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Two New Ionone Derivatives from *Rhododendron przewalskii Maxim.*

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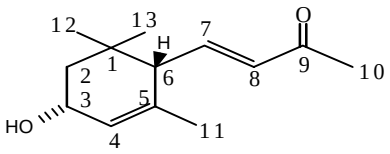
Abstract: Two new ionone derivatives, named rhododendrone and rhododendronside, were isolated from the alcoholic extract of the aerial parts of *Rhododendron przwalskii Maxim.* Their structures were elucidated on the basis of spectroscopic analysis

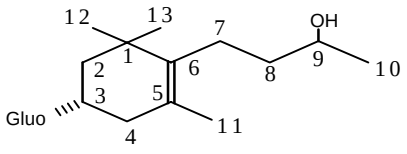
Keywords: *Rhododendron przewalskii Maxim.*, Ericaceae, rhododendrone, rhododendronside.

Rhododendron przewalskii Maxim. has been used as a folk medicine in China for the treatment of hypertension and coronary heart disease[1]. As a part of our continuing program on the study of plant-derived bioactive compounds, the chemical constituents of *R. przewalskii Maxim.* growing in Gansu were investigated. In the previous paper[2], we reported eight components from this genus. The present paper deals with the structure elucidation of two new ionone derivatives named rhododendrone **1** and rhododendronside **2** isolated from the EtOH extract of the aerial parts of *R. przewalskii.*

Figure 1 Structure of **1, 2, 3** and **4**



1



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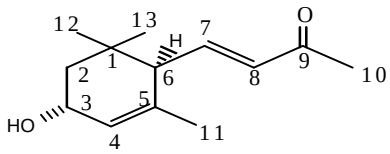

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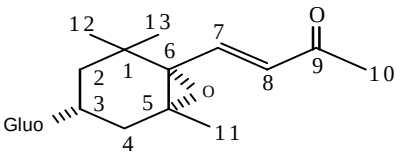

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Compound **1** was obtained as colorless oil. Its IR spectrum showed the absorption of a hydroxyl group at 3394 and a conjugated carbonyl group at 1671 cm^{-1}. Its EI mass spectrum displayed a series of fragment ions: *m/z* 193 ($M-CH_3)^+$, 175 ($M-CH_3-H_2O)^+$, 152, 125, 109 (100%), 91, 43. Its ^{1}HNMR spectrum showed the presence of four methyl groups (δ 0.88, s, 3H; δ 0.98, s, 3H; δ 1.63, s, 3H; δ 2.27, s, 3H), two conjugated olefinic proton (δ 6.08, d, 1H, J=17Hz; δ 6.64, dd, 1H, J=16, 10Hz), one trisubstituted olefinic proton (δ 5.59, m, 1H). In the ^{13}CNMR (DEPT) spectrum of **1**, thirteen carbon signals were assigned to four methyl carbons (δ 29.7, 27.2, 24.7, 22.6), one methylene carbon (δ 40.8), five methine carbons (δ 147.6, 135.4, 126.5, 66.4, 54.4) and three quaternary carbons (δ 198.2, 132.7, 35.0). Obviously, the signal at δ 198.2 were attributed to the conjugated carbonyl group. Signals at δ 147.6, 135.4, 132.7, 126.5 were due to the two conjugated olefinic carbons and the other two olefinic carbons, respectively. Thus the molecular composition of compound **1** was established as $C_{13}H_{20}O_2$. The molecular possessed four unsaturated factors, except for two olefinic bond and one carbonyl group, compound **1** might contain a ring structure in the molecular. Comparison with the ^{13}CNMR and ^{1}HNMR spectra data of the known compound **3** (3R, 6R) -3- hydroxyl -α- ionone[3] (**Table 1**), the structure of compound **1** was very similar to that of **3,** the significant differences between them were the chemical shifits of C-2, C-13 and H-6. Therefore, it is implied that **1** might be the stereo-isomer of **3.** It was reported[3] that the chemical shifit of 5-Me proton were used to make the determination of the configuration at C-3. The proton signals of 5-Me of **1** and **3** were similar (**Table 1**). Hence the structural difference between **1** and **3** might just lie in the configuration of C-6. Thus compound **1** was identified to be (3R, 6S)-3-hydroxyl-α-ionone. It is a new compound named rhododendrone.

