

Triterpenoid Saponins from *Bongardia chrysogonum*

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Two new triterpenoid saponins, 3-*O*-[β -D-glucopyranosyl-(1 \rightarrow 4)- β -D-glucopyranosyl-(1 \rightarrow 4)- α -L-arabinopyranosyl]-hederagenin (**1**) and 3-*O*-[β -D-glucopyranosyl-(1 \rightarrow 4)- β -D-glucopyranosyl-(1 \rightarrow 4)- α -L-arabinopyranosyl]-hederagenin 28-*O*-[β -L-glucopyranosyl-(1 \rightarrow 6)- β -L-glucopyranosyl] ester (**2**), together with five known saponins, were isolated from an ethanolic extract of the tubers of *Bongardia chrysogonum*. The structures of **1** and **2** were determined on the basis of spectroscopic studies.

The tubers of *Bongardia chrysogonum* (L.) Boiss. (Berberidaceae) are well-known in traditional Turkish medicine as a remedy for prostate hypertrophy. Several alkaloids have been isolated from this plant.^{1–3} This paper describes the isolation of two new saponins (**1** and **2**), together with five known saponins, leontoside A, leontoside D, hederacoside A, symphytoxide B, and 3-*O*-[β -D-glucopyranosyl-(1 \rightarrow 4)- α -L-arabinopyranosyl]-hederagenin 28-*O*-[β -D-glucopyranosyl-(1 \rightarrow 6)- β -D-glucopyranosyl] ester, from an ethanolic extract of *B. chrysogonum*.^{4–9}

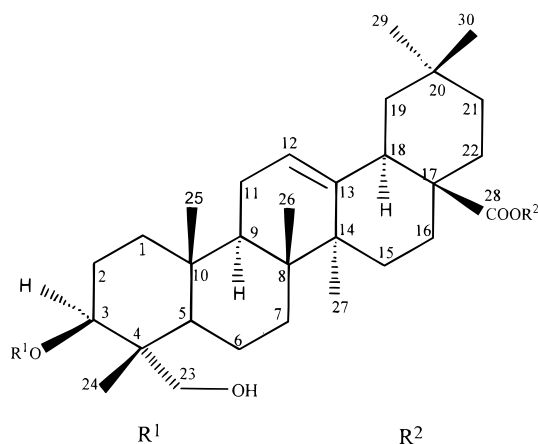
The ethanolic extract of *B. chrysogonum* was dissolved in water and partitioned with *n*-BuOH. The butanolic extract was subjected repeatedly to column chromatography on Si gel and HPLC on a reversed-phase column to afford saponins **1** and **2**, and the five above-mentioned known compounds. Acid hydrolysis of all the saponins

yielded a common aglycon, which was identified as hederagenin by comparison of spectral data in the literature.⁹

Saponin **1** was hydrolyzed with mineral acid to yield D-glucose and L-arabinose as the sugar components. The negative FABMS revealed fragments at m/z 927 [M – H][–], 765 [M – H – 162][–], 603 [M – H – 162 \times 2][–], and 471 [M – H – (162 \times 2) – 132][–]. These data suggested that a hexose was the terminal sugar, while a pentose was attached to the aglycon. The accurate mass of saponin **1** was calculated at m/z 927.4910 corresponding to C₄₇H₇₅O₁₈. The ¹H NMR spectrum of **1** showed six tertiary methyl singlets at δ 0.70, 0.78, 0.91, 0.93, 0.98, and 1.10, and one trisubstituted olefinic proton at δ 5.27. The anomeric proton signals were observed at δ 4.52 (d, $J_{1,2'} = 6.4$ Hz), 4.45 (d, $J_{1'',2''} = 7.8$ Hz), and 4.60 (d, $J_{1''',2'''} = 7.5$ Hz). These coupling constants indicated that the glycosidic linkage of arabinose was α and those of the two glucose units were both β .¹⁰

The ¹³C NMR spectrum of saponin **1** showed the presence of 47 carbon atoms in the molecule (Table 1). Sixteen carbon signals were assigned to the sugar moieties. The anomeric carbon signals at δ 102.9, 104.1, and 104.5 were consistent with the presence of trisaccharide chain. The broad-band decoupled and DEPT spectra displayed six methyl, 14 methylene, 19 methine, and eight quaternary carbon atoms. The olefinic carbon signals at δ 123.5 (CH) and 145.5 (–C–) were consistent with unsaturation at C-12 of an oleanane skeleton. The ¹³C NMR triterpenoids data were compared with the reported data of oleanane triterpenoids, which led to the identification of the aglycon as hederagenin.⁹

