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# Two New 9, 10-*seco*-Cycloartanes from the Seeds of *Sphaerophysa salsula*

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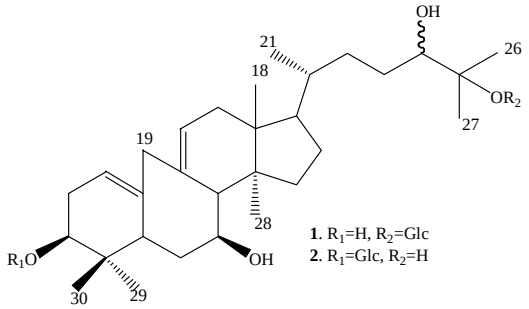
**Abstract**: Two novel compounds, named sphaerophyside SC and SD were isolated from the ethanolic extract of the seeds of *Sphaerophysa salsula*. The structures of the compounds were elucidated on the basis of the NMR data, especially the 2D NMR technique.

**Keywords**: Leguminosae, *Sphaerophysa salsula*, seeds, 9, 10-*seco*-cycloartane.

*Sphaerophysa salsula* (Pall.) DC is widely distributed in the Middle-Asian and the northwest of China. It was used as a folk medicine to treat hypertension in China. We previously reported the isoflavans[1], stilbenes[2] and 9, 19-cycloartane[3] from *S. salsula*. In our extended research, we isolated two new 9, 10-*seco*-cycloartanes from the seeds of the plant. This paper describes the isolation and structural elucidation of the compounds.

**Figure 1** Sphaerophyside SC (**1**) and SD (**2**)




Sphaerophyside SC (**1**, 6 mg), white powder from MeOH. Its molecular formula $C_{36}H_{60}O_9$ was determined on the basis of HRFABMS ($[M+H]^+$, *m/z* 637.4320, calcd. 637.4326) and $^{13}C$ NMR. After hydrolysis with 0.5 mol/L HCl, **1** afforded glucose, which was identified by TLC with authentic sample. In the $^1H$ NMR spectra of **1**, it presented 6 tertiary methyls [δ 0.73 (s, 3H, H-18), 1.24 (s, 3H, H-26), 1.21 (s, 3H, H-27), 0.92 (s, 3H, H-28), 1.02 (s, 3H, H-29), and δ 0.69 (s, 3H, H-30)] and one secondary methyl at δ 0.92 (d, 1H, J=7.5 Hz, H-21). Two olefinic protons were showed at δ 5.27

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**Table 1** NMR data of **1** and **2** (in $CD_3OD$, $^1H$ 500.0 MHz, $^{13}C$ 125.0 MHz, δppm, $J_{Hz}$)

| N | **1** ($\delta_H$) | **2** ($\delta_H$) | **1** | 2 ($\delta_C$) |
|---|---|---|---|---|
| 1 | 5.27 (br.s, 1H) | 5.27 (br.s, 1H) | 117.6 | 118.1 |
| 2 | 1.70 (m, 1H), 2.19 (m, 1H) | 2.06 (m, 1H), 2.45 (m, 1H) | 32.6 | 32.3 |
| 3 | 3.39 (dd, 1H, 9.5, 3.0 ) | 3.43 (dd, 1H, 9.5, 6.0) | 79.5 | 85.6 |
| 4 | | | 38.8 | 38.9 |
| 5 | 1.66 (m, 1H) | 1.76 (m, 1H) | 46.1 | 46.4 |
| 6 | 1.90 (m, 2H) | 1.94, 1.81 (m, 2H) | 36.8 | 37.0 |
| 7 | 3.80 (m, 1H) | 3.80 (m, 1H) | 74.9 | 74.8 |
| 8 | 2.14 (m, 1H) | 2.15 (m, 1H) | 55.9 | 55.8 |
| 9 | | | 139.3 | 137.5 |
| 10 | | | 140.6 | 140.0 |
| 11 | 5.36 (br. s, 1H) | 5.35 (br. s, 1H) | 126.6 | 126.3 |
| 12 | 2.08 (m, 1H), 1.95 (m, 1H) | 2.03 (m, 1H), 1.97 (m, 1H) | 38.5 | 38.5 |
| 13 | | | 46.7 | 46.7 |
| 14 | | | 49.3 | 49.4 |
| 15 | 1.52 (br.t, 2H, 10.0) | 1.74 (m, 2H) | 36.2 | 36.2 |
| 16 | 1.56 (m, 2H) | 1.91 (m, 2H) | 29.3 | 29.3 |
| 17 | 1.62 (m, 1H) | 1.62 (m, 1H) | 52.0 | 52.0 |
| 18 | 0.73 (s, 3H) | 0.73 (s, 3H) | 15.3 | 15.3 |
| 19 | 2.75, 3.02 (d, 1H, 14.0) | 2.73, 3.01 (d, 1H, 14.0 ) | 45.8 | 45.8 |
| 20 | 1.40 (m, 1H) | 1.38 (m, 1H) | 35.0 | 35.0 |
| 21 | 0.92 (d, 3H, 7.5) | 0.93 (d, 3H, 7.0) | 19.2 | 19.2 |
| 22 | 1.89 (m, 2H) | 1.89 (m, 2H) | 37.9 | 37.9 |
| 23 | 1.95 (m, 2H) | 1.51, 1.20 (m, 2H) | 29.3 | 29.1 |
| 24 | 3.36 (t , 1H, 9.0) | 3.15 (overlapped, 1H) | 75.5 | 80.6 |
| 25 | | | 81.9 | 73.9 |
| 26 | 1.24 (s, 3H) | 1.12 (s, 3H) | 21.3 | 24.7 |
| 27 | 1.21 (s, 3H) | 1.16 (s, 3H) | 23.8 | 25.8 |
| 28 | 0.92 (s, 3H) | 0.92 (s, 3H) | 19.5 | 19.4 |
| 29 | 1.02 (s, 3H) | 1.11 (s, 3H) | 24.9 | 25.0 |
| 30 | 0.69 (s, 3H) | 0.79 (s, 3H) | 13.4 | 14.8 |
| 1′ | 4.61 (d ,1H, 8.0) | 4.30 (d, 1H, 8.0) | 98.6 | 106.2 |
| 2′ | 3.16 (br. d, 1H, 8.0) | 3.17 (overlapped, 1H) | 75.2 | 75.6 |
| 3′ | 3.34 (m, 1H) | 3.35 (m, 1H) | 78.1 | 78.2 |
| 4′ | 3.30 (m, 1H) | 3.27 (m, 1H) | 71.6 | 71.7 |
| 5′ | 3.31 (m, 1H) | 3.29 (m, 1H) | 77.7 | 77.7 |
| 6′ | 3.64 (dd, 1H, 6.0, 12.5), 3.81 (m, 1H) | 3.64 (dd, 1H, 5.5, 11.5), 3.82 (m, 1H) | 62.6 | 62.8 |

