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Phytochemical Study of *Fagraea* spp. Uncovers A New Terpene Alkaloid with Anti-Inflammatory Properties.

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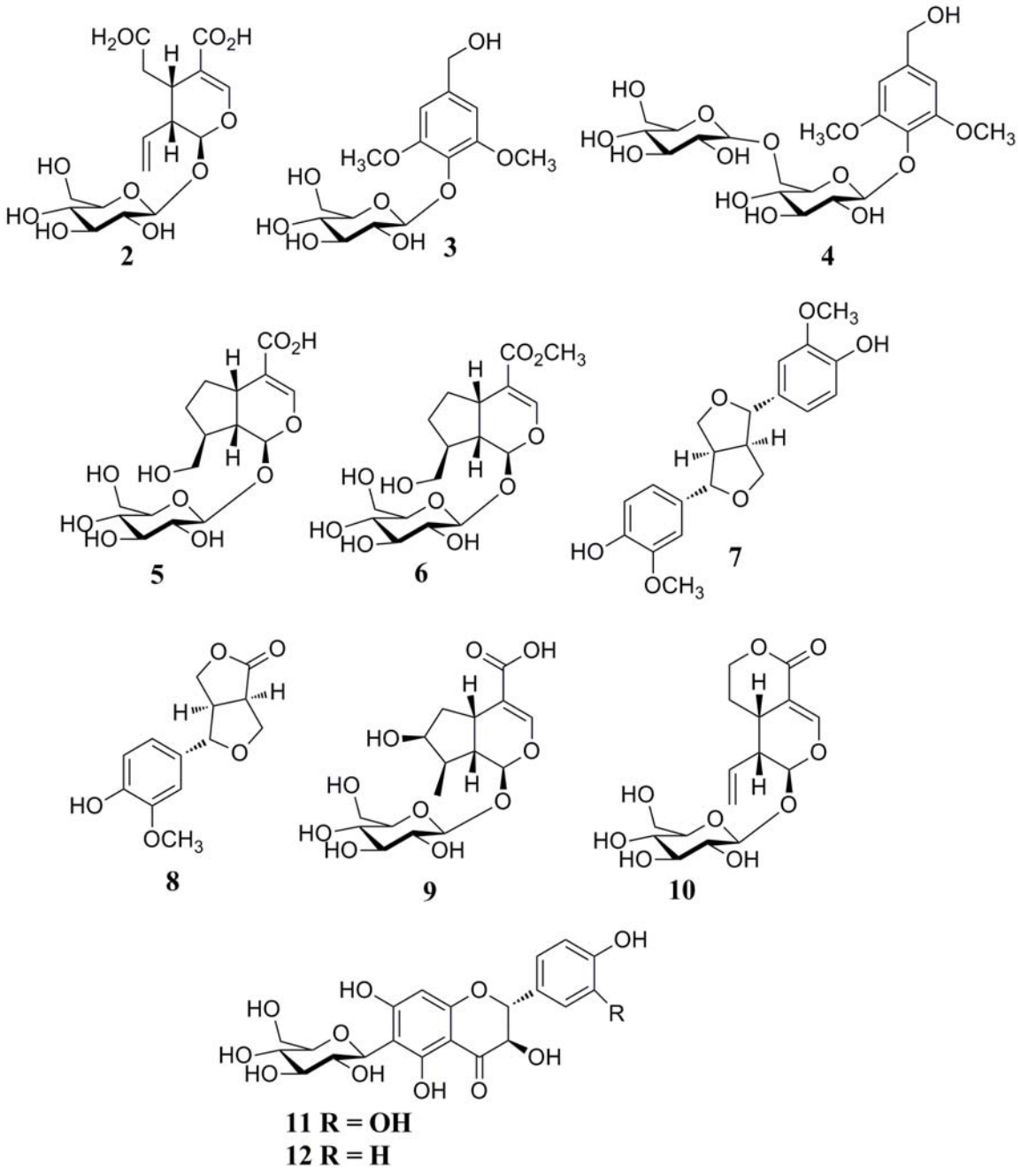
Accessory Publication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11 R = OH
12 R = H

Secologanoside (**2**)

