**Table S1. Information of *Rhodiola* samples**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **No.** | **Name** | **Genus** | **Collection part** | **Collection address** | **Acquisition time** |
| 1 | *R. crenulata* | *Rhodiola* L. of Crassulaceae | Roots and rhizomes | Yunan Province | 2020.06.27 |
| 2 | *R. kirilowii* | *Rhodiola* L. of Crassulaceae | Roots and rhizomes | Yunan Province | 2020.06.23 |
| 3 | *R. wallichiana* | *Rhodiola* L. of Crassulaceae | Roots and rhizomes | Yunan Province | 2020.06.24 |
| 4 | *R. fastigiate* | *Rhodiola* L. of Crassulaceae | Roots and rhizomes | Yunan Province | 2020.06.24 |
| 5 | *R. wallichiana var* | *Rhodiola* L. of Crassulaceae | Roots and rhizomes | Tibet Autonomous Region | 2020.09.09 |
| 6 | *R. sacra* | *Rhodiola* L. of Crassulaceae | Roots and rhizomes | Tibet Autonomous Region | 2020.08.02 |
| 7 | *R. himalensis* | *Rhodiola* L. of Crassulaceae | Roots and rhizomes | Tibet Autonomous Region | 2020.09.21 |
| 8 | *R. yunnanensis* | *Rhodiola* L. of Crassulaceae | Roots and rhizomes | Tibet Autonomous Region | 2020.11.22 |
| 9 | *R. tieghemii* | *Rhodiola* L. of Crassulaceae | Roots and rhizomes | Tibet Autonomous Region | 2021.07.26 |

**Table S2 Identification of the chemical compounds of *Rhodiola* species by UHPLC-Orbitrap Exploris 120**

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **No.** | **Identification** | **tR (min)** | **Observed Mass (Da)** | **Error (ppm)** | **Adduct** | **ESI-MS2** | **Formula** |
|
| 1 | Citric acida | 1.07 | 191.0200 | 1.44 | [M-H]- | 191.0201, 173.0095, 154.9987, 129.0197, 117.0196, 111.0090, 85.0297 | C6H8O7 |
| 2 | Gallic acida | 1.94 | 169.0143 | 0.32 | [M-H]- | 169.0144, 125.0245, 97.0296, 81.0346, 69.0347 | C7H6O5 |
| 3 | hydroxymethylfurfural | 2.04 | 125.0245 | 0.66 | [M-H]- | 125.0245, 107.0137, 97.0295, 81.0347, 69.0346 | C6H6O3 |
| 4 | *β*-glucogallin | 2.22 | 331.0676 | 1.60 | [M-H]- | 331.0677, 271.0465, 211.0253, 169.0146, 151.0039, 125.0246 | C13H16O10 |
| 5 | 4-(*β*-D-Glucopyranosyloxy)-3,5-dihydroxybenzoic acid or its isomer | 2.8 | 331.0676 | 1.60 | [M-H]- | 331.0677, 271.0464, 241.0356, 211.0252, 169.0145, 151.0047, 125.0246, 59.0140 | C13H16O10 |
| 6 | *p*-Hydroxybenzoic acid *β*-D-glucopyranoside | 3.84 | 299.0778 | 1.87 | [M-H]- | 299.0776, 239.0562, 228.1892, 179.0352, 151.0405, 137.0246, 89.0246, 59.0140 | C13H16O8 |
| 7 | Digalloyl-*β*-D-glucopyranose | 4.04 | 483.0791 | 2.22 | [M-H]- | 483.0792, 331.0678, 313.0570, 169.0146, 125.0247 | C20H20O14 |
| 8 | Protocatechuic acid | 4.08 | 153.0196 | 1.75 | [M-H]- | 153.0196, 109.0297, 81.0348 | C7H6O4 |
| 9 | Vanillic acid 4-*β*-D-glucoside | 4.15 | 329.0885 | 2.11 | [M-H]- | 329.0879, 228.1894, 167.0352, 152.0117, 123.0453, 108.0219, 59.0140 | C14H18O9 |
| 10 | *p*-Hydroxyphenacyl-*β*-D-glucopyranoside | 4.6 | 313.0936 | 2.27 | [M-H]- | 228.1791, 151.0403, 113.0246, 107.0505, 101.0247, 85.0297, 71.0140 | C14H18O8 |
| 11 | 2-(*β*-D-Glucopyranosyloxy)-1-(4-hydroxyphenyl) ethanone | 4.7 | 313.0935 | 1.95 | [M-H]- | 228.1732, 161.0460, 151.0403, 107.0505, 101.0247, 85.0297, 71.0140, 59.0140 | C14H18O8 |
| 12 | 3-*O*-*β*-D-glucopyranosylcaffeic acid | 5.64 | 341.0885 | 2.04 | [M-H]- | 341.0872, 179.0352, 135.0453, 119.0506 | C15H18O9 |
| 13 | 4-Hydroxybenzoic acid | 5.66 | 137.0246 | 1.33 | [M-H]- | 137.0246, 119.0141, 108.0218, 92.9201, 65.0400, 81.0347 | C7H6O3 |
| 14 | *p*-coumaric acid | 5.68 | 163.0403 | 1.43 | [M-H]- | 162.8394, 119.0505, 93.0350 | C9H8O3 |
