**S2 Appendix.** LC-ESI-TOF-MS/MS spectra of metabolite features putatively identified at ID level 2 (identification done at fragmentation level (MS2) by matching with online databases).



**Fig S2** a. LC-ESI-TOF-MS/MS spectra for tryptamine



**Fig S2** b. LC-ESI-TOF-MS/MS spectra for yohimbine



**Fig S2** c. LC-ESI-TOF-MS/MS spectra for akuammidine



**Fig S2** d. LC-ESI-TOF-MS/MS spectra for strictosidine



**Fig S2** e. LC-ESI-TOF-MS/MS spectra for speciofoline



**Fig S2** f. LC-ESI-TOF-MS/MS spectra for 7-hydroxymitragynine



**Fig S2** g. LC-ESI-TOF-MS/MS spectra for rynchophylline



**Fig S2** h. LC-ESI-TOF-MS/MS spectra for corynantheidine



**Fig S2** i. LC-ESI-TOF-MS/MS spectra for 11-methoxyvinorine



**Fig S2** j. LC-ESI-TOF-MS/MS spectra for hirsuteine



**Fig S2** k. LC-ESI-TOF-MS/MS spectra for mitragynine



**Fig S2** l. LC-ESI-TOF-MS/MS spectra for isopaynantheine



**Fig S2** m. LC-ESI-TOF-MS/MS spectra for brucine



**Fig S2** n. LC-ESI-TOF-MS/MS spectra for alstonine



**Fig S2** o. LC-ESI-TOF-MS/MS spectra for vomicine



**Fig S2** p. LC-ESI-TOF-MS/MS spectra for (+)-N-(methoxycarbonyl)-N-norboldine



**Fig S2** q. LC-ESI-TOF-MS/MS spectra for cinegalline



**Fig S2** r. LC-ESI-TOF-MS/MS spectra for vasicinol



**Fig S2** s. LC-ESI-TOF-MS/MS spectra for caffeine



**Fig S2** t. LC-ESI-TOF-MS/MS spectra for lumichrome



**Fig S2** u. LC-ESI-TOF-MS/MS spectra for quinate



**Fig S2** v. LC-ESI-TOF-MS/MS spectra for 5''-O-beta-D-glucosylpyridoxine



**Fig S2** w. LC-ESI-TOF-MS/MS spectra for 3-Methoxytyramine-betaxanthin



**Fig S2** x. LC-ESI-TOF-MS/MS spectra for caffeic aldehyde



**Fig S2** y. LC-ESI-TOF-MS/MS spectra for sinapate



**Fig S2** z. LC-ESI-TOF-MS/MS spectra for magnoshinin



**Fig S2** aa. LC-ESI-TOF-MS/MS spectra for glaucarubinone/soularubinone



**Fig S2** bb. LC-ESI-TOF-MS/MS spectra for 3-Oxoglycyrrhetinate



**Fig S2** cc. LC-ESI-TOF-MS/MS spectra for glabric acid



**Fig S2** dd. LC-ESI-TOF-MS/MS spectra for fatsicarpain C



**Fig S2** ee. LC-ESI-TOF-MS/MS spectra for epicatechin



**Fig S2** ff. LC-ESI-TOF-MS/MS spectra for quarcetin/6-hydroxykaempferol/ robinetin/morin/8-hydroxykaempferol



**Fig S2** gg. LC-ESI-TOF-MS/MS spectra for rutin



**Fig S2** hh. LC-ESI-TOF-MS/MS spectra for procyanidin B4/procyanidin B5



**Fig S2** ii. LC-ESI-TOF-MS/MS spectra for 2''-Hydroxygenistein/orobol



**Fig S2** jj. LC-ESI-TOF-MS/MS spectra for isoorientin 2''-O-rhamnoside



**Fig S2** kk. LC-ESI-TOF-MS/MS spectra for quarcetin/6-hydroxykaempferol/ robinetin/morin/8-hydroxykaempferol



**Fig S2** ll. LC-ESI-TOF-MS/MS spectra for myricitrin/bracteatin 6-O-glucoside/gossypetin 8-rhamnoside



**Fig S2** mm. LC-ESI-TOF-MS/MS spectra for carthamone



**Fig S2** nn. LC-ESI-TOF-MS/MS spectra for cinchonain 1a



**Fig S2** oo. LC-ESI-TOF-MS/MS spectra for 3,4-dihydroxybenzaldehyde