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CHEMICAL CONSTITUENTS FROM *Saussurea oligantha*

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More than 10 *Saussurea* species have long been used as herbal medicines in Chinese folk medicine, since they are efficacious in relieving internal heat or fever, harmonizing menstruation, alleviating pain, and increasing energy [1]. In our effort to find the biological activity of natural products as the lead molecule of drugs from Chinese medicinal plants, 11 triterpenoid compounds and three steroids were isolated from an alcoholic extract of the whole plant of *S. oligantha* Franch. We report herein the isolation and structural elucidation of all these compounds.

From an alcoholic extract of the whole plant of *S. oligantha*, lup-3β,20-ene-diol (**1**) [2], 12-en-3β-hydroxy-urs-11-one (**2**) [3], 11-keto-urs-12-en-3β-yl palmitate (**3**) [4], 12-en-3β-hydroxy-olean-11-one (**4**) [3], 11-keto-olean-12-en-3β-yl-palmitate (**5**) [3], 9(11),12-dien-urs-3β-ol (**6**) [5], 9(11),12-dien-urs-3β-yl palmitate (**7**) [6], 1β-hydroxy-ursa-9(11),12-dien-3β-yl palmitate (**8**) [7], 1β-hydroxy-olean-9(11),12-dien-3β-yl palmitate (**9**) [7], urs-3β,11β-ene-diol (**10**) [8], taraxerol (**11**) [9], ergosta-6,22-dien-3β,5α,8α-triol (**12**) [10], sitosterol (**13**), and daucosterol (**14**) were isolated and purified by repeated chromatography over silica gel column. The structure of every compound was postulated on the basis of spectroscopic analysis.

12-en-3β-Hydroxy-urs-11-one (2), colorless needle crystal, mp 206–208°C. ^{1}H NMR (400 MHz, TMS, $CDCl_3$, δ, ppm, J/Hz): 5.54 (1H, s, H-12), 3.20 (1H, dd, J = 6.4, 11.2, H-3). ^{13}C NMR (100 MHz, TMS, $CDCl_3$, δ): 40.84 (C-1), 27.2 (C-2), 78.7 (C-3), 39.1 (C-4), 54.9 (C-5), 17.4 (C-6), 32.7 (C-7), 39.2 (C-8), 61.5 (C-9), 39.1 (C-10), 199.9 (C-11), 130.4 (C-12), 164.9 (C-13), 45.4 (C-14), 26.4 (C-15), 27.2 (C-16), 33.8 (C-17), 58.9 (C-18), 39.1 (C-19), 39.2 (C-20), 30.8 (C-21), 36.4 (C-22), 28.0 (C-23), 16.5 (C-24), 18.5 (C-25), 16.4 (C-26), 20.5 (C-27), 28.7 (C-28), 17.4 (C-29), 21.1 (C-30).

12-en-3β-Hydroxy-olean-11-one (4), colorless needle, mp 229–231°C. ^{1}H NMR (400 MHz, TMS, $CDCl_3$, δ, ppm, J/Hz): 5.59 (1H, s, H-12), 3.22 (1H, dd, J = 6.4, 11.2, H-3). ^{13}C NMR (100 MHz, TMS, $CDCl_3$, δ): 47.5 (C-1), 27.4 (C-2), 78.7 (C-3), 39.2 (C-4), 54.8 (C-5), 17.4 (C-6), 32.8 (C-7), 45.1 (C-8), 61.7 (C-9), 36.9 (C-10), 200.3 (C-11), 128.0 (C-12), 170.7 (C-13), 43.3 (C-14), 26.3 (C-15), 27.2 (C-16), 32.3 (C-17), 47.5 (C-18), 45.0 (C-19), 30.8 (C-20), 34.4 (C-21), 36.4 (C-22), 28.0 (C-23), 15.5 (C-24), 16.3 (C-25), 18.6 (C-26), 23.4 (C-27), 28.7 (C-28), 32.8 (C-29), 23.4 (C-30).

