

## Supporting Information

### NMR and MS data of the known compounds from *Vitex agnus-castus*

**Vitexlactam A (1):** white crystals, mp. 207°C, C<sub>22</sub>H<sub>35</sub>NO<sub>4</sub>; [ $\alpha$ ]<sub>D</sub><sup>23.7</sup>-10.71° (c 0.42, CHCl<sub>3</sub>); IR (KBr)  $\nu_{\max}$ : 3463, 3188, 3054, 2942, 2923, 1731, 1684, 1460, 1442, 1381, 1361, 1250, 1226, 1142, 1087, 1039, 1020, 973, 962, 952, 913, 832, 781, 749, 645, 610, 598 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  see Table 3-3; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  see Table 3-4; EIMS  $m/z$  377 [M]<sup>+</sup> (3), 317 (87), 302 (5), 284 (17), 206 (13), 192 (15), 180 (72), 167 (100), 149 (18), 138 (74), 123 (22), 110 (70), 96 (56), 82 (40), 69 (50), 55 (67); HREIMS  $m/z$  found 377.2569 [M]<sup>+</sup>, calcd. 377.2566.

**Vitexlactam B (2):** white crystals, mp. 162°C, C<sub>20</sub>H<sub>33</sub>NO<sub>2</sub>; [ $\alpha$ ]<sub>D</sub><sup>23.5</sup>+18.75° (c 0.2, CHCl<sub>3</sub>); IR (KBr)  $\nu_{\max}$ : 3473, 3187, 3055, 2924, 2682, 1684, 1648, 1442, 1379, 1296, 1254, 1228, 1140, 1085, 1057, 1041, 1018, 972, 962, 943, 909, 832, 791, 777, 698 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  see Table 3-3; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  see Table 3-4; EIMS  $m/z$  319 [M]<sup>+</sup> (81), 304 (7), 286 (8), 206 (7), 194 (19), 180 (100), 167 (75), 152 (11), 138 (47), 123 (17), 110 (81), 96 (86), 82 (58), 69 (72), 55 (97); HREIMS  $m/z$  found 319.2509 [M]<sup>+</sup>, calcd. 319.2511.

**Vitexlactam C (3):** white crystals, mp. 178°C, C<sub>22</sub>H<sub>35</sub>NO<sub>4</sub>; [ $\alpha$ ]<sub>D</sub><sup>18.7</sup>-12.73° (c 0.55, CHCl<sub>3</sub>); IR (KBr)  $\nu_{\max}$ : 3364, 3297, 2925, 2867, 1711, 1670, 1465, 1426, 1383, 1362, 1271, 1256, 1228, 1203, 1152, 1125, 1097, 1039, 1024, 977, 953, 916, 849, 819 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  see Table 3-3; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  see Table 3-4; EIMS  $m/z$  377 [M]<sup>+</sup> (3), 317 (76), 302 (15), 284 (6), 260 (29), 242 (8), 222 (21), 202 (23), 187 (48), 167 (60), 150 (28), 133 (41), 119 (64), 110 (68), 96 (97), 83 (72), 69 (77), 55 (100); HREIMS  $m/z$  found 377.2547 [M]<sup>+</sup>, calcd. 377.2566.

**Vitexilactone (4):** colorless lamellar crystals, C<sub>22</sub>H<sub>34</sub>O<sub>5</sub>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  see Table 3-2; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  see Table 3-4; EIMS  $m/z$  318 [M-

$\text{CH}_3\text{COOH}]^+$  (100), 303 (18), 285 (3), 275 (7), 262 (9), 221 (5), 207 (11), 194 (21), 181 (40), 168 (32), 150 (35), 135 (34), 123 (45), 109 (50), 95 (42), 81 (45), 69 (65), 55 (57).

**Rotundifuran (5)**: colorless oil,  $\text{C}_{22}\text{H}_{34}\text{O}_4$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  see Table 3-2;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  see Table 3-4; EIMS  $m/z$  362  $[\text{M}]^+$  (7), 318 (18), 302 (81), 287 (17), 269 (8), 221 (12), 207 (21), 189 (20), 177 (33), 165 (54), 150 (89), 135 (72), 123 (100), 109 (77), 95 (69), 81 (80), 69 (61), 55 (53).

