Supplemental Information A

Characterization of the herb-derived components in rats following oral administration of *Carthamus tinctorius* extract by extracting diagnostic fragment ions (DFIs) in the MS^n chromatograms

Jin-Feng Chen,[a#] Yue-Lin Song,[b#] Xiao-Yu Guo,[a] Peng-Fei Tu,[ab] and Yong Jiang[a]*

[a] *State Key Laboratory of Natural and Biomimetic Drugs, School of Pharmaceutical Sciences, Peking University, Beijing 100191, China. E-mail: yongjiang@bjmu.edu.cn; Tel/Fax: +86-10-82802719*

[b] *Modern Research Center for Traditional Chinese Medicine, Beijing University of Chinese Medicine, Beijing 100029, China*

#: These two authors contribute equally.

Results and Discussion

1. Mass fragmentation pathways of flavones glycosides in ECT

HR-MS was used to provide accurate mass values for the precursor and the fragment ions of quinochalcone *C*-glycosides, flavonoid glycosides, and flavanone glycosides, and their fragmentation pathways were summarized according to the results obtained from the reference compounds, and from the compounds contained in the ECT.

1.1 Quinochalcone *C*-glycosides

The quinochalcone *C*-glycosides contained in ECT have the same quinochalcone skeleton, along with a hydroxyl group, and a *C*-glucosyl group at the C-5′ position. Overall, the characteristic fragmentation of these compounds primarily occurred at the *C*-*C* bond between the skeleton and the glucosyl group. In contrast to the typical cross-ring cleavage at the sugar moiety of other *C*-glycosyl flavonoids, these quinochalcone *C*-glycosides yielded a prominent fragment ion of $[M–H–Glc]^-$ under the negative ionization, attributing to the neutral loss of the C-5′ glucosyl group. In addition, the $[M–H–Glc–H_2O–CO]^-$ and $[M–H–Glc–H_2O–CO–C_4H_8O_4]^-$ ions were observed as the other major fragment ions, along with the $[M–H–C_4H_8O_4]^-$ ion, which was proved to be the characteristic $^{0,2}X$ ion of the *C*-glycosyl flavonoids [1]. The fragmentation pathways of the representative quinochalcone *C*-glycosides, HSYA is presented in Fig. S1A.

2.2 Flavonol glycosides

The major aglycones of the flavonol glycosides in ECT include quercetin, kaempferol, and their 6-hydroxylated derivatives. Most of the identified flavonol glycosides in ECT are *O*-glycosides, whereas few are *C*-glycosides. Initially, step-wise neutral losses of sugars occurred for these *O*-glycosides. Subsequently, the fragment ions of $[A–H–H_2O]^-$, $[A–H–H_2O–CO]^-$ and $[A–2CO]^-$ were given by the deprotonated aglycone $[A–H]^-$, corresponding to the cleavages that occurred at the *C*-ring. The flavonol *C*-glycosides exhibited the characteristic neutral losses of 90.03, 120.04 and 150.05 Da ($^{0,3}X$, $^{0,2}X$ and $^{0,1}X$ cleavages, respectively) due to the cross-ring cleavages of the glycosyl substituent. The fragmentation pathways of the representative flavonol glycoside, 6-hydroxykaempferol-3-*O*-rutinoside is presented in Fig. S1B.

1.3 Flavanone glycosides

The aglycones of the flavanone glycosides in ECT include carthamidin and isocarthamidin. Most of flavanone glycosides in ECT are *O*-glycosides, whereas few are *C*-glycosides. Initially, step-wise neutral losses of sugar substituents occurred for those *O*-glycosides. Subsequently, the cross-ring cleavages at the *C*-ring to afford the characteristic fragment ions of $[^{1,2}A]^-$, $[^{1,2}A–CO]^-$, $[^{1,3}A]^-$, $[^{1,3}A–CO]^-$, [M–H–B-ring]$^-$ and $[^{1,3}B]^-$ under the negative ionization. The fragmentation pathways of the representative flavanone glycoside, cathamidin-7-*O*-glucoside is presented in Fig. S1C.

2. Characterization of the ingredients of ECT

2.1 Chalcone derivatives

Fifteen chalcones were detected in the ECT. Among these chalcones, A14 and A15 were identified as isosafflomin C and safflomin C by comparison with the reference compounds. A7 was identified as HSYA, whereas A2-A6 and A8 were identified as the isomers of HSYA because they exhibited the same mass profiles as HSYA [1,2]. The molecular formulas of A1, A9, A11 and A12 were deduced as $C_{27}H_{30}O_{15}$ based on the HR-MS data (Table S1), which is the same as that of safflor yellow A. Furthermore, in comparison with the fragment ions with the data in the reference [1], the most abundant compound (A9) was identified as safflor yellow A, whereas A1, A11 and A12 were assigned as the isomers of safflor yellow A [1]. The deprotonated molecular ion of A13 was observed at *m*/*z* 1043.2664, corresponding to the elemental composition of $C_{48}H_{53}O_{26}$ (Table S1). In combination with the prominent product ions, A13 was tentatively identified as anhydroxysafflor yellow B [3]. Similarly, A10 was assigned as hydroxycarthamin [1].

2.2 Flavanone derivatives

The molecular formula of B1 and B2 was $C_{27}H_{32}O_{17}$, calculated from their HR-MS data (*m*/*z* 627.16). B2 exhibited the neutral losses of 120.04 Da (*m*/*z* 507.1142) and 162.05 Da (*m*/*z* 303.0648), indicating the presence of a *C*-glucosyl and an *O*-glucosyl groups in its structure. Therefore, B2 was assigned as 5,6,7,4′-tetrahydroxyflavanonol-*O*-glucosyl-*C*-glucoside. B1 exhibited only a neutral loss of

