**Supplementary information**

**Figure S1** The MS or MS/MS spectra of identified metabolites in the root bark extracts from tree peony.

**Figure S2** The MS/MS spectra of galloylpaeoniflorin at the different collision energies: (A) 10 eV, (B) 20 eV, (C) 30 eV and (D) 40 eV.
Figure S1

**Peak 1: Malic acid**

Peak 3: Gallic acid

Peak 5: Sucrose

Peak 7: Glucogallin

Peak 9: Muvanoside B

Peak 11: Catechim glucoside

Peak 13: Kaempferol dihexoside

Peak 15: Catechin

Peak 17: Methyl gallate

Peak 19: Saffloroside E

Peak 21: Quercetin 3,7-di-O-glucoside

**Peak 2: Citric acid**

**Peak 4: Myrosinol**

**Peak 6: Dioses**

**Peak 8: Gallicose**

**Peak 10: Muvaposide F**

**Peak 12: Procyanidin**

**Peak 14: Hydroxybenzoic acid**

**Peak 16: Oxypaeonifolin**

**Peak 18: Paeonoside**

**Peak 20: Galloyloxy paeonifolin**

**Peak 22: Muvaposide E**
Figure S2