Supplementary Material

Evaluation of raw and processed Phellodendri Chinensis Cortex using quality markers analysis strategy by UHPLC-Q-Orbitrap MS and multivariate statistical analysis

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Fig.S1The UHPLC-Q-Orbitrap MS total ion chromatograms of raw materials of *HB* in positive (A) and negative ion mode (B); The UHPLC-Q-Orbitrap MS total ion chromatograms of *YHB* in positive (C) and negative ion mode (D); The UHPLC-Q-Orbitrap MS total ion chromatograms of *THB* in positive (E) and negative ion mode (F)



**A**

**B**

**C**

**D**

**E**

**F**



**Fig.S2** S-plot of OPLS-DA model between *HB* and *YHB* in positive ion mode (A) and negative ion mode (B); S-plot of OPLS-DA model between *HB* and *THB* in positive ion mode (C) and negative ion mode (D).

Table S1. Identification of characteristic markers compounds in raw and processed materials of HB

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| No. | tR  (min) | Formula | Determined mass/Da  (m/z) | | Error/ppm | ESI- | ESI+ | Identified compounds |
| [M-H]- | [M+H]+ |
| 1 | 0.69 | C7H12O6 | 191.0554 |  | -3.645 | 189.0397[M-2H]−  173.0324[M-H-H2O] –  155.0339[M-H-2H2O] − |  | Quinic acid |
| 2 | 0.72 | C20H24NO4 |  | 342.1692 | -3.799 | \_ | 297.1118[M-OCH3-CH3 ]+ 192.1016[M-C9H11O2]+  177.0784[M-C9H11O2-CH3] + | Phellodendrine |
| 3 | 0.81 | C20H24NO4 |  | 342.1693 | -3.507 | \_ | 297.1118[M-OCH3-CH3 ]+ 192.1016[M-C9H11O2]+  177.0784[M-C9H11O2-CH3] + | Isomer of Phellodendrine |
| 4 | 0.88 | C16H18O9 | 353.0879 |  | 0.282 | 193.0602[M-C7H11O5]-  191.0553[M-C9H6O3]-  173.0447[M-C9H6O3-H2O]- | \_ | Neochlorogenic acid |
| 5 | 0.92 | C11H18NO |  | 180.1380 | -4.441 | \_ | 121.0648[M-C3H10N]+ | N-candicine |
| 6 | 1.97 | C16H18O9 | 353.0879 |  | 0.282 | 193.0602[M-C7H11O5]-  191.0554[M-C9H6O3]-  173.0445[M-C9H6O3-H2O]- |  | Chlorogenic acid |
| 7 | 2.22 | C17H20O9 | 367.1035 |  | 8.728 | 193.0500[M-H-C7H11O6]−  191.0555[M-H-C10H9O4]− 175.0389[M-H-C7H11O6-H2O]− 173.0448[M-H-C10H9O4-H2O]− 147.0289[M-H-C7H11O6-CO2-H2O]− | \_ | 3-O-feruloylquinic acid |
| 8 | 2.80 | C20H23NO4 |  | 342.1694 | -1.759 | \_ | 298.0124[M+H-CH2CH2-CH3-H]+ 268.0858[M+H-CH2CH2-CH3-2H-CO]+  192.1015[M−C9H11O2]+ 177. 0777[M−C9H11O2−CH3]+ | Tetrahydrojatrorrhizine |
| 9 | 3.37 | C20H24NO4 |  | 342.1693 | -2.052 | \_ | 297[M-(CH3)2NH]+  265[M-(CH3)2NH-CH3OH]+  192[M-(CH3)2NH-CH3OH-CO-C2H4]+ | magnoﬂorine |
| 10 | 3.49 | C17H20O9 | 367.1032 | 369.1172 | -0.815 -2.173 | 735.2122[2M-H]−  193.0497[M-H-C7H11O6]−  191.0554[M-H-C10H9O4]−  173.0448[M-H-C10H9O4-H2O]−  147.0289[M-H-C7H11O6-CO2-2H]− | \_ | 4-O-feruloylquinic acid |