| 15 | 1-*O*-*p-*Coumaroyl-*β*-D-glucopyranose | 5.7 | 325.0934 | 1.57 | [M-H]- | 163.0404, 119.0505, 93.0350 | C15H18O8 |
| 16 | Salidrosidea | 5.81 | 299.1142 | 1.92 | [M-H]- | 299.1136, 228.1894, 119.0504, 113.0246, 101.0246, 89.0246, 71.0140, 59.0140 | C14H20O7 |
| 17 | Crenulatina | 5.87 | 293.1246 | 1.65 | [M-H+HCOOH]- | 228.1946, 179.0563, 119.0353, 113.0609, 101.0246, 89.0246, 71.0140, 59.0140 | C11H20O6 |
| 18 | Gallocatechin | 6.43 | 305.0670 | 1.06 | [M-H]- | 305.0671, 228.1858, 219.0665, 179.0351, 137.0246, 125.0246 | C15H14O7 |
| 19 | 3-Methoxygallic acid | 6.46 | 183.0301 | 1.11 | [M-H]- | 183.0301, 168.0067, 124.0167 | C8H8O5 |
| 20 | Epigallocatechin | 6.53 | 305.0670 | 1.06 | [M-H]- | 305.0670, 228.1827, 219.0663, 167.0352, 137.0246, 125.0245 | C15H14O7 |
| 21 | Coniferin | 6.75 | 387.1303 | 1.84 | [M-H+HCOOH]- | 387.1302, 360.1292, 228.2005, 179.0715, 164.0482, 146.0378, 59.0140 | C16H22O8 |
| 22 | Ferulic acid | 6.75 | 193.0507 | 0.35 | [M-H]- | 193.0508, 178.0274, 149.0610, 134.0374, 61.9884 | C10H10O4 |
| 23 | 2‐(4‐Hydroxyphenyl) ‐ethyl‐*O*‐*β*‐D‐glucopyranosyl‐6‐*O*‐*β*‐D‐glucopyranoside or its isomer | 6.88 | 461.1674 | 2.06 | [M-H]- | 461.1675, 299.1140, 228.1894, 179.0562, 161.0457, 119.0351, 113.0246, 101.0246, 89.0246, 71.0140, 59.0140 | C20H30O12 |
| 24 | Catechina | 6.92 | 289.0724 | 2.21 | [M-H]- | 289.0720, 245.0825, 203.0715, 151.0403, 123.0453, 109.0296 | C15H14O6 |
| 25 | 4-*O*-*β*-D-glucopyranosylcaffeic acid | 7.04 | 341.0883 | 1.45 | [M-H]- | 341.0883, 179.0353, 135.0453 | C15H18O9 |
| 26 | Olivil-4-*O-β*-D-glucopyranoside | 7.39 | 537.1987 | 1.77 | [M-H]- | 375.1454, 360.1219, 345.0990, 312.1001, 257.0820, 228.1896, 189.0560 | C26H34O12 |
| 27 | *p*-coumaric acid 4-*O*-*β*-D-glucopyranoside | 7.46 | 325.0935 | 1.87 | [M-H]- | 228.1800, 163.0403, 119.0504 | C15H18O8 |
| 28 | 4-*O*-glucosyl-p-coumaric acid | 7.58 | 325.0936 | 2.18 | [M-H]- | 325.0933, 163.0404, 145.0297, 117.0348, 89.0247, 59.0140 | C15H18O8 |
| 29 | 6-*O*-Caffeoyl sophorose | 7.77 | 503.1416 | 1.93 | [M-H]- | 503.1415, 228.1958, 179.0352, 135.0453, 61.9885 | C21H28O14 |
| 30 | Triandrin | 7.79 | 357.1197 | 1.90 | [M-H+HCOOH]- | 357.1123, 195.0656, 136.0533, 59.0140 | C15H20O7 |
| 31 | Rhodioloside D | 7.83 | 395.1931 | 0.03 | [M-H+HCOOH]- | 349.1868, 266.9454, 228.1986, 179.0566, 161.0460, 119.0353, 89.0247, 59.0140 | C16H30O8 |
| 32 | Caffeic acida | 7.89 | 179.0353 | 1.78 | [M-H]- | 179.0352, 135.0453, 107.0504, 91.0555 | C9H8O4 |
| 33 | Procyanidin B1 | 8.53 | 577.1366 | 2.51 | [M-H]- | 577.1356, 451.1038, 425.0883, 407.0779, 289.0723, 245.0825, 161.0247, 125.0246, 109.0297 | C30H26O12 |
| 34 | Trigalloyl-*β*-D-glucopyranose | 8.59 | 635.0906 | 2.54 | [M-H]- | 635.0906, 483.0786, 465.0685, 313.0751, 295.0518, 211.0251, 169.0146, 125.0246 | C27H24O18 |
| 35 | Creoside II | 9.08 | 351.1667 | 2.10 | [M-H+HCOOH]- | 321.2056, 228.1954, 177.2400, 119.0352, 89.0248, 59.0141 | C14H26O7 |
| 36 | Epicatechina | 9.21 | 289.0723 | 1.86 | [M-H]- | 289.0722, 245.0824, 203.0715, 179.0353, 151.0403, 123.0454, 109.0297 | C15H14O6 |
| 37 | 5-*O*-Caffeoylshikimic acid | 9.49 | 335.0778 | 1.67 | [M-H]- | 305.5770, 282.7588, 228.1764, 134.0168, 86.4564, 77.1045 | C16H16O8 |
| 38 | 4,7,9,3',9'-Pentahydroxy-3-methoxyl-8-4'-oxyneolignan-3'-*O*-*β*-D-glucopyranoside or its isomer | 9.9 | 525.1992 | 2.76 | [M-H]- | 363.1453, 345.1345, 315.1244, 179.0717, 167.0716, 149.0610, 134.0376 | C25H34O12 |
| 39 | (+) ‐isolarisiresinol‐4′‐*O*‐*β*‐D‐glucopyranoside or its isomer | 10.05 | 521.2040 | 2.24 | [M-H]- | 359.1505, 344.1270, 313.1085, 283.0989, 241.0512, 109.0297 | C26H34O11 |