Amorphous solid; $[\alpha]^{20}_{D}$ -98.3 (*c* 0.12, H_2O); ^{1}H NMR (D_2O, 500 MHz) δ 6.89 (1H, d, *J* = 1.7, H-3), 5.65 (1H, ddd, *J* = 17.2, 10.2, 10.0, H-8), 5.36 (1H, d, *J* = 3.2, H-1), 5.25 (1H, dd, *J* = 17.2, 1.4, H-10a), 5.23 (1H, dd, *J* = 10.2, 1.4, H-10b), 4.76 (1H, under solvent peak, H-1'), 3.91 (1H, dd, *J* = 12.4, 1.8, H-6'a), 3.71 (1H, dd, *J* = 12.4, 6.0, H-6'b), 3.47 (2H, m, H-3', H-5'), 3.40 (1H, m, H-4'), 3.33 (1H, m, H-2'), 3.10 (1H, m, H-5), 2.80 (1H, m, H-9), 2.73 (1H, dd, *J* = 15.7, 3.5, H-6a), 1.98 (1H, dd, *J* = 15.7, 12.4, H-6b); ^{13}C NMR (D_2O, 125 MHz) δ 180.8 (C-7), 174.5 (C-11), 154.2 (C-3), 135.4 (C-8), 123.4 (C-10), 113.4 (C-4), 101.4 (C-1'), 99.7 (C-1), 79.1 (C-5'), 78.4 (C-3'), 75.4 (C-2'), 72.4 (C-4'), 63.5 (C-6'), 46.5 (C-9), 38.1 (C-6), 31.1 (C-5); LRESIMS *m*/*z* 413.2 $[M+Na]^+$.

di-O-Methylcrenatin (**3**)

White amorphous solid; $[\alpha]^{26}_{D}$ -10.7 (c 0.13, MeOH); ^{1}H NMR (MeOH-d_4, 500 MHz) δ 6.69 (2H, br s, H-3, 5), 4.55 (2H, s, H-7), 4.67 (1H, underneath water peak, H-1'), 3.85 (6H, br s, 2 x OMe), 3.76 (1H, dd, *J* = 12.0, 2.5, H-6'a), 3.66 (1H, dd, *J* = 12.0, 5.1, H-6'b), 3.47 (1H, m, H-2'), 3.40 (2H, m, H-3' overlapped H-4'), 3.19 (1H, m, H-5'); ^{13}C NMR (MeOH-d_4, 125 MHz) δ 154.2 (C-2, 6), 139.7 (C-4), 135.3 (C-1), 105.6 (C-3, 5), 105.4 (C-1'), 78.3 (C-5'), 77.8 (C-3'), 75.7 (C-2'), 71.3 (C-4'), 65.1 (C-7), 62.5 (C-6'), 57.0 (OMe); LRESIMS *m*/*z* 369 $[M+Na]^+$.

Potalioside B (**4**)

White amorphous solid; $[\alpha]^{26}_{D}$ -29.1 (c 0.10, MeOH); ^{1}H NMR (MeOH-d_4, 500 MHz) δ 6.70 (2H, br s, H-3 and H-5), 4.93 (1H, d, 7.8, H-1'), 4.56 (2H, br s, H-7), 4.15 (1H, d, 7.4, H-1"), 3.96 (1H, d, 12.0, H-6'a), 3.85 (3H, s, OMe), 3.74 (1H, m, H-5"a), 3.71 (1H, dd, 12.0, 6.0, H-6'b), 3.48 (1H, t, 4.5, H-2'), 3.39 (2H, m, H-3' and H-4"), 3.37 (1H, m, H-5'), 3.34 (1H, m, H-4'), 3.14 (1H, dt, 8.9, 8.9, H-3"), 3.06 (1H, m, H-2"), 2.96 (1H, m, H-5"b); ^{13}C NMR (MeOH-d_4, 100 MHz) δ 154.4 (C-2 and C-6), 139.6 (C-4), 134.8 (C-1), 105.6 (C-3 and C-5), 104.7 (C-1"), 104.4 (C-1'), 78.2 (C-5'), 77.8 (C-3'), 77.3 (C-3"), 75.6 (C-2'), 74.8 (C-2"), 71.4 (C-4'), 71.2 (C-4"), 68.8 (C-6'), 66.7 (C-5"), 65.2 (C-7), 56.9 (OMe); LRESIMS *m*/*z* 501 $[M+Na]^+$.

Adoxosidic acid (**5**)

White amorphous solid; $[\alpha]^{26}_{D}$ -20.5 (c 0.09, MeOH); ^{1}H NMR (MeOH-d_4, 500 MHz) δ 7.12 (1H, d, 1.4, H-3), 5.10 (1H, d, 6.2, H-1), 4.65 (1H, d, 8.0, H-1'), 3.86 (1H, dd, 12.0, 1.6, H-6'a), 3.67 (1H, dd, 12.0, 5.3, H-6'b), 3.56 (1H, dd, 10.7, 6.5, H-10a), 3.48 (1H, dd, 10.7, 7.2, H-10b), 3.37 (1H, t, 9.0, H-3'), 3.20 (1H, dd, 9.0, 8.0, H-2'), 2.88 (1H, m, H-5), 2.13 (2H, m, H-6a and H-8), 1.87 (1H, m, H-9), 1.82 (1H, m, H-7a), 1.44 (1H, m, H-6b), 1.33 (1H, m, H-7b), H-4' and H-5' underneath water peak, assigned by HSQC and HMBC; ^{13}C NMR (MeOH-d_4, 100 MHz) δ 176.3 (C-11), 147.9 (C-3), 118.5 (C-4), 100.3 (C-1'), 97.7 (C-1), 78.2 (C-5'), 77.9 (C-3'), 74.8 (C-2'), 71.5 (C-4'), 67.0 (C-10), 62.7 (C-6'), 44.9 (C-9), 44.3 (C-8), 37.3 (C-5), 33.4 (C-6), 28.7 (C-7); LRESIMS *m*/*z* 399 $[M+Na]^+$.