| 11 | 3.72 | C17H20O9 | 367.1032 | 369.1172 | -0.815 -2.173 | 735.2122[2M-H]−  193.0538[M-H-C7H11O6]−  191.0554[M-H-C10H9O4]−  175.0389[M-H-C7H11O6-H2O]− 173.0448[M-H-C10H9O4-H2O]− 147.0289[M-H-C7H11O6-CO2-CH2]− | \_ | 5-O-Feruloylquinic acid |
| 12 | 3.83 | C19H24NO3 |  | 314.1745 | -3.501 | \_ | 299.1514[M-CH3]+  283.1318[M-CH4-CH3]+  269.1169[M-CH4-CH3-CHO]+/[M-(CH3)2NH]+ | Magnocurarine |
| 13 | 3.97 | C18H22O9 | 381.1195 |  | 1.047 | 193.0498[M-H-C7H11O6]−  175.0391[M-H-C7H11O6-H2O]− | \_ | fernloylquinic acid methyl ester |
| 14 | 4.18 | C19H24NO3 |  | 314.1745 | -3.501 | \_ | 299.1514[M-CH3]+  283.1318[M-CH4-CH3]+  269.1169[M-CH4-CH3-CHO]+/[M-(CH3)2NH]+ | Lotusine |
| 15 | 4.41 | C21H26NO4 |  | 356.1850 | -3.370 | \_ | 311.0908[M-(CH3)2NH]+  279.1010[M-(CH3)2NH-CH3OH]+ | Menisperine |
| 16 | 4.68 | C21H26NO4 |  | 356.1849 | -3.650 | \_ | 311.0908[M-(CH3)2NH]+  296.1042[M−4CH3]+  279.1010[M-(CH3)2NH-CH3OH]+ 264.0778[M-(CH3)2NH-CH3OH-CH3]+ | (+)N-Methylcorydine |
| 17 | 4.94 | C21H26NO4 |  | 356.1849 | -3.650 | \_ | 311.1272[M-(CH3)2NH]+ 296.1039[M−4CH3]+  279.1013[M-(CH3)2NH-CH3OH]+ 264.0770[M-(CH3)2NH-CH3OH-CH3]+ 236.0835[M-(CH3)2NH-CH3OH-CH3]+ 192.1015[M-(CH3)2NH-CH3OH-CH3-CO-CH4]+ | Tetrahydropalmatine |
| 18 | 5.05 | C26H34O11 | 567.1780 |  | -5.802 | 521.2596[M-H]- 341.1396[M-H-Glc-H2O]- 329.1396[M -Glc-OCH3]- | \_ | (+/-)8-(4-Hydroxy-3-methoxyphenyl)-6,7-bis(hydroxymethyl)-3-methoxy-5,6,7,8-tetrahydro-2-naphthalenyl β-D-  glucopyranoside |
| 19 | 5.06 | C20H26NO3 |  | 328.1914 | 3.047 | \_ | 283.1322[M-C2H5O]+ 269.1163[M-C2H5O-CH3]+ | Armepavine |
| 20 | 5.28 | C19H18NO4 |  | 324.1223 | -4.011 | \_ | 309.0989[M-CH3]+ | demethylberberine |
| 21 | 5.32 | C20H18NO5 |  | 352.1172 | -3.692 | \_ | 337.0936[M-CH3]+ 322.1155[M-2CH3]+ 308.1354[M-CH3-CO-H]+ | Oxoberberine |
| 22 | 5.48 | C20H18NO5 |  | 352.1172 | -3.692 | \_ | 337.0936[M-CH3]+ 322.0706[M-2CH3]+ 308.0920[M-CH3-CO-H]+ | Oxoepiberberine |
| 23 | 5.49 | C17H22NO4 | 349.1525 |  | -1.973 | 334.0684[M+HCOO-CH3]- 286.0726[M-H2O]- 175.0390[M-H-CO]- | \_ | dasycarpamin |
| 24 | 5.51 | C21H21NO5 |  | 368.1488 | -1.089 | \_ | 353.1247[M+H-CH3]+ 324.1225[M+H-CH3-CO-H]+ | hydroxylpalmatine |
| 25 | 5.52 | C17H20O9 | 367.1039 |  | 1.087 | 191.0553[M-H-C7H11O6]−  173.0446[M-H-C10H9O4-H2O]− 149.0597[M-H-C7H11O6-CO2]− 134.0362[M-H-C7H11O6-CO2-CH3]− 111.0075[M-H-C7H11O6-2CO2-2H-  H2O]- | \_ | feruloylquinic acid |
| 26 | 5.54 | C21H26NO4 |  | 356.1849 | -3.650 | \_ | 311.1258[M-(CH3)2NH]+  279.1010[M-(CH3)2NH-CH3OH]+ | Xanthoplanine |
| 27 | 5.67 | C21H24NO4 |  | 354.1689 | -4.518 | \_ | 339.1080[MCH3]+  190.0859[M-2CH3-H]+ | N-Methyl canadine |
| 28 | 5.79 | C20H20NO4 |  | 338.1379 | -3.845 | \_ | 323.1144[M-CH3]+ 308.0910[M-2CH3]+ 294.1117[M-2CH3-CO-H]+ | Columbamine |