162.05 Da (*m*/*z* 465.1183) and was thereby identified as 5,6,7,4′-tetrahydroxyflavanonol-*di*-*O*-glucoside [4]. B3, B7, B8 and B9 showed the same deprotonated molecular ion at *m*/*z* 449.11, corresponding to an elemental composition of $C_{21}H_{22}O_{11}$. B7, B8 and B9 shared the same product ions at *m*/*z* 287.05, 233.06 and 181.02 (Table S1), which agree well with those of carthamidin/isocarthamidin-*O*-glucoside [4]. Whereas, B3 exhibited neutral losses of 120.04 Da and 150.05 Da, which are the diagnostic neutral losses of the *C*-glycosyl group; therefore, B3 was identified as carthamidin/isocarthamindin-*C*-glucoside [4]. B4 and B6 exhibited the same molecular composition of $C_{27}H_{32}O_{16}$, calculated from the HR-MS data, and the negative MS^n spectra showed predominant ions at *m*/*z* 521.13 and 287.05 (Table S1), indicating that these two compounds were carthamidin/isocarthamidin-*O*-glucosyl-*C*-glucoside [4]. B5 afforded the quasi-molecular ion at *m*/*z* 625.1395, corresponding to an elemental composition of $C_{27}H_{30}O_{17}$. The negative MS^n spectra of B5 showed the dominant signals at *m*/*z* 449.1058 and 287.0519 (Table S1), suggesting the step-wise losses of glucuronyl (176.05 Da) and glucosyl (162.05 Da) groups. Thus, B5 was deduced as carthamidin/isocarthamidin-*O*-glucosyl-*O*-glucuronide.

2.3 Quercetin derivatives

C3 and C4 were confirmed as rutin and quercetin-3-*O*-glucoside, respectively, using the reference compounds. C1 and C2 yielded the same product ion at *m*/*z* 317.05 in negative MS^2 spectra (Table S1), indicating that their aglycone is 6-hydroxyquercetin. Moreover, C1 showed a pseudo-molecular ion ($[M–H]^-$) at *m*/*z* 463.0884, and a

neutral loss of 146.04 Da was also observed for this compound (Table S1), indicating a structure as 6-hydroxyquercetin-*O*-rhamnoside [5]. The quasi-molecular ion of C2 was *m*/*z* 803.1869, and the product ions at *m*/*z* 641.1309, 479.0788, and 317.0258 indicated three successive neutral losses of 162.04 Da; thus, C2 was deduced as 6-hydroxyquercetin-3,6,7-*tri*-*O*-glucoside [6]. C5 exhibited a $[M+H]^+$ ion at *m/z* 625.1754 and its product ions were at *m*/*z* 149.0200 ($[^{0,3}B–H_2O]^+$) and 121.0258 ($[^{0,2}A–CO_2]^+$), indicating that its aglycone was quercetin rather than 6-hydroxylkaempferol [4]. C5 showed successive losses of the methyl and glucosyl groups, and was proposed as quercetin-*O*-methyl-*O*-glucosyl-*O*-rhamnoside [7].

2.4 Kaempferol derivatives

In comparison with the authentic compounds, D3, D4, D11, D14, D15, D17 and D18 were confirmed as 6-hydroxykaempferol-3,6,7-*tri*-*O*-glucoside, 6-hydroxykaempferol-3,6-*di*-*O*-glucosyl-7-*O*-glucuronide, 6-hydroxy-kaempferol -6,7-*di*-*O*-glucoside, 6-hydroxykaempferol-3-*O*-rutinoside, 6-hydroxykaemferol-3-*O*-glucoside, kaemferol-3-*O*-rutinoside and kaemferol-3-*O*-glucoside, respectively (Table S1). The HR-MS spectral profiles of D8 and D16 suggested that they possess the identical molecular composition of $C_{27}H_{30}O_{15}$ (Table S1). The neutral losses of 146.04 Da and 162.05 Da indicated that D8 and D16 were substituted by rhamnosyl and glucosyl; therefore, they were tentatively assigned as kaempferol-3-*O*-glucosyl-7-*O*-rhamnoside and its isomer, respectively [8]. D1, D6 and D11 shared the same deprotonated molecular ion. D1 exhibited the neutral losses of 120.04 Da and 162.05

Da, indicating this compound was substituted by a *C*-glycosyl and an *O*-glycosyl groups. Therefore, D1 was supposed as 6-hydroxykaempferol-8-*C*-glucosyl-*O*-glucoside. D6 showed the same fragment ions as D11, including *m*/*z* 463.08, 301.03, and 271.04 (Table S1); thus, D6 was assigned as 6-hydroxykaempferol-3, 7-*di*-*O*-glucoside [9, 10]. The component composition of D2 was elucidated as $C_{27}H_{30}O_{17}$. It showed the neutral losses of 120.05 Da and 150.05 Da, which was the typical cross-ring ($^{0,2}X$ and $^{0,1}X$) cleavages of *C*-glycosyl group; thus, D2 was proposed as kaempferol-*di*-*C*-glucoside. D5 and D10 afforded the same neutral losses of 308.10 Da and 162.05 Da, which resulted from the neutral losses of the rutinosyl and glucosyl groups, respectively. Moreover, D5 and D10 shared the same deprotonated aglycone ion at *m*/*z* 301.03, indicating that their aglycone was 6-hydroxykaempferol (Table S1). Therefore, D10 was assigned as 6-hydroxykaempferol-3-*O*-rutinosyl-6-*O*-glucoside [10], whereas compound D5 was assigned as 6-hydroxykaempferol-3-*O*-rutinosyl-6,7-*di*-*O*-glucoside for its additional neutral loss of 162.04 Da [10]. D7 gave the $[M–H]^–$, $[M–H–GluA]^–$ and $[M–H–GluA–Glc]^–$ ions at *m*/*z* 639.1206, 463.0836 and 301.0311, respectively; therefore, it was tentatively assigned as 6-hydroxykaempferol-3-*O*-glucosyl- 7-*O*-glucuronide [2]. Because D12 exhibited a similar mass spectral profile to D6 and D11, it was characterized as kaempferol-3, 7-*di*-*O*-glucoside. D9 and D13 shared the same molecular composition and neutral losses (162.05 Da and 176.05 Da), indicating that they were the isomers of kaemferol-3-*O*-glucosyl-7-*O*-glucuronide [2]. D19 exhibited a deprotonated ion at *m*/*z* 477.1039 and an $[A–H]^–$ ion at *m*/*z* 300.0245 (Table S1), which resulted from the successive

neutral losses of 15.02 Da and 162.05 Da; hence, D19 was assigned as 6-hydroxykaempferol-*O*-methyl-*O*-glucoside.

