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Triterpenoid Saponins from *Derris eriocarpa* How

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Abstract
*Seven new oleanane-type triterpenoid saponins, Derrisaponins D-J (**1**−**7**), were isolated from the vines of Derris eriocarpa How together with five known compounds, Derrisaponins A-C and Millettiasaponins A-B (**8**-**12**). The structures of Derrisaponins D-J (**1**−**7**) were determined based on the detailed analysis of 1D and 2D NMR as well as MS data.*
Keywords: *Derris eriocarpa How, triterpenoid saponin, derrisaponin, NMR, sweetness*

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I. Introduction

Derris eriocarpa How ('Tugancao' in Chinese) is a traditional 'Zhuang' and 'Dai' ethnopharmacy, and it is used to treat inflammation, cough, nephritis, cystitis, etc.[1-2] This medicinal plant is also used to substitute licorice for sweetness due to its similar sweet taste to licorice, which is one of the oldest well-known sweet tasting plants in the world.[1,3-4] Most recently, Millettiasaponin A and Derrisaponin A were reported from this plant and the sweetness test indicated that they are 150 and 80 times sweeter than sucrose.[1] This encouraged us to look deep into the possible analogs of Millettiasaponin A and Derrisaponin A from *D. eriocarpa* How. The goal of this research is to isolate new triterpenoid saponins from *D. eriocarpa* How and test their sweet profiles.

10 kg dried powder from the vines of *D. eriocarpa* How were extracted using 70% EtOH to yield 1.25 kg of the extract. 450 g of the extract was then separated on XAD, HP20ss, C18, and Sephadex LH20 column chromatography, and preparative RP-HPLC, respectively. Twelve triterpenoid saponins were obtained, including seven new compounds, Derrisaponins D-J (**1**−**7**), and five known analogs, Derrisaponins A-C (**8**-**10**) and Millettiasaponins A-B (**11**-**12**). The structures of the new compounds (**1**−**7**) were identified by high-resolution ESIMS and NMR analysis including 1D and 2D NMR. The known compounds (**8**−**12**) were confirmed by comparing MS and NMR data to published data.[1,5]

II. Results And Discussions

Compound **1** was obtained as a white amorphous powder, and the molecular formula was determined to be $C_{50}H_{78}O_{20}$ by HRESIMS analysis ([M-H]$^-$ at *m/z* 997.5011, calcd for $C_{50}H_{77}O_{20}$, 997.5014, Δ = 0.3 ppm). The ^{1}H and ^{13}C NMR spectra (**Tables 1** and **2**) displayed a very similar NMR data set with the co-occurrence Millettiasaponin A (**11**)[1] (see **Tables S1** and **S2** for NMR data). The only difference observed was that the hydroxymethyl group at C-24 (δ_C 64.1 and δ_H 4.27/3.26) was replaced by a methyl group (δ_C 17.3 and δ_H 1.20). Taking the MS difference of these two compounds (16 Da) into consideration, the planar structure of compound **1** was determined and the conclusion was further confirmed based on a detailed analysis of HMBC correlations, selected HMBC correlations were shown in **Figure 1**. Specifically, the linkage sites of sugar units and the aglycone were determined by the HMBC correlations from H-1′ (δ_H 5.08) to C-3 (δ_C 90.3), from H-1″ (δ_H 5.77) to C-2′ (δ_C 79.7), and from H-1‴ (δ_H 6.35) to C-2″ (δ_C 77.1) (**Figure 1**). The relative configuration of compound **1** was established based on the analysis of the ROESY correlations (**Figure 1**) and the coupling constants. The correlations of H_3-23/H-3, H-3/H-5, and H-5/H-9 indicated that these protons were in α-orientation. The correlations between H_3-24/H_3-25, and H_3-25/H_3-26 revealed that they were in β-orientation. The coupling constants of H-18 (δ_H 2.98, dd, J = 13.2, 4.6) indicated that H-18 possessed an axial direction. Together with ROESY correlations of H-12/H-18 and H-18/H_3-28, the β-orientation of these protons could be obtained. The coupling constant of one proton of H_2-19 (δ_H 2.37, d, J = 12.7) indicated that this proton was in an equatorial direction (β-oriented) and the other proton (δ_H 1.86, m) would be in the axial direction (α-oriented). Similar analysis revealed that H_2-21 (δ_H 2.88, d, J = 14.4) was in the equatorial direction (β-oriented) and the other proton (δ_H 1.80, m) would be in the axial direction (α-oriented). The correlations of H_3-29/H_{ax}-19 and H_3-29/H_{ax}-21 suggested that CH_3-29 was α-oriented and in an axial direction. The coupling constants of H-22 (δ_H

2.89, dd, J = 2.8, 3.0) indicated it was in the equatorial direction (α-oriented). The β-configurations of the GluA and Gal glycosidic bonds were established by the coupling constants of H-1′ (δ_H 5.08, d, J = 7.7 Hz) and H-1″ (δ_H 5.77, d, J = 7.7 Hz).[6] And the α-configuration of the Rha was determined by the singlet at δ_H 6.35 (H-1‴) and C-5‴ at δ_C = 70.0.[6-8] GluA and Gal were tentatively assigned as D-configuration and Rha was tentatively assigned as L-configuration following that of Millettiasaponin A (**11**) and three other co-occurrence metabolites from this plant, DerrisaponinsA-C (**8**−**10**). Consequently, compound **1** was elucidated and named Derrisaponin D.