**8-Epimanoyl oxide (6)**: colorless needles,  $\text{C}_{20}\text{H}_{34}\text{O}$ ;  $[\alpha]_{\text{D}}^{19.5} -11.82^\circ$  ( $c$  0.55,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  see Table 3-2;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  see Table 3-4; EIMS  $m/z$  290  $[\text{M}]^+$  (35), 272 (20), 257 (18), 247 (12), 232 (10), 219 (16), 203 (27), 192 (40), 177 (60), 163 (35), 149 (40), 137 (55), 123 (61), 109 (67), 95 (70), 81 (71), 69 (80), 55 (100).

**Vitetrifolin D (7)**: colorless oil,  $\text{C}_{24}\text{H}_{38}\text{O}_5$ ;  $[\alpha]_{\text{D}}^{19.1} +139.58^\circ$  ( $c$  0.6,  $\text{CHCl}_3$ ); IR (KBr)  $\nu_{\text{max}}$ : 3499, 2967, 2928, 2865, 1740, 1465, 1369, 1249, 1028, 978, 941, 920, 874, 743, 695, 484  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  see Table 3-1;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  see Table 3-4; EIMS  $m/z$  346  $[\text{M}-\text{CH}_3\text{COOH}]^+$  (31), 328 (23), 304 (28), 286 (20), 271 (26), 248 (24), 201 (27), 188 (33), 178 (30), 136 (33), 121 (100), 109 (30), 95 (33), 79 (32), 69 (36), 55 (41).

**Spathulenol (8)**:  $\text{C}_{15}\text{H}_{24}\text{O}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.22 (1H, m, H-1 $\alpha$ ), 0.46 (1H, dd,  $J = 9.5, 11.3$  Hz, H-6 $\alpha$ ), 0.73 (1H, m, H-7 $\alpha$ ), 2.41 (1H, dd,  $J = 7.4, 16.5$  Hz, H-9 $\beta$ ), 1.03 (3H, s, H-12), 1.05 (3H, s, H-13), 4.68 (1H, s, H-14a), 4.66 (1H, s, H-14b), 1.27 (3H, s, H-15);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  53.4 (d, C-1), 26.7 (t, C-2), 41.7 (t, C-3), 81.0 (s, C-4), 54.3 (d, C-5), 29.9 (d, C-6), 27.4 (d, C-7), 24.8 (t, C-8), 38.8 (t, C-9), 153.4 (s, C-10), 20.2 (s, C-11), 16.3 (q, C-12), 28.6 (q, C-13), 106.2 (t, C-14), 26.0 (q, C-15); Positive FABMS  $m/z$  203 (100)  $[\text{M}-\text{H}_2\text{O}]^+$ , 187 (4), 175 (6), 159 (15), 147 (14), 138 (8), 113 (2), 99 (9), 84 (2), 59 (3).

**Cis-dihydro-dehydro-diconiferylalcohol-9-O- $\beta$ -D-glucoside (9)**: colorless syrup,  $\text{C}_{26}\text{H}_{34}\text{O}_{11}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  6.99 (1H, d,  $J = 1.7$  Hz, H-2), 6.75 (1H, d,  $J = 8.0$  Hz, H-5), 6.85 (1H, dd,  $J = 1.8, 8.1$  Hz, H-6), 5.57 (1H, d,  $J = 6.5$  Hz, H-7), 3.65 (1H, m, H-8), 4.10 (1H, t,  $J = 8.0$  Hz, H-9a), 3.83 (1H, overlap, H-9b), 6.71 (1H, s, H-2'), 6.79 (1H, s, H-6'), 2.61 (2H, t,  $J = 7.3$  Hz, H<sub>2</sub>-7'), 1.80 (2H, m, H<sub>2</sub>-8'), 3.56 (2H, t,  $J = 6.5$

