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TRITERPENOIDAL SAPONINS FROM *DUMASIA TRUNCATA*

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Key Word Index—*Dumasia truncata*; Leguminosae; saponin; triterpene; glucuronic acid.

Abstract—Extraction of the aerial parts of *Dumasia truncata* Sieb *et* Zucc. afforded two new triterpenoidal saponins, together with four known ones. The structures of the new compounds were elucidated by spectral analysis as 3-*O*-α-L-rhamnopyranosyl-(1 → 3)-β-D-glucuronopyranosy-28-*O*-β-D-glucopyransoyl hederagenin and 3-*O*-β-D-xylopyranosyl-(1 → 2)-[α-L-rhamnopyranosyl (1 → 3)]-β-D-glucuronopyranosyl oleanic acid.

INTRODUCTION

There are eight species of *Duamasia* in Africa and Asia [1]. *Dumasia truncata* Sieb *et* Zucc. is a climbing herb with yellow flowers distributed in Japan. Chemical examination of this plant has identified some phytoalexins [2] and a alkaloid [3]. There are few reports on the saponins of *Dumasia*. As a part of our study on leguminous plants, we investigated the saponins of *D. truncata*. We now report the isolation and structural determination of two new saponins along with four known saponins.

RESULTS AND DISCUSSION

A methanolic extract of the aerial parts of *D. truncata* provided compounds **1**–**6** after chromatography. Compounds **3**–**6** were identified as saponin 3 (chikusetsusaponin IVa [4]) (**3**), saponin 1 (**4**), saponin 4 (**5**) and saponin 6 (**6**) by comparison with various data of molluscicidal saponins from *Swartzia simplex* (Leguminosae) [5].

Compound **1** showed a peak due to $[M - H]^-$ at *m/z* 955 in the negative FAB-mass spectrum. Acid hydrolysis of **1** gave hederagenin, glucuronic acid, glucose and rhamnose. In the ^{13}C NMR spectrum of **1**, signals due to the sugar moiety were identical with those of **5**. As the signals ascribable to the aglycone were superimposable on those of the 3, 28-*O*-bisdesmoside of hederagenin [6], the structure of **1** was deduced to be 3-*O*-α-L-rhamnopyranosyl-(1 → 3)-β-D-glucuronopyranosyl-28-*O*-β-D-glucopyranosyl hederagenin.

Compound **2** was identified as prosapogenin **6a** [5] which was derived from alkaline hydrolysis of saponin **6**. This paper is the first report on the isolation of this natural product.

EXPERIMENTAL

General. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in pyridine-d_5. TMS was used as int. standard, FAB-mass spectrum (negative ion mode) was measured with glycerol matrix. CC were performed with silica gel (230–400 mesh, Merck).

Plant material. The aerial parts of *D. truncata* were collected in Kumamoto prefecture.

Extraction and isolation. The dried aerial parts of *D. truncata* (200 g) was percolated with MeOH. The MeOH extract (17 g) was concentrated and partitioned between EtAOc and 40% MeOH. The combination of silica gel chromatography [$CHCl_3$–MeOH–H_2O; 9:1:0.1 → 6:4:1 and *n*-BuOH–HOAc–H_2O; 4:1:5 (upper layer] are 40% MeOH fr. afforded compound **1** (17 mg), **2** (20 mg), **3** (13 mg), **4** (24 mg), **5** (225 mg) and **6** (51 mg).

3-O-α-L-*Rhamnopyranosyl*-(1 → 3)-β-D-*glucuronopyranosyl*-28-O-β-D-*glucopyranosyl hederagenin* (**1**). Amorphous power. $[\alpha]_D$ − 10.4° (MeOH; *c*. 0.37). FAB-MS *m/z*: 955 $[M - H]^-$. ^1H NMR: δ6.29 (1H, *d*, *J* = 7.9 Hz, glc H-1), 6.24 (1H, *s*, rha H-1), 5.41 (1H, *br s*, H-12), 5.06 (1H, *d*, *J* = 7.9 Hz, glc A H-1), 1.70 (3H, *d*, *J* = 6.1 Hz, rha H_3-6), 1.22, 1.10, 0.91, 0.90, 0.89, 0.88 (each 3H, *s*, Me-24, 25, 26, 27, 29, 30). ^{13}C NMR: δ38.6, 26.1, 81.5, 43.4, 47.4, 18.1, 32.8, 39.9, 48.1, 36.8, 24.0, 122.8, 144.1, 42.1, 28.3, 23.2, 47.0, 41.7, 46.1, 30.7, 34.0, 32.5, 64.1, 13.5, 16.1, 17.5, 26.1, 176.4, 33.1, 23.6 (C-1 ~ 30). 105.6, 75.6, 82.1, 72.7, 77.2, 174.0 (glc A C-1-6), 102.5, 71.7, 72.4, 74.1, 69.9, 18.6 (rha C-1 ~ 6), 95.7, 74.1, 79.2, 71.1, 78.8, 62.2 (glc C-1 ~ 6).

Acid hydrolysis of **1**. This was carried out in a sealed tube with 1 M HCl for 1 hr at 100°. After filtration, the residue was identified as hederagenin [6] by comparison

Part XLVIII in a series of studies on the constituents of the leguminous plants.

