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CHEMICAL CONSTITUENTS OF *Saxifraga umbellulata*

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Saxifraga umbellulata belongs to the genus *Saxifraga*, which has about 203 species in China [1]. In China *Saxifraga umbellulata* grows mainly in high cold areas such as the southwest of Qinghai, Gansu Province [2]. It is used as a herb medicine to treat hepatitis, cholecystitis, infuenza, fever, skin ulcer, and so on. As part of the continuous research on *S. umbellulata* [3, 4], eight compounds were isolated from *Saxifraga umbellulata* for the first time.

The powder of *S. umbellulata* [3] was extracted by ethanol refluxing repeatedly (12 L × 2, 2 h the first time, 1 h the second time). The EtOH extract was concentrated under reduced pressure to give a residue (320 g), and the residue was sequentially partitioned with petroleum ether (PE) (90–100°C) (0.5 L × 4), EtOAc (0.5 L × 4), and *n*-BuOH (0.5 L × 4).

The EtOAc fraction (45 g) was chromatographed on a silica gel column (4.0 × 120 cm) eluted with PE–acetone (50:1–0:1) gradually to yield 10 fractions (Frs.1–10) according to TLC analysis. Fraction 8 (0.5 g) was retreated on a silica gel (300–400 mesh, 15 g) column eluted with $CHCl_3$–MeOH (20:1) and then retreated on an LH-20 (20–150 μm, 25 g) column eluted with $CHCl_3$–MeOH (1:1) repeatedly to obtain compounds **1** (10 mg) and **2** (12 mg).

The PE fraction (70 g) was chromatographed on a silica gel column (5.0 × 150 cm) eluted with PE–EtOAc (100:1–0:1) gradually to yield eight fractions (Frs. 1–8) according to TLC analysis. Fraction 1 (1.5 g) was retreated on a silica gel (300–400 mesh, 50 g) column eluted with PE–EtOAc (60:1) to obtain **3** (8 mg). Fraction 3 (2.0 g) was retreated on a silica gel (300–400 mesh, 60 g) column eluted with PE–EtOAc (40:1) to obtain **4** (8 mg). Fraction 4 (4.5 g) was retreated on a silica gel (300–400 mesh, 120 g) column eluted with PE–EtOAc (30:1) to obtain **5** (15 mg).

The *n*-BuOH fraction (75 g) was chromatographed on a silica gel column (5.0 × 150 cm) eluted with $CHCl_3$–MeOH (15:1–0:1) gradually to yield 10 fractions (Frs. 1–10) according to TLC analysis. Fraction 3 (1.0 g) was retreated on an LH-20 (20–150 μm, 25 g) column eluted with $CHCl_3$–MeOH (1:1) to obtain **6** (6 mg). Fraction 5 (5.0 g) was retreated on an LH-20 (20–150 μm, 25 g) column eluted with $CHCl_3$–MeOH (1:1) and then on an LH-20 (20–150 μm, 25 g) column eluted with H_2O–MeOH (1:1) to obtain **7** (5 mg). Fraction 10 (2.0 g) was retreated on an LH-20 (20–150 μm, 25 g) column eluted with $CHCl_3$–MeOH (1:1) and then on an LH-20 (20–150 μm, 25 g) column eluted with H_2O–MeOH (1:1) to obtain **8** (5 mg).

Daucosterol (1), $C_{35}H_{60}O_6$, white powder, mp 294–296°C. MS *m/z*: 576 $[M]^+$, 558 ($M^+ - 18$). IR (KBr, ν_{max}, cm^{-1}): 3410 (OH), 2960, 2940, 2868, 1630, 1463, 1370 [5].