| 40 | Ethyl gallate | 10.52 | 197.0459 | 1.79 | [M-H]- | 197.0459, 169.0145, 162.8394, 124.0168 | C9H10O5 |
| 41 | 2-phenylethyl-6-*O*-*α*-L-arabinofuranosyl-*β*-D-glucopyranoside | 10.69 | 461.1675 | 1.04 | [M-H+HCOOH]- | 415.1614, 228.1966, 191.0563, 149.0457, 131.0350, 101.0246, 89.0246, 59.0140 | C19H28O10 |
| 42 | Catechin-(4*α*-8)-catechin-3′-*O*-gallate | 10.91 | 729.1472 | 1.50 | [M-H]- | 729.1465, 577.1347, 407.0779, 289.0723, 169.0146 | C37H30O16 |
| 43 | Epigallocatechin- (4*β* → 8) -epigallocatechin | 11.01 | 729.1469 | 1.09 | [M-H+HCOOH]- | 729.1469, 577.1356, 559.1025, 451.1040, 425.0867, 407.0781, 289.0724, 125.0247 | C37H30O16 |
| 44 | 3-(*β*-D-glucopyranuronosyloxy)-8-(*β*-D-glucopyranosyloxy)-4',5,7-trihydroxyflavone | 11.01 | 639.1208 | 0.80 | [M-H]- | 639.1210, 477.0696, 463.0888, 300.0277, 271.0250, 255.0302 | C27H28O18 |
| 45 | 6'-*O*-Galloylsalidrosidea | 11.08 | 451.1254 | 1.81 | [M-H]- | 451.1256, 313.0572, 271.0473, 211.0250, 169.0146, 151.0039, 124.0169 | C21H24O11 |
| 46 | (7*R*,8*S*)-Dihydrodehydrodiconiferyl-alcohol-3′-*O*-*β*-D-glucopyranoside | 11.09 | 507.1883 | 2.20 | [M-H]- | 507.1897, 477.1774, 345.1352, 327.1242, 315.1243, 300.1009, 167.0716 | C25H32O11 |
| 47 | Pharienside | 11.18 | 451.1255 | 2.03 | [M-H]- | 451.1255, 313.0564, 271.0457, 228.1986, 169.0147, 151.0040, 124.0168, 59.0140 | C21H24O11 |
| 48 | 3-*O*-Galloyl quinic acid butyl ester | 11.59 | 399.1305 | 2.08 | [M-H]- | 399.1304, 329.0521, 228.1794, 177.0407, 169.0145, 125.0246 | C18H24O10 |
| 49 | 3-(4-Hydroxyphenyl) acryloyl 6-*O*-galloyl-*β*-D-glucopyranoside | 11.71 | 477.1046 | 1.57 | [M-H]- | 477.1045, 313.0572, 169.0146, 163.0404, 125.0247, 119.0505, | C22H22O12 |
| 50 | (7*R*,8*S*)-Dihydrodehydrodiconiferyl-alcohol-4-*O*-*β*-D-glucopyranoside | 11.75 | 507.1884 | 2.40 | [M-H]- | 507.1907, 489.1775, 477.1774, 462.1534, 327.1243, 228.1814, 59.0140 | C25H32O11 |
| 51 | Herbacetin-3-*O*-*β*-D-glucopyranose-7-*O*-*β*-D-glucopyranose (1-3)-*α*-L-rhamnopyranoside | 11.81 | 771.2006 | 2.16 | [M-H]- | 463.0890, 300.0280, 271.0253, 243.0302, 139.0038 | C33H40O21 |
| 52 | Rhodionidin | 11.87 | 609.1478 | 2.78 | [M-H]- | 609.1474, 463.0892, 447.0943, 300.0277, 271.0253, 255.0303, 243.0304, 165.9910 | C27H30O16 |
| 53 | 4-Hydroxybenzyl-*β*-D-glucopyranoside | 11.96 | 285.0986 | 2.19 | [M-H]- | 285.0984, 228.1901, 209.0456, 197.0459, 138.0325 | C13H18O7 |
| 54 | Rhodalidin | 12.34 | 595.1321 | 2.76 | [M-H]- | 595.1320, 300.0280, 271.0253, 255.0302, 151.0039 | C26H28O16 |
| 55 | 1,2,3,6-Tetra-*O*-galloyl glucose | 12.59 | 787.1014 | 1.85 | [M-H]- | 787.1013, 635.0899, 617.0796, 465.0684, 313.0573, 193.0143, 169.0145, 125.0246 | C34H28O22 |
| 56 | 5′-Methoxy-8′-hydroxyl-(+)-isolariciresinol-4′-*O*-*β*-D-glucopyranoside | 12.69 | 567.2094 | 1.91 | [M-H]- | 567.1404, 415.1256, 359.1493, 329.1400, 228.1886, 175.0770 | C27H36O13 |
| 57 | Tecomin | 12.81 | 343.1042 | 2.17 | [M-H]- | 343.0452, 181.0509, 166.0274, 138.0324 | C15H20O9 |
| 58 | Epicatechingallate-(4*β*-8)-epicatechingallate | 12.9 | 881.1590 | 2.19 | [M-H]- | 881.1595, 729.1473, 577.1311, 559.1254, 407.0779, 269.0460, 169.0146, 125.0246 | C44H34O20 |
| 59 | 4,7,9,3′,9′-Pentahydroxy-3-methoxyl-8-4′-oxyneolignan | 12.92 | 363.1457 | 2.13 | [M-H]- | 327.1241, 315.1241, 221.0827, 179.0717, 167.0717, 149.0611, 134.0377, 122.0376 | C19H24O7 |
| 60 | Epicatechin gallatea | 13.14 | 441.0835 | 1.77 | [M-H]- | 441.0835, 289.0723, 245.0823, 169.0145, 125.0247, 109.0296 | C22H18O10 |