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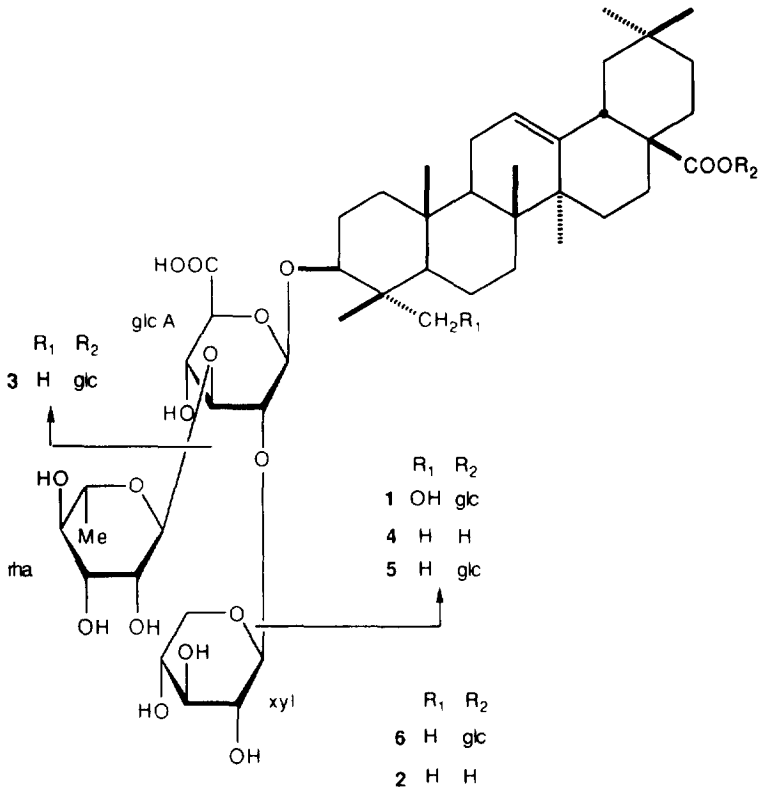

with authentic sample (via TLC). After neutralization, the filtrate was also confirmed to contain glucuronic acid, glucose and rhamnose, again by comparison with authentic sample.

3-O-β-D-*Xylopyranosyl*-(1 → 2)-[α-L-*rhamnopyranosyl*-(1 → 3)]-β-D-*glucuronopyranosyl oleanolic acid* (**2**). Amorphous power. $[\alpha]_D$ −7.1° (70% MeOH; *c* 0.36). FAB-MS *m/z*: 909 $[M-H]^-$, 763 $[M-H-rha]^-$, 631 $[M-H-rha-xyl]^-$. ^{1}H NMR: δ6.15 (1H, *s*, rha H-1), 5.24 (1H, *d*, *J* = 7.3 Hz, xyl H-1), 1.68 (3H, *d*, *J* = 6.2 Hz, rha H_3-6), 1.31, 1.16, 1.03, 1.01, 0.97, 0.96, 0.78 (each 3H, *s*, Me-23, 24, 25, 26, 27, 29, 30). ^{13}C NMR: δ38.5, 26.5, 89.8, 39.6, 55.7, 18.4, 33.1, 39.6, 47.9, 36.9, 23.7, 122.5, 144.7, 42.0, 28.0, 23.7, 46.6, 41.9, 46.4, 30.9, 34.2, 33.1, 27.6, 15.4, 16.3, 17.3, 26.1, 180.1, 33.2, 23.7 (C-1 ~ 30), 104.7, 79.0, 84.6, 72.7, 77.7, 172.4 (glc A C-1 ~ C), 105.2, 75.7, 78.4, 71.2, 67.1 (xyl C-1 ~ 5), 103.5, 71.7, 72.5, 73.9, 70.3, 18.4 (rha C-1 ~ 6).

Chikusetsusaponin IVa (**3**). Amorphous powder. $[\alpha]_D$ +0.2° (70% MeOH; *c* 0.34). FAB-MS *m/z*: 793 $[M-H]^-$. ^{1}H NMR: δ6.34 (1H, *d*, *J* = 7.9 Hz, glc H-1), 5.45 (1H, *s*, H-12), 5.05 (1H, *d*, *J* = 7.3 Hz, glc A H-1), 1.34, 1.31, 1.12, 1.03, 0.94, 0.92, 0.87 (each 3H, *s*, Me-23, 24, 25, 26, 27, 28, 29, 30). ^{13}C NMR: δ38.7, 26.6, 89.0, 39.5, 55.7, 18.5, 33.1, 39.9, 48.0, 36.9, 23.7, 122.7, 144..1, 42.1, 28.0, 23.4, 47.0, 41.7, 46.2, 30.7, 34.0, 32.5, 28.2, 15.5, 16.9, 17.5, 26.1, 176.4, 33.1, 23.6 (C-1 ~ 30). 107.2, 75.5, 78.1, 73.4, 77.8, 172.8 (glc A C-1 ~ 6), 95.7, 74.1, 79.1, 71.1, 78.9, 62.2 (glc C-1 ~ 6).