1β-Hydroxy-ursa-9(11),12-dien-3β-yl palmitate (8): colorless gum. IR (KBr, ν_{max}, cm^{-1}): 3499 (OH). UV (MeOH, λ, nm) (log ε): 199.4 (3.57). ^{1}H NMR (400 MHz, TMS, $CDCl_3$, δ, ppm, J/Hz): 3.94 (1H, dd, J = 11.6, 4.4, H-1), 1.81 (1H, m, H-2α), 1.94 (1H, m, H-2β), 4.55 (1H, dd, J = 12.0, 4.4, H-3), 6.20 (1H, d, J = 5.6, H-11), 5.47 (1H, d, J = 6.0, H-12), 0.87 (3H, s, H-23), 0.88 (3H, s, H-24), 0.90 (3H, s, H-25), 0.80 (3H, s, H-26), 0.92 (3H, s, H-27), 0.93 (3H, s, H-23), 0.85 (3H, d, J = 6.4, H-29), 0.82 (3H, d, J = 6.4, H-30), 2.31 (2H, t, J = 7.2, H-2′), 1.75 (2H, m, H-3′), 1.28 (2H, br.s, H-4′-15′), 0.89 (3H, t, J = 7.2, H-16′). ^{13}C NMR (100 MHz, TMS, $CDCl_3$, δ): 75.6 (C-1), 34.7 (C-2), 76.8 (C-3), 38.0 (C-4), 48.8 (C-5), 18.4 (C-6), 31.0 (C-7), 43.3 (C-8), 152.1 (C-9), 44.1 (C-10), 117.4 (C-11), 123.5 (C-12), 141.7 (C-13), 40.9 (C-14), 26.2 (C-15), 28.3 (C-16), 33.7 (C-17), 57.3 (C-18), 39.4 (C-19), 39.1 (C-20), 31.2 (C-21), 41.3 (C-22), 28.7 (C-23), 16.2 (C-24), 18.6 (C-25), 17.8 (C-26), 22.2 (C-27), 27.7 (C-28), 17.4 (C-29), 21.5 (C-30), 173.5 (C-1′), 34.5 (C-2′), 25.1 (C-3′), 29.2–29.8 (C-4′-13′), 31.9 (C-14′), 22.7 (C-15′), 14.1 (C-16′).

1β-Hydroxy-oleana-9(11),12-dien-3β-yl palmitate (9): colorless gum, $[\alpha]_D^{20}$ +62.0° (*c* 0.33, $CHCl_3$). IR (KBr, ν_{max}, cm^{-1}): 3526, 3413 (OH). UV (MeOH, λ, nm) (log ε): 199.4 (3.76). ^{1}H NMR (400 MHz, TMS, $CDCl_3$, δ, ppm, J/Hz): 3.94 (1H, dd, J = 11.6, 4.4, H-1), 4.55 (1H, dd, J = 12.0, 4.4, H-3), 6.52 (1H, d, J = 5.6, H-11), 5.52 (1H, d, J = 6.0, H-12), 0.85 (3H, s, H-23), 0.86 (3H, s, H-24), 0.93 (3H, s, H-25), 0.80 (3H, s, H-26), 0.99 (3H, s, H-27), 0.93 (3H, s, H-23), 0.82 (3H, s, H-29), 0.98 (3H, s, H-30), 2.31 (2H, t, J = 7.2, H-2′), 1.75 (2H, m, H-3′), 1.28 (2H, br.s, H-4′-15′), 0.89 (3H, t, J = 7.2, H-16′).

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^{13}C NMR (100 MHz, TMS, $CDCl_3$, δ): 75.6 (C-1), 34.7 (C-2), 76.7 (C-3), 38.0 (C-4), 48.9 (C-5), 18.4 (C-6), 31.2 (C-7), 42.9 (C-8), 151.9 (C-9), 44.8 (C-10), 118.3 (C-11), 121.1 (C-12), 147.4 (C-13), 40.8 (C-14), 27.2 (C-15), 25.8 (C-16), 32.2 (C-17), 45.6 (C-18), 46.8 (C-19), 31.1 (C-20), 34.6 (C-21), 37.0 (C-22), 28.7 (C-23), 16.2 (C-24), 18.6 (C-25), 20.3 (C-26), 33.7 (C-27), 27.8 (C-28), 33.2 (C-29), 21.8 (C-30), 173.5 (C-1′), 34.6 (C-2′), 25.2 (C-3′), 29.2–29.8 (C-4′-13′), 31.9 (C-14′), 22.7 (C-15′), 14.1 (C-16′).

