1154 Chinese Chemical Letters Vol. 14, No. 11, pp 1154 – 1155, 2003
http://www.imm.ac.cn/journal/ccl.html

A Novel Monoterpene Glycoside from *Swertia mileensis*

Ying Tong DI, Xun LIAO, Shu Lin PENG, Jian LIANG, Li Sheng DING*

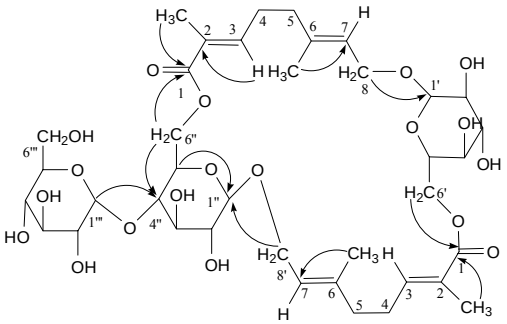
Chengdu Institute of Biology, Chinese Academy of Sciences, Chengdu 610041

Abstract: A novel monoterpene glycoside, mileenside, was isolated from *Swertia mileensis* by repeated normal and reverse phase silica gel chromatography and its structure was elucidated mainly based on spectral evidence.

Keyword: *Swertia mileensis*, *Gentianaceae*, monoterpene glycoside, mileenside.

The plant *Swertia mileensis* T. N. He *et* W. L. Shi (*Gentianaceae*) is used as a folk medicine for the treatment of virus induced hepatitis in Yunnan province. The chemical investigations of this plant led to the isolation of various compounds such as xanthones, flavonoids, iridoid and secoiridoid glycosides and terpenoids[1,2]. This paper reports the structural elucidation of the novel monoterpene glycoside, named mileenside **1**, isolated from the whole title plant.

Figure 1 The key HMBC correlations of **1** (H to C)



Mileenside (**1**), $[\alpha]_D^{20}$ -10 (*c* 1.0, MeOH), was obtained from the ethanolic extracts as a white amorphous powder by repeated normal and reverse phase silica gel chromatography. It possessed the molecular formula $C_{38}H_{58}O_{19}$ from its quasi-molecular ion peaks at *m/z* 841 in positive ESIMS due to $[M+Na]^+$ and *m/z* 817 in negative ESIMS due to $[M-H]^-$. Only 27 peaks were observed in ^{13}C NMR spectrum, suggesting the existence of partially symmetric structure in the molecule. By comparison of the NMR data with those of the similar compounds, **1** was suggested to be a glycoside of 2,6-

* E-mail: lsding@cib.ac.cn

dimethyl-8-hydroxy- 2E,6E-octadienoic acid[3]. The sugar obtained from acid hydrolysis was identified as D-glucose by comparison with the authentic sample in TLC. The ^{1}H NMR signals at δ 4.14, 4.08 (each d, 1H, J = 8 Hz) and 4.24 (d, 1H, J = 7.6 Hz) suggested the presence of three β-D-glucopyranosyl moieties in the compound. Tandem ESIMS of **1** (*m/z* 817 $[M - H]^- \rightarrow$655 $[M - glc]^- \rightarrow$489 [655 − monoterpene moiety]$^-$) and signals of C-8 (δ_C 63.3) and C-8' (δ_C 63.5) suggested there were two monoterpene moieties in the molecule. According to HMBC and HMQC experiment, carbonyls of both monoterpene moieties were linked to C-6' and C-6" of two glucoses, and C-8 of both monoterpene moieties to the anomeric carbons (C-1' and C-1") of those glucoses respectively, which resulted in the formation of a macrocyclic structure. In addition, correlation peaks was also observed in HMBC between H'"-1 and C"-4 and H"-6 and C"-4, confirmed that the outer glucose was attached to the C-4 of an inner one.

Table 1 ^{1}H and ^{13}C NMR Data (DMSO-d_6) of **1** (δ ppm, J_{Hz})

No	δ_C	δ_H	No	δ_C	δ_H
1	166.6		5'	76.4	3.13(m)
2	127.3		6'	64.3	4.45(d, 10), 4.04(m)
3	141.3	6.61(t, 7.2)	1"	100.6	4.14(d, 8.0)
4	25.6	2.28(m)	2"	72.0	3.54(m)
5	37.4	2.15(m)	3"	72.9	2.98(m)
6	139.2		4"	81.3	3.24(m)
7	121.1	5.28(m)	5"	74.9	3.31(m)
8	63.3	4.08(m)	6"	63.8	4.55(d, 10), 4.21(m)
8'	63.5	3.97(m)	1"'	103.3	4.24(d, 7.6)
2-Me	12.3	1.76(s)	2"'	73.1	2.96(m)
6-Me	15.3	1.51(s)	3"'	76.4	3.13(m)
1'	100.7	4.08(d, 8.0)	4"'	70.3	3.01(m)
2'	73.1	2.96(m)	5"'	76.8	3.20(m)
3'	73.7	3.23(m)	6"'	61.0	3.69(d, 10), 3.35(m)
4'	70.8	2.98(m)			

Therefore the molecular structure was determined as showed in **Figure 1**. Furthermore, two basic hydrolysis products of **1**, 2,6-dimethyl-8-hydroxy-2E, 6E-octadienoic acid 8- *O*-glucosyl (1→4) glucoside (*m/z* 507 $[M–H]^- \rightarrow$345 $[M–glc]^- \rightarrow$165, 179) and 2,6-dime thyl-8-hydroxy-2E, 6E-octadienoic acid 8-*O*-glucoside (*m/z* 345$[M–H]^- \rightarrow$165, 179) also confirmed the above proposed structure.

References

1. Y. Wang, J. S. Yang, *Nat. Prod. Res. & Dev.*, **1992**, *4*, 99.
2. N. Pant, D. C. Jain, R. S. Bhakuni, *Indian J. Chem.*, **2000**, *39B*, 565.
3. X. Ming, M. H. Qiu, R. L. Nie, G. L. Zhang, *Chin. Chem. Lett.*, **2000**, *11*, 709.

Received 14 November, 2002