(+)-Pinoresinol (**7**)

White amorphous solid; $[\alpha]^{22}_{D}$ +93.2 (c 0.19, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.88 (2H, d, *J* = 1.8, H-2, H-2'), 6.87 (1H, d, *J* = 8.1, H-5, H-5'), 6.80 (1H, dd, *J* = 8.1, 1.8, H-6, H-6'), 5.58 (2H, br s, OH, D_2O-exchangeable) 4.72 (2H, d, *J* = 4.4, H-7, H-7'), 4.23 (2H, dd, *J* = 9.2, 7.0, H-9a, H-9'a), 3.89 (6H, s, 2xOMe), 3.86 (2H, dd, *J* = 9.2, 3.8, H-9b, H-9'b), 3.08 (2H, m, H-8, H-8'); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 146.7 (C-3, C-3'), 145.2 (C-4, C-4'), 132.9 (C-1, C-1'), 119.0 (C-6, C-6'), 114.3 (C-5, C-5'), 108.6 (C-2, C-2'), 85.9 (C-7, C-7'), 71.7 (C-9, C-9'), 56.0 (OMe), 54.2 (C-8, C-8'); HRESIMS *m*/*z* 381.1308 $[M+Na^+]$ (calcd. for $C_{20}H_{22}O_6$ Na 381.1416).

Salicifoliol (**8**)

White amorphous solid; $[\alpha]^{22}_{D}$ +18.1 (c 0.36, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.89 (1H, d, *J* = 8.1, H-5'), 6.87 (1H, d, *J* = 1.9, H-2'), 6.79 (1H, dd, *J* = 8.1, 1.9, H-6'), 4.60 (1H, d, *J* = 7.0, H-2), 4.48 (1H, dd, *J* = 9.8, 7.0, H-8a), 4.34 (1H, t, *J* = 9.1, H-4a), 4.31 (1H, dd, *J* = 9.8, 2.2, H-8b), 4.17 (1H, dd, *J* = 9.1, 3.8, H-4b), 3.89 (3H, s, OMe), 3.42 (1H, m, H-5), 3.10 (1H, m, H-1); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 178.0 (C-6), 146.7 (C-3'), 145.6 (C-4'), 130.4 (C-1'), 118.8 (C-6'), 114.2 (C-5'), 108.2 (C-2'), 85.9 (C-2), 69.8 (C-4), 69.6 (C-8), 55.9 (OMe), 48.0 (C-1), 45.8 (C-5); LRESIMS *m*/*z* 273.1 $[M+Na]^+$.

Loganic acid (**9**)

White amorphous solid; $[\alpha]^{23}_{D}$ -53.7 (c 0.05, MeOH); ^{1}H NMR (MeOH-d_4, 500 MHz) δ 7.38 (1H, d, *J* = 1.3, H-3), 5.27 (1H, d, *J* = 4.5, H-1), 4.65 (1H, d, *J* = 7.9, H-1'), 4.05 (1H, m, H-7), 3.89 (1H, dd, *J* = 11.9, 1.9, H-6'a), 3.65 (1H, dd, *J* = 11.9, 5.7, H-6'b), 3.36 (1H, m, H-3'), 3.29 (1H, m, H-5'), 3.28 (1H, m, H-4'), 3.18 (1H, m, H-2'), 3.09 (1H, m, H-5), 2.23 (1H, m, H-6), 2.02 (1H, m, H-9), 1.87 (1H, m, H-8), 1.65 (1H, m, H-6), 1.09 (3H, d, *J* = 7.0, H-10); ^{13}C NMR (MeOH-d_4, 125 MHz) δ 170.5 (C-11), 151.8 (C-3), 113.8 (C-4), 99.8 (C-1'), 97.4 (C-1), 78.0 (C-5'), 77.7 (C-3'), 74.8 (C-7), 74.5 (C-2'), 71.4 (C-4'), 62.5 (C-6'), 46.4 (C-9), 42.5 (C-6), 41.9 (C-8), 31.9 (C-5), 13.4 (C-10); LRESIMS *m*/*z* 375.2 $[M-H]^-$.