| 29 | 5.88 | C20H20NO4 |  | 338.1362 | -8.872 | \_ | 323.1095[M-CH3]+ 308.1235[M-2CH3]+ 280.2636[M-2CH3-CO]+ | Jatrorrhizine |
| 30 | 5.95 | C19H15NO4 |  | 322.1069 | -0.934 | \_ | 307.0834[M-CH3]+ 292.0602[M-H-CO]+ 278.0809[M-CH3-CO]+ | berberrubine |
| 31 | 5.97 | C22H28NO4 |  | 370.2007 | -2.971 | \_ | 206.1172[M-CH3-C9H7O2]+ | 1,2,9,10-Tetramethoxy-6,6-dimethyl-5,6,6a,7-tetrahydro-4H-dibenzo[de,g]quinolinium |
| 32 | 6.01 | C20H18NO4 |  | 336.1221 | -4.463 | \_ | 321.0987[M-CH3]+ 306.0756[M-2CH3]+ 292.0960[M-CH3-H-CO]+ 278.0791[M-2CH3-CO]+ | Berberine |
| 33 | 6.07 | C20H18NO4 |  | 336.1221 | -4.463 | \_ | 321.0986[M-CH3]+ 306.0759[M-2CH3]+ 292.0958[M-CH3-H-CO]+ 278.0771[M-2CH3-CO]+ | Isomer of berberine |
| 34 | 6.30 | C19H34O15 | 501.1841 |  | 3.186 | 457.1869[M-CO2]- 413.1978[M-2CO2]- 395.1863[M-2CO2-H2O]- 371.1861[M-2CO2-H2O-CH3]- | \_ | γ-hydroxybutenolide deniatives II |
| 35 | 6.31 | C20H18NO4 |  | 336.1223 | -3.868 |  | 321.0988[M-CH3]+ 306.0759[M-2CH3]+ 292.0958[M-CH3-H-CO]+ 278.0783[M-2CH3-CO]+ | Isomer of berberine |
| 36 | 6.42 | C19H18O11 | 421.0759 |  | -4.028 | 377.1060[M-CO2]-  301.1446[M-C4H8O4]- | \_ | Mangiferin |
| 37 | 6.61 | C26H30O9 | 531.1849 |  | -4.731 | 485.1826 [M-H]- 423.1819[M-H-H2O-CO2]- 411.2003[M-H-H2O-C2O2]- 327.2176[M-C10H7O2]- | \_ | Rutaevin |
| 38 | 6.63 | C20H18NO4 |  | 336.1224 | -3.570 | \_ | 321.0988[M-CH3]+ 306.0765[M-2CH3]+ 292.0962[M-CH3-H-CO]+ | Isomer of berberine |
| 39 | 6.71 | C18H34O5 | 329.2333 |  | 0 | 311.2226[M-H-HO]- 293.2119[M-H-2HO]- 229.1442[M-H-HO-C6H10O]-  211.1334[M-H-CO2-(CH2)4CH3]- 171.1018[M-H-OH-(CH2)8CH3OH]- | \_ | Sanleng acid |
| 40 | 7.05 | C26H30O8 | 470.1910 |  | -6.593 | 515.1920[M+HCOO]- 469.1872[M -H]- 425.2195[M -H-CO2]- 409.2359[M -H-CO2-CH4]- | \_ | Obaculactone |
| 41 | 7.20 | C21H22NO4 | 352.1569 |  | 5.679 | \_ | 337.0938[M-CH3]+ 308.0916[M-CH4-CO]+ 292.0981[M-4CH3]+ | Palmatine |
| 42 | 7.27 | C31H46O5 | 497.3378 |  | -4.816 | 423.1821[M-CO2-2H-CO]- | \_ | Poricoic acid A |
| 43 | 7.36 | C16H18O9 | 353.0871 |  | 8.960 | 193.0602[M-C7H11O5]- 191.0553[M-C9H6O3]- 173.0447[M-C9H6O3-H2O]- | \_ | Cryptochlorogenic acid |
| 44 | 7.71 | C13H16O10 | 331.0658 |  | -3.915 | 313.2386[M-H-H2O]- 168.0408[M-H-GLc]- 149.0460[M-H-H2O-H]- 125.0346[M-C7H4O5-2H2O]- | \_ | b-Glucogallin |
| 45 | 7.82 | C26H30O7 |  | 455.2051 | -2.862 | \_ | 427.2062[M+H-CO]+ 409.2000[M+H-CO-H2O]+ | Obacunone |
| 46 | 7.84 | C17H20N2O | 313.1568 |  | 3.729 | 253.9937[M+HCOO-CH3]- 148.0506[M+HCOO-CH3-C7H8N]- | \_ | Bis-[4-(dimethylamino)phenyl]methanone |
| 47 | 8.64 | C18H32O2 | 279.2312 |  | -6.423 | 265.2159[M-CH2]- 232.1539[M-CH2-H2O-CH3]- | \_ | cis-9-cis-12-Linoleic acid |
| 48 | 9.18 | C9H8O2 |  | 149.0231 | -6.450 | \_ | 131.0491[M-H2O]+ 103.0544[M-HCOOH]+ | cinnamic acid |