Compound **2** was purified as a white amorphous powder, and the HRESIMS peak at *m/z* 999.5140 ([M-H]$^-$) suggested its molecular formula as $C_{50}H_{80}O_{20}$ (calcd for $C_{50}H_{79}O_{20}$, 999.5170, Δ = 3.0 ppm). Detailed ^{1}H and ^{13}C NMR data analysis (**Tables 1** and **2**) indicated compound **2** was an analog of Millettiasaponin A (**11**)[1] (see **Tables S1** and **S2** for NMR data), and their NMR data were very similar to each other. The only difference observed was that the C-30 carbonyl signal (δ_C 180.0) was replaced by that of a hydroxymethyl group (δ_C 68.5 and δ_H 3.89/3.84). This observation together with MS difference of these two compounds (14 Da) revealed the planar structure of compound **2,** and the conclusion was further confirmed by a detailed analysis of ^{1}H-^{1}H COSY and HMBC analysis. The HMBC correlation from H_3-29 to C-30 (**Figure S1**) confirmed the reduction of the carboxylic acid to a hydroxymethyl group. The HMBC correlation from H-1‴(δ_H 6.32) to C-2″ (δ_C 78.1) confirmed the linkage of Rha and Gal, and the ROESY correlations between H-1′ (δ_H 5.00) and H-3 (δ_H 3.40), and between H-1″ (δ_H 5.83) and H-2′ (δ_H 4.63) revealed the attach position of GluA to the aglycone and that of Gal to GluA. (**Figure S1**). The relative configuration of the aglycone was confirmed by the detailed analysis of ROESY correlations (**Figure S2**) and coupling constants of H-18, H_2-19, H_2-21, and H-22. Specifically, the β-orientation of the new hydroxymethyl group was deduced from the ROESY correlation between H-18 and H-30. The β-configurations of the GluA and Gal glycosidic bonds were established by the coupling constants of H-1′ (δ_H 5.00, d, J = 6.6 Hz) and H-1″ (δ_H 5.83, d, J = 7.5 Hz),[6] and they were tentatively assigned as D-configuration. The α-configuration of the Rha was determined by the singlet at δ_H 6.32 (H-1‴) and C-5‴ at δ_C =69.9.[6-8] And it was tentatively assigned as L-configuration. Thus, compound **2** was confirmed and named Derrisaponin E.

Compound **3** was isolated as a white amorphous powder, and the molecular formula was determined to be $C_{51}H_{80}O_{21}$ by HRESIMS analysis ([M-H]$^-$ at *m/z* 1027.5159, calcd for $C_{51}H_{79}O_{21}$, 1027.5119, Δ = 3.9 ppm). The comparison of ^{1}H and ^{13}C NMR data (**Tables 1** and **2**) indicated that it shared a very similar NMR data set with Millettiasaponin A (**11**)[1] (see **Tables S1** and **S2** for NMR data). The exception observed was the presence of an additional methoxy group (δ_C 52.5 and δ_H 3.77). The position of the methoxy group was confirmed based on its correlation with C-6′ in the HMBC spectrum (**Figure S1**). The linkage points of sugar units and the aglycone were confirmed by the HMBC correlations from H-1‴ (δ_H 6.32) to C-2″ (δ_C 78.1), from H-1″ (δ_H5.82) to C-2′ (δ_C 77.0), and from H-1′ (δ_H 4.96) to C-3 (δ_C 91.8) (**Figure S1**). The relative configuration of the aglycone was obtained from ROESY correlations (**Figure S2**) and detailed analysis of the coupling constants of H-18, H_2-19, H_2-21, and H-22. The β-configurations of the GluA and Gal glycosidic bonds were established based on the coupling constants of H-1′ (δ_H 4.96, d, J = 7.5 Hz) and H-1″ (δ_H 5.82, d, J = 7.5 Hz),[6] and they were tentatively assigned as D-configuration. The α-configuration of the Rha was determined by the singlet at δ_H 6.32 (H-1‴) and C-5‴ at δ_C = 69.9.[6-8] The Rha was tentatively assigned as L-configuration. Thus, compound **3** was confirmed and named Derrisaponin F.