Hz, H<sub>2</sub>-9'), 4.35 (1H, d, *J* = 7.8 Hz, H-1''), 3.24 (1H, t, *J* = 8.8 Hz, H-2''), 3.36 (1H, t, *J* = 8.8 Hz, H-3''), 3.30 (1H, overlap, H-4''), 3.28 (1H, m, H-5''), 3.87 (1H, dd, *J* = 2.0, 12.2 Hz, H-6a), 3.68 (1H, dd, *J* = 5.4, 11.9 Hz, H-6b), 3.81 (3H, s, 3-OCH<sub>3</sub>), 3.85 (3H, s, 3'-OCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>OD) δ 134.6 (s, C-1), 111.0 (d, C-2), 149.0 (s, C-3), 147.4 (s, C-4), 116.1 (d, C-5), 119.8 (d, C-6), 99.1 (d, C-7), 52.8 (d, C-8), 72.3 (t, C-9), 136.9 (s, C-1'), 114.3 (d, C-2'), 145.1 (s, C-3'), 147.4 (s, C-4'), 129.7 (s, C-5'), 118.2 (d, C-6'), 32.8 (t, C-7'), 35.9 (t, C-8'), 62.3 (t, C-9'), 104.2 (d, C-1''), 75.1 (d, C-2''), 78.2 (d, C-3''), 71.6 (d, C-4''), 77.9 (d, C-5''), 62.7 (t, C-6''), 56.9 (q, 3'-OCH<sub>3</sub>), 56.5 (q, 3-OCH<sub>3</sub>); Negative FABMS *m/z* 522 [M]<sup>+</sup> (27), 357 (12), 341 (100), 327 (29), 311 (14), 297 (7), 179 (54), 119 (37).

**Luteolin-7-O-glucoside (10)**: yellow needles, C<sub>21</sub>H<sub>20</sub>O<sub>11</sub>; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 6.74 (1H, s, H-3), 6.43 (1H, d, *J* = 2.0 Hz, H-6), 6.78 (1H, d, *J* = 2.5 Hz, H-8), 7.40 (1H, d, *J* = 2.0 Hz, H-2'), 6.89 (1H, d, *J* = 8.0 Hz, H-5'), 7.44 (1H, dd, *J* = 2.5, 8.0 Hz, H-6'), 5.06 (1H, d, *J* = 7.5 Hz, H-1''), 3.17 (1H, t, *J* = 8.5, H-2''), 3.40 (1H, overlapped by water, H-3''), 3.29 (1H, overlap, H-4''), 3.25 (1H, m, H-5''), 3.70 (1H, d, *J* = 10.5 Hz, H-6''a), 3.43 (1H, overlapped by water, H-6''b), 12.96 (1H, s, 5-OH); <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ 164.6 (s, C-2), 103.2 (d, C-3), 182.0 (s, C-4), 161.2 (s, C-5), 99.6 (d, C-6), 163.0 (s, C-7), 94.8 (d, C-8), 157.0 (s, C-9), 105.4 (s, C-10), 121.4 (s, C-1'), 113.6 (d, C-2'), 145.8 (s, C-3'), 150.0 (s, C-4'), 116.1 (d, C-5'), 119.3 (d, C-6'), 100.0 (d, C-1''), 73.2 (d, C-2''), 77.2 (d, C-3''), 69.6 (d, C-4''), 76.4 (d, C-5''), 60.7 (t, C-6''); Negative FABMS *m/z* 447 [M-H]<sup>+</sup> (100), 433 (10), 325 (9), 285 (34), 202 (4).

**5-Hydroxy-3, 6, 7, 4'-tetramethoxyflavone (11)**: pale yellow blocks, C<sub>19</sub>H<sub>18</sub>O<sub>7</sub>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 6.48 (1H, s, H-8), 8.05 (2H, dd, *J* = 3.0, 12.0 Hz, H-2' and H-6'), 7.00 (2H, dd, *J* = 2.5, 11.5 Hz, H-3' and H-5'), 12.6 (1H, s, 5-OH), 3.94, 3.91, 3.88 and 3.85 (each 3H, s, 4×OCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 152.2 (s, C-2), 138.6 (s, C-3), 178.8 (s, C-4), 152.7 (s, C-5), 132.3 (s, C-6), 158.7 (s, C-7), 90.3 (d, C-8), 155.9 (s, C-9), 106.5 (s, C-10), 122.7 (s, C-1'), 130.0 (2C, d, C-2' and C-6'), 114.0 (2C, d, C-3' and C-5'), 161.7 (s, C-4'), 60.7, 60.0, 56.2 and 55.3 (each q, 4×OCH<sub>3</sub>); EIMS *m/z* 358 [M]<sup>+</sup> (100), 343 (56), 339 (26), 328 (8), 315 (13), 300 (8), 297 (8), 285 (6), 272 (3), 229 (3), 201 (4), 181 (10), 153 (12), 135 (25), 119 (13), 107 (8), 92 (9), 77 (17), 69 (20).

