**Supporting Information**

**Unveiling the phytochemical profile and antioxidant activity of roots from six *Polygala* species**

Yiyao Jinga, Benxiang Hub, Haiyue Jia,b, Fan Zhaoc, Bo Lia, Yao Luoa, Han Zhanga, Gang Zhanga, Yonggang Yana, Xiaolin Dangb, Bingyue Yanga,\*, Liang Penga,\*

*a Key Laboratory for Research of "Qin medicine" of Shaanxi Administration of Traditional Chinese Medicine, Shaanxi Qinling Application Development and Engineering Center of Chinese Herbal Medicine, College of Pharmacy, Shaanxi University of Chinese Medicine, Xi’an 712046, China*

*b Shaanxi Institute of International Trade & Commerce, Xi’an 712046, China*

*c Yulin No.5 Hospital, Yulin 719000, China*

\* Corresponding authors.

E-mail addresses: bingyyang@126.com (B.Y. Yang), ppengliang@126.com (L. Peng)

**Table S1** Mass spectrometric information and the post-acquisition strategies of the chemical components in six *Polygala* species detected by UPLC-Q-TOF-MS/MS

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Pe | RT | Molecular | Measured | Calculated | Errors | ESI-MSn | Identified |  |  |  |  |  |  |  |
| ak | (min) | formula | (m/z) | (m/z) |  | （-） | compounds | Class | PT | PS | PJ | PF | PA | PG |
| 1  | 6.743  | C13H8O5 | 243.0292  | 243.0299  | 0.0007  | MS2[243]161,93 | Gentitein  | Xan | - | - | - | - | √ | - |
| 2  | 4.353  | C14H64O29  | 257.0727  | 257.0528  | -0.0199  | MS2[257]223,205,195,163 | 1,3-Dihydroxyl-2-methoxanthone/1,7-Dihydroxy-3-methoxyxanthone\* | Xan | √ | - | - | √ | - | - |
| 3  | 0.379  | C14H10O6 | 273.0392  | 273.0405  | 0.0013  | MS2[273]175 | 1,3,7-Trihydroxy-2-methoxyxanthone | Xan | - | - | √ | √ | √ | √ |
| 4  | 3.086  | C15H12O6 | 287.0861  | 287.0561  | -0.0300  | MS2[287]272,259  | 1,5-Dihydroxy-2,3-dimethoxyxanthone /1,6-Dihydroxy-3,7-dimethoxyxanthone /3-Hydroxy-2,8-dimethoxyxanthone\* | Xan | √ | - | √ | - | - | - |
| 5  | 3.093  | C15H12O6 | 287.0546  | 287.0561  | 0.0015  | MS2[287]273,257  | 1,7-Dihydroxy-2,3-dimethoxyxanthone | Xan | √ | - | √ | - | - | - |
| 6  | 0.434  | C16H14O6 | 301.2064  | 301.0718  | -0.1346  | MS2[301]285,215,131 | 1-Hydroxy-3,6,7-trimethoxyxanthone /Onjixanthone I\* | Xan | - | √ | - | - | - | - |
| 7  | 7.919  | C15H12O7 | 303.1294  | 303.0510  | -0.0783  | MS2[303]273,258 | Onjixanthone II | Xan | √ | √ | - | - | - | - |
| 8  | 7.948  | C15H12O7 | 303.0503  | 303.0518  | 0.0015  | MS2[303]273,258 | 1,6,7-Trihydroxoy-2,3-dimethoxyxanthone | Xan | √ | √ | - | - | - | - |
| 9  | 7.969  | C15H12O7 | 303.0294  | 303.0520  | 0.0226  | MS2[303]273,223 | 1,3,7-Trihydroxy-2,6-dimethoxyxanthone | Xan | √ | √ | - | - | - | - |
| 10  | 3.434  | C16H14O7 | 317.1449  | 317.0686  | -0.0763  | MS2[317]287 | 6, 8-Dihydroxy-1, 2, 4-trimethoxyxanthone | Xan | √ | √ | √ | √ | √ | √ |