Compound **4** was obtained as a white amorphous powder, and the HRESIMS peak at *m/z* 1145.5405 ([M-H]$^-$) suggested its molecular formula as $C_{55}H_{86}O_{25}$ (calcd for $C_{55}H_{85}O_{25}$, 1145.5380, Δ = 2.2 ppm). The comparison of ^{1}H and ^{13}C NMR data of compound **4** (**Tables 1** and **2**) with that of Derrisaponin A (**8**)[1] (see **Tables S1** and **S2** for NMR data) indicated that a fourth sugar unit was incorporated into this compound. The additional sugar unit was identified as D-xylose based on the NMR data (H-1⁗−5⁗, δ_H 5.04, 4.08, 4.09, 4.17, and 4.27/3.65; C-1⁗−5⁗, δ_C 107.2, 75.3, 78.7, 71.5, and 67.5) (**Tables 1** and **2**).[6] The linkage positions of sugar units were deduced from the HMBC correlations from H-1‴ (δ_H 6.22) to C-2″ (δ_C77.6) and from H-1″ (δ_H 5.87) and C-2′ (δ_C 77.0), and the ROESY correlation between H-1⁗ (δ_H 5.04) and H-3″ (δ_H 4.13) (**Figure S1**). The attached position of the oligosaccharide chain to the aglycone was confirmed based on the ROESY correlation between H-1′ (δ_H 5.01) and H-3 (δ_H 3.40) (**Figure S1**). The relative configuration of the aglycone was confirmed by the extensive analysis of ROESY correlations (**Figure S2**) and coupling constants of H-18, H_2-19, H_2-21, and H-22. The β-configurations of the GluA, Gal, and Xyl glycosidic bonds were established by the coupling constants of H-1′ (δ_H 4.96, d, J = 7.5 Hz), H-1″ (δ_H 5.82, d, J = 7.5 Hz), and H-1⁗ (δ_H 5.04, d, J = 6.5 Hz), respectively.[6] And they were tentatively assigned as D-configuration. The α-configuration of the Rha was determined by the singlet at δ_H 6.22 (H-1‴) and C-5‴ at δ_C = 69.9.[6-8] And it was tentatively assigned as L-configuration. Thus, compound **4** was confirmed and named Derrisaponin G.

Compound **5** was isolated as a white amorphous powder, and the molecular formula ($C_{50}H_{76}O_{21}$) was concluded from the HRESIMS data ([M-H]$^-$ at *m/z* 1011.4801, calcd for $C_{50}H_{75}O_{21}$, 1011.4806, Δ = 0.5 ppm). Due to poor solubility, the NMR data of Compound **5** was collected in DMSO-d_6. For comparison, NMR data of the co-occurrence Millettiasaponin A (**11**) was also collected in DMSO-d_6. These two compounds showed very similar ^{1}H and ^{13}C NMR spectra (**Tables 1**, **2**, **S1**, and **S2**) with the difference at C-24: the hydroxymethyl group (CH_2OH-24: δ_C 62.8, δ_H 3.91/3.70) *vs* the aldehyde group (CHO-24: δ_C 207.1, δ_H 9.90). The replacement was confirmed by the HMBC correlations from H_3-23 to C-24, and from H-24 to C-4 (**Figure S1**). The linkage sites of sugar units and the aglycone were established by the HMBC correlation from H-1‴ (δ_H 4.99) to C-2″ (δ_C 74.9) and by the ROESY correlations between H-1′ (δ_H 4.18) and H-3 (δ_H 3.26) and between H-1″ (δ_H 4.67) and H-2′ (δ_H 3.38) (**Figure S1**). The relative configuration of the aglycone was confirmed by the detailed analysis of ROESY data (**Figure S2**) and coupling constants of H-18, H_2-19, H_2-21, and H-22. The *β*-configurations of the GluA and Gal glycosidic bonds were established by the coupling constants of H-1′ (δ_H 4.50, d, *J* = 7.2 Hz) and H-1″ (δ_H 4.60, d, *J* = 7.8 Hz)[6] [these data were from the ^{1}H NMR spectrum collected in D_2O]. And they were tentatively assigned as D-configuration. The *α*-configuration of the Rha was determined by the singlet at δ_H 4.99 (H-1‴) and C-5‴ at δ_C = 68.4.[6-8] The configuration of Rha was tentatively assigned to be L. Thus, compound **5** was confirmed and named Derrisaponin H.