The points of attachment of the sugar units in the molecule **1** were determined from the ¹³C NMR chemical shifts. The downfield carbon signal at δ 82.3 (CH) indicated glycosidation at C-3 of the aglycon.¹¹ A comparison of the chemical shift of C-4 of arabinose (C-4, δ 79.5) with that of methyl arabinose (C-4, δ 69.4) allowed the assignment of a 1 \rightarrow 4 linkage between arabinose and the inner glucose unit Glc I.^{12,13} The downfield ¹³C NMR chemical shift of C-4 of Glc I at δ 79.5 and small upfield shift of C-5 of Glc I at δ 77.9 indicated a 1 \rightarrow 4 linkage between Glc I and Glc II.^{11,14} The correspondence of the ¹³C NMR chemical shift of Glc II with corresponding methyl glycosides suggested that it was a terminal sugar.¹² The nature of the interglycosidic linkage was further confirmed by the HMBC spectrum, which showed ² J_{CH} interactions of the protons at δ 3.85 (H-4') and 3.95 (H-4'') with the anomeric carbons at δ 104.5 (C-1'') and 102.9 (C-1'''), in agreement with the



| | R ¹ | R ² |
|----------|---|-----------------------------|
| 1 | Ara (4 \rightarrow 1) Glc (4 \rightarrow 1) Glc | H |
| 2 | Ara (4 \rightarrow 1) Glc (4 \rightarrow 1) Glc | Glc (6 \rightarrow 1) Glc |
| 3 | H | H |

Ara = α -L-arabinopyranosyl; Glc = β -D-glucopyranosyl

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Table 1. ¹H NMR Data for Compounds **1** and **2**

| position | 1 | | 2 | |
|-------------|----------|---------------|----------|-------------------|
| | δC | HMBC (C→H) | δC | HMBC (C→H) |
| C-3 sugars | | | | |
| Ara | | | | |
| 1' | 104.1 | H-3, H-5' | 104.4 | H-3, H-2', H-5' |
| 2' | 73.5 | | 73.8 | H-1' |
| 3' | 71.4 | | 71.5 | H-1', H-5' |
| 4' | 79.5 | H-5', H-1'' | 79.04 | H-1'' |
| 5' | 62.5 | H-4' | 64.85 | H-3', H-4' |
| Glc I | | | | |
| 1'' | 104.5 | H-2'', H-4' | 104.5 | H-2'', H-4' |
| 2'' | 75.1 | | 75.1 | |
| 3'' | 78.2 | | 77.8 | |
| 4'' | 79.5 | H-1''', H-2 | 78.3 | H-1'' |
| 5'' | 77.9 | | 78.2 | |
| 6'' | 62.2 | H-4'' | 63.0 | H-5'' |
| Glc II | | | | |
| 1''' | 102.9 | H-2''', H-4'' | 106.2 | H-1'' |
| 2''' | 75.5 | | 75.7 | |
| 3''' | 78.0 | | 75.7 | |
| 4''' | 71.6 | | 71.5 | H-6''' |
| 5''' | 78.3 | | 78.5 | |
| 6''' | 62.7 | H-5''' | 62.8 | |
| C-28 sugars | | | | |
| Glc III | | | | |
| 1'''' | | | 95.8 | H-2''''', H-5'''' |
| 2'''' | | | 73.6 | |
| 3'''' | | | 78.0 | |
| 4'''' | | | 71.5 | H-5''''', H-6'''' |
| 5'''' | | | 77.9 | H-4''''', H-6'''' |
| 6'''' | | | 69.5 | H-2''''', H-1'''' |
| Glc IV | | | | |
| 1''''' | | | 104.6 | H-2''''', H-6'''' |
| 2''''' | | | 75.4 | |
| 3''''' | | | 78.0 | |
| 4''''' | | | 71.0 | |
| 5''''' | | | 78.0 | |
| 6''''' | | | 62.8 | |

presence of (1→4) linkages between Ara-Glc I and Glc I-Glc II. From these results the structure of compound **1** was elucidated as 3-*O*-[β-D-glucopyranosyl-(1→4)-β-D-glucopyranosyl-(1→4)-α-L-arabinopyranosyl]-hederagenin.