Sweroside (**10**)

Brown amorphous solid; $[\alpha]^{26}_{D}$ -106.7 (c 0.23, MeOH); ^{1}H NMR (D_2O, 500 MHz) δ 7.62 (1H, d, 2.4, H-3), 5.56 (1H, br s, H-1), 5.53 (1H, ddd, 16.9, 10.4, 9.8, H-8), 5.33 (1H, d, 16.9, H-10a), 5.28 (1H, d, 10.4, H-10b), 4.83 (1H, d, 8.1, H-1'), 4.49 (1H, m, H-7a), 4.40 (1H, dt, 11.8, 11.8, H-7b), 3.91 (1H, d, 12.3, H-6'a), 3.72 (1H, dd, 12.3, 6.0, H-6'b), 3.49 (2H, m, H-3' and H-5'), 3.39 (1H, m, H-4'), 3.28 (1H, t, 8.8, H-2'), 3.05 (1H, m, H-5), 2.79 (1H, m, H-9), 1.81 (1H, m, H-6a), 1.73 (1H, dddd, 4.4, 4.3, 4.4, 4.3, H-6b); ^{13}C NMR (D_2O, 100 MHz) δ 172.5 (C-11), 156.2 (C-3), 134.2 (C-8), 123.4 (C-10), 107.5 (C-4), 101.1 (C-1'), 100.4 (C-1), 79.1 (C-5'), 78.3 (C-3'), 75.4 (C-2'), 72.4 (C-7 and C-4'), 63.5 (C-6'), 29.3 (C-5), 26.7 (C-6); LRESIMS *m*/*z* 381 $[M+Na]^+$.

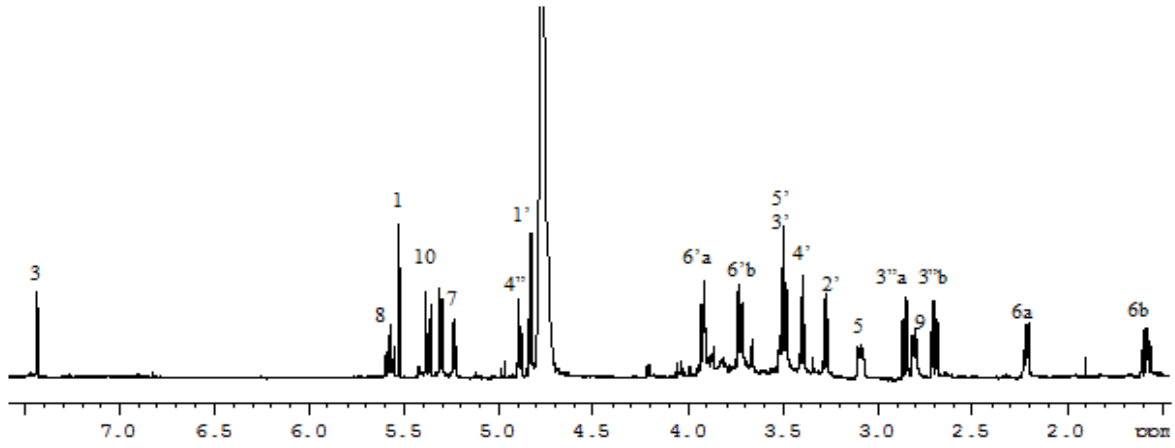
Taxifolin-6-C-glucoside (**11**)

Yellow amorphous powder; $[\alpha]^{23}_{D}$ +6.0 (c 0.53, MeOH); ^{1}H NMR (MeOH-d_4, 500 MHz) δ 6.94 (1H, d, 2.0, H-6'), 6.83 (1H, dd, 8.2, 2.0, H-2'), 6.79 (1H, d, 8.2, H-3'), 5.95 (1H, s, H-8), 4.92 (1H, d, 11.4, H-2), 4.79 (1H, d, 10.0, H-1"), 4.50 (1H, d, 11.4, H-3), 4.11 (1H, m, H-2"), 3.85 (1H, dd, 12.1, 2.2, H-6"a), 3.70 (1H, dd, 12.1, 5.5, H-6"b), 3.43 (2H, m, H-3" and H-4"), 3.37 (1H, m, H-5"); ^{13}C NMR (MeOH-d_4, 125 MHz) δ 198.8 (C-4), 167.6 (C-7), 164.1 (C-5), 163.9 (C-9), 147.2 (C-4'), 146.6 (C-5'), 129.7 (C-1'), 120.9 (C-3'), 116.1 (C-2'), 115.9 (C-6'), 106.3 (C-6), 101.8 (C-10), 96.5 (C-8), 85.1 (C-2), 82.5 (C-5"), 80.2 (C-3"), 75.1 (C-1"), 73.6 (C-3), 72.5 (C-2"), 71.8 (C-4"), 62.9 (C-6"); LRESIMS *m*/*z* 463.3 $[M-H]^-$.