Compound **6** was obtained as a white amorphous powder, and the molecular formula was established to be $C_{54}H_{84}O_{25}$ based on HRESIMS data ([M-H]$^-$ at *m/z* 1131.5282, calcd for $C_{54}H_{83}O_{25}$, 1131.5229, Δ = 4.7 ppm). Compound **6** gave a very similar 1D NMR data set (**Tables 1** and **2**) with that of Millettiasaponin B (**12**)[5] (see **Tables S1** and **S2** for NMR data) except for the presence of an additional sugar unit. The additional unit was determined to be D-glucose based on the MS difference (162 Da) and the NMR data (H-1⁗−6⁗, δ_H 5.16, 4.07, 4.21, 4.22, 3.91, and 4.47/4.35; C-1⁗−6⁗, δ_C 106.4, 75.5, 78.7, 72.0, 78.7, and 63.1). The linkage of sugar units was determined from the HMBC correlations of H-1⁗ (δ_H 5.16) to C-3‴ (δ_C 73.3), H-1‴ (δ_H 6.21) to C-2″ (δ_C 77.7), and H-1″ (δ_H 5.79) to C-2′ (δ_C 76.9) (**Figure S1**). The attached position of the oligosaccharide chain to the aglycone was confirmed based on the HMBC correlation from H-1′ (δ_H 4.97) to C-3 (δ_C 91.7) (**Figure S1**). The partial structure of the five-membered lactone ring was confirmed from the HMBC correlations from H-29 (δ_H 4.24, 3.80)/H-22 (δ_H 4.30) to C-20 (δ_C 48.9)/C-30 (δ_C 179.5) (**Figure S1**). The relative configuration of the aglycone was confirmed by the detailed analysis of ROESY data (**Figure S2**) and coupling constants of H-18, H_2-19, H_2-21, and H-22. The *β*-configurations of the GluA, Gal, and Glc glycosidic bonds were established by the coupling constants of H-1′ (δ_H 4.97, d, *J* = 7.4 Hz), H-1″ (δ_H 5.79, d, *J* = 7.6 Hz), and H-1⁗ (δ_H 5.16, d, *J* = 7.8 Hz), respectively.[6] And they were tentatively assigned as D-configuration. The *α*-configuration of the Rha was determined by the singlet at δ_H 6.21 (H-1‴) and C-5‴ at δ_C = 69.7.[6-8] And it was tentatively assigned as L-configuration. Thus, compound **6** was confirmed and named Derrisaponin I.

Compound **7** was purified as a white amorphous powder, and the molecular formula was determined to be $C_{48}H_{72}O_{21}$ by HRESIMS analysis ([M-H]$^-$ at *m/z* 983.4510, calcd for $C_{48}H_{71}O_{21}$, 983.4493, Δ = 1.7 ppm). The 1D NMR of this compound (**Tables 1** and **2**) was very similar to Millettiasaponin B (**12**)[5] (see **Tables S1** and **S2** for NMR data) except for the disappearance of resonances for the hydroxymethyl group (CH_2OH-29, δ_C 63.9 and δ_H 4.23/3.90) and the presence of a carbonyl carbon (δ_C 173.0). Taking the MS difference (14 Da) and downfield of C-27 (δ_C 49.5 to 53.8) into consideration, CH_2OH-29 in Millettiasaponin B (**12**) was replaced by COOH-29 in compound **7**. The linkage positions of sugar units and the aglycone were established by the HMBC correlations from H-1‴ (δ_H 6.30) to C-2″ (δ_C 78.2), from H-1″ (δ_H 5.82) to C-2′ (δ_C77.1), and from H-1′ (δ_H 5.00) to C-3 (δ_C 91.5) (**Figure S1**). The partial structure of the five-membered lactone ring was confirmed from the HMBC correlations from H-22 (δ_H 4.43) to C-20 (δ_C 53.8)/C-30 (δ_C 176.1). The relative configuration of the aglycone was confirmed by the correlations from the ROESY spectrum (**Figure S1**) and extensive analysis of the coupling constants of H-18, H_2-19, H_2-21, and H-22. The *β*-configurations of the GluA and Gal glycosidic bonds were established by the coupling constants of H-1′ (δ_H 5.00, d, *J* = 7.5 Hz) and H-1″ (δ_H 5.82, d, *J* = 7.5 Hz).[6] And they were tentatively assigned as D-configuration. The *α*-configuration of the Rha was determined by the singlet at δ_H 6.30 (H-1‴) and C-5‴ at δ_C = 69.8.[6-8] And the Rha was tentatively assigned as L-configuration. Thus, compound **7** was confirmed and named Derrisaponin J.

III. EXPERIMENTAL

General: NMR spectra were acquired on a Varian 500 MHz spectrometer with TMS as the internal standard. High-resolution electrospray ionization (HRESIMS) accurate mass measurements were carried out on a Waters ACQUITY UPLC-I-class Xevo G2-XS-QTof instrument. Column chromatography (CC) separations were carried out using Amberlite™, XAD, Diaion™, HP20ss, Sephadex® LH-20, and Biotage® C18 SNAP cartridge. Preparative HPLC was performed on a D-7000 HSM with a L-7455 detector using Phenomenex Luna 5 μm C_{18} columns (250 mm × 21.2 mm and 250 mm × 10.0 mm).

Plant Material. Different parts from *D. eriocarpa* How (leaves, vines, roots) were collected in small scales from three locations (Liuqiu, Yulin, and Meishuling) in Guangxin, China. The dried powder was extracted using 70% EtOH by ultrasonic for 1h, the extract was analyzed using HRESIMS, respectively. The HRMS of known derrisaponins and their fragmentations were used for candidate selection. As a result, dried vines of *Derris eriocarpa* were collected in November 2018 in Yulin, Guangxi, China.

