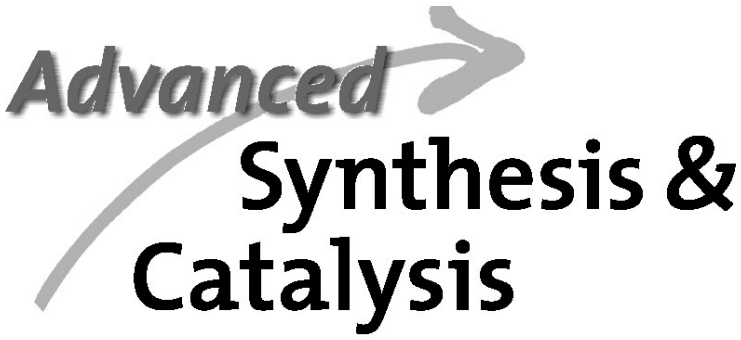

Supporting Information

Biocatalyzed generation of molecular diversity:
selective modification of the saponine asiaticoside

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Supporting Information

Characterization data of compounds **1**-**8**.

Asiaticoside (1) [19]

^{1}H-NMR (CD_3OD) selected data δ: 5.31 (1H, d, *J* = 8.0 Hz, H-1'); 5.27 (1H, br t, *J* = 4.4 Hz, H-12); 4.87 (1H, d, *J* = 1.7 Hz, H-1'''); 4.39 (1H, d, *J* = 7.9 Hz, H-1''); 4.09 (1H, dd, J_1 = 10.2 Hz, J_2 = 1.5 Hz, H-6'); 3.98 (1H, dq, J_1 = 8.5 Hz, J_2 = 7.0 Hz, H-5'''); 2.26 (1H, d, *J* = 11.3 Hz, H-18); 1.29 (3H, d, *J* = 6.2 Hz, CH_3-6'''); 1.15 (3H, s, CH_3-27); 1.07 (3H, s, CH_3-25); 1.00 (3H, br s, CH_3-30); 0.92 (3H, d, *J* = 6.5 Hz, CH_3-29); 0.85 (3H, s, CH_3-26); 0.72 (3H, s, CH_3-24). ^{13}C-NMR: 178.0 (C-28); 139.4 (C-13); 127.0 (C-12); 104.5 (C-1''); 102.9 (C-1'''); 95.9 (C-1'); 79.6 (C-4''); 78.3 and 78.2 (C-3 and C-3'); 78.0 (C-5'); 76.9 (C-5''); 76.8 (C-3''); 75.3 (C-2''); 73.8 (C-2' and C-4'''); 72.5 (C-2'''); 72.3 (C-3'''); 71.1 (C-4'); 70.7 (C-5'''); 69.7 (C-2 and C-6'); 66.5 (C-23); 62.0 (C-6''); 54.1 (C-18); 50.3 (C-9 and C-17); 48.1 (C-5); 47.7 (C-1); 44.1 (C-4); 43.4 (C-14); 41.0 (C-8); 40.4 (C-20); 40.3 (C-19); 39.0 (C-10); 37.6 (C-22); 33.6 (C-7); 31.7 (C-21); 29.3 (C-15); 25.3 (C-16); 24.5 (C-11); 24.0 (C-27); 21.6 (C-30); 19.1 (C-6); 18.1 (C-26); 17.9 (C-25); 17.8 (C-6'''); 17.7 (C-29); 13.9 (C-24).

Desrhamno-asiaticoside (2)

Amorphous solid. R_f, 0.29 ($CHCl_3$-MeOH-H_2O = 8 : 3 : 0.5). ESI-MS 835,44252 [M + Na^+] (theoretic: 835,44504). ^{1}H-NMR (CD_3OD) selected data δ: 5.33 (1H, d, *J* = 8.0 Hz, H-1'); 5.27 (1H,