Aromadendrin 6-C-glucoside (**12**)

Yellow powder; $[\alpha]^{23}_{D}$ +3.4 (c 0.92, MeOH) ^{1}H NMR (MeOH-d_4, 500 MHz) δ 7.33 (2H, d, 8.6, H-2' and H-6'), 6.81 (2H, d, 8.6, H-3' and H-5'), 5.78 (1H, s, H-8), 4.89 (obscured by water peak, H-2), 4.76 (1H, d, 9.7, H-1"), 4.45 (1H, d, 11.2, H-3), 4.25 (1H, m, H-2"), 3.82 (1H, dd, 12.0, 2.0, H-6"a), 3.71 (1H, dd, 12.0, 4.0, H-6"b), 3.48 (1H, m, H-4"), 3.42 (1H, m, H-3"), 3.35 (1H, m, H-5"); ^{13}C NMR (MeOH-d_4, 125 MHz) δ 194.7 (C-4), 169.5 (C-7), 163.2 (C-5), 162.2 (C-9), 157.7 (C-4'), 128.8 (C-2' and C-6'), 128.3 (C-1'), 114.7 (C-3' and C-5'), 105.8 (C-6), 98.2 (C-10), 97.4 (C-8), 83.1 (C-2), 80.7 (C-5"), 79.1 (C-3"), 74.0 (C-1"), 72.0 (C-3), 70.8 (C-2"), 70.2 (C-4"), 61.4 (C-6"); LRESIMS *m*/*z* 473.1$[M+Na]^{+}$.

^{1}H NMR spectrum for compound **1**



^{13}C NMR spectrum for compound **1**

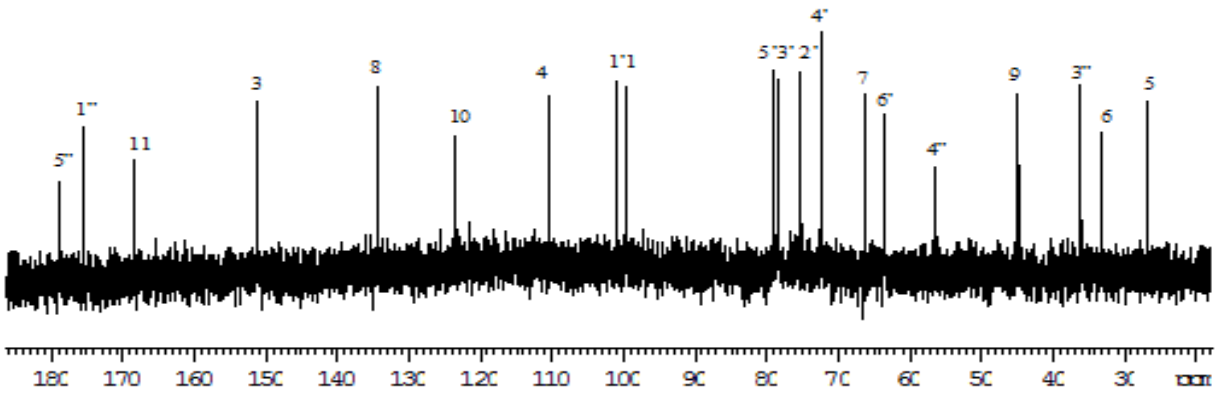
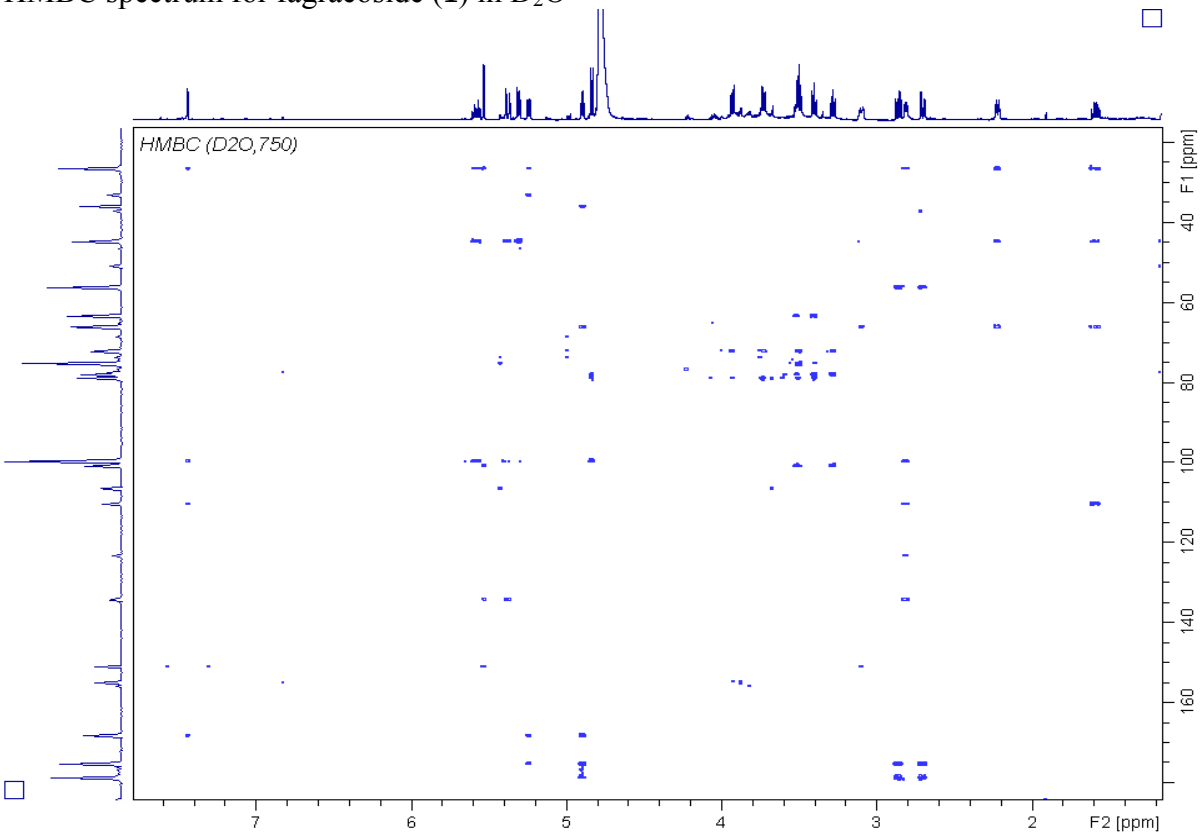


