Chinese Chemical Letters Vol. 16, No. 7, pp 928-930, 2005
http://www.imm.ac.cn/journal/ccl.html

Two New Glycosides from the Roots of *Ranunculus ternatus*

Jing Kui TIAN*, Feng SUN, Yi Yu CHENG

Deptment of Chinese Medicine Science & Engineering, Zhejiang University, Hangzhou 310027

Abstract: Two new glycosides named as ternatoside A **1** and ternatoside B **2** were isolated from the roots of *Ranunculus ternatus,* the structures were determined by 1D and 2D NMR, ESI-MS techniques, and chemical methods.

Keywords: *Ranunculus ternatus,* ternatoside A and ternatoside B.

Ranunculus ternatus Thunb. is a plant of *Ranunculus* genus used for treatment of tuberculosis[1]. Some fatty acid esters and γ-keto-δ-valerolactone have been isolated from this plant[2,3]. In this paper, we reported two new glycosides named ternatoside A **1** and B **2**. Their structures were identified on the basis of spectroscopic and chemical methods.

Compound **1** was obtained as a colorless gum, and gave positive result to Molish test. In the positive and negative ESIMS, it showed quasi-molecular ion peaks at *m/z* 373.2 $[M+Na]^+$, 189.2 $[M-162+H]^+$ and 349.3 $[M-H]^-$, respectively. Its molecular formula $C_{15}H_{26}O_9$ was deduced from HRFABMS (373.1426 $[M+Na]^+$, calcd. 373.1475), ^{13}CNMR and MS data. Glucose was detected after the acid hydrolysis and compared with standard sugar on TLC. The ^{1}H, ^{13}CNMR and HMQC indicated that this compound possesses three methylenes, one butanol, one carbonyl ketone, one carbonyl ester, and one (*β*-D) glucosyl group (**Table 1**). Analysis of ^{1}H-^{1}HCOSY and HMBC spectra enabled deduction the structure. In HMBC spectrum of **1**, ^{13}C-^{1}H long range correlation signals were found between C-1 and H-2, H-3, H-6; C-4 and H-2, H-3, H-5; C-3 and H-5; The anomeric proton of *β*- D-glucosyl group at δ 4. 91 (d, 1H, J=7.5 Hz) was correlated to C-5 of aglycone (**Figure 1**). In ^{1}H-^{1}HCOSY spectrum of **1**, correlation signals were found between H-2 and H-3; H-6 and H-7; H-7 and H-8; H-8 and H-9. Thus compound **1** was identified as 4-carbonyl-(*O*-*β*-D-glucopyranosyl)-pentanoic acid-1-*O*-butyl ester. It is a new compound, named as ternatoside A.

Compound **2** was obtained as the brown gum, and gave positive result to Molish test. In the positive and negative ESIMS, it showed *quasi*-molecular ion peaks at *m/z* 439.2 $[M+Na]^+$, 255.2 $[M-162+1]^+$ and 415.3 $[M-H]^-$, respectively. Its molecular formula $C_{19}H_{28}O_{10}$ was deduced from HRFABMS (439.1551 $[M+Na]^+$, calcd. 439.1580), ^{13}CNMR and MS data. Glucose was detected after the acid hydrolysis and compared

* E-mail: tjk@zju.edu.cn

Table 1 NMR spectral data of **1** (^{1}H, 500 MHz; ^{13}C, 125MHz; in DMSO-d_6, δ ppm, J Hz)

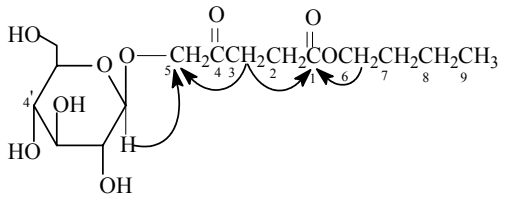
No.	δ_H	δ_C	No.	δ_H	δ_C
1		172.9	9	0.87(t, 3H, 7.5)	14.0
2	2.48 (t, 2H, 6.5)	27.7	1′	4.91(d, 1H, 7.5)	103.3
3	2.78(t, 2H, 6.5)	34.1	2′	3.04(t, 1H, 7.5)	74.0
4		207.9	3′	3.17(t, 1H, 7.5)	77.2
5	4.30, 4.22(d, 2H, 17.0)	73.7	4′	3.07(t, 1H, 7.5)	70.7
6	3.99(t, 2H, 7.5)	64.2	5′	3.25(m, 1H, 7.5)	77.5
7	1.52(m, 2H, 7.5)	30.8	6′	3.99, 3.66(dd, 2H, 13.5,7.5)	61.7
8	1.31(m, 2H, 7.5)	19.1			