| 11  | 23.980  | C16H14O7 | 317.1603  | 317.0611  | -0.0992  | MS2[317]287 | 1,3-Dihydroxy-2,4,7-trimethoxyxanthone | Xan | √ | √ | √ | √ | √ | √ |
| 12  | 25.083  | C16H14O7 | 317.1765  | 317.0649  | -0.1116  | MS2[317]287 | 6,8-Dihydroxy-1,2,3-trimethoxyxanthone | Xan | √ | √ | √ | √ | √ | √ |
| 13  | 24.315  | C16H14O7 | 317.1931  | 317.0652  | -0.1279  | MS2[317]287 | 1,8-Dihydroxy-2,3,6-trimethoxyxanthone | Xan | √ | √ | √ | √ | √ | √ |
| 14  | 24.215  | C16H14O7 | 317.1593  | 317.0689  | -0.0904  | MS2[317]287 | 1,6-Dihydroxy-3,5,7-trimethoxyxanthone | Xan | √ | √ | √ | √ | √ | √ |
| 15  | 24.585  | C16H14O7 | 317.1049  | 317.0679  | -0.0370  | MS2[317]287 | 3,6-Dihydroxy-1,2,7-trimethoxyxanthone | Xan | √ | √ | √ | √ | √ | √ |
| 16  | 3.952  | C17H16O7 | 331.0813  | 331.0823  | 0.0011  | MS2[331]301,295，245,235,223 | 6-Hydroxy-1,2,3,7-tetramethoxyxanthone | Xan | √ | √ | - | - | √ | √ |
| 17  | 3.904  | C17H16O7 | 331.0821  | 331.0842  | 0.0021  | MS2[331]301,293 | 2-(3,4-Dimethoxyphenyl)-3,5,7-trihydroxychroman-4-one | Xan | √ | √ | - | - | √ | √ |
| 18  | 0.457  | C12H22O11 | 341.1059  | 341.1089  | 0.0030  | MS2[341]198,179,161 | Sucrose | Oth | √ | √ | √ | √ | √ | √ |
| 19  | 4.360  | C19H18O10  | 405.1887  | 405.0822  | -0.1065  | MS2[405]357,341,315,285 | Lancerin | Xan | √ | √ | - | - | - | - |
| 20  | 4.935  | C19H18O11 | 421.3305  | 421.0776  | -0.2529  | MS2[421]205 | Mangiferin or isomer | Xan | - | - | √ | - | - | - |
| 21  | 6.005  | C20H20O11 | 435.0954  | 435.0933  | -0.0021  | MS2[435]405,399 | 7-*O*-Methylmangiferin | Xan | √ | √ | √ | - | - | - |
| 22  | 0.651  | C19H20O12 | 439.1717  | 439.0882  | -0.0835  | MS2[439]306,195,191,179 | Hydroxy-dihydromangiferin | Xan | √ | √ | - | √ | √ | √ |
| 23  | 1.242  | C19H26O13 | 461.2418  | 461.1295  | -0.1123  | MS2[461]281,239,179,137 | Sibiricose A3 | Oli | √ | √ | √ | √ | √ | √ |
| 24  | 0.444  | C17H30O15 | 473.1611  | 473.1512  | -0.0099  | MS2[473]341,131 | Galactopyranosyl-galactopyranosyl-arabinose | Oth | - | √ | √ | √ | - | - |
| 25  | 6.117  | C20H28O13 | 475.0560  | 475.1452  | 0.0892  | MS2[476]439,355,315,219,120 | Polygalatenoside D | Oli | - | - | √ | - | - | √ |
| 26  | 6.026  | C18H32O16 | 503.2291  | 503.1618  | -0.0673  | MS2[503]491,315,272,205,190,163 | Maltotriose | Oth | √ | √ | √ | √ | - | √ |
| 27  | 2.411  | C22H30O14 | 517.1561  | 517.1563  | 0.0002  | MS2[517]437 | Arillanin B | Oli | - | √ | √ | √ | √ | - |
| 28  | 2.253  | C22H30O14 | 517.3157  | 517.3229  | 0.0073  | MS2[517]193,175,160 | Sibiricose A5 | Oli | √ | √ | √ | √ | √ | √ |
| 29  | 5.257  | C24H26O14 | 537.1612  | 537.1245  | -0.0367  | MS2[537]417,405,387 | Sibiricaxanthone A | Xan | √ | √ | √ | √ | √ | √ |
| 30  | 5.278  | C24H26O14 | 537.2345  | 537.1294  | -0.1051  | MS2[537]387,315,267 | Sibiricaxanthone B | Xan | √ | √ | √ | √ | √ | √ |