Air-dried and ground whole plants of *S. oligantha* Franch (5.0 kg) were extracted seven times with 85% EtOH at room temperature, each time lasting three days. The combined extracts were evaporated to dryness under reduced pressure. The residue (130 g) was then suspended in H_2O (1.0 L) and extracted with petroleum ether (1.2 L × 6), ethyl acetate (1.2 L × 3), and *n*-butanol (1.2 L × 5). The petroleum ether extract (60 g) was subjected to column chromatography on silica gel (200–300 mesh, 600 g) using petroleum ether with increasing volume of acetone (v/v, from 25:1 to 1: 1) as eluent to give six fractions (Fr. 1–6). Fraction 1 (v/v, from 30: 1 to 25: 1) was chromatographed on silica gel column using petroleum ether–chloroform (v/v, 10:1) as eluent to yield pure compound **1** (9 mg), compound **2** (12 mg), and compound **13** (25 mg). Fraction 2 (v/v, from 25:1 to 20:1) was eluted with petroleum ether–ethyl acetate (v:v 18:1) to give Fr. 2a, 2b, and 2c. Fraction 2a was repeatedly purified by CC over silica gel with petroleum ether–acetone (v/v, 20:1) as eluent to give pure compound **3** (12 mg) and compound **12** (28 mg). Fraction 2b was chromatographed on silica gel column with petroleum ether–ethyl acetate (v/v, 12:1) as eluent to give compound **4** (8 mg). Fraction 2c was chromatographed on silica gel column with petroleum ether–ethyl acetate (v/v, 10:1) as eluent to give compound **5** (12 mg). Fraction 3 (v/v, from 20:1 to 15:1) was eluted with petroleum ether–ethyl acetate (v/v 15:1) to give compound **6** (17 mg) and compound **7** (15 mg). Fraction 4 (v/v, from 15:1 to 12:1) gave compound **8** (9 mg) and compound **9** (10 mg) after CC on silica gel eluted with petroleum ether–acetone (v/v, 10:1). Fraction 5 (v/v, from 12:1 to 10:1) was chromatographed using petroleum ether–acetone (v/v, 10:1) as eluent to afford compound **10** (10 mg). Fraction 6 (v/v, from 10:1 to 5:1) was chromatographed using petroleum ether–acetone (v/v, 8:1) as eluent to afford compound **11** (10 mg) and compound **14** (15 mg).

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REFERENCES

1. Jiangsu College of New Medicine, *A Dictionary of the Traditional Chinese Medicines*, Shanghai Science and Technology Press, Shanghai (1977), pp. 23–24.
2. M. J. R. Segura, M. M. Meyer, and S. P. T. Matsuda, *Org. Lett.*, **2**, 2257 (2000).
3. W. M. Bandaranayake, *Phytochemistry*, **19**, 255 (1980).
4. M. A. Ouyang, H. Q. Wang, and J. H. Su, *Nat. Prod. Res. Dev.*, **9**, 19 (1997).
5. S. B. Mahato and A. P. Kundu, *Phytochemistry*, **33** (6), 1517 (1994).
6. S. Sakuma and J. Shoji, *Chem. Pharm. Bull.,* **30**, 810 (1982).
7. X. H. Li, J. T. Feng, and Y. P. Shi, *Can. J. Chem.,* **86**, 281 (2008).
8. A. M. Yang, X. Liu, R. H. Lu, and Y. P. Shi, *Pharmazie*, **61**, 70 (2006).
9. X. Du, Y. P. Shi, and Z. G. Li, *Chin. Trad. Herb. Drugs*, **35**, 245 (2004).
10. N. Chaurasia and M.Wichtl, *J. Nat. Prod.* **50**, 881 (1987).