2.5 Other compounds

O1 and O3 showed an $[M-H]^-$ ion at *m*/*z* 325.09 (Table S1), corresponding to a molecular formula of $C_{15}H_{18}O_8$. In addition, these two compounds showed a neutral loss of 162.05 Da; therefore, they were proposed as 4-*O*-glucosylcinnamic acid and its isomer, respectively [11]. Similarly, O2 was assigned as 4-*O*-glucosyl-phenyl propionic acid (Table S1).

3. Characterization of the metabolites of the single compounds in rats

To summarize the metabolites of the representative single compound by LC-IT-TOF-MS^n and to propose the metabolic pathways of the major chemical types, HSYA, 6-hydroxykaempferol-3-*O*-rutinoside and kaempferol-3-*O*-rutinoside were orally administered to rats. Through comparison of the plasma samples at different blood sampling time points after the administration of ECT, most of the metabolites were found to show the highest concentrations at 1.5 h. Therefore, blood sampling was performed at 1.5 h, whereas the urine samples from 0 to 24 h were collected for LC/MS analysis. The metabolites were identified or tentatively characterized based on their response value and the high-accuracy mass spectral data.

3.1 Characterization of the metabolites of kaempferol-3-*O*-rutinoside in rats

Thirty-seven metabolites were found for kaempferol-3-*O*-rutinoside, including 13 flavanonol- or chalcone-type metabolites (A1-A13), 3 quercetin-type metabolites (C1-C3), 17 kaempferol-type metabolites (D1-D17) and 4 other compounds (O1-O4) (Table S2). Most of the metabolites were glucuronidates and sulfonates. The proposed metabolic pathways are illustrated in Fig. S5.

A1, A8 and A12 were proposed as dihydrogalangin or α,2,4,6-tetrahydroxychalcone-type metabolites due to observation of the $[A–H]^-$ ion at *m*/*z* 271.04 and $[^{1,3}A]^-$ ion at *m*/*z* 151.00 (Table S2), indicating that the 4′-OH of dihydrokaempferol or α,2,4,4′, 6-pentahydroxychalcone can be dehydroxylated by the intestinal bacteria [12]. Among them, A1 and A12 were sulfonated conjugates because they exhibited an obvious neutral loss of 79.95 Da. A8 was identified as the *di*-glucuronidated conjugate due to the successive neutral losses of 176.05 Da. Because kaempferol can be metabolized to dihydrokaempferol and α,2,4,4′,6-pentahydroxychalcone by the intestinal bacteria [13], the $[A–H]^-$ ion at *m*/*z* 287.05and the $[^{1,3}A]^-$ ion at *m*/*z* 151.00 (Table S2) suggested that A2, A3, A4, A5, A6, A7, A9, A10 and A11 were the corresponding metabolites mediated by the intestinal bacteria. A2 was proposed as the *di*-glucuronidated conjugates because of the successive neutral losses of 176.05 Da. A3, A5, A6 and A7 were assigned as glucuronidated conjugates due to the neutral loss of 176.05 Da. A9, A10 and A11 were assigned as sulfonates based on the neutral loss of 79.95 Da. A4 was assigned as glucuronidated and sulfonated conjugates due to the neutral loss of 176.05 and 79.95 Da. Moreover, A13 exhibited the $[A–H]^-$ ion at *m*/*z* 255.0642 (Table S2), which was 31.99 Da less

than dihydrokaempferol or α,2,4,4′,6-pentahydroxychalcone. In addition, the neutral loss of 79.95 Da suggested the sulfonate conjugation. Collectively, A13 was deduced as α, 2-*di*-hydroxychalcone-*O*-glucuronide or 3,5-dihydroxyflavanone-*O*-glucuronide.

Three metabolites (C1-C3) were identified as quercetin-type metabolites generated from the oxidation of kaempferol by the intestinal bacteria [14]. The $[A–H]^-$ ion at *m*/*z* 301.03 and the product ions $[^{0,3}B]^-$ and $[^{1,3}A]^-$ at *m*/*z* 165.02 and 151.00, respectively (Table S2) were in good agreement with the mass spectral profile of quercetin [4]. Hence, C1 and C2 were identified as quercetin-*O*-glucuronide due to the observation of the neutral loss of 176.05 Da, whereas C3 was identified as quercetin-*O*-methyl-*O*-glucuronide because of an additional loss of 15.02 Da.

Seventeen components (D1-D17) were identified as kaempferol-type metabolites because they showed a diagnostic $[A–H]^-$ ion at *m*/*z* 285.04 and the $[A–H–CO]^-$ and $[A–H–H_2O]^-$ ions (Table S2). Among these components, D10 was characterized as the prototype with the reference compound. D1, D2, D4, D5, D6 and D7 were characterized as *di*-glucuronidated conjugates because their MS^2 spectra exhibited the characteristic step-wise neutral losses of 176.05 Da. D3 and D8 yielded the same product ions at *m*/*z* 447.08 and 285.04 (Table S2), which resulted from the neutral loss of the glucosyl group. D3 was identified as kaempferol-3-*O*-glucosyl-*O*-glucuronide because it showed another neutral loss of 176.05 Da, whereas D8 was proposed as kaempferol-3-*O*-glucosyl-*O*-sulfonate because it showed an additional neutral loss of 79.95 Da. D9 and D13 were proposed as glucuronidated and sulfonated

products due to the observation of $[M–H–GluA]^-$ and $[M–H–GluA–SO_3]^-$ ions at *m*/*z* 461.0645 and 285.0414, respectively. D11, D12 and D14 were proposed as glucuronidates because they exhibited the neutral loss of 176.05 Da. D16 and D17 showed the same molecular formula of $C_{22}H_{20}O_{12}$ and the fragment ion at *m*/*z* 284.02 $[M–H–GluA–Me]^-$ (Table S2); therefore, these two components were identified as kaempferol-*O*-methyl-*O*-glucuronide.

O1/O2 and O3/O4 were proposed as the derivatives of *4*-hydroxybenzoic acid and 2,4,6-trihydroxybenzoic acid, respectively, which were the ring-fission products of kaempferol by the intestinal bacteria [15,16]. O1 was identified as *4*-sulfo-benzoic acid due to the observation of the neutral loss of 79.95 Da, whereas O2 was identified as *4*-hydroxybenzoic acid-*O*-methyl-*O*-sulfonate based on the additional radical cleavage of 15.02 Da. O3/O4 were assigned as glucuronidated of 2,4,6-trihydroxybenzoic acid due to the neutral loss of 176.05 Da.