Saponin **2** afforded D-glucose and L-arabinose on mineral acid hydrolysis. The FABMS gave [M - 1]⁻ at *m/z* 1251, corresponding to C₅₉H₉₅O₂₈ (peak matching calcd value, *m/z* 1251.5990). The fragment ions were observed at *m/z* 1089 [M - H - 162]⁻, 927 [M - H - (162 × 2)]⁻, 765 [M - H - 162 × 3]⁻, 603 [M - H - (162 × 4)]⁻, and 471 [M - H - (162 × 4) - 132]⁻ representing the sequential loss of four hexose units and one pentose unit from the molecular ion. The ¹H NMR spectrum of **2** showed anomeric signals due to the sugar moieties resonating at δ 4.48 (d, *J*_{1'',2''} = 7.6 Hz, H-1'''), 4.35 (d, *J*_{1''',2'''} = 7.7 Hz, H-1''''), 4.55 (d, *J*_{1',2'} = 6.3 Hz, H-1'), 4.63 (d, *J*_{1'',2''} = 7.7 Hz, H-1''), and 5.35 (d, *J*_{1''',2'''} = 7.9 Hz, H-1'''). The coupling constants of these protons indicated a trans-diaxial relationship of the C-1 and C-2 protons of the sugar moieties. Therefore, a β configuration was suggested for the D-glucose unit, and an α configuration for the L-arabinose moieties.¹⁰

In the ¹³C NMR spectrum of **2**, signals due to the aglycon moiety were in good agreement with the occurrence of a bisdesmoside saponin. The downfield signals at δ 84.1 (CH) and 178.1 (-C-) suggested glycosidation at C-3 and C-28 of the aglycon. In hederagenin, the signals for C-3 and C-28 are observed at δ 74.3 and 183.1, respectively.⁹ The broadband decoupled ¹³C NMR spectrum (Table 1) of **2** showed 59 carbon signals, including 6 methyl, 16 methylene, 29 methine, and eight quaternary carbon atoms. The anomeric signals due to the sugar moieties resonated at δ 95.8 (C-

1'''), 104.4 (CH-1'), 104.5 (C-1''), 104.6 (C-1'''), and 106.2 (C-1'''). The two protons of a hydroxymethyl group appeared at δ 3.28 (d, *J*_{23a,23b} = 12.3 Hz) and 3.60 (d, *J*_{23b,23a} = 12.3 Hz). On alkaline hydrolysis, saponin **2** yielded a prosapogenin.¹ Comparison of the spectral data of the prosapogenin with saponin **1** indicated that both compounds have identical structures.

The sugar linkages in **2** were determined using the glucosidation rule.^{11,13,14} The ¹³C NMR spectrum of **2** showed significant displacement of signals for C-3 (+10.2 ppm) of the aglycon, for C-4' (+10.7 ppm) of the arabinopyranosyl moiety,⁹ for C-4'' of the inner glucose (Glc I) (+10.1 ppm), and for C-6''' of the glucopyranosyl moiety (Glc IV) (+7.0 ppm), in comparison to the reported values for hederagenin¹⁴ and methyl pyranoside due to glycosidation at these positions. The nature of the interglycosidic linkage was further confirmed by the HMBC spectrum, which showed ²*J*_{CH} interaction of the protons at δ 3.85 (H-4') and 3.95 (H-4'') with the anomeric carbons at δ 104.5 (C-1') and 106.2 (C-1'''), which confirmed the presence of (1→4) linkages between Ara-Glc I and Glc I-Glc II. Another strong ²*J*_{CH} interaction of δ 4.35 (H-1''') with the carbon at δ 69.5 (C-6''') was in agreement with the presence of a (1→6) linkage between Glc III-Glc IV. Analysis of all the available evidence suggested that the structure of saponin **2** is 3-*O*-[β-D-glucopyranosyl-(1→4)-β-D-glucopyranosyl-(1→4)-α-L-arabinopyranosyl]-hederagenin 28-*O*-[β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl] ester.

