

PREPARATIVE SEPARATION OF C₁₉-DITERPENOID ALKALOIDS FROM *Aconitum carmichaelii* DEBX BY pH-ZONE-REFINING COUNTER-CURRENT CHROMATOGRAPHY

Dahui Liu

Institute of Medicinal Plants, Yunnan Academy of Agricultural Sciences, Kunming 650231, China

Xikai Shu, Xiao Wang*, Lei Fang and Luqi Huang

Shandong Analysis and Test Center, Shandong Academy of Sciences, 19 Keyuan Street, Jinan, Shandong 250014, China

Xingjun Xi and Zhenjia Zheng

China National Institute of Standardization, 4 Zhichun Road, Beijing 100088, China

Compound I: ESI-MS: m/z 632.7 [M+H]⁺. ¹H-NMR (600 MHz, CD₃OD): δ 1.38(3H, s, 8-OAc), 1.47(1H, dt, $J=12$, 6, H-2b), 1.96(1H, brd, $J=12$, H-2a), 2.06(1H, dd, $J=19$, 6.6, H-3), 2.38(1H, d, $J=13$, H-12b), 2.52(1H, d, $J=18$, H-12a), 2.94(3H, s, NCH₃), 2.96(1H, d, $J=6$, H-9), 2.99(1H, d, $J=12$, H-5), 3.17(1H, s, H-20a), 3.74, 3.38, 3.31, 3.25 (each 3H, s, 4 × OCH₃), 3.52(1H, d, $J=8.4$, H-16), 3.56(1H, brs, H-17), 4.21 (1H, d, $J=6.6$ Hz, H-6), 4.52 (1H, d, $J=5.4$ Hz, H-15a), 4.97 (1H, d, $J=4.8$ Hz, H-14), 7.40–8.03 (5H, m, H-Ar). ¹³C-NMR (125 MHz, CD₃OD): δ 83.3(C-1), 35.7(C-2), 71.1(C-3), 43.4(C-4), 46.5(C-5), 82.5(C-6), 44.2(C-7), 91.6(C-8), 43.4(C-9), 40.6(C-10), 49.9(C-11), 34.3(C-12), 74.2(C-13), 79.2(C-14), 79.3(C-15), 90.2(C-16), 62.4(C-17), 76.5(C-18), 49.6(C-19), 42.7(N-Me), 56.6(C1-OMe), 58.3(C6-OMe), 61.4(C16-OMe), 59.5(C18-OMe), 172.6, 21.6(OAc), 166.2, 129.5, 129.4, 128.4, 133.1(OBz).

Compound II: ESI-MS: m/z 616.7 [M+H]⁺. ¹H-NMR (600 MHz, CD₃OD): δ 1.41(3H, s, 8-OAc), 1.49(1H, dt, $J=12$, 6, H-2b), 1.86(1H, dt, $J=12$, 6, H-3b), 1.99(1H, brd, $J=12$, H-2a), 2.04(1H, dd, $J=19$, 6.6, H-3a), 2.35(1H, d, $J=13$, H-12b), 2.53(1H, d, $J=18$, H-12a), 2.93(3H, s, NCH₃), 2.94(1H, d, $J=6$, H-9), 2.99(1H, d, $J=12$, H-5), 3.19(1H, s, H-20a), 3.74, 3.38, 3.31, 3.25 (each 3H, s, 4 × OCH₃), 3.50(1H, d, $J=8.4$, H-16), 3.54(1H, brs, H-17), 4.20 (1H, d, $J=6.6$ Hz, H-6), 4.53 (1H, d, $J=5.4$ Hz, H-15a), 4.98 (1H, d, $J=4.8$ Hz, H-14), 7.40–8.03 (5H, m, H-Ar). ¹³C-NMR (125 MHz, CD₃OD): δ 85.12(C-1),

26.5(C-2), 35.2(C-3), 39.1(C-4), 48.5(C-5), 83.3(C-6), 44.7(C-7), 92.3(C-8), 43.4(C-9), 41.2(C-10), 49.6(C-11), 36.1(C-12), 74.4(C-13), 78.5(C-14), 78.6(C-15), 90.4(C-16), 62.4(C-17), 80.5(C-18), 56.6(C-19), 42.4(N-Me), 56.4(C1-OMe), 58.5(C6-OMe), 61.6(C16-OMe), 59.7(C18-OMe), 172.2, 21.3 (OAc), 166.2, 129.5, 129.4, 128.4, 133.1(OBz).

Compound III: ESI-MS: m/z 630.8 [M+H]⁺. ¹H-NMR (600 MHz, CD₃OD): δ 1.43(3H, s, 8-OAc), 1.48(1H, dt, $J=9$, 7.2, H-2b), 1.51(3H, t, H-21), 1.76(1H, dd, $J=12.6$, 5.4, H-12b), 1.80(1H, dd, $J=18$, 6, H-3b), 1.92(1H, dd, $J=10.2$, 4.5, H-2a), 1.96(1H, dd, $J=14.5$, 6, H-3a), 2.39(1H, dd, $J=13.8$, 12.6, H-12a), 2.58(1H, ddd, $J=10.8$, 7.2, 6.6, H-10), 2.94(1H, d, $J=7.2$, H-5), 3.05(1H, dd, $J=10.8$, 6, H-9), 3.10(1H, brs, H-7), 3.74, 3.39, 3.31, 3.25 (each 3H, s, 4 × OCH₃), 3.29(1H, brd, $J=7.2$, H-19b), 3.32(1H, m, H-20b), 3.38(1H, d, $J=6.6$, H-18b), 3.49(1H, brd, $J=6$, H-19a), 3.52(1H, d, $J=7.8$, H-18a), 3.59(1H, brs, H-17), 4.23(1H, d, $J=6$, H-6), 4.55(1H, d, $J=4.5$, H-15), 7.40–8.03 (5H, m, H-Ar). ¹³C-NMR (125 MHz, CD₃OD): δ 85.3(C-1), 25.9(C-2), 35.3(C-3), 39.2(C-4), 49.5(C-5), 83.6(C-6), 45.2(C-7), 92.4(C-8), 44.7(C-9), 41.0(C-10), 49.9(C-11), 36.8(C-12), 74.2(C-13), 79.2(C-14), 79.3(C-15), 90.6(C-16), 61.4(C-17), 80.5(C-18), 53.4(C-19), 42.7, 13.5(N-Et), 56.0(C1-OMe), 58.1(C6-OMe), 61.4(C16-OMe), 59.5(C18-OMe), 172.6, 21.4(OAc), 166.2, 129.5, 129.4, 128.4, 133.1(OBz).