3.2 Characterization of the metabolites of 6-hydroxykaempferol-3-*O*-rutinoside in rats

Twenty-three metabolites were identified or tentatively characterized, including 11 flavanonol- or chalcone-type metabolites (A1-A11), 2 kaempferol-type metabolites (D1-D2) and 10 6-hydroxykaempferol-type metabolites (E1-E10) (Table S3). Most of the metabolites were glucuronidated products. The proposed metabolic pathways are illustrated in Fig. 2B.

Eleven metabolites (A1-A11) were identified as flavanonol- or chalcone-type

metabolites. Because 6-hydroxykaempferol-3-*O*-rutinoside shared the same metabolites with kaempferol-3-*O*-rutinoside at 24.070, 34.605, 37.765, 38.680, 41.665, 54.435, 59.115 and 64.495 min, the 6-OH of 6-hydroxykaempferol-3-*O*-rutinoside was speculated to be expelled by the intestinal bacteria [12,17]. Therefore, A1, A2, A3, A4, A7, A8 and A9 were identified as the dihydrokaempferol or α,2,4,4′,6-pentahydroxychalcone-type metabolites. Due to the successive neutral losses of 176.02 Da, A1 was assigned as the *di*-glucuronidated conjugate. A2, A3, A4 and A7 were identified as glucuronidated conjugates in view of the neutral loss of 176.02 Da, whereas A8 and A9 were identified as sulfonated conjugates due to the obvious neutral loss of 79.95 Da. The aglycone of A5, A6, A10 and A11 were proposed as dihydrogalangin or α,2,4,6-tetrahydroxychalcone since they exhibited $[A–H]^-$ and $[^{1,3}A]^-$ ions at *m*/*z* 271.06 and 151.01, respectively (Table S3). A5 and A6 were *di*-glucuronidated conjugates based on the successive neutral losses of 176.02 Da, whereas A10 and A 11 were characterized as glucuronidative sulfonated conjugates in view of the successive neutral losses of 176.02 Da and 79.95 Da.

D2 was identified as kaempferol-*O*-glucuronide since it shared the same retention time and fragment ions with one of the metabolite of kaempferol-3-*O*-rutinoside. Owing that D1 exhibited the same $[A–H]^-$ ion with D2, it was identified as kaempferol-*O*-sulfo-*O*-glucuronide due to the successive neutral losses of 176.05 Da and 79.95 Da.

Ten components (E1-E10) were identified as 6-hydroxykaempferol-type metabolites. These components shared the same $[A–H]^-$, $[A–CO]^-$ and $[A–H_2O–CO]^-$

ions. E1 was identified as 6-hydroxykaempferol-*tri*-*O*-glucuronide due to the successive neutral losses of 176.05 Da. E2 was identified as 6-hydroxykaempferol-*O*-methyl-*di*-*O*-glucuronide based on its mass spectral profile. E3, E4, E5 and E6 were assigned as 6-hydroxykaempferol-*di*-*O*-glucuronide because they shared the same fragment pathway (Table S3). E7 and E10 were identified as 6-hydroxykaempferol-*O*-glucuronide since they exhibited an obvious neutral loss of 176.05 Da; whereas, E8 and E9 were deduced as 6-hydroxykaempferol-*O*-methyl-*O*-glucuronide because they showed an additional radical cleavage of 15.02 Da compared with E7.

3.3 Characterization of the metabolites of HSYA in rat

Fourteen metabolites were identified or tentatively characterized based on their high accuracy mass spectral profiles (Table S4). Most of the metabolites were glucuronidates. The proposed metabolic pathways are illustrated in Fig. 2C.

Thirteen metabolites (A1-A11) were identified as chalcone-type, which were generated by hydrolysis, dehydroxylation [12,17] and reduction [13] of HSYA in combination with certain further metabolic pathways. A1 was determined as prototypes by comparison with the reference compounds. A2, A4, A8, A10 and A11 showed the same $[A–H]^-$ ion at *m*/*z* 255.06 (Table S4); thus, their aglycone was deduced as 2,4,6-trihydroxychalcone, which resulted from dehydroxylation of the 5-OH and the 4′-OH [12,17] of 2,4,4′,5,6-pentahydroxychalcone. A2, A4 and A10 were identified as the glucuronidated conjugates because they exhibited an obvious neutral loss of 176.05 Da, whereas A8 and A11 were identified as sulfonated derivatives due

to the obvious neutral cleavage of 79.95 Da. A3, A5 and A9 showed the same molecular composition ($C_{22}H_{22}O_{12}$) along with the $[M–H–GluA]^-$, $[A–H–CO]^-$ and $[A–H–CO–Me]^-$ ions at *m*/*z* 301.07, 273.07 and 258.06 (Table S4), respectively; thus, they were supposed as the isomers of 2,4,4′,5,6-pentahydroxychalcone-*O*-methyl- *O*-glucuronide. A6 and A7 exhibited the same $[A–H]^-$ ion at *m*/*z* 271.06 (Table S4), which was 15.99 Da less than that of 2, 4, 4′, 5, 6-pentahydroxychalcone. It was reported that 5-OH and 4′-OH of 2, 4, 4′, 5, 6-pentahydroxychalcone can be expelled by the intestinal bacteria [12,17], and the 5-OH is the preferred site to occur dehydroxylation. Hence, A6 and A7 were proposed as 2,4,4′,6-tetrahydroxychalcone-*O*-glucuronide because of the obvious neutral loss of 176.05 Da (Table S4).

Three metabolites (O1-O3) were identified as 4-hydroxycinnamic acid-type metabolites, which were the ring-fission products of 2,4,4′,5,6-pentahydroxychalcone (Table S4). O1 was assigned as 4-sulfo-*O*-methyl phenylacetic acid. O3 was 4-sulfo-cinnamic acid due to its formula composition ($C_9H_{12}O_6S$) and neutral loss of sulfonate (79.95 Da). Meanwhile, O2 was identified as 4-sulfo-phenylpropionic acid, the hydrogenated product of O3 by the intestinal bacteria.