Extraction and Isolation: 10 kg dried powder from the vines of *D. eriocarpa* How were extracted using 70% EtOH to yield 1.25 kg of the extract. 450 g of extract was chromatographed over XAD, HP20ss, Sephadex LH20, and C18 columns, followed by preparative HPLC and/or semi-preparative HPLC (details see Supporting Information) to yield compounds **1** (7.7 mg), **2** (5.5 mg), **3** (6.4 mg), **4** (19.2 mg), **5** (5.5 mg), **6** (18.5 mg), **7** (23.9 mg), **8** (23.2 mg), **9** (31.3 mg), **10** (16.9 mg), **11** (36.3 mg), and **12** (25.6 mg).

Derrisaponin D (1): white amorphous powder. HRESIMS: *m/z* $[M-H]^-$ 997.5011 (calcd for $C_{50}H_{77}O_{20}$, 997.5014, Δ = 0.3 ppm). ^1H and ^{13}C NMR: **Tables 1** and **2**.

Derrisaponin E (2): white amorphous powder. HRESIMS: *m/z* $[M-H]^-$ 999.5140, calcd for $C_{50}H_{79}O_{20}$, 999.5170, Δ = 3.0 ppm). ^1H and ^{13}C NMR: **Tables 1** and **2**.

Derrisaponin F (3): white amorphous powder. HRESIMS: *m/z* $[M-H]^-$ 1027.5159 (calcd for $C_{51}H_{79}O_{21}$, 1027.5119, Δ = 3.9 ppm). ^1H and ^{13}C NMR: **Tables 1** and **2**.

Derrisaponin G (4): white amorphous powder. HRESIMS: *m/z* $[M-H]^-$ 1145.5405, calcd for $C_{55}H_{85}O_{25}$, 1145.5380, Δ = 2.2 ppm). ^1H and ^{13}C NMR: **Tables 1** and **2**.

Derrisaponin H (5): white amorphous powder. HRESIMS: *m/z* $[M-H]^-$ 1011.4801, calcd for $C_{50}H_{75}O_{21}$, 1011.4806, Δ = 0.5 ppm). ^1H and ^{13}C NMR: **Tables 1** and **2**.

Derrisaponin I (6): white amorphous powder. HRESIMS: *m/z* $[M-H]^-$ 1131.5282, calcd for $C_{54}H_{83}O_{25}$, 1131.5229, Δ = 4.7 ppm). ^1H and ^{13}C NMR: **Tables 1** and **2**.

Derrisaponin J (7): white amorphous powder. HRESIMS: *m/z* $[M-H]^-$ 983.4510, calcd for $C_{48}H_{71}O_{21}$, 983.4493, Δ = 1.7 ppm).^1H and ^{13}C NMR: **Tables 1** and **2**.

Supplementary data: Supplementary data, such as detailed separation procedure, NMR data for the known compounds, and HRESIMS and NMR spectra for the new compounds, are included in the Supporting Information.

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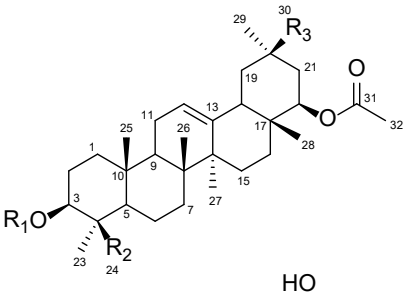
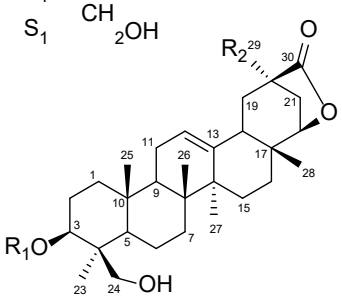
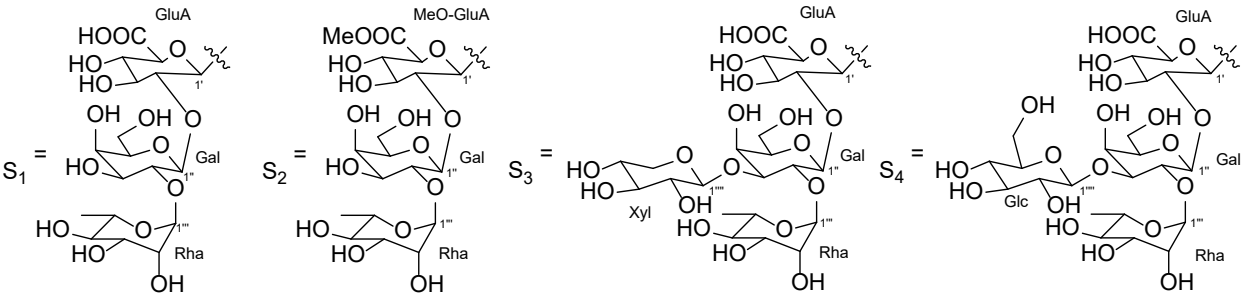
Structure chart