Table 1 ^{1}H and ^{13}CNMR (DEPT) data for compound **1** (400MHz, $CDCl_3$, δppm)

position	**1**	**3**	**1**	**3**
1			35.0	33.9
2	1.38 (1H, dd, J=13.4, 10Hz)	1.38 (1H, dd, J=13.5, 6.4Hz)	40.8	43.9
	1.71 (1H, dd,J=13.5, 6.0Hz)	1.81 (1H, dd, J=13.5, 6.0Hz)		
3	4.25 (1H,m)	4.24 (1H, m)	66.4	65.5
4	5,59 (1H,m)	5.60 (1H m)	126.5	125.9
5			132.7	133.3
6	2.28 (1H, d, J=10Hz)	2.47 (1H, d, J=10Hz)	54.4	54.4
7	6.64 (1H, dd, J=16, 10Hz)	6.49 (1H, dd, J=16, 10Hz)	147.6	147.0
8	6.08 (1H, d, J=17Hz)	6.07 (1H, d, J=17Hz)	135.4	135.4
9			198.2	198.0
10	2.27 (3H, S)	2.23 (3H,S)	27.0	27.2
11	1.63 (3H, S)	1.59 (3H,S)	22.4	22.6
12	0.88 (3H, S)	0.86 (3H,S)	29.1	29.7
13	0.98 (3H, S)	1.00 (3H,S)	27.0	24.7

Table 2 ^{13}CNMR (DEPT) data of compound **2** (100MHz, CD_3OD, δ ppm)

C	**2** (DEPT)	**4** (DEPT)	C	**2** (DEPT)	**4** (DEPT)
1	38.8 (C)	35.5 (C)	11	30.2 (CH_3)	29.0 (CH_3)
2	47.5 (CH_2)	44.7 (CH_2)	12	23.2 (CH_3)	25.4 (CH_3)
3	73.3 (CH)	71.4 (CH)	13	20.0 (CH_3)	20.0 (CH_3)
4	40.7 (CH_2)	37.8 (CH_2)	G-1	102.4	103.2
5	125.0 (C)	67.0 (C)	G-2	75.2	75.2
6	138.6 (C)	69.8 (C)	G-3	78.1	78.7
7	25.5 (CH_2)	142.9 (CH)	G-4	71.7	71.7
8	39.8 (CH_2)	133.3 (CH)	G-5	77.8	78.3
9	69.1 (CH)	197.0 (C)	G-6	62.8	62.8
10	28.8 (CH_3)	27.7 (CH_3)			

Compound **2** was obtained as colorless oil; EIMS of **2** exhibited a series of ion fragments at *m/z* 194 (M-Glu-H_2O)$^+$, 177 (M-Glu-2H_2O)$^+$, 161 (M-Glu-2H_2O-CH_3)$^+$, 136, 121 (100%). Acidic hydrolysis of **2** yielded one glucose and one aglycone, and thus **2** was a glycoside confirmed by six carbon signals (δ 102.4, 75.2, 78.1, 71.7, 77.8, 62.8). Its IR spectrum showed the absorption of a hydroxyl (3433) and an olefinic bond (1636 cm^{-1}). The ^{13}CNMR and DEPT showed the presence of four CH_3, five CH_2, seven CH and three C. Then the molecular formula of compound **2** was deduced to be $C_{19}H_{34}O_7$, which could be a single ring glucoside except for one glucose and one olefinic bond. The aglycone ($C_{13}H_{23}O_2$) of **2** might possess the similar skeleton of **1** ($C_{13}H_{20}O_2$). In ^{1}HNMR spectrum of **2**, an anomeric proton signal was found at δ 4.43 (d, 1H, J=7.8Hz), therefore, the glucoside linkage should be in β configuration. The signals at δ 1.04 (s, 3H), 1.06 (s, 3H), 1.17 (d, 3H, J=6.1Hz) and 1.64 (s, 3H) were due to four methyl groups, and obviously, the signal at δ 1.17 and 1,64 were due to 9-Me protons and 5-Me protons. The absence of the olefinic proton signals suggested that the olefinic bond of **2** was quartersubstitued which was confirmed by two quaternary carbon signals (δ 125.0, 138.6) of ^{13}CNMR spectrum data of **2**. Comparison with the known compound 1,1,5-trimethyl-3-O-(β-D-glucopyranosyl)-5α, 6α-epoxy-6- (butene-1– one -3)-cyclo- hexane[4] **4**, the obvious difference lied in C-5, C-6, C-7, C-8(**Table 2**), that meant there might be some structural varites at C-5, C-6, C-7, C-8 of **2**, olefinic group might placed for the epoxyl group of **4** in C-5 and C-6 position , the –CH_2-CH_2- group might replaced for the olefinic bond group of **4** in C-7 and C-8, CHOH group replaced for the carbonyl group of **4** in C-9, which were coincident with the ^{13}CNMR data of **2** and **4**. The remaining problem was the glucoside position. Analyzing the ^{13}CNMR spectrum data of the similar compounds[5,6]. It was found that the chemical shifts C-5 and C-9 often appeared at δ 64.0 and 69.0 in the ionone compounds. However, the formation of glucoside in C-3 or C-9 will make the chemical shift to be changed to downfield 8 ppm approximately. The carbon signals attributed to C-3 and C-9 of **2** were 73.3 and 69.2, respectively, therefore, the glucose moiety should be connected to C-3. Compound **2** was thus identified as 1,1,5 trimethyl-3-O- (β-D- glucopyranosyl) –6- (butanol-3) -cyclohexene-5. It is a new compound named rhododendronside.

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