(br.s,1H, H-1) and δ 5.36 (br.s, 1H, H-11). It also exhibited an anomeric proton at δ 4.61 (d, 1H, J=8.0 Hz, H-1′), so the configuration of the glucose is β. Three oxygen substituted methine protons were observed at δ 3.39 (dd, 1H, J=9.5, 3.0 Hz, H-3), 3.80 (m, 1H, H-7) and δ 3.36 (t, 1H, J=9.0 Hz, H-24). The $^1H$ NMR spectrum also revealed a pair of doublets at δ 2.75 and δ 3.02 (d, each 1H, J=14.0, H-19). In the $^{13}C$ NMR and DEPT (90°, 135°) of **1**, it revealed 36 carbon signals (7×$CH_3$, 9×$CH_2$, 14×CH and 6×C), 6 of them were in good accordance with the presence of a β–D-glucose moiety. Four olefinic carbons at δ 117.6 (C-1), 140.6 (C-10), 139.3 (C-9) and δ 126.6 (C-11) and four oxygen-bearing carbons at δ 79.5 (C-3), 74.9 (C-7), 75.5 (C-24), 81.9 (C-25) were

presented. However, the characteristic proton signals due to the three membered ring of 9, 19-cycloartane were not found. From the above data and literature data[4], this compound was determined to be a 9, 10-*seco* related derivative of sphaerophysone A[3]. In the HMQC spectrum of **1**, it presented the correlated peaks between proton δ 5.27 (br.s, 1H, H-1) and carbon δ 117.6 (C-1), 5.36 (br. s, 1H, H-11) and δ 126.6 (C-11), and the proton at δ 2.75 and δ 3.02 (d, 1H, J=14.0, H-19) are correlated with the carbon δ 45.8 (C-19). In the HMBC spectra of **1**, the protons at δ 2.75 and δ 3.02 (d, 1H, J=14.0, H-19) showed correlated with the carbons at δ 117.6 (C-1), 46.1 (C-5), 139.3 (C-9), 140.6 (C-10), 55.9 (C-8) and δ 126.6 (C-11). The proton δ 5.27 (br.s, 1H, H-1) has the long-range correlations with the carbons at δ 140.6 (C-10), 45.8 (C-19) and δ 46.1 (C-5). It also displayed that proton δ 5.36 (br. s, 1H, H-11) correlated with the carbons δ 45.8 (C-19), 55.9 (C-8) and δ 139.3 (C-9), However there is no HMBC correlations between proton δ 5.27 (br.s, 1H, H-1) and carbon δ 139.3 (C-9), proton δ 5.36 (br. s, 1H, H-11) and carbon δ 140.6 (C-10), which confirmed that the structure is a *seco*-cycloartane type triterpene. In the HMBC spectra of **1**, the anomeric proton showed long-range correlation with C-25 (δ 81.9). So the C-25 was substituted by a glucosyl group. And in the NOESY spectra of **1**, the cross peaks between proton δ 3.39 (dd, 1H, J=9.5, 3.0 Hz, H-3) and proton δ 1.66 (m, 1H, H-5), proton δ 3.80 (m, 1H, H-7) with δ 0.92 (s, 3H, H-28) were exhibited, so the configuration of 3, 7-OH are β-orientations. However, orientation of the hydroxyl group at the side chain is difficult to determine. On the basis of 2D NMR, the NMR data of the compound **1** were assigned.

Sphaerophyside SD (**2**, 2 mg**)** has the same molecular formula as **1**. In the $^{1}$H NMR, it presented H-19 protons at δ 2.73 and δ 3.01 (d, each 1H, J=14.0 Hz), suggested it is a 9, 10-*seco*-cycloartane glucoside. The anomeric proton at δ 4.30 (d, 1H, J=8.0 Hz) has the correlation with carbon δ 85.6 (C-3) in HMBC spectrum. So the glycosic linkage is at C-3. The configuration of 3, 7-OH were determined by NOESY spectrum. The NMR data were also assigned by 2D NMR. (see **Table 1**.)

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