4. Characterization of the metabolites of ECT in rat

One hundred fifty-six metabolites were identified or tentatively characterized, based on their high resolution mass spectral profile (Table 3), among which 17 compounds were prototypes and the other 139 compounds were metabolites. Most of the

metabolites were glucuronidated and sulfonated products. The detailed mass data of the primary metabolites are illustrated in Table S5.

4.1 Flavanonol- or chalcone-type metabolites

The chemical composition of A4 was calculated as $C_{21}H_{20}O_8$, and it was proposed as chalcone-2-*O*-glucuronide with the obvious neutral loss of 176.05 Da. The formula of the aglycone of A8, A9 and A14 was determined to be $C_{15}H_{14}O_7$ (Table S5), which was consistent with that of 6-hydroxykaempferolchalcone and 3,5,6,7,4′-pentahydroxyflavanonol. The neutral loss of 176.05 Da indicated that A9 was the glucuronidated conjugate. Due to an additional neutral loss of 15.02 Da compared with A9, A8 was deduced to be with the glucuronyl and methyl substituents. A14 was characterized as the sulfonated and methylated conjugate since it exhibited successive neutral losses of 79.95 Da and 15.02 Da. Similarly, A12 and A17 were deduced as 2, 4, 6-trihydroxychalcone-*O*-sulfo-*O*-glucuronide and 2,4,4',6-tetrahydroxychalcone-*O*-glucuronide, respectively. In sight that A19 and A20 exhibited the same $[A–H]^-$ ion at *m*/*z* 271.06 (Table S5), their aglycone was deduced as dihydrogalangin or α, 2, 4, 6-tetrahydroxychalcone, A19 was proposed as a glucuronidated conjugate, and A20 was deduced as a glucuronyl and sulfonyl substituted product due to the additional neutral loss of 79.95 Da (Table S5).

4.2 Carthamidin- or isocarthamidin-type (flavanonol-type) metabolites

B2, B3, and B7 were identified as glucuronidative glycosylated conjugates because

they showed the successive neutral losses of 176.05 Da and 162.05 Da (Table S5). Similarly, B4, B5, and B8 were proposed as the *di*-glucuronidated conjugates due to the successive neutral losses of 176.05 Da (Table S5). In view of the neutral cleavage of 176.05 Da, B9 and B15 were assigned as the glucuronidated conjugates. Subsequently, B13 and B14 were supposed as the glucuronidative sulfonated conjugates owing to the observation of the additional neutral loss of 79.95 Da. The molecular formula of B10 was determined to be $C_{15}H_{12}O_6$. Because the typical fragment ions at *m*/*z* 193.0073, 153.0973 and 139.0423 were in good agreement with carthamidin or isocarthamidin, B10 was assigned as carthamidin or isocarthamidin. Moreover, B17 and B19 shared an identical molecular composition ($C_{22}H_{22}O_{12}$) and the same sequential neutral losses of 176.05 Da and 15.02 Da (Table S5); thus, they were identified as glucuronidative methylated conjugates. Owing that B16 and B18 exhibited an additional neutral cleavage of 79.95 Da compared with B17 and B19, all of the glucuronyl, methyl and sulfonyl groups were substituted at B16 and B18. The molecular formula of B20 and B21 was determined as $C_{15}H_{12}O_9S$ based on their HR-MS data, and they were assigned as sulfonated conjugates with the neutral loss of 79.95 Da. The molecular composition of B22 exhibited an additional 15.02 Da compared with B20; hence, it was assigned as the methylated product of B20.

4.3 Kaempferol-type metabolites

D1 was prototype by comparing with the ECT. D2 was identified as kaempferol-*di*-*O*-glucuronide because it exhibited the successive neutral losses of 176.05 Da, whereas

D4 was proposed as kaempferol-*O*-glucosyl-*O*-glucuronide due to the observation of the step-wise neutral losses of 162.05 Da and 176.05 Da (Table S5). D8 and D16 were characterized as glucuronidated conjugates because they exhibited the diagnostic neutral loss of 176.05 Da. All of the glucuronyl, sulfonyl and methyl groups were proposed to be present in D14 because its MS^n spectra exhibited successive cleavages of 176.05 Da, 79.95 Da and 15.02 Da (Table S5). D15 and D17 were proposed as glucuronidated and methylated metabolites due to the detection of the $[M–H–GluA]^–$ and $[M–H–GluA–Me]^–$ ions (Table S5). Accordingly, D10 and D13 were assigned as glucuronidated and sulfonated metabolites due to the detection of the neutral loss of 179.95 Da and 176.05 Da (Table S5).

4.4 6-Hydroxykaempferol- or quercetin-type metabolites

E1 was prototype by comparing with the ECT. Due to the similar mass spectral profiles between 6-hydroxykaempferol and quercetin, the aglycone of E5, E6, E14, E15, E17 and E18 was proposed as 6-hydroxykaempferol or quercetin. Due to the occurrence of neutral losses of 15.02 Da and 176.05 Da, E5, E14 and E15 were proposed as the methylative glucuronidated conjugates (Table S5). E18 was characterized as the sulfonated product of E15 since it showed an additional cleavage of 79.95 Da (Table S5). Similarly, E6 was deduced as the glycosylative glucuronidated metabolite and E17 was identified as the glucuronidated conjugate (Table S5).

4.5 Other flavone-type metabolites

Among the 14 flavone-type metabolites (G1-G14), G1-G5 were classified as dihydroxyflavone-type metabolites (Table S5). G2 and G5 were assigned as glucuronidated conjugates since they exhibited an obvious neutral loss of 176.05 Da (Table S5). Similarly, G4 was supposed as the sulfonated conjugate because it showed a neutral loss of 79.95 Da. G1 and G3 were deduced as the glucuronidated products of G4 due to the observation of an additional neutral loss of 176.05 Da (Table S5).

G6–G14 were sorted as galangin-type metabolites (Table S5). Owing that the neutral loss of 176.05 Da was exhibited in the G11 and G13 mass spectral profiles, these two components were proposed as galangin-*O*-glucuronides, while G8 and G9 were deduced as the sulfonated products of G11 due to the detection of an additional neutral loss of 79.05 Da (Table S5). Similarly, G6, G10 and G12 were supposed as the methylated products of G8 because they showed the successive neutral cleavages of 176.05 Da, 79.95 Da and 15.02 Da. The molecular composition of G7 was determined to be $C_{22}H_{20}O_{11}$; thus, it was identified as galangin-*O*-methyl-*O*-glucuronide according to the observation of the neutral losses of 176.05 Da and 15.02 Da. Accordingly, G14 was assigned as galangin-*O*-methyl-*O*-sulfonate (Table S5).