| 61 | Rhodioloside E | 13.17 | 511.2408 | 2.93 | [M-H]- | 465.2355, 311.0991, 228.1894, 191.0565, 149.0457, 131.0351, 89.0246, 59.0140 | C21H38O11 |
| 62 | Rosavina | 13.37 | 473.1676 | 2.69 | [M-H+HCOOH]- | 427.1613, 293.0882, 228.1761, 191.0566, 149.0459, 125.0247, 101.0249, 89.0246, 59.0140 | C20H28O10 |
| 63 | (*E*)-2-methyl-4-(((2*R*,3*R*,4*S*,5*S*,6*R*)-3,4,5-trihydroxy-6-(((3,4,5-trihydroxybenzoyl) oxy) methyl) tetrahydro-2H-pyran-2-yl) oxy) but-2-en-1-yl-3,4,5-trihydroxybenzoate or its isomer | 13.52 | 567.1371 | 2.75 | [M-H]- | 567.1369, 521.2047, 415.1253, 313.0576, 271.0466, 228.2009, 169.0146, 124.0168 | C25H28O15 |
| 64 | Lariciresinol-4-*O*-*β*-D-glucopyranoside | 13.56 | 521.2042 | 2.62 | [M-H]- | 521.2038, 457.1736, 359.1512, 329.1425, 311.0921, 228.1821, 169.0144, 101.0248, 59.0142 | C26H34O11 |
| 65 | Catechin gallatea | 13.6 | 441.0840 | 2.90 | [M-H]- | 441.0833, 331.0465, 289.0724, 245.0820, 169.0146, 151.0403, 125.0246, 61.9885 | C22H18O10 |
| 66 | Creoside IV | 13.82 | 395.1932 | 2.35 | [M-H]- | 395.1931, 263.1505, 161.0460, 131.0353, 113.0247, 101.0247, 71.0140, 59.0140 | C17H32O10 |
| 67 | Procyanidin B2 | 13.97 | 577.1367 | 2.69 | [M-H]- | 577.1360, 451.1040, 425.0889, 407.0779, 289.0722, 245.0824, 161.0246, 125.0246 | C30H26O12 |
| 68 | Isoquercitrina | 14.11 | 463.0892 | 2.16 | [M-H]- | 463.0890, 300.0280, 271.0253, 255.0303, 242.0299, 151.0038 | C21H20O12 |
| 69 | 5-Methoxy-(+)-isolariciresinol-4'-O-β-D-glucopyranoside | 14.26 | 551.2143 | 1.63 | [M-H]- | 505.2664, 359.1503, 208.0743, 149.0457, 89.0245 | C27H36O12 |
| 70 | Rhodioloside A | 14.32 | 347.1721 | 2.76 | [M-H]- | 347.1719, 228.1887, 167.1080, 119.0351, 101.0247, 89.0246, 71.0140, 59.0140 | C16H28O8 |
| 71 | luteolin 7-*O*-*β*-D-glucoside | 14.33 | 447.0945 | 2.72 | [M-H]- | 447.0939, 285.0406, 256.0376, 228.2010, 151.0038, 133.0299 | C21H20O11 |
| 72 | Creoside III | 14.38 | 383.1357 | 2.47 | [M-H]- | 383.1353, 228.1971, 203.0715, 137.0246, 92.0270, 59.0140 | C18H24O9 |
| 73 | 1,2,3,4,6-Penta-*O*-galloyl glucose | 15.36 | 939.1124 | 1.59 | [M-H]- | 939.1125, 769.0909, 617.0793, 465.0690, 228.1890, 169.0145, 125.0246 | C41H32O26 |
| 74 | 3,4,5-trimethoxycinnamic acida | 15.44 | 237.0772 | 1.49 | [M-H]- | 237.0773, 228.1890, 193.0873, 178.0637, 150.0324, 138.0325, 124.0167 | C12H14O5 |
| 75 | Salidroside-3',6'-gallate | 15.55 | 603.1370 | 2.42 | [M-H]- | 603.1367, 451.1254, 433.1138, 313.0573, 169.0145, 124.0168 | C28H28O15 |
| 76 | Rosin | 15.85 | 341.1252 | 3.41 | [M-H+HCOOH]- | 341.1223, 228.1976, 202.8174, 161.0460, 133.0664, 101.0249, 71.0143 | C15H20O6 |
| 77 | Quercitrina | 16.1 | 447.0947 | 3.17 | [M-H]- | 447.0942, 284.0332, 255.0305, 227.0352, 143.1398 | C21H20O11 |
| 78 | Sachalinoside A | 16.16 | 483.1886 | 2.93 | [M-H]- | 483.1884, 271.0491, 211.0253, 169.0146, 124.0168 | C23H32O11 |
| 79 | Rhodiolgidin | 16.75 | 625.1425 | 2.36 | [M-H]- | 625.1407, 317.0309, 299.02, 228.1820, 166.9989, 139.0040, 111.0091 | C27H30O17 |
| 80 | 3,5-Digalloylcatechin | 16.97 | 593.0953 | 2.73 | [M-H]- | 593.0951, 441.0833, 423.0731, 289.0720, 271.0616, 169.0145, 125.0246 | C29H22O14 |
| 81 | Gossypetin-7-*O*-*α*-rhamnopyranoside | 17.01 | 463.0894 | 2.59 | [M-H]- | 463.0878, 317.0309, 194.9940, 166.9989, 139.0039, 111.0090 | C21H20O12 |
| 82 | Epicatechin-(4*β*-8) epicatechingallate | 17.1 | 729.1479 | 2.46 | [M-H]- | 729.1476, 577.1295, 451.1041, 407.0782, 289.0724, 125.0246 | C37H30O16 |
| 83 | Procyanidin B 2 3′-*O*-gallate | 17.2 | 729.1476 | 2.05 | [M-H]- | 729.1476, 577.1307, 451.1044, 425.0887, 407.0778, 289.0722, 169.0145, 125.0246 | C37H30O16 |