Table 2 NMR spectral data of **2** (^{1}H, 500 MHz; ^{13}C, 125MHz; in DMSO-d_6, δ ppm, J Hz)

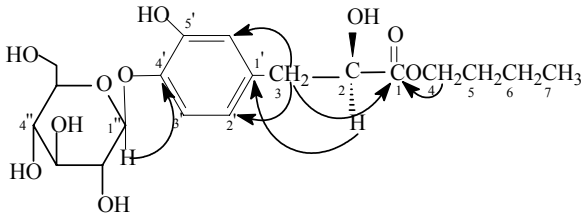
No.	δ_H	δ_C	No.	δ_H	δ_C
1		174.3	4′		146.0
2	4.16 (t, 1H, 6.0)	72.0	5′	6.67(1H, br.)	116.1
3	2.81,2.69(dd, 2H, 14.5,6.0)	40.0	6′	6.69(1H, br.)	124.4
4	3.96(t, 2H, 7.0)	64.3	1″	4.61(d, 1H, 7.5)	103.2
5	1.49(m, 2H, 7.0)	30.8	2″	3.27(t, 1H, 7.5)	74.0
6	1.26(m, 2H, 7.0)	19.2	3″	3.25(t, 1H, 7.5)	76.6
7	0.89(t, 3H, 7.0)	14.2	4″	3.18(t, 1H, 7.5)	70.3
1′		129.0	5″	3.29(m, 1H, 7.5)	77.8
2′	6.95(1H, br.)	118.7	6″	3.72,3.63(dd, 2H, 11.7,7.5)	61.4
3′		145.5			

with the standard sugar on TLC. In ^{13}CNMR spectrum of **2**(**Table 2**), 19 carbon signals including one methylene, one methine, one phenyl, one *n*-butanol, one (*β*-D) glucosyl group, one carbonyl ester groups were found. In the HMBC of compound **2**, ^{13}C-^{1}H long range correlation signals were found between C-1 and H-2, H-3, H-4; C-3 and H-2, H-2′, H-6′; C-1′ and H-2, H-3, H-2′, H-5′, H-6′; C-4′ and H-2′, H-5′, H-6′; The anomeric proton of *β*-D-glucosyl group at δ 4.61(d, 1H, J=7.5 Hz) was correlate to C-4′ of phenyl (**Figure 1**). In ^{1}H-^{1}HCOSY spectrum of **2**, correlation signals were found between H-2 and H-3; H-5′ and H-6′; H-4 and H-5; H-5 and H-6; H-6 and H-7. Comparison of ^{13}CNMR data of **2** with that of the known (*R*)-3-[3-hydroxy-4-(-*O*-*β*-D-glucopyranosyl) phenyl]-2-hydroxypropanoic acid[4], both compounds showed very similar ^{13}CNMR data, but **2** has a group of butanol signal and C-1 of **2** is up-shifted for 10.90 ppm**,** indicating that the carboxyl was esterified by butanol. Therefore, compound **2** was identified as (*R*)-3-[3-hydroxy-4-(*O*-*β*-D-glucopyranosyl)phenyl]-2-hydroxypropanoic acid butyl ester. It is a new compound, named as ternatoside B.

Figure 1 Key HMBC correlations of ternatoside A and B



ternatoside A



ternatoside B

Acknowledgments

This research was supported by the National Natural Science Foundation of China (Grant No. 30400584).

References

1. S. H. Zhu, *Commercial Science of Chinese Medical Materials*, First edition, People Healthy Publishing House, Beijing, **1990**, 212.
2. D. Q. Jiang, X. M. Huang, *China Journal of Chinese Materia Medica*, **1993**, *18*(9), 550.
3. X. M. Guo, Z. L. Zhou, Y. F. Hong, *Acta Pharm. Sin.,* **1995**, *30*(12), 931.
4. T. Satake, *et al*., *Chem. Pharm. Bull.,* **1999,** *47*, 1444.

Received 23 September, 2004