br t, J = 3.6 Hz, H-12); 4.36 (1H, d, J = 7.8 Hz, H-1''); 4.12 (1H, dd, J_1=11.8 Hz, J_2= 1.8 Hz, H-6_a'); 3.87 (1H, dd, J_1 = 12.0 Hz, J_2= 2.2 Hz, H-6_a''); 3.76 (1H, dd, J_1= 11.8 Hz, J_2= 4.7 Hz, H-6_b[1]); 3.67 (1H, dd, J_1= 12.0 Hz, J_2= 5.2 Hz, H-6_b''); 2.24 (1H, d, J = 11.2 Hz, H-18); 1.42 (1H, m, H-19); 1.15 (3H, s, CH_3-27); 1.07 (3H, s, CH_3-25); 0.98 (3H, br s, CH_3-30); 0.92 (3H, d, J = 6.4 Hz, CH_3-29); 0.86 (3H, s, CH_3-26); 0.73.(3H, s, CH_3-24). ^{13}C-NMR (CD_3OD) δ: 176.6 (C-28); 138.0 (C-13); 125.6 (C-12); 103.4 (C-1''); 96.9 (C-1'); 77.1 e 76.9 (C-3'' e C-5''); 76.7, 76.6 and 76.4 (C-3, C-3' and C-5'); 73.8 (C-2''); 72.5 (C-2'); 70.3 (C-4''); 69.8 (C-4'); 68.4 (C-6'); 68.3 (C-2); 65.3 (C-23); 61.5 (C-6''); 52.8 (C-18); 42.7 (C-4); 42.1 (C-14); 39.6 (C-8); 39.0 (C-20); 38.8 (C-19); 37.6 (C-10); 36.2 (C-22); 32.3 (C-7); 30.3 (C-21); 27.9 (C-15); 23.9 (C-16); 23.1 (C-11); 22.6 (C-27); 20.1 (C-30); 17.7 (C-6); 16.7 (C-26); 16.5 (C-25); 16.2 (C-29); 12.5 (C-24).

Desrhamno-desgluco-asiaticoside (3)

Amorphous solid. R_f, 0.57 ($CHCl_3$-MeOH-H_2O = 8 : 3 : 0.5). ESI-MS 673,39134 [M + Na^+] (theoretic: 673,39222). ^{1}H-NMR (CD_3OD) selected data δ: 5.37 (1H, d, J = 8.0 Hz, H-1'); 5.28 (1H, br t, J = 3.6 Hz, H-12); 3.81 (1H, dd, J_1 = 12.0 Hz, J_2 = 2.3 Hz, H-6_a'); 3.71 (1H, dt, J_I = 11.0 Hz, J_2 = 4.5 Hz, H-2); 3.70 (1H, dd, J_1 = 12.0 Hz, J_2 = 4.4 Hz, H-6_b); 3.53 (1H, d, J = 13.0 Hz, H-23_a); 3.44 - 3.31 (6H, m); 3.29 (1H, d, J = 13.0 Hz, H-23_b); 2.26 (1H, d, J = 11.2 Hz, H-18); 2.10 (1H, dt, J_1 = 13.3 Hz, J_2 = 4.1 Hz, H-16_a); 1.78 (1H, dt, J_1 = 13.1 Hz, J_2 = 3.0 Hz, H-16_b); 1.15 (3H, s, CH_3-17); 1.07 (3H, s, CH_3-25); 0.99 (3H, br s, CH_3-30); O.92 (3H, d, J = 6.4 Hz, CH_3-29); 0.86 (3H, s, CH_3-26); 0.73 (3H, s, CH_3-24). ^{13}C-NMR (CD_3OD) δ: 176.6 (C-28); 138.0 (C-13); 125.8 (C-12); 94.4 (C-1'); 77.3, 77.2, 77.1 (C-3, C-3', C-5'); 72.6 (C-2'); 70.0 (C-4'); 68.4 (C-2); 65.4 (C-23); 61.3 (C-6'); 52.9 (C-18); 47.1 (C.-5); 42.8 (C-4); 42.2 (C-14); 39.8 (C-8); 39.1 (C-20); 39.0 (C-19); 37.7 (C-10); 36.2 (C-22); 32.4 (C-7); 30.4 (C-21); 28.0 (C-15); 24.0 (C-16); 23.2 (C-11); 22.7 (C-27); 20.2 (C-30); 17.8 (C-6); 16.7 (C-26); 16.5 (C-25); 16.3 (C-29); 12.6 (C-24).

Asiatic acid (4)

^{1}H-NMR (CD_3OD) selected data δ: 5.23 (1H, br t, J = 4.4 Hz, H-12); 3.67 (1H, dt, J_1 = 9.5 Hz, J_2 = 4.0 Hz, H-2); 3.46 and 3.26 (1H each, d each, J = 10.5 Hz, H-23a and H-23b); 3.33 (1H, d, J = 9.5 Hz, H-3); 2.20 (1H, d, J = 11.3 Hz, H-18); 1.13 (3H, s, CH_3-27); 1.04 (3H, s, CH_3-25); 0.96 (3H, br s, CH_3-30); 0.89 (3H, d, J = 6.5 Hz, CH_3-29); 0.84 (3H, s, CH_3-26); 0.69 (3H, s, CH_3-24). ^{13}C-NMR: 181.6 (C-28); 139.8 (C-13); 126.7 (C-12); 78.3 (C-3); 69.7 (C-2); 66.4 (C-23); 54.4 (C-18); 44.1 (C-4); 43.4 (C-14); 40.8 (C-8); 40.4 (C-20 and C-19); 39.0 (C-10); 38.1 (C-22); 33.7 (C-7); 31.8 (C-21); 29.2 (C-15); 25.3 (C-16); 24.5 (C-11); 24.2 (C-27); 21.6 (C-30); 19.1 (C-6); 17.9 (C-26); 17.7 (C-25); 17.6 (C-29); 13.9 (C-24).