| 84 | 2-(4-Hydroxyphenyl) ethyl 3,4,5-trihydroxybenzoate | 17.51 | 289.0726 | 2.90 | [M-H]- | 289.0722, 228.1814, 169.0146, 125.0246, 107.0141 | C15H14O6 |
| 85 | Kaempferol-7-*O*-neohesperidoside | 17.93 | 593.1529 | 2.88 | [M-H]- | 593.1526, 285.0409, 257.0458, 229.0511, 185.0608 | C27H30O15 |
| 86 | Nicotiflorina | 18.16 | 593.1526 | 2.37 | [M-H]- | 593.1510, 285.0410, 257.0461, 229.0509 | C27H30O15 |
| 87 | Catechingallate-(4*α*-8)- catechingallate | 18.42 | 881.1584 | 1.51 | [M-H]- | 881.1605, 729.1476, 577.1152, 559.1253, 541.1147, 407, 0779, 289.0719, 169.0145, 125.0245 | C44H34O20 |
| 88 | Afzelina | 18.5 | 431.0991 | 1.69 | [M-H]- | 431.0991, 285.0406, 255.0303, 227.0353 | C21H20O10 |
| 89 | Luteolin-7-*O*-*α*-L-rhamnoside | 18.59 | 431.0994 | 2.39 | [M-H]- | 431.0992, 285, 0406, 255.0302, 227.0353 | C21H20O10 |
| 90 | Quercetin-3-*O*-glucuronide | 18.99 | 477.0689 | 3.01 | [M-H]- | 477.0680, 301.0356, 228.1830 | C21H18O13 |
| 91 | Rhodiosina | 19.26 | 609.1483 | 3.60 | [M-H]- | 301.0356, 255.0305, 201.0559 | C27H30O16 |
| 92 | Herbacetina | 19.28 | 303.0508 | 2.87 | [M+H]+ | 303.0512, 228.2104, 169.0140, 121.0290 | C15H10O7 |
| 93 | Kaempferol 3,7-digalactoside | 19.49 | 609.1475 | 2.29 | [M-H]- | 301.0359, 283.0261 | C27H30O16 |
| 94 | Rhodionin | 19.75 | 447.0946 | 2.94 | [M-H]- | 447.0846, 301.0357 | C21H20O11 |
| 95 | Eriodictyola | 19.81 | 287.0568 | 2.40 | [M-H]- | 287.0565, 228.1763, 151.0039, 135.0453, 107.0140, 83.0140, 65.0034 | C15H12O6 |
| 96 | Rhodiolatuntoside | 19.85 | 447.0941 | 1.82 | [M-H]- | 447.0944, 301.0358, 255.0313, 139.0040 | C21H20O11 |
| 97 | myrtenol-*O*-*α*-L-pyran arabinose (1-6)-*O*-*β*-D-glucopyranoside | 20.04 | 491.2144 | 1.98 | [M-H+HCOOH]- | 445.2088, 313.1658, 228.1986, 149.0457, 131.0352, 101.0245, 59.0140 | C21H34O10 |
| 98 | Sachaloside Ⅱ | 20.1 | 445.2090 | 2.43 | [M-H]- | 445.2088, 313.1660, 233.0671, 191.0563, 161.0457, 13.0351, 101.0246, 71.0140, 59.0140 | C21H34O10 |
| 99 | Crenuloside | 20.75 | 593.1529 | 2.88 | [M-H]- | 285.0408, 228.2016, 151.0036 | C27H30O15 |
| 100 | Quercetina | 21.06 | 301.0360 | 2.07 | [M-H]- | 301.0357, 178.9989, 151.0038, 121.0296, 107.0140, 65.0034 | C15H10O7 |
| 101 | Luteolina | 21.26 | 285.0409 | 1.54 | [M-H]- | 285.0407, 175.0399, 151.0039, 133.0296, 107.0140 | C15H10O6 |
| 102 | Kaempferol-7-*O*-*α*-L-rhamnoside | 22.12 | 431.0998 | 3.32 | [M-H]- | 431.0990, 2850405, 257.0460, 151.0038, 136.0162, 107.0140 | C21H20O10 |
| 103 | Rhodiooctanoside | 22.32 | 423.2244 | 1.96 | [M-H]- | 423.2242, 291.1817, 228.1816, 191.0050, 161.0457, 131.0351, 113.0246, 101.0246, 85.0297, 71.0139, 59.0140 | C19H36O10 |
| 104 | Kenposide A | 22.49 | 493.2300 | 3.32 | [M-H+HCOOH]- | 447.2249, 228.1890, 191.0564, 149.0457, 131.0352, 101.0246, 89.0246 | C21H36O10 |
| 105 | Rhodioloside C | 22.65 | 493.2298 | 1.52 | [M-H]- | 523.1139, 447.2246, 228.1792, 191.0567, 149.0457, 131.0351, 101.0245, 89.0247, 71.0140, 59.0140 | C22H38O12 |
| 106 | Rhodioloside B | 22.74 | 493.2303 | 2.54 | [M-H]- | 447.2241, 228.1891, 191.0567, 149.0457, 131.0352, 89.0246, 59.0140 | C22H38O12 |
| 107 | Creoside V | 24.73 | 495.2463 | 1.96 | [M-H+HCOOH]- | 449.2401, 317.1977, 228.1805, 131.0353, 101.0246, 89.0246, 71.0140 | C21H38O10 |
| 108 | Kaempferola | 25.15 | 285.0410 | 1.89 | [M-H]- | 285.0409, 228.1891, 151.0036 | C15H10O6 |
| 109 | 6-Feruloyloxyhexanoic acid | 27.29 | 307.1196 | 2.89 | [M-H]- | 307.1194, 228.1893, 193.0509, 175.0404, 160.0169, 134.0376, 85.0662 | C16H20O6 |

a Identification by reference compounds.