4.6 Phenolic acid-type metabolites

Thirty-six phenolic acids (O1-O36) were identified by MS^n E(DFI)Cs of *m*/*z* 125.02, 137.02, 141.02, 151.04, 163.04 and 165.04 (Table 2), which were the DFIs of the phenolic acid-type metabolites. Most of them were the ring-fission metabolites of flavonoids.

4.6.1 Hydroxylphenyl-acetic acid

Initially, O6 was identified by a comparison with the metabolic profile of kaempferol-3-*O*-rutinoside (Table S2). Then, O1 was assigned as (3-*O*-sulfo-phenyl)-acetic acid because it shared the same molecular composition and fragment ions with O6 in Table S5 [18]. The molecular formula of O5 was determined as $C_9H_{10}O_3S$. In the MS^2 spectra, the neutral losses of 18.01 Da and 43.98 Da were observed, suggesting O5 as 4-hydroxyphenyl propionic acid. The molecular composition of O3 was 15.99 Da more than O5, indicating that O3 was 3,4-dihydroxyphenylacetic acid. O2 and O4 shared the same molecular composition ($C_{14}H_{16}O_{10}$) and fragment ions (Table S5), which were in accordance with hydroxyphenyl acetic acid-*O*-glucuronide, suggesting that these two compounds were the isomers of 3-hydroxyphenylacetic acid-*O*-glucuronide. In a previous study, it has been confirmed that 3-coumaric acid is a major metabolite in rats compared with 4-coumaric acid [19]. Therefore, O2 (with a response value of 15,548,811 cps) with a higher response was identified as 3-hydroxyphenylacetic acid-*O*-glucuronide, and O4 (with a response value of 4,109,329 cps) was thereby inferred to be 4-hydroxyphenylacetic acid-*O*-glucuronide.

4.6.2 2, 3, 4, 6-Tetrahydroxy-benzoic acid

The molecular formula of O7, O8 and O9 was determined to be $C_{13}H_{14}O_{12}$ (Table S5). The characteristic neutral losses of 18.01 Da and 176.05 Da assigned O7, O8 and O9 as 2,3,4,6-tetrahydroxybenzoic acid-*O*-glucuronide. O10 was deduced as the

methylated conjugate of 2,3,4,6-tetrahydroxybenzoic acid (Table S5).

4.6.3 2, 4, 6-Trihydroxybenzoic acid

The molecular formula of O11 and O14 was determined to be $C_{15}H_{18}O_{11}$. Moreover, the diagnostic neutral losses of 15.02 Da and 176.05 Da were observed; hence, O11 and O14 were assigned as 2,4,6-trihydroxybenzoic acid-*di*-*O*-methyl-*O*-glucuronide. Similarly, O13 and O15 were assigned as 2,4,6-trihydroxybenzoic acid-*di*-*O*-methyl-*O*-sulfonate. In addition, the molecular composition of O12 was characterized as $C_8H_8O_8S$, and the $[M-H-CO_2]^-$, $[M-H-SO_3]^-$ and $[M-H-SO_3-Me]^-$ ions were observed; therefore, it was identified as 2,4,6-trihydroxybenzoic acid-*O*-methyl-*O*-sulfonate (Table S5).

4.6.4 3,4-Dihydroxybenzoic acid

Based on the HR-MS, the molecular composition of O16 was $C_{13}H_{16}O_8$; therefore, it was tentatively identified as 4-hydroxybenzoic acid-*O*-glucoside with the neutral loss of 162.05 Da. Similarly, O17 was deduced as 3, 4-dihydroxybenzoic acid-*O*-methyl-*O*-sulfonate.

4.6.5 4-Hydroxyphenylpropionic acid

O22 was identified as 4-hydroxyphenylpropionic acid-*O*-sulfonate by a comparison with the metabolite profile of HSYA (Table S4). O23, O25 and O26 shared an identical element composition and fragment ions with O22, and these three

components were thus assigned as the isomers of 4-hydroxyphenylpropionic acid-*O*-sulfonate (Table S5). The molecular formula of O20 and O24 was calculated as $C_{15}H_{18}O_9$ based on their HR-MS data. In sight that the fragment ion at *m*/*z* 165.05 was formed by the neutral loss of 176.05 Da, O20 and O24 were identified as the glucuronidated products of 4-hydroxyphenylpropionic acid (Table S5). O18 and O21 showed the same $[M-H]^-$ ion at *m*/*z* 371.09, and the obvious neutral losses of 176.05 Da and 15.02 Da indicated that they were the isomers of 4-hydroxyphenyl acetic acid-*di*-*O*-methyl-*O*-glucuronide. Similarly, O19 was identified as the glycosylative product of 4-hydroxyphenyl propionic acid due to the neutral losses of 162.04 Da.

4.6.6 1,2,3,5-Tetraolbenzene

The molecular composition of O27 was $C_9H_{12}O_7S$, calculated from its HR-MS data, and the ions of $[M-H-SO_3]^-$, $[M-H-SO_3-Me]^-$ and $[M-H-SO_3-2Me]^-$ were observed; hence, O27 was identified as benzene-1,2,3,5-tetraol-*tri*-*O*-methyl-*O*-sulfonate.

4.6.7 Coumaric acid

O29 was identified as 4-sulfo-coumaric acid by a comparison with the metabolite profile of HSYA (Table S4). Because O30 and O31 shared the same molecular composition and fragment ions with O29, they were assigned as the isomers of 4-sulfo-coumaric acid, which were the metabolites of 3, 4-dihydroxycoumaric acid [18]. The molecular formula of compound O28 was calculated as $C_9H_8O_3$ based on the HR-

MS data (Table S5), and a product ion at *m*/*z* 119.0579 (Table S5), which was afforded by the neutral loss of CO_2 (43.99 Da) was observed. Therefore, O28 was assigned as 4-coumaric acid.