| 31  | 2.566  | C23H32O15 | 547.0785  | 547.1663  | 0.0878  | MS2[547]341,299,223,205,190，175 | Sibiricose A6 | Oli | √ | √ | √ | √ | √ | √ |
| 32  | 10.442  | C23H32O15 | 547.2416  | 547.1668  | -0.0748  | MS2[547]367,295,265, 205 | Sibiricose A1 | Oli | √ | √ | √ | √ | √ | √ |
| 33  | 3.520  | C24H34O15 | 561.6109  | 561.1820  | -0.4289  | MS2[562]562,559 | Sibiricose A2 | Oli | √ | √ | √ | - | - | - |
| 34  | 5.179  | C25H28O15 | 567.1400  | 567.1397  | -0.0003  | MS2[567]345,315,272 | Polygalaxanthone III | Xan | √ | √ | √ | - | √ | √ |
| 35  | 4.367  | C25H28O15 | 567.1360  | 567.1355  | -0.0005  | MS2[567]461,285 | Wubangziside C | Xan | √ | √ | √ | - | √ | - |
| 36  | 9.121  | C26H30O15 | 581.1942  | 581.1506  | -0.0436  | MS2[581]273,257 | Polygalaxanthone V | Xan | √ | √ | - | √ | √ | √ |
| 37  | 46.809  | C27H32O15 | 595.2945  | 595.1663  | -0.1282  | MS2[595]365 | Polygalaxanthone IV | Xan | √ | √ | √ | √ | √ | - |
| 38  | 9.690  | C27H32O16 | 611.2104  | 611.1612  | -0.0492  | MS2[611]303,287 | Polygalaxanthone VII | Xan | √ | √ | - | - | - | √ |
| 39  | 11.674  | C29H34O15 | 621.1539  | 621.1819  | 0.0280  | MS2[621]499,337 | ReinioseB/ C\* | Oli | √ | - | - | √ | - | √ |
| 40  | 11.814  | C29H34O15 | 621.5603  | 621.1825  | -0.3778  | MS2[621]598,595 | Reiniose C/B\* | Oli | √ | - | - | - | - | - |
| 41  | 7.592  | C29H34O16  | 637.2643  | 637.1774  | -0.0869  | MS2[637]547,529,461 | Sibiricaxanthone F | Xan | √ | √ | √ | - | √ | - |
| 42  | 10.597  | C30H36O16 | 651.1979  | 651.1937  | -0.0042  | MS2[651]443 | Unknown | Oli | - | √ | √ | √ | - | - |
| 43  | 10.735  | C30H36O16 | 651.2006  | 651.1925  | -0.0081  | MS2[651]443 | 3'-Sinapoyl-6-benzoylsucrose | Oli | √ | √ | - | - | √ | √ |
| 44  | 7.393  | C30H36O17 | 667.1933  | 667.1844  | -0.0089  | MS2[667]461,205 | Tenuifoliside B | Oli | √ | √ | √ | √ | √ | √ |
| 45  | 8.561  | C30H36O17 | 667.3523  | 667.1879  | -0.1644  | MS2[667]461,357,205,190,137 | Tenuifoliside B2 | Oli | - | - | √ | - | - | - |
| 46  | 2.732  | C36H56O12 | 679.3143  | 679.3694  | 0.0551  | MS2[679]547,503,461,277,167 | Tenuifiolin | Sap | √ | √ | √ | √ | - | √ |
| 47  | 11.900  | C31H38O17 | 681.2026  | 681.2031  | 0.0005  | MS2[681]443 | Tenuifoliside A | Oli | √ | √ | √ | √ | √ | √ |
| 48  | 8.763  | C32H38O17 | 693.3674  | 693.2036  | -0.1638  | MS2[693]675,601,175 | Glomeratose B | Oli | √ | √ | - | √ | √ | - |
| 49  | 8.903  | C32H38O17 | 693.3674  | 693.2036  | -0.1638  | MS2[693]675,601,175 | 3-(3,4-Dimethoxyphenylpropionyl)fructose (2→1) 6-(4-methoxycinnamyl) glucose | Oli | √ | √ | - | √ | √ | - |
| 50  | 16.069  | C32H40O18 | 711.2145  | 711.2136  | -0.0009  | MS2[711]701,665,543 | Telephiose C | Oli | √ | - | √ | - | - | √ |
| 51  | 8.298  | C33H40O18 | 723.1199  | 723.2146  | 0.0947  | MS2[723]547,493 | 1'-Sinapoyl-3'-feruloylsucrose | Oli | - | √ | - | - | - | - |
