14β, 16α-pentol-3-*O*-β-D- glucopyranoside.

Figure 1 The structure for rhodomoside A **1**



Acknowledgment

This work was supported by the National Natural Science Foundation of China (Grant No. 30170104)

References

1. J. Sakakibara, N. Shirai, T. Kaiya, Y. Iitaka, *Phytochemistry*, **1980**, *19*, 1495.
2. L. Q. Wang, S. N. Chen, K. F. Cheng, C. J. Li, G. W. Qin, *Phytochemistry*, **2000**, *54*, 847.
3. L. Q. Wang, G. W. Qin, S. N. Chen, C. J. Li, *Fitoterapia*, **2001**, *72*, 779.
4. S. F. El-Naggark, R. W. Doskotch, T. M .Odell, L. Girard, *J. Nat. Prod.*, **1980,** *43*, 617.

Received 14 January, 2002