**Table S1.** Identification of the differential secondary metabolites in *D. nobile* by UPLC-Q/TOF-MS.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| No. | RT | Adducts | Experimental | Theoretical | Molecular formula | Identification | MS/MS |
| 1 | 3.09 | [M+H]+ | 264.1969 | 264.1958 | C16H25NO2 | Dendrobine | 218.1910; 176.1441; 145.1014;105.0699; 70.0655. |
| 2 | 3.00 | M+ | 278.2118 | 278.2115 | C17H28NO2+ | *N*-Methyl-dendrobine | 250.2194;220.1355;187.0016;133.1005;105.0689;84.0807 |
| 3 | 3.32 | [M+H]+ | 280.1917 | 280.1907 | C16H25NO3 | 6-Hydroxydendrobine | 263.1884;220.1326;136.1118 |
| 4 | 3.43 | [M+H]+ | 294.2068 | 294.2064 | C17H27NO3 | Nobilonine | 249.1491;203.1425;175.1484;95.085 |
| 5 | 4.22 | [M]+ | 332.2597 | 332.2584 | C21H34NO2+ | N-Isopentenyl-dendrobine | 264.1965;218.1890;176.1431;69.0697 |
| 6 | 2.22 | [M+H]+ | 280.1905 | 280.1907 | C16H25NO3 | Dendrobine-*N*-oxide | 262.1797;218.1888;190.0745;133.0998;119.0855;79.0529 |
| 7 | 6.67 | [M-H]- | 233.1554 | 233.1619 | C15H22O2 | Confertifolin | NA |
| 8 | 6.59 | [M+H]+ | 223.2056 | 223.1983 | C15H26O | Elemol | NA |
| 9 | 3.91 | [M-H]- | 563.3060 | 563.3073 | C27H48O12 | Dendronobiloside A | 401.2472;113.0229;101.0231;71.0131;59.0131 |
| 10 | 4.07 | [M-H]- | 417.2482 | 417.2494 | C21H38O8 | Dendronobiloside B | 345.0209;191.0538;161.0454;123.0449;101.0238;89.0239 |
| 11 | 3.77 | [M-H]- | 559.2741 | 559.2760 | C27H44O12 | Dendronobiloside C | 179.0559;119.0347;89.0244;59.0135 |
| 12 | 3.51 | [M-H]- | 559.2730 | 559.2760 | C27H44O12 | Dendronobiloside D | 379.2067;179.0552;119.0338;89.0239;71.0142 |
| 13 | 3.02 | [M-H]- | 445.2073 | 445.2079 | C21H34O10 | Dendronobiloside E | 413.2148;281.1389;221.1548;162.0436;89.0240;59.0133 |
| 14 | 2.98 | [M-H]- | 413.2173 | 413.2181 | C21H34O8 | Dendromoniliside A | 350.1051;293.1501;265.1447;216.1370;101.0241;59.0132 |
| 15 | 1.98 | [M+Na]+ | 483.1829 | 483.1837 | C21H32O11 | Dendromoniliside B | 387.1636;321.1310;275.1248;203.0527;171.1129;105.0690 |
| 16 | 2.66 | [M+Na]+ | 467.1885 | 467.1888 | C21H32O10 | Dendromoniliside C | 305.1365;247.1288;173.1321;107.0492;57.0706 |
| 17 | 2.75 | [M-H]- | 445.2073 | 445.2079 | C21H34O10 | Dendromoniliside D | 385.1810;299.1479;265.1439;239.1656;181.1235 |
| 18 | 3.28 | [M-H]- | 415.2329 | 415.2337 | C21H36O8 | Dendroside A/C | 265.1444;101.0239;71.0142;59.0135 |
| 19 | 3.43 | [M-H]- | 415.233 | 415.2337 | C21H36O8 | Dendroside E | 267.1615;113.0238;85.0294;71.0142;59.0131 |
| 20 | 2.02 | [M-H]- | 429.2119 | 429.213 | C21H34O9 | Dendroside F  | 395.1842;354.0869;197.9128;137.0592;85.0289;59.0137 |
| 21 | 2.24 | [M-H]- | 445.2069 | 445.2079 | C21H34O10 | Dendroside G | 357.0653;283.1540;219.1390;113.0238;89.0241;59.0130 |

**Table S2.** The information of qRT-PCR primers.

|  |  |  |
| --- | --- | --- |
| Gene name |  | Primer |
| UGT73C3 | F | ACGAGGAGGTGAAGAAGTGG |
| R | CTCAGCACCTCTACCACCAA |
| UGT74F1 | F | TCCTCAGCCATCTTCGTCTC |
| R | ACCAGTTGCCAGAATCTCCA |
| UGT86A1 | F | GCCATTTTGCGTCGGATGATAA |
| R | CGAGGTGTCGGTGTCTTGAA |
| RhGT1 | F | CTTTGTCGCCCTCTTCAACC |
| R | CAAAGCAGAGGAAGACGACG |
| 5GT | F | CTTCAAAGGCCACCAATGCT |
| R | CTCATTGTAGGCGGAGAGGT |
| SB20O07.14 | F | TGAGTCCTACGCCTTCTGTG |
| R | TCTCGGCAGGTGTTGATGAT |
| AS | F | GTCACCTTCATCACCTTCGC |
| R | GCGGATGGAGACTATGGACA |
| PF3R | F | CGAACACGGCAGATGAGATG |
| R | TGCCTATCGAGCCAATCCAT |
| LOC110100769 | F | GAGGTGGAGAGCGAGTTTCT |
| R | TTGTTGACATGGTGCCGAAG |

Table S3. Molecular docking binding energies of sesquiterpene glycosides with UDP-glycosyltransferases (kcal/mol).

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Compounds | 5GT | AS | PF3R4 | RhGT1 | SB20O07.14 | UGT73C3 |
| Dendronobiloside A | -7.2 | -9.7 | -8.8 | -9.2 | -7.2 | -9.0 |
| Dendronobiloside B | -6.7 | -8.5 | -7.3 | -7.9 | -6.6 | -7.2 |
| Dendronobiloside C | -8.0 | -8.7 | -8.5 | -9.1 | -7.5 | -8.6 |
| Dendronobiloside D | -6.9 | -8.6 | -8.8 | -8.7 | -8.1 | -9.7 |
| Dendronobiloside E | -6.5 | -9.2 | -9.8 | -8.6 | -7.4 | -6.4 |
| Dendromoniliside A | -7.2 | -9.3 | -7.7 | -8.1 | -6.9 | -6.8 |
| Dendromoniliside B | -6.5 | -7.8 | -7.1 | -8.8 | -7.2 | -6.8 |
| Dendromoniliside C | -7.2 | -8.8 | -8.3 | -8.2 | -7.8 | -6.5 |
| Dendromoniliside D | -6.8 | -9.6 | -7.9 | -8.5 | -7.1 | -8.6 |
| Dendroside A | -6.9 | -8.8 | -8.9 | -8.4 | -6.6 | -9.1 |
| Dendroside C | -6.7 | -8.6 | -8.8 | -8.4 | -6.9 | -8.9 |
| Dendroside E | -6.9 | -8.6 | -8.2 | -8.3 | -7.4 | -9.0 |
| Dendroside F | -6.4 | -9.6 | -9.7 | -8.6 | -7.1 | -8.5 |
| Dendroside G | -7.1 | -8.4 | -8.1 | -8.9 | -7.7 | -7.0 |