**Casticin (12):** C<sub>19</sub>H<sub>18</sub>O<sub>8</sub>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.44 (1H, s, H-8), 7.63 (1H, d, *J* = 2.2 Hz, H-2'), 6.89 (1H, d, *J* = 8.4 Hz, H-5'), 7.64 (1H, dd, *J* = 2.2, 10.9 Hz, H-6'), 3.92, 3.90, 3.87 and 3.81 (each 3H, s, 4×OCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 152.3 (s, C-2), 139.0 (s, C-3), 178.9 (s, C-4), 152.7 (s, C-5), 132.3 (s, C-6), 158.8 (s, C-7), 90.4 (d, C-8), 155.6 (s, C-9), 106.6 (s, C-10), 123.5 (s, C-1'), 110.5 (d, C-2'), 145.6 (s, C-3'), 148.9 (s, C-4'), 114.4 (d, C-5'), 121.5 (d, C-6'), 60.8, 60.1, 56.3 and 56.0 (each q, 4×OCH<sub>3</sub>); EIMS *m/z* 374 [M]<sup>+</sup> (100), 359 (65), 345 (9), 331 (16), 316 (7), 301 (8), 285 (5), 273 (8), 245 (5), 217 (5), 181 (13), 164 (16), 151 (23), 135 (16), 121 (11), 109 (8), 93 (13), 77 (14), 69 (33).

**Artemetin (13):** yellow needles, C<sub>20</sub>H<sub>20</sub>O<sub>8</sub>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.49 (1H, s, H-8), 7.67 (1H, d, *J* = 2.0 Hz, H-2'), 6.98 (1H, d, *J* = 8.4 Hz, H-5'), 7.72 (1H, dd, *J* = 2.0, 8.8 Hz, H-6'), 12.6 (1H, *br s*, 5-OH), 3.85, 3.91, 3.95, 3.96 and 3.97 (each 3H, s, 5×OCH<sub>3</sub>); EIMS *m/z* 388 [M]<sup>+</sup> (100), 373 (58), 165 (15).

**Aucubin (14):** colorless syrup, C<sub>15</sub>H<sub>22</sub>O<sub>9</sub>; <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD) δ 4.94 (1H, d, *J* = 7.0 Hz, H-1), 6.30 (1H, dd, *J* = 2.0, 6.1 Hz, H-3), 5.08 (1H, dd, *J* = 2.0, 6.1 Hz, H-4), 2.65 (1H, m, H-5), 4.43 (1H, *br dd*, *J* = 1.6, 3.2 Hz, H-6), 5.76 (1H, *br s*, H-7), 2.89 (1H, *br t*, *J* = 7.4 Hz, H-9), 4.34 (1H, d, *J* = 15.3 Hz, H-10a), 4.16 (1H, d, *J* = 15.4 Hz, H-10b), 4.67 (1H, d, *J* = 8.0 Hz, H-1'), 3.22 (1H, t, *J* = 8.4 Hz, H-2'), 3.39 (1H, t, *J* = 8.6 Hz, H-3'), 3.30 (1H, overlap, H-4'), 3.28 (1H, m, H-5'), 3.85 (1H, dd, *J* = 1.2, 12.2 Hz, H-6'a), 3.64 (1H, dd, *J* = 5.4, 12.1 Hz, H-6'b); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>OD) δ 97.8 (d, C-1), 141.5 (d, C-3), 105.7 (d, C-4), 46.1 (d, C-5), 82.8 (d, C-6), 130.3 (d, C-7), 147.9 (s, C-8), 47.9 (d, C-9), 61.3 (t, C-10), 100.0 (d, C-1'), 74.8 (d, C-2'), 78.1 (d, C-3'), 71.5 (d, C-4'), 77.8 (d, C-5'), 62.6 (t, C-6'); Negative FABMS *m/z* 345 [M-H]<sup>+</sup> (5), 339 (90), 325 (100), 311 (61), 239 (4), 197 (4), 157 (3), 119 (2), 80 (15).