**Table S3 Distribution of identified chemical compounds in *Rhodiola* species**

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **No.** | **Identification** | ***Rhodiola species*** | | | | | | | | |
| ***R. crenulata*** | ***R. tieghemii*** | ***R. wallichiana*** | ***R.***  ***fastigiate*** | ***R. sacra*** | ***R.***  ***wallichiana var*** | ***R. yunnanensis*** | ***R. himalensis*** | ***R. kirilowii*** |
| 1 | Citric acida | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| 2 | Gallic acida |  | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| 3 | hydroxymethylfurfural |  | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| 4 | *β*-glucogallin | ✓ |  |  |  | ✓ | ✓ | ✓ |  |  |
| 5 | 4-(*β*-D-Glucopyranosyloxy)-3,5-dihydroxybenzoic acid or its isomer | ✓ |  |  |  |  |  |  |  |  |
| 6 | *p*-Hydroxybenzoic acid *β*-D-glucopyranoside | ✓ |  |  |  |  |  |  | ✓ |  |
| 7 | Digalloyl-*β*-D-glucopyranose | ✓ |  |  |  |  |  |  |  |  |
| 8 | Protocatechuic acid | ✓ |  |  |  |  |  |  |  |  |
| 9 | Vanillic acid 4-*β*-D-glucoside | ✓ |  |  |  |  |  |  |  |  |
| 10 | *p*-Hydroxyphenacyl-*β*-D-glucopyranoside | ✓ |  |  |  |  |  |  |  | ✓ |
| 11 | 2-(*β*-D-Glucopyranosyloxy)-1-(4-hydroxyphenyl) ethanone | ✓ |  |  |  |  |  |  |  |  |
| 12 | 3-*O*-*β*-D-glucopyranosylcaffeic acid | ✓ | ✓ | ✓ |  | ✓ |  |  | ✓ |  |
| 13 | 4-Hydroxybenzoic acid | ✓ |  | ✓ |  | ✓ | ✓ | ✓ |  |  |
| 14 | *p*-coumaric acid | ✓ |  |  |  |  |  |  |  |  |
| 15 | 1-*O*-*p-*Coumaroyl-*β*-D-glucopyranose | ✓ |  |  |  |  |  |  | ✓ |  |
| 16 | Salidrosidea | ✓ |  | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| 17 | Crenulatina | ✓ |  | ✓ | ✓ |  |  | ✓ | ✓ | ✓ |
| 18 | Gallocatechin |  | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| 19 | 3-Methoxygallic acid | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| 20 | Epigallocatechin |  | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| 21 | Coniferin | ✓ |  |  | ✓ | ✓ | ✓ | ✓ | ✓ |  |
| 22 | Ferulic acid |  |  | ✓ |  |  | ✓ | ✓ |  | ✓ |
| 23 | 2‐(4‐Hydroxyphenyl) ‐ethyl‐*O*‐*β*‐D‐glucopyranosyl‐6‐*O*‐*β*‐D‐glucopyranoside or its isomer | ✓ |  |  |  | ✓ |  |  |  | ✓ |
| 24 | Catechina |  |  |  |  | ✓ |  |  |  |  |
| 25 | 4-*O*-*β*-D-glucopyranosylcaffeic acid | ✓ |  |  |  |  |  |  |  |  |
| 26 | Olivil-4-*O-β*-D-glucopyranoside | ✓ | ✓ |  | ✓ | ✓ |  | ✓ | ✓ | ✓ |
| 27 | *p*-coumaric acid 4-*O*-*β*-D-glucopyranoside | ✓ | ✓ |  | ✓ | ✓ |  | ✓ | ✓ | ✓ |
| 28 | 4-*O*-glucosyl-p-coumaric acid | ✓ |  |  |  |  |  |  |  |  |
| 29 | 6-*O*-Caffeoyl sophorose | ✓ |  |  |  |  |  |  |  |  |
| 30 | Triandrin |  | ✓ |  |  |  | ✓ | ✓ | ✓ | ✓ |
| 31 | Rhodioloside D | ✓ |  |  |  | ✓ | ✓ | ✓ |  | ✓ |
| 32 | Caffeic acida | ✓ |  |  |  |  |  |  | ✓ | ✓ |
| 33 | Procyanidin B1 | ✓ |  |  |  | ✓ |  |  |  |  |
| 34 | Trigalloyl-*β*-D-glucopyranose | V |  |  |  | ✓ |  |  |  |  |
| 35 | Creoside II | ✓ |  |  | ✓ | ✓ | ✓ |  |  |  |
| 36 | Epicatechina | ✓ |  |  |  | ✓ |  |  | ✓ |  |
| 37 | 5-*O*-Caffeoylshikimic acid | ✓ |  |  |  |  |  |  |  |  |
| 38 | 4,7,9,3',9'-Pentahydroxy-3-methoxyl-8-4'-oxyneolignan-3'-*O*-*β*-D-glucopyranoside or its isomer | ✓ |  | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| 39 | (+) ‐isolarisiresinol‐4′‐*O*‐*β*‐D‐glucopyranoside or its isomer | ✓ | ✓ |  |  | ✓ |  |  |  | ✓ |
| 40 | Ethyl gallate | ✓ |  | ✓ |  | ✓ |  |  | ✓ | ✓ |
| 41 | 2-phenylethyl-6-*O*-*α*-L-arabinofuranosyl-*β*-D-glucopyranoside | ✓ | ✓ |  | ✓ | ✓ |  | ✓ | ✓ | ✓ |
| 42 | Catechin-(4*α*-8)-catechin-3′-*O*-gallate |  |  |  |  | ✓ |  |  |  |  |
| 43 | Epigallocatechin-(4*β* → 8)-epigallocatechin | ✓ | ✓ |  |  |  |  |  |  |  |
| 44 | 3-(*β*-D-glucopyranuronosyloxy)-8-(*β*-D-glucopyranosyloxy)-4',5,7-trihydroxyflavone |  |  | ✓ |  |  | ✓ |  | ✓ |  |
| 45 | 6'-*O*-Galloylsalidrosidea | ✓ |  |  | ✓ |  |  |  | ✓ | ✓ |
| 46 | (7*R*,8*S*)-Dihydrodehydrodiconiferyl-alcohol-3′-*O*-*β*-D-glucopyranoside | ✓ |  | ✓ |  | ✓ |  |  |  | ✓ |
| 47 | Pharienside | ✓ |  |  | ✓ |  |  | ✓ | ✓ |  |