| 52  | 10.557  | C33H40O18 | 723.2148  | 723.2142  | -0.0006  | MS2[723]547,517，205 | Arillanin A | Oli | √ | √ | √ | √ | √ | √ |
| 53  | 5.921  | C33H40O18 | 723.2159  | 723.2221  | 0.0062  | MS2[723]485,335,237 | 3'-Feruloy-6-sinapoylsucrose or isomer | Oli | - | √ | - | √ | √ | - |
| 54  | 17.840  | C34H42O18 | 737.3286  | 737.2293  | -0.0993  | MS2[737]499 | Reiniose A | Oli | √ | - | - | √ | √ | √ |
| 55  | 2.372  | C35H36O18  | 743.1217  | 743.1829  | 0.0612  | MS2[743]731,727 | Unknown | Oli | √ | - | - | - | - | - |
| 56  | 5.932  | C34H40O19 | 751.3131  | 751.2086  | -0.1045  | MS2[751]465,427,315,272 | Glomeratose E | Oli | - | - | √ | √ | √ | √ |
| 57  | 9.363  | C34H42O19 | 753.1604  | 753.2247  | 0.0643  | MS2[753]631,581,273 | Sibiricose A4 | Oli | √ | √ | √ | √ | √ | √ |
| 58  | 9.366  | C34H42O19 | 753.2266  | 753.2258  | -0.0008  | MS2[753]611,553,545 | 3,6'-Disinapoylsucrose | Oli | - | √ | - | - | - | - |
| 59  | 14.308  | C35H44O19 | 767.4602  | 767.2399  | -0.2203  | MS2[767]529,265,223，205 | Tenuifolioside C | Oli | √ | √ | √ | √ | √ | √ |
| 60  | 8.858  | C36H44O20 | 795.2121  | 795.2347  | 0.0226  | MS2[795]753,629,509,465 | 3-Acetyl-3',6-O-disinapoylsucrose | Oli | - | - | √ | - | - | - |
| 61  | 16.145  | C37H44O20  | 807.2368  | 807.2341  | -0.0027  | MS2[807]237,175 | Unknown | Sap | √ | √ | - | - | - | - |
| 62  | 18.505  | C39H46O21 | 849.3311  | 849.3830  | 0.0519  | MS2[849]819,779 | Unknown | Oth | √ | - | - | √ | - | - |
| 63  | 24.443  | C40H46O21 | 861.2534  | 861.2459  | -0.0075  | MS2[861]473,257 | Unknown | Oli | √ | √ | - | √ | √ | - |
| 64  | 3.441  | C41H48O22 | 891.3143  | 891.2559  | -0.0584  | MS2[891]861,753 | Tenuifoliside E | Oli | - | - | √ | - | - | √ |
| 65  | 8.532  | C40H52O24  | 915.7362  | 915.2776  | -0.4586  | MS2[915]651,561 | Reiniose F | Oli | √ | √ | √ | √ | √ | √ |
| 66  | 1.441  | C48H76O20 | 971.4835  | 971.4857  | 0.0022  | MS2[971]962 | Polygalasaponin XIV or isomer | Sap | √ | - | √ | - | - | - |
| 67  | 6.153  | C48H78O20 | 973.4192  | 973.5008  | 0.0816  | MS2[973]861,794,771 | Polygalasaponin VI | Sap | - | - | √ | - | - | - |
| 68  | 16.640  | C53H84O24 | 1103.4472  | 1103.5269  | 0.0797  | MS2[1103]957 | PolygalasaponinXXVIII | Sap | - | - | √ | √ | √ | √ |
| 69  | 6.467  | C54H86O24 | 1117.5446  | 1117.5431  | -0.0015  | MS2[1118]1093,1074 | Polygalasapion XXIV | Sap | √ | - | - | - | - | √ |
| 70  | 18.372  | C54H64O29  | 1175.3846  | 1175.3455  | -0.0391  | MS2[1175]1104,999,879 | Glomeratose F | Oli | √ | √ | √ | - | √ | √ |
| 71  | 14.102  | C55H68O31  | 1223.3968  | 1223.3672  | -0.0296  | MS2[1223]1077 | Tenuifoliose S | Oli | √ | √ | √ | √ | - | - |
| 72  | 22.534  | C53H70O33 | 1233.4521  | 1233.3727  | -0.0794  | MS2[1233]1203 | TenuifolioseV | Oli | - | √ | - | - | - | - |