Galactosyl-desrhamno-asiaticoside (5)

R_f, 0.15 ($CHCl_3$-MeOH-H_2O = 8 : 3 : 0.5). ESI-MS: 997.48762 $[M + Na]^+$ (theoretic: 997.49787). ^{1}H-NMR (CD_3OD) selected data δ: 5.32 (1H, d, *J* = 8.1 Hz, H-1'); 5.27 (1H, br t, *J* = 3.6 Hz, H-12); 4.39 (1H, d, *J* = 8 Hz) e 4.37 (1H, d, *J*=7.8 Hz): H-1'' and H-1'''; 4.12 (1H, dd, J_1 = 11.5 Hz, J_2 = 1.7 Hz, H-6_a'); 3.92 (1H, dd, J_1 = 12.1 Hz, J_2 = 2.5 Hz, H-6_a'''); 3.86 (1H, dd, J_1 = 12.1 Hz, J_2= 4.3 Hz, H-6_a''); 2.26 (1H, d, *J* = 11.4 Hz, H-18); 1.15 (3H, s, CH_3-27); 1.08 (3H, s, CH_3-25); 0.99 (3H, br s, CH_3-30); 0.92 (3H, d, *J* = 6.4 Hz, CH_3-26); 0.86 (3H, s, CH_3-26); 0.73 (3H, s, CH_3-24). ^{13}C-NMR (CD_3OD) selected data δ: 176.5 (C-28); 138.1 (C-13); 125.7 (C-12); 103.7 (C-1'' e C-1'''); 94.1 (C-1'), 68.3 (C-6'); 61.3 (C-6''); 60.8 (C-6''').

Galactosyl-desrhamno-desgluco-asiaticoside (6)

R_f, 0.35 ($CHCl_3$-MeOH-H_2O = 8 : 3 : 0.5). ESI-MS: 835,44434 $[M + Na]^+$ (theoretic: 835.444504). ^{1}H-NMR (CD_3OD) selected data δ: 5.40 (1H, d, *J* = 8.2 Hz, H-1'); 5.28 (1H, br t, *J* = 3.6 Hz, H-12); 4.41 (1H, d, *J*=7.6 Hz, H-1''); 2.24 (1H, *J* = 11.9 Hz, H-18); 1.15 (3H, s, CH_3-27); 1.07 (3H, s, CH_3-25); 0.99 (3H, s, CH_3-30); O.92 (3H, d, *J* = 6.4 Hz, CH_3-29); 0.87 (3H, s, CH_3-26); 0.74 (3H, s, CH_3-24). ^{13}C-NMR (CD_3OD) δ: 176.5 (C-28); 138.0 (C-13); 125.8 (C-12); 103.7 (C-1''); 94.2 (C-1); 68.3 (C-2); 61.1 (C-6'); 60.9 (C-6''); 52.8 (C-18); 42.8 (C-4); 42.0 (C-14); 39.1 (C-8); 39.0 (C-20); 38.9 (C-19); 37.6 (C-10); 36.1 (C-22); 32.3 (C-7); 30.3 (C-21); 27.8 (C-15); 23.8 (C-16); 23.1 (C-11); 22.7 (C-27); 20.1 (C-30); 17.7 (C-6); 16.6 (C-26); 16.4 (C-25); 16.2 (C-29); 12.5 (C-24).

4'''-*O*-acetyl asiaticoside (7)

Amorphous solid. R_f, 0.22 ($CHCl_3$-MeOH-H_2O = 8 : 3 : 0.5). ESI-MS: 1023.5145 $[M + Na]^+$ (theoretic: 1023.51352).. ^{1}H-NMR (CD_3OD) selected data δ: 5.28 (1H, d, J = 7.8 Hz, H-1'); 5.24 (1H, br t, J = 4.4 Hz, H-12); 4.94 (1H, t, J = 9.8 Hz, H-4''); 4.87 (1H, d, J = 1.7 Hz, H-1'''); 4.39 (1H, d, J = 7.8 Hz, H-1''); 4.31 (1H, dq, J_1 = 8.5 Hz, J_2 = 7.0 Hz, H-5'''); 4.06 (1H, dd, J_1 = 9.2 Hz, J_2 = 1.5 Hz, H-6'); 2.23 (1H, d, J = 11.2 Hz, H-18); 1.13 (3H, d, J = 6.2 Hz, CH_3-6'''); 1.12 (3H, s, CH_3-27); 1.05 (3H, s, CH_3-25); 0.97 (3H, br s, CH_3-30); 0.89 (3H, d, J = 6.4 Hz, CH_3-29); 0.83 (3H, s, CH_3-26); 0.69 (3H, s, CH_3-24). ^{13}C-NMR: 178.0 (C-28); 139.4 (C-13); 127.0 (C-12); 104.4 (C-1''); 102.6 (C-1'''); 95.9 (C-1'); 79.0 (C-4''); 78.2 (C-3 and C-3'); 78.1 (C-5'); 77.0 and 76.7 (C-5''and C-3''); 75.5 and 75.4 (C-2'' and C-4'''); 73.8 (C-2'); 72.5 (C-2'''); 71.1 (C-4'); 70.4 (C-3'''); 69.7 and 69.6 (C-2 and C-6'); 68.3 (C-5'''); 66.4 (C-23); 61.9 (C-6''); 54.1 (C-18); 50.3 (C-9 and C-17); 48.1 (C-5); 47.7 (C-1); 44.1 (C-4); 43.4 (C-14); 41.0 (C-8); 40.4 (C-20); 40.3 (C-19); 39.0 (C-10); 37.7 (C-22); 33.6 (C-7); 31.7 (C-21); 29.3 (C-15); 25.3 (C-16); 24.6 (C-11); 24.0 (C-