4.6.8 Phloroglucinol

Corresponding to the proposed metabolic pathway of HSYA, phloroglucinol was assigned as the ring-fission product of HSYA. In the case of ECT, the molecular composition of O32 was deduced as $C_6H_6O_6S$ based on its HR-MS data (Table S5). In combination with the observation of the neutral loss of 79.95 Da, O32 was assigned as phloroglucinol-*O*-sulfonate. Similarly, O35 and O36 were identified as the sulfonated and methylated conjugated metabolites owing to the observation of an additional cleaveage of 15.02 Da (Table S5). Moreover, O33 and O34 were proposed as phloroglucinol-*di*-*O*-methyl-*O*-glucuronide because they exhibited successive losses of 176.05 Da and 15.02 Da (Table S5).

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Table S1 Detailed LC/MS data for characterization of the chemical constituents from ECT.

No.[a]	t_R (min)	Identification	Formula	$[M+H]^+/[M-H]^-$ Ion mode	Meas. (Da)	Calcd. (Da)	Error (ppm)	Major fragment ions	Ref.
A1	7.400	Isomer of safflor yellow A	$C_{27}H_{30}O_{15}$	neg	593.1510	593.1512	-0.34	503.1151 $[M-H-C_3H_6O_3]^-$, 473.1060 $[M-H-C_4H_8O_4]^-$, 341.0624 $[M-H-C_3H_6O_3\text{-}Glc]^-$, 297.0686 $[M-H-C_3H_6O_3\text{-}Glc\text{-}CO_2]^-$, 353.0504 $[M-H-2C_4H_8O_4]^-$	1
A2	14.572	Isomer of hydroxysafflor yellow A	$C_{27}H_{32}O_{16}$	neg	611.1620	611.1617	0.49	491.1120 $[M-H-C_4H_8O_4]^-$, 473.1003 $[M-H-C_4H_8O_4\text{-}H_2O]^-$, 325.0897 $[M-H-C_4H_8O_4\text{-}CO]^-$, 313.0650 $[^{0,1}X\text{-}CO]^-$, 283.0698 $[M-H-C_4H_8O_4\text{-}CO\text{-}C_2H_2O]^-$, 257.0366	1,2
A3	18.200	Isomer of hydroxysafflor yellow A	$C_{27}H_{32}O_{16}$	neg	611.1620	611.1617	0.49	491.1155 $[M-H-C_4H_8O_4]^-$, 473.1042 $[M-H-C_4H_8O_4\text{-}H_2O]^-$,	1,2

A4	18.768	Isomer of hydroxysafflor yellow A	$C_{27}H_{32}O_{16}$	neg	611.1614	611.1617	-0.49	403.0961 [^{0,4}X-CO]$^-$, 325.0652 [M-H-$C_4H_8O_4$-CO]$^-$, 313.0611 [^{0,1}X-CO]$^-$, 283.0598 [M-H-$C_4H_8O_4$-CO-C_2H_2O]$^-$, 265.0845 491.1137 [M-H-$C_4H_8O_4$]$^-$, 403.0966 [^{0,4}X-CO]$^-$, 473.1039 [M-H-$C_4H_8O_4$-H_2O]$^-$, 353.0593 [M-H-2$C_4H_8O_4$-H_2O]$^-$,	1,2
A5	19.612	Isomer of hydroxysafflor yellow A	$C_{27}H_{32}O_{16}$	neg	611.1614	611.1617	-0.49	325.0810 [M-H-$C_4H_8O_4$-CO]$^-$, 313.0666 [^{0,1}X-CO]$^-$, 283.0585 [M-H-$C_4H_8O_4$-CO-C_2H_2O]$^-$ 491.1181 [M-H-$C_4H_8O_4$]$^-$, 403.1098 [^{0,4}X-CO]$^-$, 473.1080 [M-H-$C_4H_8O_4$-H_2O]$^-$, 325.0714 [M-H-$C_4H_8O_4$-CO]$^-$, 313.0773 [^{0,1}X-CO]$^-$,	1,2
A6	30.732	Isomer of hydroxysafflor yellow A	$C_{27}H_{32}O_{16}$	neg	611.1616	611.1617	0.65	283.0584 [M-H-$C_4H_8O_4$ -CO-C_2H_2O]$^-$, 257.0366 491.1152 [M-H-$C_4H_8O_4$]$^-$,	1,2

A7[b]	32.272	Hydroxysafflor yellow A	$C_{27}H_{32}O_{16}$	neg	611.1621	611.1617	0.65	473.1163 [M-H-$C_4H_8O_4$-H_2O]$^-$, 403.1011 [^{0,4}X-CO]$^-$, 325.0726 [M-H-$C_4H_8O_4$-CO]$^-$, 313.0686 [^{0,1}X-CO]$^-$, 303.0669, 295.0581 [^{0,1}X-CO-H_2O]$^-$, 283.0611 [M-H-$C_4H_8O_4$-CO-C_2H_2O]$^-$ 491.1138 [M-H-$C_4H_8O_4$]$^-$, 473.1130 [M-H-$C_4H_8O_4$-H_2O]$^-$, 403.1017 [^{0,4}X-CO]$^-$, 325.0655 [M-H-$C_4H_8O_4$-CO]$^-$, 313.0685 [^{0,1}X-CO]$^-$, 295.0644 [^{0,1}X-CO-H_2O]$^-$, 283.0598 [M-H-$C_4H_8O_4$-CO-C_2H_2O]$^-$	1,2
A8	33.438	Isomer of hydroxysafflor yellow A	$C_{27}H_{32}O_{16}$	neg	611.1613	611.1617	-0.65	491.1128 [M-H-$C_4H_8O_4$]$^-$, 473.0966 [M-H-$C_4H_8O_4$-H_2O]$^-$, 403.0935 [^{0,4}X-CO]$^-$, 325.0644 [M-H-$C_4H_8O_4$-CO]$^-$, 313.0674 [^{0,1}X-CO]$^-$,	1,2