| 73  | 31.448  | C58H92O28 | 1235.4486  | 1235.5691  | 0.1205  | MS2[1235]1205 | Arilloside B | Sap | √ | √ | - | - | √ | - |
| 74  | 31.462  | C58H92O28 | 1235.4238  | 1235.5702  | 0.1464  | MS2[1235]1205 | Arillatanoside A | Sap | √ | √ | - | - | - | - |
| 75  | 31.483  | C58H92O28 | 1235.4286  | 1235.5736  | 0.1450  | MS2[1235]1205 | Polygalasaponin XXII | Sap | √ | √ | - | - | - | √ |
| 76  | 8.964  | C59H94O28 | 1249.5850  | 1249.5854  | 0.0004  | MS2[1250]1217,1158 | Onjisaponin TF | Sap | - | - | √ | - | - | - |
| 77  | 13.620  | C56H70O32 | 1253.3512  | 1253.3798  | 0.0286  | MS2[1253]1077 | Tenuifoliose T | Oli | - | - | √ | - | - | - |
| 78  | 14.593  | C56H70O32 | 1253.4512  | 1253.3766  | -0.0746  | MS2[1253]1077 | Tricornose K | Oli | √ | - | - | - | √ | √ |
| 79  | 45.505  | C59H92O29 | 1263.5950  | 1263.5646  | -0.0304  | MS2[1264]1232 | OnjisaponinMF | Sap | - | - | - | - | - | √ |
| 80  | 45.065  | C59H94O29 | 1265.4223  | 1265.3850  | -0.0373  | MS2[1265]1250,1174 | Polygalasaponin XVI/DesacylsenegasaponinB\* | Sap | - | - | - | - | √ | - |
| 81  | 15.321  | C57H70O32 | 1265.3843  | 1265.3766  | -0.0077  | MS2[1265]1119 | Tenuifoliose K | Oli | √ | √ | √ | - | √ | √ |
| 82  | 52.513  | C57H72O33 | 1283.3851  | 1283.3883  | 0.0032  | MS2[1283]1253,1245 | Tenuifoliose X | Oli | √ | - | - | √ | - | √ |
| 83  | 52.899  | C57H72O33 | 1283.0372  | 1283.3919  | 0.3547  | MS2[1283]1253,1245 | Senegose D | Oli | √ | - | - | √ | - | - |
| 84  | 11.729  | C58H72O33 | 1295.3878  | 1295.3872  | -0.0006  | MS2[1295]1165,1147,1087 | Senegose K | Oli | - | √ | - | - | - | - |
| 85  | 11.744  | C58H72O33 | 1295.3883  | 1295.3873  | -0.0010  | MS2[1295]1119 | TenuifolioseC2 | Oli | - | √ | - | - | - | - |
| 86  | 11.779  | C58H72O33 | 1295.3829  | 1295.3872  | 0.0043  | MS2[1295]1119,1087,795 | Tenuifoliose E/C\* | Oli | - | √ | - | - | - | - |
| 87  | 15.748  | C58H72O33 | 1295.4205  | 1295.3896  | -0.0309  | MS2[1295]1119 | Tenuifoliose C/E\* | Oli | √ | √ | - | - | - | - |
| 88  | 15.558  | C58H74O33 | 1297.4205  | 1297.4040  | -0.0165  | MS2[1297]1119,958 | Tricornose I | Oli | - | - | - | √ | √ | √ |
| 89  | 16.467  | C59H72O33 | 1307.5212  | 1307.3872  | -0.1340  | MS2 [1307]1265 | Tenuifoliose J | Oli | √ | √ | √ | - | √ | - |
| 90  | 20.185  | C59H72O33 | 1307.5463  | 1307.3883  | -0.1580  | MS2[1307]1161 | Tenuifoliose I | Oli | √ | √ | √ | - | √ | - |
| 91  | 17.573  | C61H96O30 | 1308.4688  | 1307.5908  | -0.8780  | MS2[1308]1130 | PolygalasaponinXXXVII | Sap | - | - | - | √ | - | - |
| 92  | 29.672  | C65H96O28 | 1323.3630  | 1323.6010  | 0.2380  | MS2[1323]1292 | Onjisaponin TH | Sap | - | √ | - | √ | √ | - |
| 93  | 16.218  | C59H74O34 | 1325.7630  | 1325.3983  | -0.3647  | MS2[1325]1149 | Tenuifoliose P、senegoseB/C\* | Oli | √ | - | - | - | - | - |
| 94  | 13.148  | C60H74O34 | 1337.4599  | 1337.3988  | -0.0611  | MS2[1337]1161,1295 | Tenuifoliose D | Oli | √ | √ | - | - | √ | - |