The known saponins, leontoside A, leontoside D, hederacoside A, symphytoxide B, and 3-*O*-[β-D-glucopyranosyl-(1→4)-α-L-arabinopyranosyl]-hederagenin 28-*O*-[β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl] ester were also isolated and were identified by comparison of their spectral data (¹H NMR, ¹³C NMR, HMQC, FABMS) with those of reported compounds.⁴⁻⁹

Experimental Section

General Experimental Procedures. Optical rotations were measured in MeOH with a JASCO DIP-360 digital polarimeter. UV (MeOH) and IR (KBr) spectra were measured on Shimadzu UV-240 and JASCO A-302 spectrophotometers, respectively. ¹H NMR spectra were recorded in CD₃OD on a Bruker AM-300, AM-400, and AMX-500 instruments operating at 300, 400, and 500 MHz, respectively. ¹³C NMR spectra were recorded in CD₃OD on Bruker AM-400 and AMX-500 spectrometers operating at 100 and 125 MHz, respectively. The negative ion FABMS were recorded on a JEOL JMS HX-110 spectrometer using MeOH as a solvent and glycerol as matrix. Si gel type 60 (70–230 mesh) was used for column chromatography. Precoated Si gel cards (GF₂₅₄, 0.25 mm thickness) were used for TLC. The HPLC system consisted of a Shimadzu model LC-6A pump and SPD 6AV UV and RID 6A IR detectors, while a Waters RP₁₈ reversed-phase column was used for purification. Injections were made using a Shimadzu SIL-6A autoinjector, and fractions were collected on Shimadzu FCV-100B fraction collector.

Plant Material. The tubers of *B. chrysogonum* were collected near Gaziantep, Turkey, by one of us (K.H.C.B.) in September 1995. The plant was identified at the Faculty of Pharmacy, Anadolu University, Eskisehir, Turkey, where a voucher specimen is preserved.

Extraction and Isolation. The tubers (15 kg) were extracted with ethanol. After removal of the solvent by evaporation, the combined extracts were dissolved in water (1 L) and then extracted with *n*-BuOH (4.5 L). The combined *n*-BuOH layers were concentrated to dryness affording a crude *n*-BuOH fraction (16.5 g). The extract was subjected to column chromatography over a Si gel column, which was eluted with a gradient mixture of CHCl₃-MeOH. The combined fractions obtained on elution with CHCl₃-MeOH (9:1) were evaporated

and subjected to vacuum-layer chromatography (VLC) over Si gel, by elution with mixtures of CHCl_3 -MeOH. The fraction collected on elution with CHCl_3 -MeOH (9:1) was evaporated and recrystallized in MeOH to yield saponin **1** (42 mg, $2.8 \times 10^{-6}\%$ yield). Leontoside A was obtained on elution with CHCl_3 -MeOH (99:1) (8 mg, $5.3 \times 10^{-7}\%$ yield). A fraction obtained on elution with CHCl_3 -MeOH (95:5) was evaporated at room temperatures and recrystallized in MeOH to yield hederacoside A (70 mg, $4.6 \times 10^{-6}\%$ yield). A fraction collected in CHCl_3 -MeOH (80:20) was concentrated and subjected to HPLC on a reversed-phase semipreparative (RP₁₈) column. Elution was carried out at a flow rate of 2 mL/min under isocratic conditions with MeOH-H₂O (6:4) as the mobile phase. The fraction obtained at a retention time of 18.7 min on evaporation yielded saponin **2** as a white amorphous powder (20 mg, $1.36 \times 10^{-6}\%$ yield). Other known compounds were identified as 3-*O*-[β -D-glucopyranosyl-(1 \rightarrow 4)- α -L-arabinopyranosyl]-hederagenin 28-*O*-[β -D-glucopyranosyl-(1 \rightarrow 6)- β -D-glucopyranosyl] ester (23.2 mg, $1.5 \times 10^{-6}\%$ yield) (retention time 24.8 min), leontoside D (43 mg, $2.9 \times 10^{-6}\%$ yield) (retention time 20.3 min), and symphitoxide B (35 mg, $2.3 \times 10^{-6}\%$ yield) (retention time 15.3 min).