| 48 | 3-*O*-Galloyl quinic acid butyl ester | ✓ |  |  | ✓ |  |  |  |  |  |
| 49 | 3-(4-Hydroxyphenyl)acryloyl 6-*O*-galloyl-*β*-D-glucopyranoside | ✓ |  |  |  |  |  |  | ✓ |  |
| 50 | (7*R*,8*S*)-Dihydrodehydrodiconiferyl-alcohol-4-*O*-*β*-D-glucopyranoside | ✓ |  |  | ✓ |  |  |  |  |  |
| 51 | Herbacetin-3-*O*-*β*-D-glucopyranose-7-*O*-*β*-D-glucopyranose(1-3)-*α*-L-rhamnopyranoside | ✓ |  |  |  |  |  |  |  |  |
| 52 | Rhodionidin | ✓ |  |  | ✓ |  |  | ✓ |  |  |
| 53 | 4-Hydroxybenzyl-*β*-D-glucopyranoside | ✓ |  |  |  |  |  |  |  |  |
| 54 | Rhodalidin | ✓ |  |  |  |  |  |  |  |  |
| 55 | 1,2,3,6-Tetra-*O*-galloyl glucose | ✓ |  |  | ✓ |  |  |  | ✓ |  |
| 56 | 5′-Methoxy-8′-hydroxyl-(+)-isolariciresinol-4′-*O*-*β*-D-glucopyranoside | ✓ | ✓ |  |  | ✓ |  | ✓ |  |  |
| 57 | Tecomin | ✓ |  |  | ✓ |  |  |  |  |  |
| 58 | Epicatechingallate-(4*β*-8)-epicatechingallate | ✓ |  |  | ✓ | ✓ |  |  |  |  |
| 59 | 4,7,9,3′,9′-Pentahydroxy-3-methoxyl-8-4′-oxyneolignan |  |  |  |  |  | ✓ |  | ✓ |  |
| 60 | Epicatechin gallatea |  |  | ✓ |  | ✓ |  | ✓ |  |  |
| 61 | Rhodioloside E | ✓ |  |  |  |  | ✓ |  |  | ✓ |
| 62 | Rosavina | ✓ |  |  |  |  |  | ✓ |  | ✓ |
| 63 | (*E*)-2-methyl-4-(((2*R*,3*R*,4*S*,5*S*,6*R*)-3,4,5-trihydroxy-6-(((3,4,5-trihydroxybenzoyl) oxy) methyl) tetrahydro-2H-pyran-2-yl) oxy) but-2-en-1-yl-3,4,5-trihydroxybenzoate or its isomer | ✓ |  |  |  |  |  |  |  |  |
| 64 | Lariciresinol-4-*O*-*β*-D-glucopyranoside | ✓ |  | ✓ |  | ✓ | ✓ |  |  | ✓ |
| 65 | Catechin gallatea | ✓ |  |  |  | ✓ |  |  |  |  |
| 66 | Creoside IV | ✓ |  |  |  |  |  | ✓ |  | ✓ |
| 67 | Procyanidin B2 | ✓ |  |  |  | ✓ |  |  |  |  |
| 68 | Isoquercitrina | ✓ |  |  |  | ✓ |  |  |  |  |
| 69 | 5-Methoxy-(+)-isolariciresinol-4'-O-β-D-glucopyranoside |  |  | ✓ |  |  |  |  |  |  |
| 70 | Rhodioloside A | ✓ |  |  |  |  |  |  |  | ✓ |
| 71 | luteolin 7-*O*-*β*-D-glucoside | ✓ |  |  |  |  |  |  | ✓ | ✓ |
| 72 | Creoside III | ✓ |  |  |  |  |  |  |  |  |
| 73 | 1,2,3,4,6-Penta-*O*-galloyl glucose | ✓ |  |  |  |  |  |  |  |  |
| 74 | 3,4,5-trimethoxycinnamic acida | ✓ |  |  | ✓ |  |  |  | ✓ | ✓ |
| 75 | Salidroside-3',6'-gallate | ✓ |  |  |  |  |  |  |  |  |
| 76 | Rosin | ✓ |  |  | ✓ |  |  |  |  | ✓ |
| 77 | Quercitrina | ✓ |  |  |  | ✓ |  |  | ✓ |  |
| 78 | Sachalinoside A | ✓ |  |  |  |  |  |  |  |  |
| 79 | Rhodiolgidin |  |  |  |  | ✓ |  | ✓ |  |  |
| 80 | 3,5-Digalloylcatechin | ✓ |  |  |  |  |  |  |  |  |
| 81 | Gossypetin-7-*O*-*α*-rhamnopyranoside | ✓ |  |  |  | ✓ |  |  |  |  |
| 82 | Epicatechin-(4*β*-8) epicatechingallate | ✓ |  |  |  | ✓ |  |  |  |  |
| 83 | Procyanidin B 2 3′-*O*-gallate | ✓ |  |  |  |  |  |  |  |  |
| 84 | 2-(4-Hydroxyphenyl) ethyl 3,4,5-trihydroxybenzoate | ✓ |  |  |  | ✓ |  | ✓ |  |  |
| 85 | Kaempferol-7-*O*-neohesperidoside | ✓ |  |  |  |  |  |  |  |  |
| 86 | Nicotiflorina | ✓ |  |  |  |  |  |  |  |  |
| 87 | Catechingallate-(4*α*-8)- catechingallate | ✓ |  |  | ✓ | ✓ |  |  |  |  |
| 88 | Afzelina | ✓ |  |  |  |  |  | ✓ |  |  |
| 89 | Luteolin-7-*O*-*α*-L-rhamnoside | ✓ |  |  |  |  |  |  |  |  |
| 90 | Quercetin-3-*O*-glucuronide | ✓ |  |  |  |  |  | ✓ | ✓ |  |
| 91 | Rhodiosina | ✓ |  |  |  | ✓ |  | ✓ |  |  |
| 92 | Herbacetina | ✓ |  |  |  |  |  |  |  |  |
| 93 | Kaempferol 3,7-digalactoside |  |  |  |  |  |  |  |  | ✓ |
| 94 | Rhodionin | ✓ |  | ✓ |  | ✓ |  | ✓ | ✓ |  |
| 95 | Eriodictyola | ✓ |  |  | ✓ | ✓ |  | ✓ | ✓ |  |
| 96 | Rhodiolatuntoside | ✓ |  | ✓ |  | ✓ |  | ✓ | ✓ |  |
| 97 | myrtenol-*O*-*α*-L-pyran arabinose (1-6)-*O*-*β*-D-glucopyranoside | ✓ |  | ✓ | ✓ | ✓ |  | ✓ | ✓ |  |
| 98 | Sachaloside Ⅱ | ✓ |  |  |  |  |  | ✓ | ✓ |  |
| 99 | Crenuloside | ✓ |  |  |  |  |  | ✓ |  |  |
| 100 | Quercetina | ✓ |  |  |  | ✓ |  |  | ✓ |  |
| 101 | Luteolina | ✓ |  |  | ✓ | ✓ | ✓ | ✓ | ✓ |  |
| 102 | Kaempferol-7-*O*-*α*-L-rhamnoside | ✓ |  |  |  |  |  | ✓ |  |  |
| 103 | Rhodiooctanoside | ✓ |  | ✓ | ✓ |  | ✓ | ✓ |  |  |
| 104 | Kenposide A | ✓ | ✓ | ✓ |  | ✓ | ✓ | ✓ |  | ✓ |