| 95  | 16.948  | C60H74O34 | 1337.3581  | 1337.3978  | 0.0397  | MS2[1337]1295 | Tenuifoliose B | Oli | √ | √ | - | - | - | - |
| 96  | 15.086  | C61H74O34 | 1349.3710  | 1349.3978  | 0.0268  | MS2[1349]1223 | Tenuifoliose H | Oli | √ | √ | - | - | - | - |
| 97  | 13.018  | C61H76O35 | 1367.3954  | 1367.4083  | 0.0129  | MS2[1367]1307,1205,1161 | Reiniose I | Oli | - | √ | - | - | - | - |
| 98  | 13.029  | C61H76O35 | 1367.4099  | 1367.4094  | -0.0005  | MS2[1367]1337 | Senegose A | Oli | - | √ | - | - | - | - |
| 99  | 18.048  | C61H76O35 | 1367.4773  | 1367.4139  | -0.0634  | MS2[1367]1337  | Tenuifoliose O | Oli | √ | √ | - | - | - | - |
| 100  | 19.103  | C62H76O35 | 1379.4282  | 1379.4083  | -0.0199  | MS2[1379]1203,1337 | Tenuifoliose A/A2\* | Oli | √ | √ | - | - | - | - |
| 101  | 18.422  | C64H100O32 | 1379.8894  | 1379.6114  | -0.2780  | MS2[1380]1307,1175 | Onjisaponin TG | Sap | √ | √ | - | - | - | - |
| 102  | 14.956  | C64H102O32  | 1381.6282  | 1381.6281  | -0.0001  | MS2[1381]1351 | Polygalasaponin XIX | Sap | √ | - | √ | - | - | √ |
| 103  | 16.834  | C64H102O33 | 1397.6061  | 1397.6315  | 0.0254  | MS2[1398]1235,1103 | Arilloside D | Sap | √ | - | - | - | - | - |
| 104  | 16.855  | C64H102O33 | 1397.6361  | 1397.6225  | -0.0136  | MS2[1398]1235,1103 | Polygalasaponin XXIX | Sap | √ | - | - | √ | - | - |
| 105  | 19.374  | C63H78O36 | 1409.4764  | 1409.4189  | -0.0575  | MS2[1409]1233 | OnjisaponinY | Sap | √ | √ | - | - | - | - |
| 106  | 19.495  | C63H78O36 | 1409.4484  | 1409.3832  | -0.0652  | MS2[1409]1221,1201 | Tenuifoliose N | Oli | √ | √ | - | - | - | - |
| 107  | 16.841  | C64H100O34 | 1411.7932  | 1411.6018  | -0.1914  | MS2[1412]1412 | Desacylsenegin III | Sap | √ | - | √ | √ | - | - |
| 108  | 23.751  | C69H102O31 | 1425.3450  | 1425.6327  | 0.2877  | MS2[1425]1395 | Senegasaponin B | Sap | - | - | - | √ | - | √ |
| 109  | 45.045  | C65H114O34 | 1427.3205  | 1427.6191  | 0.2986  | MS2[1427]1397 | Unknown | Sap | √ | √ | √ | - | √ | √ |
| 110  | 17.500  | C66H104O34 | 1439.6355  | 1439.6331  | -0.0024  | MS2[1440]1019 | Arilloside E | Sap | - | √ | √ | - | - | - |
| 111  | 12.787  | C67H78O35 | 1441.5328  | 1441.4246  | -0.1082  | MS2[1442]753,643 | Glomeratose G | Oli | - | - | √ | - | - | √ |
| 112  | 13.048  | C65H82O37 | 1453.4470  | 1453.4462  | -0.0008  | MS2[1453]1337,1307,1161,653 | Tenuifoliose M | Oli | √ | √ | √ | √ | - | - |
| 113  | 13.063  | C65H82O37 | 1453.4980  | 1453.4451  | -0.0529  | MS2[1453]1337,1307,1161,653 | Tenuifoliose Q | Oli | √ | √ | - | - | - | - |
| 114  | 32.266  | C68H80O35  | 1455.6439  | 1455.6312  | -0.0127  | MS2[1456]1429 | OnjisaponinTH | Sap | √ | √ | √ | - | √ | √ |
| 115  | 32.401  | C68H80O35  | 1455.6946  | 1455.4402  | -0.2544  | MS2[1456]1151 | SeneginII/onjisaponin G\* | Sap | √ | √ | √ | - | - | √ |