3-O-α-L-*Rhamnopyranosyl*-(1 → 3)-β-D-*glucuronopyranosyl oleanolic acid* (**4**). [7]. Amorphous powder. $[\alpha]_D$ −6.2° (MeOH; *c* 0.37). FAB-MS *m/z*: 777 $[M-H]^-$, 631 $[M-H-rha]^-$. ^{1}H NMR: δ6.31 (1H, *s*, rha H-1), 5.46 (1H, *s*, H-12), 1.72 (3H, *d*, *J* = 6.1 Hz, rha H_3-6), 1.32, 1.26, 1.01, 0.98, 0.96, 0.94, 0.79 (each 3H, Me-23, 24, 25, 26, 27, 29, 30). ^{13}C NMR: δ38.6, 26.5, 89.2, 39.5, 55.7, 18.5, 33.2, 39.7, 48.0, 36.9, 23.8, 122.8, 144.8, 42.2, 28.3, 23.8, 46.7, 42.0, 46.5, 31.0, 34.3, 33.2, 28.1, 15.4, 16.9, 17.4, 26.2, 180.2, 33.3, 23.8 (C-1 ~ 30), 107.0, 75.9, 82.4, 72.8, 77.7, 173.1 (glc A C-1 ~ 6), 102.9, 71.7, 72.6, 74.2, 69.8, 18.6 (rha C-1 ~ 6).

3-O-α-L-*Rhamnopyranosyl*-(1 → 3)-β-D-*glucuronopyranosyl*-28-O-β-D-*glucopyranosyl oleanolic acid* (**5**) [7]. Amorphous powder. $[\alpha]_D$ −11.4° (MeOH; *c* 0.42). FAB-MS *m/z*: 939 $[M-H]^-$, 793 $[M-H-rha]^-$, 777 $[M-H-glc]^-$. ^{1}H NMR: δ6.31 (1H, *d*, *J* = 7.3 Hz, glc H-1), 6.29 (1H, *s*, rha H-1), 5.41 (1H, *br s*, H-12), 4.91 (1H, *d*, *J* = 7.9 Hz, glc A H-1), 1.72 (3H, *d*, *J* = 6.1 Hz, rha H_3-6), 1.28, 1.25, 1.08, 0.95, 0.92, 0.88, 0.81 (each 3H, *s*, Me-23, 24, 25, 26, 27, 29, 30). ^{13}C NMR: δ38.5, 26.4, 89.1, 39.3, 55.5, 18.4, 32.9, 39.7, 47.8, 36.7, 23.5, 122.7, 143.9, 41.9, 28.1, 23.2, 46.8, 41.6, 46.0, 30.6, 33.8, 32.3, 27.9, 15.3, 16.7, 17.3, 25.9, 176.3, 32.9, 23.5 (C-1 ~ 30), 106.8, 75.6, 82.2, 72.5, 77.6, 172.6 (glc A C-1 ~ 6), 102.7, 71.4, 72.3, 73.9, 69.6, 18.4 (rha C-1 ~ 6), 95.5, 73.9, 79.1, 70.9, 78.6, 62.0 (glc C-1 ~ 6).

3-O-β-D-*Xylopyranosyl*-(1 → 2)-[α-L-*rhamnopyranosyl*-(1 → 3)]-β-D-*glucuronopyranosyl*-28-O-β-D-*glucopyranosyl*

oleanolic acid (**6**). Amorphous powder. $[\alpha]_D$ −15.9° (70% MeOH; *c* 0.36). FAB-MS *m/z*: 1071 $[M-H]^-$, 909 $[M-H-glc]^-$, 777 $[M-H-glc-xyl]^-$. ^1H NMR: δ6.30 (1H, *d*, *J* = 7.9 Hz, glc H-1), 6.10 (1H, *s*, rha H-1), 5.41 (1H, *br s*, H-12), 5.20 (1H, *d*, *J* = 7.3 Hz, xyl H-1), 1.65 (3H, *d*, *J* = 6.1 Hz, rha H_3-6), 1.27, 1.15, 1.07, 1.03, 0.92, 0.89, 0.81 (each 3H, *s*, Me-23, 24, 25, 26, 27, 28, 29, 30). ^{13}C NMR: δ 38.5, 26.4, 89.8, 39.5, 55.7, 18.3, 33.0, 39.8, 47.9, 36.8, 23.6, 122.8, 144.0, 42.0, 28.1, 23.3, 46.9, 41.6, 46.1, 30.6, 33.9, 32.4, 27.6, 15.4, 16.2, 17.3, 26.0, 176.3, 33.0, 23.5 (C-1 ~ 30), 104.5, 79.0, 84.4, 72.6, 77.4, 174.0 (glc A C-1 ~ 6), 105.0, 75.5, 78.2, 71.0, 67.0 (xyl C-1 ~ 5), 103.2, 71.8, 72.4, 73.8, 70.1, 18.3 (rha C-1 ~ 6), 95.6, 74.0, 79.2, 71.0, 78.7, 62.1 (glc C-1 ~ 6).

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