Digalactosyl-diacylglycerol (2), yellow oil. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 5.11 (1H, m, H-2), 4.90 (1H, s, OH), 4.73 (2H, s, OH), 4.68 (1H, d, J = 4.0, H-1‴), 4.53 (1H, s, OH), 4.50 (1H, s, OH), 4.38 (2H, s, OH), 4.31 and 4.15 (each 1H, m, H-1), 4.13 (1H, d, J = 7.2, H-1‴), 3.82 and 3.62 (each 1H, m, H-3), 2.28 (4H, t, J = 6.8, H-2′, 2″), 1.27 (4H, m, H-4′, 4″), 1.28 (4H, m, H-ω-2′, 2″), 1.24 (4H, m, H-3′, 3″), 0.86 (4H, t, J = 7.2, H-ω′,ω″). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 173.3 (C-1′, 1″), 104.3 (C-1‴), 100.2 (C-1⁗), 73.8 (C-2‴), 73.7 (C-5‴), 71.9 (C-4‴), 70.9 (C-4⁗), 70.5 (C-2), 70.2 (C-2⁗), 69.5 (C-3‴), 69.0 (C-5⁗), 68.6 (C-3⁗), 67.2 (C-3), 67.10 (C-6‴), 63.0 (C-1), 61.2 (C-6⁗), 34.1 (C-2′, 2″), 31.24 (C-3′, 3″), 29.7 (C-5′–C-ω-2′, C-5″–C-ω-2″), 29.1 (C-4′, 4″), 22.7 (C-ω-1′, 1″), 14.61 (C-ω′, ω″) [6].

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α-Palmitoyl-β-linoleoyl-α'-linoleoyl-glycerol (3), colorless oil, $C_{55}H_{98}O_6$. ESI-MS *m/z* 855 $[M + H]^+$. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm, J/Hz): 4.31 (2H, dd, J = 11.8, 4.4, -OC$\underline{H}_2$-CH(O)-CH_2-O), 4.16 (2H, dd, J = 11.8, 5.8, OCH_2-CH(O)-C$\underline{H}_2$-O), 2.33 (2H, t, J = 7.2, H-2), 2.31 (4H, t, J = 7.2, 2 × CH_2), 1.60–1.63 (6H, m, 3 × CH_2), 1.28–1.47 (52H, m, 26 × CH_2), 5.31–5.40 (8H, m, -CH=CH-), 2.79 (4H, t, J = 6.4, H-11), 2.07 (8H, q, J = 6.8, H-8, 14), 0.86–0.99 (9H, m, 3 × CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 62.1 (OCH_2-CH(O)-$\underline{C}H_2$-O), 68.8 (1H, m, OCH_2-$\underline{C}$H(O)-CH_2-O-COO), 173.2 (OCH_2-CH(O)-CH_2-O-$\underline{C}$OO), 33.9, 34.1 (CH_2-2), 24.8, 22.6, 29.0, 29.2, 29.5, 29.6, 31.4 (CH_2 groups), 127.8, 128.0, 129.9, 130.1 (-CH=CH-), 25.5 (CH_2-11), 27.1 (CH_2-8), 14.0 (CH_3 groups) [7].

Pentadecanoic acid heptadecyl ester (4), white powder, $C_{32}H_{64}O_3$, mp 38–39°C (PE). EI-MS m/z: 481 $[M + H]^+$, 285, 257, 239, 224, 196. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm, J/Hz): 4.05 (2H, t), 2.29 (2H, t), 1.27 (50H, br), 1.61 (4H, m), 0.88 (6H, t). ^{13}C NMR (400 MHz, $CDCl_3$, δ, ppm): 174.00 (C=O), 64.39 (-CH_2-O), 34.43 (CH_2), 31.92 (CH_2), 29.69 (CH_2), 29.36 (CH_2), 29.26 (CH_2), 28.67 (CH_2), 25.94 (CH_2), 25.04 (CH_2), 22.68 (CH_2), 14.10 (CH_3) [8].

Phytyl-1-hexanoate (5), white powder, $C_{26}H_{50}O_2$. EI-MS *m/z*: 396 $[M+2]^+$, 379, 364, 351, 278, 239, 71, 57. IR (KBr, ν_{max}, cm^{-1}): 2944, 1721, 1660, 1459, 1379, 1168, 1113, 1040. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.84 (3H, t, J = 7.6, H-5′), 0.85 (6H, d, J = 6.4, H-18, 19), 0.86 (6H, d, J = 6.8, H-16, 17), 1.68 (3H, s, H-20), 1.99 (2H, t, J = 6.5, H-4), 2.28 (2H, t, J = 7.2, H-1′), 4.58 (2H, d, J = 7.6, H-1), 5.34 (1H, ddd, J = 1.6, 7.2, 7.2, H-2) [9].