| 116  | 15.915  | C71H106O32 | 1469.4555  | 1469.6583  | 0.2028  | MS2[1469]1222 | Onjisaponin Z | Sap | - | √ | - | - | √ | √ |
| 117  | 10.914  | C67H106O35 | 1469.8177  | 1469.6437  | -0.1740  | MS2[1470]1308,1097,1061 | Polygalasaponin XXXXII | Sap | - | √ | √ | - | - | √ |
| 118  | 13.098  | C66H84O38 | 1483.0972  | 1483.4557  | 0.3585  | MS2[1483]1453,1337,1307,1161 | Tenuifoliose G | Oli | √ | √ | - | - | √ | - |
| 119  | 13.440  | C71H106O33 | 1485.4339  | 1485.6533  | 0.2194  | MS2[1485]1238,679,287 | Onjisaponin E | Sap | - | - | √ | - | √ | - |
| 120  | 15.065  | C67H84O38 | 1495.3064  | 1495.4557  | 0.1493  | MS2[1495]1349 | Tenuifoliose L | Oli | √ | - | - | - | - | - |
| 121  | 13.112  | C34H42O19 | 1507.3190  | 1507.4568  | 0.1378  | MS2[1507]1420,1354,1148 | 3,6’-Disinapoyl sucrose | Oth | - | √ | - | - | √ | √ |
| 122  | 12.607  | C69H108O36 | 1511.3190  | 1511.6437  | 0.3247  | MS2[1511]904 | Reinioside F | Sap | √ | - | √ | - | - | - |
| 123  | 19.331  | C67H86O39 | 1513.9326  | 1513.4667  | -0.4659  | MS2[1513]1367 | Tenuifoliose W | Oli | √ | - | √ | √ | √ | - |
| 124  | 18.857  | C68H86O39 | 1525.8528  | 1525.6668  | -0.1860  | MS2[1526]1337 | Onjisaponion TE | Oli | √ | √ | - | - | - | - |
| 125  | 14.992  | C68H86O39 | 1525.9490  | 1525.4662  | -0.4828  | MS2[1525]1495,1379,1349,1203 | Tenuifoliose F | Oli | √ | √ | √ | - | - | - |
| 126  | 14.688  | C74H110O34 | 1541.4565  | 1541.6800  | 0.2235  | MS2[1541]1511 | Onjisaponin H | Sap | √ | √ | √ | - | √ | - |
| 127  | 53.453  | C74H110O35 | 1557.1086  | 1557.1755  | 0.0669  | MS2[1557]1506,1436 | SenegasaponinA | Sap | √ | - | - | - | - | - |
| 128  | 41.322  | C75H112O35 | 1572.4461  | 1571.6906  | -0.7555  | MS2[1572]1558 | Onjisaponin B | Sap | √ | √ | - | √ | - | √ |
| 129  | 54.001  | C75H110O36 | 1585.2409  | 1585.2794  | 0.0385  | MS2[1585]1566,1516 | Unknown | Sap | √ | - | - | - | - | - |
| 130  | 22.698  | C75H112O36 | 1587.4208  | 1587.4861  | 0.0653  | MS2[1587]1559 | Onjisaponin F | Sap | √ | √ | √ | √ | - | √ |
| 131  | 43.810  | C75H112O36 | 1588.2409  | 1587.6855  | -0.5554  | MS2[1588]1456 | Onjisaponin Wg | Sap | √ | - | √ | √ | - | √ |
| 132  | 34.786  | C76H112O36 | 1599.6883  | 1599.6805  | -0.0078  | MS2[1600]962,889 | Onjisaponin Gg/K\* | Sap | √ | √ | - | - | - | - |
| 133  | 34.822  | C76H112O36 | 1599.9565  | 1599.6855  | -0.2710  | MS2[1600]962,889 | Onjisaponin K/Gg\* | Sap | √ | √ | - | - | - | - |
| 134  | 33.250  | C76H114O36  | 1601.3883  | 1601.7110  | 0.3227  | MS2[1601]1310 | Unknown | Sap | √ | - | - | √ | - | - |
| 135  | 38.441  | C76H114O37 | 1617.4275  | 1617.6966  | 0.2691  | MS2[1617]198.163,100 | Onjisaponin R | Sap | √ | √ | - | √ | √ | √ |
| 136  | 15.670  | C77H122O41 | 1629.2464  | 1629.6955  | 0.4491  | MS2[1629]1599 | Senegasaponin C | Sap | √ | - | - | - | - | √ |
