A Novel Ursane Triterpene from *Rubus swinhoei*

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Abstract: A novel ursane triterpene, named swinhoeic acid, was isolated from the roots of *Rubus swinhoei*. Its structure was elucidated as 18, 19-seco, 2α, 3β- dihydroxy- 19 -oxo- urs- 11, 13(18)- dien- 28- oic acid by means of MS, 1DNMR and 2DNMR.

Keywords: *Rubus swinhoei*, swinhoeic acid.

As a part of investigation on the plant of *Rubus*, we studied the chemical constituents of the roots of *R. swinhoei.* A novel ursane triterpene, named swinhoeic acid, was isolated and converted into its methyl-ester with CH_2N_2. This paper deals with its structure elucidation.

Figure 1 The structure of **1** and **1a**

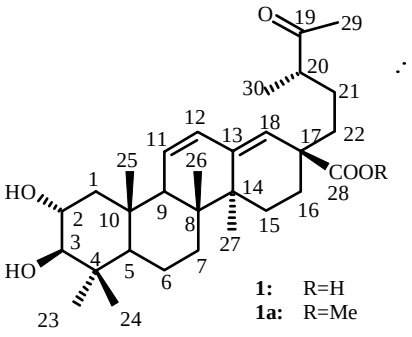
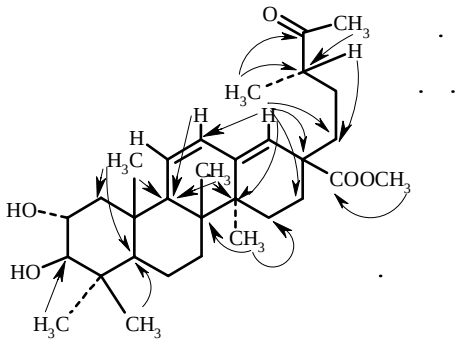


Figure 2 The key HMBC correlations



Compound **1a**, was obtained as white powder, $[\alpha]_D^{20}$ - 66 (c 0.1, $CHCl_3$). Its molecular formula was assigned as $C_{31}H_{48}O_5$ by HR-EIMS ($[M]^+$ *m/z* 500.3487, calc. 500.3502). A positive Liebermannn-Burchard test indicated **1a** was a triterpene. The IR spectrum of **1a** showed the presence of hydroxyl (3421 cm^{-1}), carbonyl group (1727 cm^{-1}) and double bond (1672 cm^{-1}). ^{1}HNMR signals between δ_H 0.6 and δ_H 2.2 suggested the presence of seven methyl groups, one of which was a doublet (δ_H 1.08, J = 7.2Hz) and the others were singlet. So **1a** was not an oleanane triterpene. ^{13}CNMR signals showed **1a** has two carbonyl groups and two double bonds. **1a** should be a tetra-cyclic triterpene according to the degree of unsaturation. A comparison of ^{13}CNMR data with analogue revealed that ring A had 2α, 3β-dihydroxyl groups [1]. HMBC confirmed this part of structure. The chemical shifts of C-26 and H-26 were assigned from the correlation with C-9, which also had correlation with H-25 in HMBC.

In the same way, C-27 was assigned. The rings B, C and D were determined by the following correlations in HMBC: H- 26 with C-7, 8, 9, 14; H-27 with C- 8, 13, 14, 15; H-11 with C-8, 9, 10, 13; H-12 with C- 9, 13; H- 18 with C-12, 14, 16, 17, 22. C- 28 was a carboxyl group by the correlation of H-22 with C-16, 20, 28. The structure of side chain was determined by the correlations of H-29 with C- 19, 20 and H- 30 (d, J = 7.2Hz) with C-19, 21, 29, 30. Therefore, the structure of **1a** was elucidated as shown in **Figure 1**. It was an E-ring opened derivative between C-18 and C-19. So the absolute configuration of C-17 and 20 were determined according to biogenesis. The original compound **1** should be 18, 19-seco, 2α, 3β-dihydroxyl-19-oxo-urs-11, 13(18)-dien-28-oic acid, named swinhoeic acid.

Table 1 ^{1}H and ^{13}CNMR of compound **1a** (in $CDCl_3$)

C	δ_C	δ_H	HMBC	^{1}H-^{1}H COSY
1	46.0(t)	1a : 2.22, dd, J=12, 4 Hz	C- 2, 3, 5, 10	H- 1b, 2
		1b: 0.98, br	C- 3, 25	H- 1a, 2
2	68.9(d)	3.75, ddd, J=9.6, 12, 4.4 Hz		H- 1a, 1b, 3
3	83.9(d)	3.02, d, J=9.6Hz	C- 2, 23, 24	H- 2
4	39.2(s)			
5	55.0(d)	1.40, m	C- 1, 6	H- 6
6	18.1(t)	1.66, m		H- 5, 7
7	32.0(t)	1.22, m		H- 6
8	40.5(s)			
9	54.1(d)	2.01, br	C- 25	H- 11, 12
10	38.0(s)			
11	127.0(d)	5.62, dd, J=10, 1.6Hz	C- 8, 9, 10, 13	H- 9, 12
12	130.0(d)	5.97, dd, J=10, 3.2Hz	C- 9, 13	H- 9, 11
13	142.8(s)			
14	41.1(s)			
15	26.0(t)			
16	27.0(t)			
17	47.1(s)			
18	126.6(d)	5.54, s	C- 12, 14, 16, 17,	
19	212.2(s)		22	
20	47.3(d)	2.49, m		H- 30
21	27.5(t)	1.25, br	C- 19, 21, 22, 30	H- 22
22	38.2(t)	1.65, m	C- 20, 30	H- 21
23	16.2(q)	0.81, s	C- 16, 17, 28	
24	28.3(q)	1.03, s	C- 3, 4, 5, 24	
25	19.1(q)	0.96, s	C- 3, 4, 5, 23	
26	16.2(q)	0.69, s	C- 1, 5, 9, 10	
27	19.8(q)	0.93, s	C- 7, 8, 9, 14	
28	176.0(s)		C- 8, 13, 14, 15	
29	28.1(q)	2.12, s		
30	16.2(q)	1.08, d, J=7.2	C- 19, 20	H- 20
MeO	51.9(q)	3.64, s	C- 19, 20, 21	
			C- 28	

Acknowledgments

This work was financially supported by the Sichuan Sci & Tech Foundation for Young Scientists.

Reference

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Received 12 July, 2000