Figure **S1**. ^{1}H and ^{13}C NMR spectra for fagraeoside (**1**) in D_2O

HMBC spectrum for fagraeoside (**1**) in D_2O



HMBC spectrum for fagraeoside (**1**) in DMSO-d_6

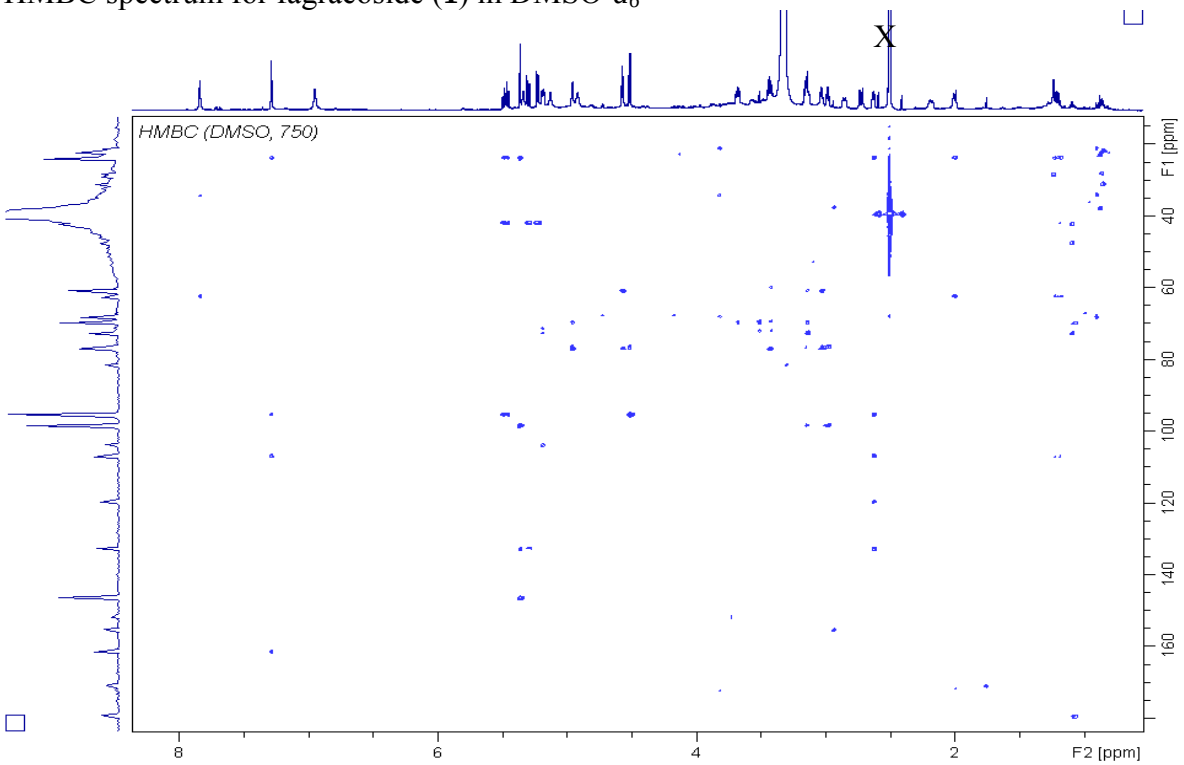
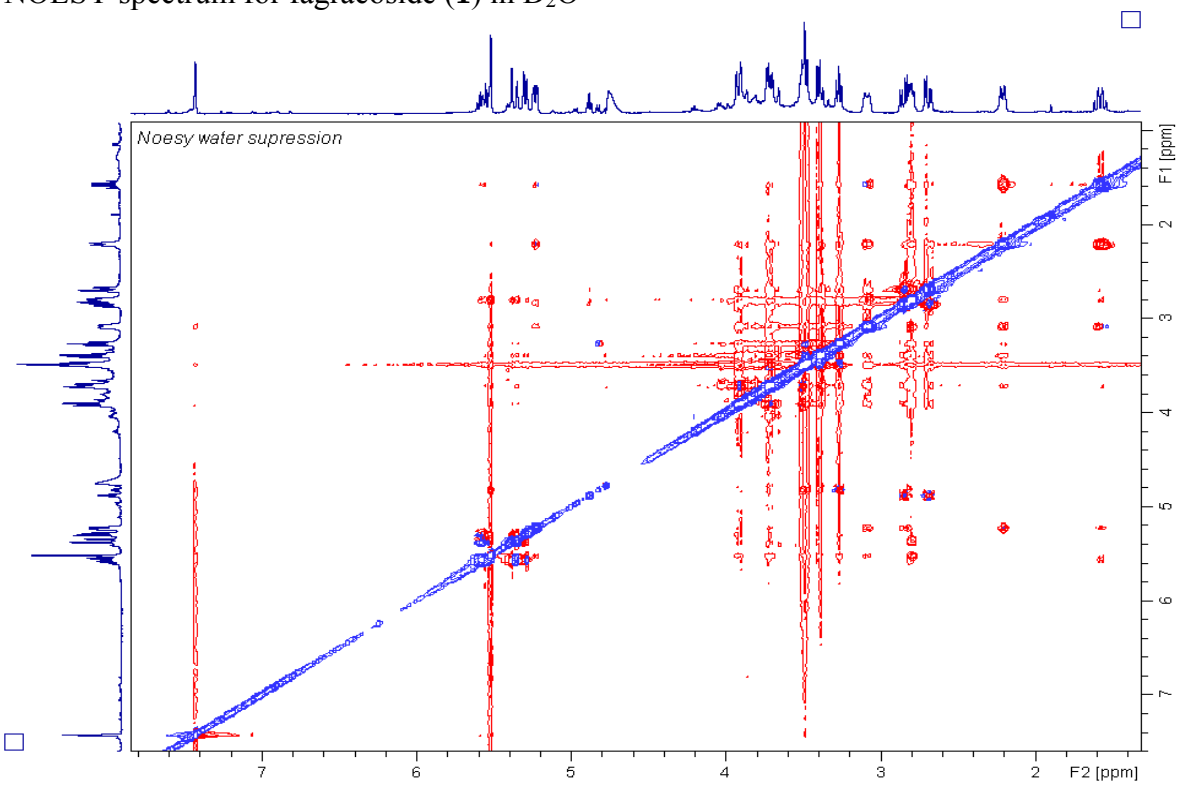