| 137  | 44.216  | C77H116O37 | 1631.4275  | 1631.7117  | 0.2842  | MS2[1631]1498,1396,1324 | Onjisaponin O | Sap | - | √ | √ | √ | - | √ |
| 138  | 34.362  | C78H116O38 | 1659.5477  | 1659.1000  | -0.4477  | MS2[1660]1494,1296 | Polygalasaponin XLV | Sap | √ | - | √ | - | - | - |
| 139  | 43.291  | C79H118O38 | 1673.7212  | 1673.7228  | 0.0016  | MS2[1674]1542 | Polygalasaponin XXXII | Sap | √ | - | - | - | - | - |
| 140  | 43.366  | C79H118O38 | 1673.8225  | 1673.7223  | -0.1002  | MS2[1674]1486,1470 | Tenuifoside A | Sap | √ | - | - | - | - | - |
| 141  | 43.431  | C76H118O41 | 1686.0000  | 1685.7071  | -0.2929  | MS2[1686]1674 | Onjisaponin Ng | Sap | √ | √ | √ | - | - | - |
| 142  | 15.463  | C79H118O39 | 1689.3487  | 1689.7328  | 0.3841  | MS2[1689]1543,1325 | MyrtifoliosideA1 | Sap | √ | - | - | - | - | - |
| 143  | 38.915  | C80H120O39 | 1703.6912  | 1703.7329  | 0.0417  | MS2[1704]1588,851 | Senegin IV | Sap | √ | √ | - | √ | √ | √ |
| 144  | 39.086  | C80H120O39 | 1703.7315  | 1703.7334  | 0.0019  | MS2[1704]1588,851 | Onjisaponin A | Sap | √ | √ | - | √ | √ | √ |
| 145  | 43.996  | C81H120O40 | 1731.5855  | 1731.7278  | 0.1423  | MS2[1732]1600,1410 | Onjisaponin W | Sap | √ | √ | √ | - | - | √ |
| 146  | 44.046  | C81H120O40 | 1731.7270  | 1731.7283  | 0.0013  | MS2[1732]1600 | Onjisaponin Fg | Sap | √ | √ | - | - | - | √ |
| 147  | 32.665  | C81H122O40 | 1733.4855  | 1733.7440  | 0.2585  | MS2[1733]958 | Onjisaponin S | Sap | √ | √ | - | - | √ | √ |
| 148  | 30.394  | C82H122O41 | 1762.3658  | 1761.7388  | -0.6270  | MS2[1762]1618 | Onjisaponin V | Sap | √ | √ | - | - | - | √ |
| 149  | 30.650  | C82H122O41 | 1762.1863  | 1761.7384  | -0.4479  | MS2[1762]1618 | Onjisaponin Vg | Sap | √ | √ | - | - | - | √ |
| 150  | 34.267  | C83H124O42 | 1791.3788  | 1791.7489  | 0.3701  | MS2[1791]1567 | Onjisaponin T | Sap | √ | - | - | - | - | √ |
| 151  | 43.532  | C85H126O42 | 1817.9973  | 1817.7646  | -0.2327  | MS2[1818]1686 | Onjisaponin J | Sap | √ | √ | - | - | - | - |
| 152  | 37.184  | C86H128O43 | 1847.7829  | 1847.9955  | 0.2126  | MS2[1848]1780,1734 | Onjisaponin L | Sap | - | √ | - | - | - | - |
| 153  | 44.360  | C87H130O44 | 1877.6660  | 1877.7851  | 0.1191  | MS2[1877]1732 | Onjisaponin Sg | Sap | √ | √ | - | - | - | √ |
| 154  | 36.066  | C87H130O45 | 1893.5631  | 1893.7806  | 0.2175  | MS2[1894]1851 | Onjisaponin Ug/X\* | Sap | - | √ | - | - | - | - |

Note\*: trace characterized, Xan: Xanthones, Oli: Oligosaccharide esters, Sap: Saponins, Oth: Other chemicals, √: contain, -: exclusive.



**Figure S1** Screening of differential metabolites between PT and the remaining five *Polygala* species (A, PS vs. PT; B, PJ vs. PT; C, PF vs. PT; D,FG vs. PT; and E, PA vs. PT, the criteria was set to satisfy VIP values≥1, Fold change≥2, *p*≤0.05).