	R1	R2	R3
1.	S_1	CH_3	COOH
2.	S_1	CH_2OH	CH_2OH
3.	S_2	CH_2OH	COOH
4.	S_3	CH_2OH	COOH
5.	S_1	CHO	COOH
8.	S_4	CH_2OH	COOH
9.	S_1	CH_2OH	S
10.	S_4	CH_2OH	S_5
11.	S_1	CH_2OH	COOH



	R1	R2
6.	S_4	CH_2OH
7.	S_1	COOH
12.	S_1	CH_2OH





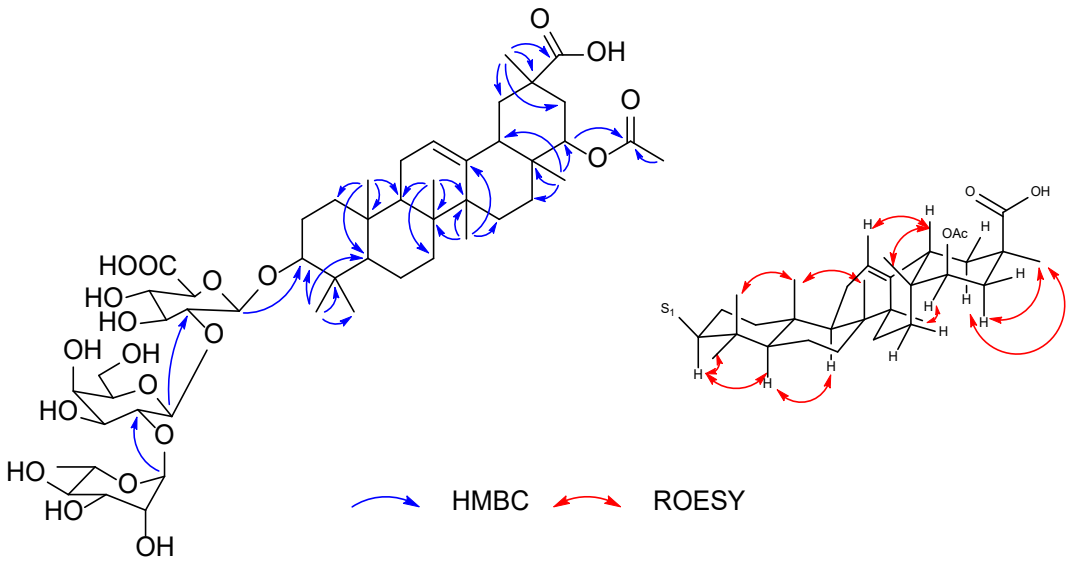


Figure 1. Selected HMBC and ROESY correlations for Derrisaponin D (1)

Table 1.^{1}H NMR Spectroscopic Data for Derrisaponins D-J (1-7)