27); 21.6 (C-30); 19.1 (C-6); 18.1 (C-26); 17.9 (C-25); 17.7 (C-6’’’); 17.6 (C-29); 14.0 (C-24); acetyl moiety: 172.5 and 21.0.

Mixture of 2‘‘‘-O-acetyl- and 3‘‘‘-O-acetyl-asiaticoside

^{1}H-NMR (MeOD) selected data δ: ma*J*or product: 4.91 (1 H, b s, H-1”’); 4.94 (1 H, dd, J_1= 9.9 Hz J_2= 3.1 Hz, H-3”’); 4.02 (1 H, b s, H-2”’); 1.32 (3 H, d, *J*=6.0 Hz, CH_3-5”’); minor product: 5.03 (1 H, b s, H-2”’); 4.87 (1 H, b s, H-1”’), 1.29 (3 H, d, J=6.1 Hz, CH_3-5”’). ESI-MS: 1023 [acetyl asiaticoside + Na^+].

Laccase-oxidized asiaticoside (8)

Amorphous solid. R_f 0.13 (eluent AcOEt-MeOH-H_2O 10 : 3 : 1). ESI-MS 1017,45970 [M - H + 2 Na^+] (theoric: 1017,46416). ^{1}H-NMR (CD_3OD) selected data δ: 5.33 (1H, d, *J* = 8.0 Hz, H-1’); 5.28 (1H, br t, *J* = 3.4 Hz, H-12); 4.81 (1H, d, *J* = 1.0 Hz, H-1’’’); 4.37 (1H, d, *J* = 7.7 Hz, H-1’’); 4.11 (1H, dd, J_1 = 10.2 Hz, J_2 = 1.8 Hz, H-6’); 4.01 (1H, dq, J_1 = 8.5 Hz, J_2 = 7.0 Hz, H-5’’’); 3.88 (br dd, 1H, H-2’’’); 3.75 (1H, dd, J_1 = 10.2 Hz, J_2 = 4.8 Hz, H-6_b’); 3.32 (1H, d, *J* = 10.3 Hz, H-5); 2.26 (1H, d, *J* = 11.3 Hz, H-18); 1.27 (3H, d, *J* = 6.2 Hz, CH_3-6’’’); 1.15 (3H, s, CH_3-27); 1.07 (3H, s, CH_3-25); 0.99 (3H, br s, CH_3-30); 0.91 (3H, d, *J* = 6.5 Hz, CH_3-29); 0.85 (3H, s, CH_3-26); 0.72 (3H, s, CH_3-24). ^{13}C-NMR: 178.9 (C-28); 140.3 (C-13); 128.0 (C-12); 105.6 (C-1’’); 103.6 (C-1’’’); 96.7 (C-1’); 82.4 (C-4’’); 79.6 (C-5’); 79.1 (C-3); 78.7 (C-5’’); 77.7 (C-3’’); 76.1 (C-3’ and C-2’’); 75.0 and 74.8 (C-2’ and C-4’’’); 73.1 (C-2’’’ and C-3’’’); 72.4 (C-4’); 71.2 (C-5’’’); 70.8 (C-6’); 70.6 (C-2); 67.8 (C-23); 55.1 (C-18); 45.0 (C-4); 44.4 (C-14); 42.0 (C-8); 41.3 (C-20); 41.1 (C-19); 40.0 (C-10); 38.5 (C-22); 34.6 (C-7); 32.6 (C-21); 30.3 (C-15); 26.2 (C-16); 25.5 (C-11); 25.0 (C-27); 22.4 (C-30); 20.1 (C-6); 19.0 (C-26); 18.8 (C-25); 18.5 (C-6’’’ and C-29); 14.7 (C-24).