5-*O*-Butylhirusutanonol (6), yellow amorphous powder. ESI-MS *m/z* 400.9 $[M - H]^-$. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 0.88 (3H, t, J = 6.8, H-4‴), 1.32 (2H, m, H-3‴), 1.42 (2H, m, H-2‴), 1.61 (2H, m, H-6), 2.43 (1H, m, H-4), 2.43 (2H, m, H-7), 2.61 (1H, dd, J = 7.6, 15.6, H-4), 2.67 (4H, m, H-1, 2), 3.65 (1H, m, H-5), 3.65 (2H, m, H-1‴), 6.39 (1H, dd, J = 2.0, 8.0, H-6″), 6.41 (1H, dd, J = 2.0, 8.0, H-6′), 6.55 (1H, d, J = 2.0, H-2′), 6.57 (1H, d, J = 2.0, H-2″), 6.60 (1H, d, J = 8.0, H-5″), 6.62 (1H, d, J = 8.0, H-5′). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 30.1 (C-1), 46.2 (C-2), 210.9 (C-3), 48.7 (C-4), 76.6 (C-5), 37.4 (C-6), 31.7 (C-7), 134.9 (C-1′), 116.2 (C-2′), 144.4 (C-3′), 146.0 (C-4′), 116.3 (C-5′), 120.6 (C-6′), 134.0 (C-1″), 116.5 (C-2″), 144.2 (C-3″), 146.1 (C-4″), 116.3 (C-5″), 120.5 (C-6″), 70.0 (C-1‴), 33.2 (C-2‴), 19.9 (C-3‴), 14.2 (C-4‴) [10].

(5*S*)-1,7-Bis(3,4-dihydroxyphenyl)-5-hydroxyheptan-3-one-5-*O*-β-D-glucopyranoside (7), brown oil, $C_{25}H_{32}O_{11}$. FAB-MS *m/z* 507 $[M - H]^-$. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.67–1.64 (2H, m, H-6), 2.40, 2.62 (each 1H, m, H-4), 2.46 (1H, m, H-7), 2.51, 2.57 (each 1H, m, H-2), 2.52 (2H, m, H-1), 4.07 (1H, m, H-5), 4.32 (1H, br.d, J = 7.2, H-1‴), 6.30 (1H, dd, J = 2.0, 8.0, H-6′), 6.46 (1H, dd, J = 2.0, 8.0, H-6″), 6.52 (1H, d, J = 2.0, H-2′), 6.60 (1H, d, J = 2.0, H-2″), 6.60 (1H, d, J = 8.0, H-5′), 6.64 (1H, d, J = 8.0, H-5″) [11].

3,5-Dicaffeoylquinic acid (8), yellow powder, $C_{25}H_{24}O_{12}$, mp 139–141°C. ESI-MS *m/z*: 515 $[M - H]^-$, 353 $[M - 162]^-$. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 1.94 (1H, dd, J = 9.6, 13.2, H-6β), 1.96 (1H, dd, J = 3.2, 14.4, H-2α), 2.13 (1H, dd, J = 4.0, 13.2, H-6α), 2.15 (1H, dd, J = 3.2, 14.4, H-2β), 4.15 (1H, dd, J = 3.6, 9.6, H-4), 5.20 (1H, ddd, J = 3.6, 9.6, 10.2, H-5), 5.35 (1H, ddd, J = 3.2, 3.6, 4.0, H-3), 6.17 (1H, d, J = 16.0, H-8″), 6.25 (1H, d, J = 16.0, H-8′), 6.77 (1H, d, J = 8.0, H-5″), 6.79 (1H, d, J = 8.0, H-5′), 6.99 (1H, dd, J = 2.0, 8.0, H-6″), 7.00 (1H, dd, J = 2.0, 8.0, H-6′), 7.05 (1H, d, J = 2.0, H-2′), 7.06 (1H, d, J = 2.0, H-2″), 7.49 (1H, d, J = 16.0, H-7′), 7.50 (1H, d, J = 16.0, H-7″). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 74.6 (C-1), 36.3 (C-2), 72.6 (C-3), 70.6 (C-4), 72.1 (C-5), 37.7 (C-6), 177.2 (C-7), 127.6 (C-1′), 115.1 (C-2′), 146.7 (C-3′), 149.5 (C-4′), 116.3 (C-5′), 123.0 (C-6′), 147.3 (C-7′), 115.3 (C-8′), 168.4 (C-9′), 127.8 (C-1″), 115.2 (C-2″), 146.7 (C-3″), 149.6 (C-4″), 116.5 (C-5″), 123.0 (C-6″), 147.0 (C-7″), 115.6 (C-8″), 168.9 (C-9″) [12].

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