NO.	1[a]	2[a]	3[a]	4[a]	5[b]	6[a]	7[a]
1	1.41 m; 0.87 m	1.35 m; 0.83 m	1.35 m; 0.83 m	1.34 m; 0.84 m	1.62 m; 0.98 m	1.32 m; 0.82 m	1.33 m; 0.84 m
2	2.20 m; 1.87 m	2.21 m; 1.88 m	2.09 m; 1.85 m	2.21 m; 1.86 m	2.08 m; 1.88 m	2.18 m; 1.86 m	2.22 m; 1.88 m
3	3.33 dd (11.8, 4.4)	3.40 dd (11.7, 3.9)	3.38 dd (12, 4.6)	3.40 dd (12.1, 3.7)	3.26 m	3.38 dd (11.7, 4.6)	3.41 dd (11.8, 4.6)
5	0.82 m	0.86 m	0.86 m	0.88 m	0.98 m	0.85 m	0.85 m
6	1.56 m; 1.35 m	1.55 m; 1.25 m	1.56 m; 1.25 m	1.63 m; 1.33 m	1.66 m; 1.24 m	1.61 m; 1.30 m	1.56 m; 1.24 m
7	1.53 m; 1.27 m	1.48 m; 1.28 m	1.50 m; 1.27 m	1.52 m; 1.30 m	1.42 m; 1.25 m	1.47 m; 1.32 m	1.44 m; 1.29 m
9	1.65 m	1.58 m	1.61 m	1.63 m	1.55 m	1.56 m	1.54 m
11	1.86 m	1.77 m	1.83 m	1.84 m	1.84 m	1.74 m	1.72 m
12	5.58 brs	5.26 brs	5.57 brs	5.57 brs	5.22 brs	5.14 dd (3.6, 3.8)	5.16 dd (3.6, 3.7)
15	1.81 m; 1.01 m	1.74 m; 1.00 m	1.78 m; 1.00 m	1.79 m; 1.02 m	1.70 m; 0.94 m	1.70 m; 0.98 m	1.69 m; 1.01 m
16	1.95 m; 1.01 m	1.93 m; 1.13 m	1.95 m; 1.03 m	1.95 m; 1.02 m	1.87 m; 0.94 m	1.87 m; 1.07 m	1.88 m; 1.08 m
18	2.98 dd (13.2, 4.6)	2.41 dd (13.2, 3.9)	2.97 dd (13.1, 4.4)	2.98 dd (13.0, 3.9)	2.36 brd (12.9)	2.24 dd (13.2, 6.8)	2.32 d (13.2, 5.5)
19	2.37 d (12.7); 1.86 m	1.84 m; 1.57 m	2.35 d (11.9); 1.86 m	2.36 brd (12.8); 1.85 m	1.75 m; 1.59 m	2.02 dd (13.5, 13.3); 1.59 m	2.59 m; 2.35 dd (13.3
21	2.88 d (14.4), 1.80 m	2.13 m; 1.56 m	2.87 d (14.3); 1.82 m	2.88 d (14.9); 1.80 m	2.15 d (14.0); 1.59 m	2.69 dd (11.9, 5.2); 2.39 d (11.9)	3.06 dd (11.2, 7.2); 2.69 d (12.0)
22	4.89 dd (3.0, 2.8)	4.97 dd (3.5, 3.2)	4.88 t (2.6)	4.89 brs	4.35 brs	4.30 m	4.43 m
23	1.44 s	1.46 s	1.46 s	1.47 s	1.19 s	1.43 s	1.45 s
24	1.20 s	4.27 d (11.3); 3.26 d (11.3)	4.26 d (11.4); 3.25 d (11.4)	4.29 m; 3.34 d (11.3)	9.90 s	4.29 m; 3.34 d (11.4)	4.27 d (11.4); 3.25 d (
25	0.84 s	0.69 s	0.69 s	0.71 s	0.70 s	0.70 s	0.68 s
26	0.96 s	0.90 s	0.92 s	0.93 s	0.86 s	0.84 s	0.82 s
27	1.32 s	1.29 s	1.33 s	1.34 s	1.13 s	1.22 s	1.21 s
28	1.02 s	0.99 s	1.02 s	1.02 s	0.70 s	1.02 s	1.02 s
29	1.37 s	1.20 s	1.36 s	1.36 s	1.03 s	4.24 m, 3.90 m	
30		3.89 d (10.3), 3.84 d (10.3)					
32	2.05 s	2.12 s	2.05 s	2.05 s	1.89 s		
1'	5.08 d (7.7)	5.00 d (6.6)	4.96 d (7.5)	5.01 d (6.6)	4.18 m	4.97 d (7.4)	5.00 d (7.5)
2'	4.55 m	4.63 m	4.55 m	4.65 m	3.38 m	4.62 m	4.63 m
3'	4.67 m	4.64 m	4.57 m	4.62 m	3.37 m	4.62 m	4.62 m
4'	4.54 m	4.49 m	4.32 m	4.48 m	3.09 m	4.47 m	4.49 m
5'	4.66 m	4.64 m	4.53 m	4.64 m	3.21 m	4.63 m	4.65 m
OCH_3			3.77 s				
1"	5.77 d (7.7)	5.83 d (7.5)	5.82 d (7.5)	5.87 d (7.6)	4.67 m	5.79 d (7.6)	5.82 d (7.5)
2"	4.69 m	4.59 m	4.58 m	4.63 m	3.37 m	4.58 m	4.58 dd (9.7, 7.6)
3"	4.21 dd (9.5, 3.5)	4.13 dd (9.5, 3.0)	4.13 dd (9.6, 3.4)	4.13 m	3.24 m	4.18 m	4.12 dd (9.6, 3.3)
4"	4.51 m	4.42 m	4.41 m	4.73 brs	3.57 m	4.71 d (3.1)	4.42 m
5"	3.94 dd (6.2, 6.3)	3.95 dd (6.0, 6.1)	3.95 t (6.1)	4.02 dd (6.0, 6.2)	3.21 m	3.92 dd (5.8, 5.9)	3.95 dd (6.0, 6.1)
6"	4.51 m, 4.43 m	4.44 dd (11.5, 5.1); 4.33 dd (11.0, 5.4)	4.43 m; 4.34 m	4.43 m; 4.32 m	3.48 m; 3.34 m	4.29 m; 4.23 m	4.43 m; 4.34 m
1"'	6.35 s	6.32 s	6.32 s	6.22 s	4.99 s	6.21 s	6.30 s
2"'	4.81 dd (3.6, 1.6)	4.83 dd (3.3, 1.4)	4.82 dd (3.4, 1.4)	4.93 m	3.64 m	4.93 brs	4.83 m
3"'	4.74 dd (9.3, 3.5)	4.69 m	4.66 dd (9.3, 3.4)	4.65 m	3.51 m	4.65 m	4.70 dd (9.3, 3.4)
4"'	4.34 dd (9.4, 9.3)	4.36 (t, 9.3)	4.35 m	4.31 m	3.13 m	4.31 m	4.36 m
5"'	5.07 dd (9.4, 6.2)	5.01 m	4.98 m	4.96 m	3.93 m	4.94 m	5.02 m
6"'	1.80 d (6.2)	1.80 d (6.5)	1.79 d (6.5)	1.75 d (6.3)	1.06 d (6.2)	1.73 d (6.2)	1.80 d (6.2)
1""				5.04 d (6.5)		5.16 d (7.8)	
2""				4.08 m		4.07 dd (8.1, 8.2)	
3""				4.09 m		4.21 m	
4""				4.17 m		4.22 m	
5""				4.27 m; 3.65 dd (10.6, 10.5)		3.91 m	
6""						4.47 m; 4.35 m	