**Agnuside (15):** white powders, C<sub>22</sub>H<sub>26</sub>O<sub>11</sub>; <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD) δ 4.98 (1H, d, *J* = 7.4 Hz, H-1), 6.33 (1H, dd, *J* = 2.0, 6.0 Hz, H-3), 5.11 (1H, dd, *J* = 3.8, 6.1 Hz, H-4), 2.70 (1H, m, H-5), 4.46 (1H, *br dd*, *J* = 1.5, 3.6 Hz, H-6), 5.82 (1H, *br s*, H-7), 2.98 (1H, *br t*, *J* = 7.4 Hz, H-9), 5.08 (1H, d, *J* = 15.7 Hz, H-10a), 4.90 (1H, d, *J* = 15.7 Hz, H-10b), 4.70 (1H, d, *J* = 7.7 Hz, H-1'), 3.25 (1H, t, *J* = 9.0 Hz, H-2'), 3.39 (1H, t, *J* = 8.9 Hz, H-3'), 3.31 (1H, overlap, H-4'), 3.27 (1H, m, H-5'), 3.85 (1H, dd, *J* = 1.9, 12.2 Hz, H-6'a),

3.66 (1H, dd,  $J = 5.3, 12.0$  Hz, H-6'b), 7.90 (2H, dd,  $J = 2.0, 8.8$  Hz, H-3'' and H-7''), 6.83 (2H, dd,  $J = 2.0, 8.8$  Hz, H-4'' and H-6'');  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  98.0 (d, C-1), 141.7 (d, C-3), 105.5 (d, C-4), 46.2 (d, C-5), 82.8 (d, C-6), 132.5 (d, C-7), 142.8 (s, C-8), 48.8 (d, C-9), 63.6 (t, C-10), 100.3 (d, C-1'), 74.9 (d, C-2'), 77.9 (d, C-3'), 71.5 (d, C-4'), 78.1 (d, C-5'), 62.8 (t, C-6'), 167.8 (s, C-1''), 122.2 (s, C-2''), 132.9 (2C, d, C-3'' and C-7''), 116.3 (2C, d, C-4'' and C-6''), 163.6 (s, C-5''); Negative FABMS  $m/z$  466  $[\text{M-H}]^+$  (100), 447 (4), 404 (10), 384 (4), 339 (51), 325 (44), 250 (3), 116 (2), 94 (2).

**$\beta$ -Sitosterol (16)**: colorless needles,  $\text{C}_{29}\text{H}_{50}\text{O}$ ; EIMS  $m/z$  414  $[\text{M}]^+$  (100), 396 (54), 381 (32), 369 (14), 351 (14), 329 (36), 314 (12), 303 (46), 289 (10), 273 (34), 255 (43), 231 (21), 213 (32), 173 (17), 159 (34), 145 (38), 119 (30), 107 (43), 95 (39), 81 (42), 69 (39), 55 (56).

***p*-Hydroxybenzoic acid (17)**: white plates,  $\text{C}_7\text{H}_6\text{O}_3$ ;  $^1\text{H}$  NMR (400 MHz, Acetone- $d_6$ )  $\delta$  7.92 (2H, d,  $J = 8.6$  Hz, H-3 and H-7), 6.92 (2H, d,  $J = 8.6$  Hz, H-4 and H-6);  $^{13}\text{C}$  NMR (100 MHz, Acetone- $d_6$ )  $\delta$  169.0 (s, C-1), 122.3 (s, C-2), 132.8 (2C, d, C-3 and C-7), 116.0 (2C, d, C-4 and C-6), 162.7 (s, C-5); EIMS  $m/z$  138  $[\text{M}]^+$  (95), 121 (100), 110 (22), 93 (75), 81 (40), 74 (28), 65 (86), 53 (84).

***p*-Hydroxybenzoic acid glucose ester (18)**: white powders,  $\text{C}_{13}\text{H}_{16}\text{O}_8$ ;  $^1\text{H}$  NMR (400 MHz, Pyridine- $d_5$ )  $\delta$  8.24 (2H, d,  $J = 8.5$  Hz, H-3 and H-7), 7.15 (2H, d,  $J = 8.5$  Hz, H-4 and H-6), 6.65 (1H, d,  $J = 6.3$  Hz, H-1'), 4.37-4.54 (6H, m, H-2' to H-6');  $^{13}\text{C}$  NMR (100 MHz, Pyridine- $d_5$ )  $\delta$  165.8 (s, C-1), 121.2 (s, C-2), 132.9 (2C, d, C-3 and C-7), 116.2 (2C, d, C-4 and C-6), 164.0 (s, C-5), 96.4 (d, C-1'), 74.5 (d, C-2'), 78.7 (d, C-3'), 71.2 (d, C-4'), 79.6 (d, C-5'), 62.3 (t, C-6'); Negative FABMS  $m/z$  283  $[\text{M-OH}]^+$  (7), 245 (45), 212 (18), 186 (6), 116 (6), 79 (33).