3-*O*-[β -D-Glucopyranosyl-(1 \rightarrow 4)- β -D-glucopyranosyl-(1 \rightarrow 4)- α -L-arabinopyranosyl]-hederagenin (1): white crystals; $[\alpha]_{\text{D}}^{25} -2.5^\circ$ (*c* 0.16, MeOH); IR (KBr) ν_{max} 3410 (OH), 1755 (COOH), 1600 (C=C) cm^{-1} ; ¹H NMR (CD_3OD , 500 MHz) C-3 sugars, Ara δ 4.52 (1H, d, $J_{1,2} = 6.4$ Hz, H-1'), 3.83 (1H, dd, $J_{2,3} = 9.5$ Hz, $J_{2,1} = 6.4$ Hz, H-2'), 3.25 (1H, d, $J_{3,4} = 6.2$ Hz, H-3'), 3.85 (1H, dd, $J_{4,5} = 2.1$ Hz, $J_{4,3} = 6.2$ Hz, H-4'), 3.52 (1H, dd, $J_{5,\alpha,5\beta} = 12.1$ Hz, $J_{5,\alpha,4} = 2.7$ Hz, H-5 α), 4.15 (1H, dd, $J_{5\beta,4} = 11.1$ Hz, $J_{5\beta,5\alpha} = 4.5$ Hz, H-5 β); Glc I δ 4.60 (1H, dd, $J_{1,2} = 7.5$ Hz, H-1''), 3.20 (1H, dd, $J_{2,3} = 4.8$ Hz, $J_{2,1} = 7.5$ Hz, H-2''), 3.40 (1H, m, H-3''), 3.95 (1H, br s, H-4''), 3.40 (1H, m, H-5''), 3.68 (1H, d, $J_{6,a,6'b} = 9.4$ Hz, H-6''a), 3.85 (1H, d, $J_{6'b,6'a} = 9.4$ Hz, H-6''b), Glc II δ 4.45 (1H, d, $J_{1,2} = 7.8$ Hz, H-1'''), 3.25 (1H, d, $J_{2,3} = 6.2$ Hz, H-2'''), 3.30 (1H, dd, $J_{3,4} = 5.2$ Hz, $J_{3,2} = 6.2$ Hz, H-3'''), 3.32 (1H, t, $J_{4,5} = 4.2$ Hz, H-4'''), 3.40 (1H, m, H-5'''), 3.68 (1H, d, $J_{6,a,6'b} = 9.4$ Hz, H-6'''a), 3.85 (1H, d, $J_{6'b,6'a} = 9.4$ Hz, H-6'''b); ¹³C NMR, see Table 1; FABMS m/z 927 [M - H]⁻, 765 [M - H - 162]⁻, 603 [M - H - (162 \times 2)]⁻, 471 [M - H - (162 \times 2) - 132]⁻; HRFABMS m/z 927. 4910 (calcd for C₄₇H₇₅O₁₈, 927.4952).

3-*O*-[β -D-Glucopyranosyl-(1 \rightarrow 4)- β -D-glucopyranosyl-(1 \rightarrow 4)- α -L-arabinopyranosyl]-hederagenin 28-*O*-[β -D-glucopyranosyl-(1 \rightarrow 6)- β -D-glucopyranosyl] ester (2): white amorphous powder; $[\alpha]_{\text{D}}^{25} -3.8^\circ$ (*c* 0.31, MeOH); IR (KBr) ν_{max} 3420 (OH), 1725 (COOR), 1610 (C=C), 1100-1000 (C-O-C) cm^{-1} ; ¹H NMR (CD_3OD , 500 MHz) C-3 sugars, Ara δ 4.55 (1H, d, $J_{1,2} = 6.3$ Hz, H-1'), 3.82 (1H, dd, $J_{2,3} = 8.7$ Hz, $J_{2,1} = 6.3$ Hz, H-2'), 3.23 (1H, t, $J_{3,2} = 8.7$ Hz, H-3'), 3.85 (1H, dd, $J_{4,5} = 1.9$ Hz, $J_{4,3} = 3.1$ Hz, H-4'), 3.55 (1H, m, H-5 α), 4.12 (1H, dd, $J_{5,\alpha,5\beta} = 12.3$ Hz, $J_{5,\alpha,4} = 2.9$ Hz, H-5 β); Glc I δ 4.63 (1H, d, $J_{1,2} = 7.7$ Hz, H-1''), 3.20 (1H, d, $J_{2,3} = 9.1$ Hz, $J_{2,1} = 7.7$ Hz, H-2''), 3.40 (1H, d, $J_{3,4} = 5.1$ Hz, H-3''), 3.95 (1H, br s, H-4''), 3.30 (1H, m, H-5''), 3.64 (1H, dd, $J_{6,a,6'b} = 11.8$ Hz, $J_{6'a,5} = 3.7$ Hz, H-6''a), 3.80 (1H, dd, $J_{6'b,6'a} = 11.8$ Hz, $J_{6'b,5} = 2.3$ Hz, H-6''b); Glc II δ 4.48 (1H, d, $J_{1,2} = 7.6$ Hz, H-1'''), 3.25 (1H, dd, $J_{2,3} = 8.5$ Hz, $J_{2,1} = 7.6$ Hz, H-2'''), 3.20 (1H, d, $J_{3,4} = 8.5$ Hz, H-3'''), 3.30 (1H, m, H-4'''), 3.32 (1H, m, H-5'''),