[a]recorded in pyridine-d_5; [b]recorded in DMSO-d_6

Table 2. ^{13}C NMR Spectroscopic Data for Derrisaponins D-J (1-7)

NO.	1[a]	2[a]	3[a]	4[a]	5[b]	6[a]	7[a]
1	39.2	38.9	38.9	39.0	37.7	38.9	38.9
2	26.9	27.1	26.7	27.1	26.3	27.0	27.0
3	90.3	91.6	91.8	91.8	86.5	91.7	91.5
4	40.2	44.3	44.3	44.4	52.8	44.3	44.3
5	56.3	56.4	56.4	56.5	56.5	56.5	56.4
6	19.0	18.9	18.9	19.0	18.8	18.9	18.8
7	33.2	33.4	33.2	33.3	32.4	33.7	33.6
8	40.7	40.4	40.5	40.6	39.7	40.0	40.0
9	48.3	48.1	48.1	48.2	46.1	48.0	47.9
10	37.3	36.8	36.8	36.9	36.6	36.9	36.9
11	24.3	24.4	24.5	24.6	24.0	24.4	24.4
12	123.8	123.5	123.5	123.7	122.7	125.5	126.0
13	144.6	144.3	144.6	144.6	144.0	141.3	140.9
14	42.4	42.4	42.3	42.4	41.8	43.2	43.1
15	26.8	26.5	26.7	26.8	25.9	25.5	25.5
16	26.8	28.0	26.7	26.8	25.8	26.9	26.8
17	36.7	37.2	36.6	36.7	35.8	37.2	36.8
18	44.7	45.1	44.5	44.6	43.7	45.2	45.1
19	42.2	41.9	42.1	42.2	41.0	38.4	37.8
20	41.3	36.2	41.2	41.3	40.2	49.6	53.8
21	35.7	34.3	35.6	35.7	34.5	34.2	36.8
22	78.6	78.8	78.5	78.6	77.4	85.2	86.3
23	28.9	23.4	23.4	23.6	21.7	23.4	23.4
24	17.3	64.0	63.9	64.1	207.1	64.0	64.0
25	16.1	16.2	16.1	16.2	16.3	16.1	16.1
26	17.4	17.2	17.1	17.2	16.9	17.1	17.1

27	27.2	26.4	27.0	27.1	26.5	25.3	25.2
28	21.9	21.3	21.8	21.9	21.3	24.0	23.7
29	30.3	28.6	30.2	30.3	29.4	63.9	173.0
30	179.9	68.5	179.8	179.9	178.5	179.5	176.1
31	170.8	170.8	170.7	170.8	170.2		
32	21.5	21.7	21.5	21.5	21.3		
1'	105.8	105.9	105.9	106.0	103.7	105.9	105.8
2'	79.7	77.1	77.0	77.0	77.9	76.9	77.1
3'	79.4	79.0	78.7	79.1	77.6	78.8	78.9
4'	74.0	74.3	74.0	74.4	72.7	74.2	74.2
5'	77.9	78.2	77.3	78.1	74.1	78.1	78.0
6'	173.2	172.9	170.9	173.1	172.8	172.8	172.8
OCH_3			52.5				
1''	103.2	102.2	102.1	102.0	101.0	101.9	102.2
2''	77.1	78.1	78.1	77.6	74.9	77.7	78.2
3''	76.7	77.1	76.9	84.5	74.9	84.1	77.0
4''	71.0	71.6	71.6	71.6	68.9	71.6	71.6
5''	76.7	76.9	76.9	77.0	75.0	77.0	76.9
6''	62.4	62.0	62.0	61.9	60.2	62.2	62.0
1'''	102.6	102.9	102.9	103.5	100.5	103.4	102.9
2'''	72.9	72.8	72.9	73.0	71.0	72.9	72.8
3'''	73.3	73.2	73.2	73.4	71.0	73.3	73.2
4'''	74.9	74.8	74.7	74.8	72.8	74.7	74.8
5'''	70.0	69.9	69.9	69.9	68.4	69.7	69.8
6'''	19.5	19.4	19.9	19.5	18.5	19.4	19.4
1''''				107.2		106.4	
2''''				75.3		75.5	
3''''				78.7		78.7	
4''''				71.5		72.0	
5''''				67.5		78.7	
6''''						63.1	

[a]recorded in pyridine-d_5; [b]recorded in DMSO-d_6