Figure **S2**. HMBC spectra for fagraeoside (**1**) in D_2O and DMSO-d_6

NOESY spectrum for fagraeoside (**1**) in D_2O



ROESY spectrum for fagraeoside (**1**) in DMSO-d_6

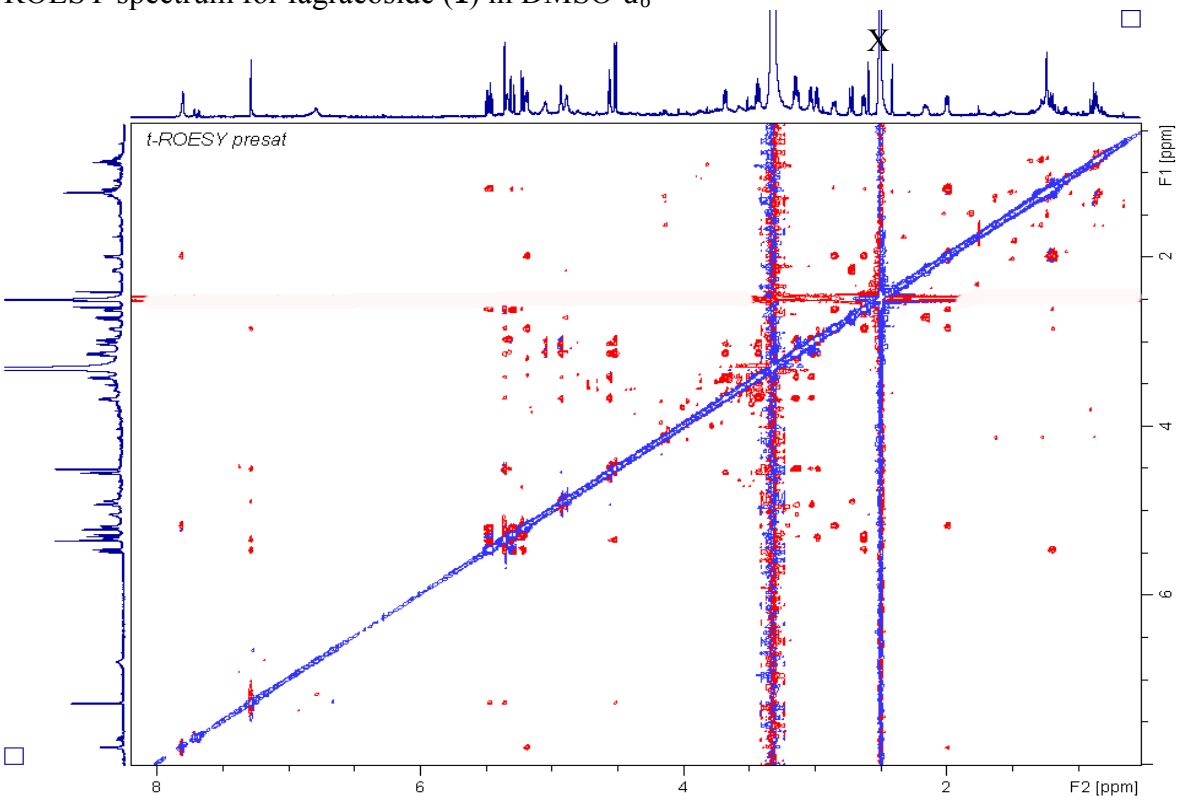
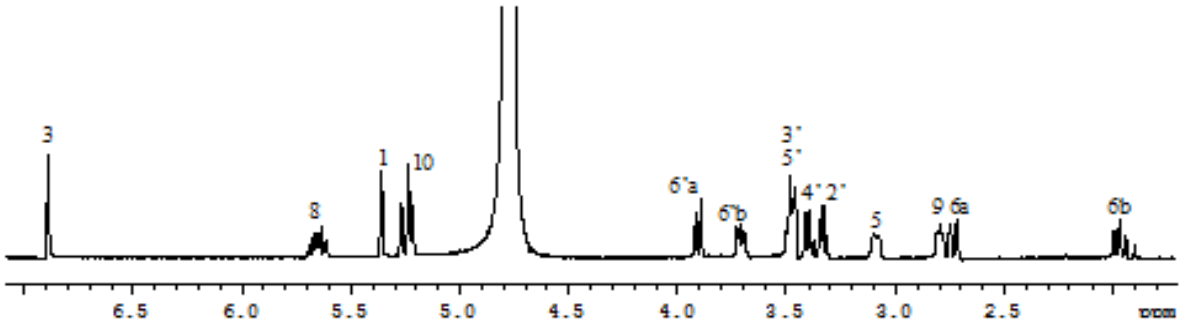


Figure **S3**. NOESY (D_2O) and ROESY (DMSO-d_6) spectra for fagraeoside (**1**)

^{1}H NMR spectrum for secologanoside (**2**) in D_2O



^{13}C NMR spectrum for secologanoside (**2**) in D_2O

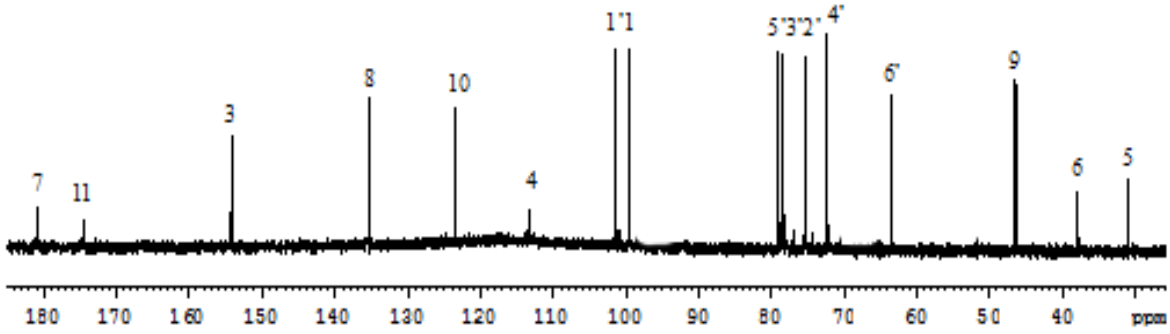


Figure **S4**. ^{1}H and ^{13}C NMR spectrum for secologanoside (**2**) in D_2O