3.60 (1H, dd, $J_{6'a,6'b} = 12.5$ Hz, $J_{6'a,5} = 4.3$ Hz, H-6'''a), 3.83 (1H, dd, $J_{6'b,6'a} = 12.5$ Hz, $J_{6'b,5} = 1.8$ Hz, H-6'''b); C-28 sugars Glc III δ 5.35 (1H, d, $J_{1,2} = 7.9$ Hz, H-1''''), 3.30 (1H, m, H-2''''), 3.38 (1H, t, $J_{3,2} = 5.3$ Hz, H-3''''), 3.40 (1H, d, $J_{4,5} = 5.1$ Hz, H-4''''), 3.50 (1H, m, H-5''''), 3.78 (1H, dd, $J_{6'a,6'b} = 11.3$ Hz, $J_{6'a,5} = 4.7$ Hz, H-6a''''), 4.10 (1H, dd, $J_{6'b,6'a} = 2.9$ Hz, $J_{6'b,5} = 11.3$ Hz, H-6b''''), Glc IV δ 4.35 (1H, d, $J_{1,2} = 7.7$ Hz, H-1'''''), 3.20 (1H, dd, $J_{2,3} = 9.1$ Hz, $J_{2,1} = 7.7$ Hz, H-2'''''), 3.23 (1H, t, $J_{3,4} = 8.7$ Hz, H-3'''''), 3.30 (1H, m, H-4'''''), 3.24 (1H, m, H-5'''''), 3.62 (1H, dd, $J_{6'a,6'b} = 11.8$ Hz, $J_{6'a,5} = 4.3$ Hz, H-6a'''''), 3.83 (1H, dd, $J_{6'b,6'a} = 11.8$ Hz, $J_{6'b,5} = 4.8$ Hz, H-6b'''''); ¹³C NMR, see Table 1; FABMS m/z 1251 [M - H]⁻, 1089 [M - H - 162]⁻, 927 [M - H - (162 \times 2)]⁻, 765 [M - H - (162 \times 3)]⁻, 603 [M - H - (162 \times 4)]⁻, 471 [M - H - (162 \times 4) - 132]⁻; HRFABMS m/z 1251.5990 (calcd for C₅₉H₉₅O₂₈, 1251.6009).

Acid Hydrolysis of 1 and 2. Each saponin (10 mg) was heated with 2M HCl-MeOH (10 mL). The reaction mixture was diluted with H₂O and extracted with CHCl_3 . The sapogenins were detected in the CHCl_3 layer by TLC. The water layer was neutralized with Na₂CO₃, concentrated, and subjected to co-TLC analysis with authentic samples. The sample of sugars isolated was identified by co-TLC with authentic samples of D-glucose, L-arabinose, D-xylose, D-galactose, and L-rhamnose. For TLC analysis H₂O-MeOH-AcOH-EtOAc (15:15:20:65) was used. Detection was carried out with an aniline phthalate spray.

Alkaline Hydrolysis of 2. Saponin **2** (10 mg) was also subjected to alkaline hydrolysis by adding 2% methanolic KOH (4 mL), and the resulting solution was refluxed for 2 h. Methanol was evaporated, and the reaction mixture was diluted with H₂O (5 mL), neutralized with 10% HCl, and extracted with *n*-BuOH. The *n*-BuOH layer was washed with H₂O and concentrated to yield a prosapogenin (**1**).

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