| 105 | Rhodioloside C |  | ✓ |  | ✓ |  |  |  | ✓ | ✓ |
| 106 | Rhodioloside B | ✓ |  |  |  |  |  |  |  |  |
| 107 | Creoside V | ✓ |  | ✓ |  |  | ✓ |  |  |  |
| 108 | Kaempferola |  |  |  | ✓ | ✓ |  | ✓ | ✓ |  |
| 109 | 6-Feruloyloxyhexanoic acid | ✓ |  | ✓ |  | ✓ | ✓ | ✓ |  |  |

**Table S4 Information of 12 active components**

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **No.** | **Name** | **CAS number** | **Degree** | **No.** | **Name** | **CAS number** | **Degree** |
| c52 | Luteolin | 491-70-3 | 246 | c50 | Afzelin | 482-39-3 | 207 |
| c31 | Epicatechin gallate | 1257-08-5 | 222 | c38 | Nicotiflorin | 17650-84-9 | 201 |
| c32 | Catechin gallate | 130405-40-2 | 222 | c41 | Rhodiosin | 86831-54-1 | 199 |
| c26 | 6'-*O*-Galloylsalidroside | 83013-86-9 | 211 | c7 | Salidroside | 10338-51-9 | 198 |
| c42 | Isoquercitrin | 21637-25-2 | 209 | c17 | Catechin | 154-23-4 | 198 |
| c48 | Eriodictyol | 552-58-9 | 208 | c20 | Epicatechin | 490-46-0 | 198 |

**Table S5 Condition parameters of mass spectrometry analysis of 12 active components in *Rhodiola*.**

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **No.** | **Active ingredients** | **Formula** | **Parent** | **Daughters** | **CV** | **CE** | **Detection mode** |
| 1 | Luteolin | C15H10O6 | 287.02 | 152.98 | 46 | 30 | positive |
| 2 | Epicatechin gallate | C22H18O10 | 440.99 | 168.9 | 52 | 18 | negative |
| 3 | Catechin gallate | C22H18O10 | 442.93 | 122.93 | 2 | 20 | positive |
| 4 | 6'-*O*-Galloylsalidroside | C21H24O11 | 451.04 | 123.84 | 84 | 34 | negative |
| 5 | Isoquercitrin | C21H20O12 | 465 | 302.92 | 4 | 8 | positive |
| 6 | Eriodictyol | C15H12O6 | 288.97 | 152.98 | 42 | 24 | positive |
| 7 | Afzelin | C21H20O10 | 433.2 | 287.05 | 8 | 10 | positive |
| 8 | Nicotiflorin | C27H30O15 | 593.06 | 284.88 | 76 | 30 | negative |
| 9 | Rhodiosin | C27H30O16 | 611.12 | 303.03 | 32 | 28 | positive |
| 10 | Salidroside | C14H20O7 | 299.03 | 118.97 | 44 | 12 | negative |
| 11 | Catechin | C15H14O6 | 288.98 | 245.08 | 54 | 14 | negative |
| 12 | Epicatechin | C15H14O6 | 291.17 | 138.94 | 2 | 14 | positive |

**Table S6 The contents of active components in *Rhodiola* species**

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| ***Rhodiola* species** (mg/g) | ***R.***  ***crenulata*** | ***R.***  ***kirilowii*** | ***R. wallichiana*** | ***R.***  ***fastigiate*** | ***R.***  ***wallichiana var*** | ***R.***  ***sacra*** | ***R. himalensis*** | ***R. yunnanensis*** | ***R.***  ***tieghemii*** |
| Salidroside | 14.23 ± 0.27 | 11.16 ± 0.27 | 0.18 ± 0.01 | 0.51 ± 0.02 | 0.18 ± 0.00 | 1.36 ± 0.01 | N.D. | N.D. | N.D. |
| Epicatechin gallate | 0.67 ± 0.02 | N.D. | N.D. | N.D. | N.D. | 0.70 ± 0.00 | N.D. | N.D. | N.D. |
| Catechin gallate | 0.96 ± 0.01 | N.D. | N.D. | N.D. | N.D. | 0.98 ± 0.03 | N.D. | N.D. | N.D. |
| Rhodiosin | 0.97 ± 0.01 | 0.04 ± 0.00 | 0.02 ± 0.00 | 0.02 ± 0.00 | 0.03 ± 0.00 | 0.04 ± 0.00 | 0.01 ± 0.00 | 0.88 ± 0.02 | N.D. |
| Luteolin | 0.07 ± 0.00 | 0.22 ± 0.02 | 0.02 ± 0.00 | 0.03 ± 0.00 | 0.05 ± 0.00 | 0.03 ± 0.00 | 0.02 ± 0.00 | 0.02 ± 0.00 | 0.01 ± 0.00 |
| Epicatechin | 0.33 ± 0.01 | N.D. | N.D. | N.D. | N.D. | 0.26 ± 0.00 | 0.02 ± 0.00 | N.D. | 0.01 ± 0.00 |
| Isoquercitrin | 0.02 ± 0.00 | N.D. | N.D. | N.D. | N.D. | N.D. | 0.02 ± 0.00 | 0.02 ± 0.00 | N.D. |
| Afzelin | 0.14 ± 0.00 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | 0.06 ± 0.00 | N.D. |
| Nicotiflorin | 0.12 ± 0.01 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | 0.01 ± 0.00 | N.D. |
| Catechin | 0.16 ± 0.01 | N.D. | N.D. | N.D. | N.D. | 0.13 ± 0.00 | N.D. | N.D. | N.D. |
| 6'-*O*-Galloylsalidroside | 0.38 ± 0.02 | 0.18 ± 0.01 | 0.03 ± 0.00 | N.D. | N.D. | 9.25 ± 0.06 | 0.01 ± 0.00 | 0.01 ± 0.00 | N.D. |
| Eriodictyol | 0.06 ±0.01 | 0.04 ± 0.00 | N.D. | 0.01 ± 0.00 | 0.02 ± 0.00 | 0.01 ± 0.00 | 0.03 ± 0.00 | N.D. | N.D. |
| Note: values are expressed as the mean ± SD of three parallel samples. N.D. = not detected. | | | | | | | | | |