								283.0557 [M-H-$C_4H_8O_4$-CO-C_2H_2O]$^-$	
A9	41.258	Safflor yellow A	$C_{27}H_{30}O_{15}$	pos	595.1493	595.1477	2.69	577.1411 [M+H-H_2O]$^+$,	1
								433.1063 [M+H-Glc]$^+$,	
								415.1022 [M+H-Glc-H_2O]$^+$,	
								397.0901 [M+H-Glc-H_2O-H_2O]$^+$,	
								385.0909 [M+H-Glc-H_2O-CH_2O]$^+$,	
								355.0755 [M+H-Glc-H_2O-2CH_2O]$^+$,	
								313.0553 [M+H-Glc-$C_4H_8O_4$]$^+$,	
								301.0626 [M+H-Glc-$C_5H_8O_4$]$^+$,	
								181.0392 [M+H-Glc-$C_5H_8O_4$-$C_4H_8O_4$]$^+$,	
								147.0422 [B ring]$^+$,	
A10	47.717	Hydroxycartormin	$C_{27}H_{31}NO_{14}$	neg	592.1663	592.1672	-1.52	472.1055 [M-H-$C_4H_8O_4$]$^-$,	1
								446.1200 [M-H-$C_3H_6O_3$-2CO]$^-$,	
								364.0774 [M-H-$C_4H_8O_4$-$C_3H_6O_3$-H_2O]$^-$,	
								244.0235 [M-H-$C_4H_8O_4$-$C_3H_6O_3$-H_2O]$^-$,	
								339.0694 [M-H-$C_4H_8O_4$-NH_3-2CO]$^-$	
A11	50.585	Isomer of safflor yellow A	$C_{27}H_{30}O_{15}$	neg	593.1512	593.1512	0.00	473.0994 [M-H-$C_4H_8O_4$]$^-$,	1

								447.1121,327.0720,	
								297.0786 [M-H-$C_3H_6O_3$-Glc-CO_2]$^-$,	
								353.0592 [M-H-2$C_4H_8O_4$]$^-$	
A12	52.167	Isomer of safflor yellow A	$C_{27}H_{30}O_{15}$	pos	595.1658	593.1677	-3.19	433.1073 [M+H-Glc]$^+$,	1
								415.0996 [M+H-Glc-H_2O]$^+$,	
								397.0932 [M+H-Glc-H_2O-H_2O]$^+$,	
								385.0872 [M+H-Glc-H_2O-CH_2O]$^+$,	
								355.0755 [M+H-Glc-H_2O-2CH_2O]$^+$,	
								313.0587 [M+H-Glc-$C_4H_8O_4$]$^+$,	
								301.0681 [M+H-Glc-$C_5H_8O_4$]$^+$,	
								181.0093 [M+H-Glc-$C_5H_8O_4$-$C_4H_8O_4$]$^+$,	
								147.0431 [B ring]$^+$	
A13	56.067	Anhydrosafflor yellow B	$C_{48}H_{52}O_{26}$	neg	1043.2664	1043.2674	-0.96	1025.2487 [M-H-H_2O]$^-$, 923.2116 [M-H-$C_4H_8O_4$]$^-$,	1
								863.1964 [M-H-H_2O-Glc]$^-$, 449.1038 [A ring]$^-$,	
								299.0468 [A ring-$C_5H_{10}O_5$]$^-$	
A14 [b]	69.122	Isosafflomin C	$C_{30}H_{30}O_{14}$	neg	613.1564	613.1563	0.16	567.1840 [M-H-CO-H_2O]$^-$,	1
								551.1483 [M-H-CO_2-H_2O]$^-$,	

									533.1381 [M-H-CO_2-H_2O-H_2O]$^-$,	
									467.1187 [M-H-$C_6H_{10}O_4$]$^-$,	
									431.1029 [M-H-CO_2-H_2O-$C_4H_8O_4$]$^-$,	
									361.1009 [M-H-CO_2-H_2O-$C_4H_8O_4$-$C_3H_6O_3$]$^-$,	
									317.1020 [M-H-$C_6H_{10}O_4$-$C_5H_{10}O_5$]$^-$,	
									299.0533 [M-H-$C_6H_{10}O_4$-$C_5H_{12}O_6$]$^-$,	
									287.0638 [^{0,2}X-C_2H_2O-H_2O]$^-$,	
									241.0483 [^{0,2}X-C_2H_2O-CO]$^-$,	
A15 [b]	70.628	Safflomin C	$C_{30}H_{30}O_{14}$	neg	613.1560	613.1563	-0.49		567.2725 [M-H-CO-H_2O]$^-$,	1
									551.1515 [M-H-CO_2-H_2O]$^-$,	
									533.1381 [M-H-CO_2-H_2O-H_2O]$^-$,	
									467.1537 [M-H-$C_6H_{10}O_4$]$^-$,	
									431.0880 [M-H-CO_2-H_2O-$C_4H_8O_4$]$^-$,	
									361.1042 [M-H-CO_2-H_2O-$C_4H_8O_4$-$C_3H_6O_3$]$^-$,	
									317.1121 [M-H-$C_6H_{10}O_4$-$C_5H_{10}O_5$]$^-$,	
									299.0513 [M-H-$C_6H_{10}O_4$-$C_5H_{12}O_6$]$^-$	
									287.0629 [^{0,2}X-C_2H_2O-H_2O]$^-$,	

								241.0490 [^{0,2}X-C_2H_2O-CO]$^-$,	
B1	15.032	5,6,7,4′-Tetrahydroxy-flavanonol -*di*-*O*-glucoside	$C_{27}H_{32}O_{17}$	neg	627.1542	627.1567	-3.99	465.1183 [M-H-Glc]$^-$,	4
B2	28.163	5,6,7,4′-Tetrahydroxy-flavanonol -*O*-glucosyl-*C*-glucoside	$C_{27}H_{32}O_{17}$	neg	627.1571	627.1567	0.64	507.1142 [M-H-$C_4H_8O_4$]$^-$, 303.0648 [M-H-2Glc]$^-$, 489.0972, 419.0895, 315.0749, 299.0530, 281.0403, 257.0670	4
B3	36.512	Carthamidin/Isocarthamidin -*C*-glucoside	$C_{21}H_{22}O_{11}$	neg	449.1082	449.1089	-1.56	359.0781 [M-H-$C_3H_6O_3$]$^-$, 329.0596 [M-H-$C_4H_8O_4$]$^-$, 287.0485 [M-H-Glc]$^-$, 223.0206 [M-H-Glc]$^-$, 139.0088 [^{1,3}A-CO]$^-$	4
B4	38.212	Carthamidin/Isocarthamidin -*O*-glucosyl-*C*-glucoside	$C_{21}H_{22}O_{11}$	neg	611.1616	611.1617	-0.16	521.1247 [M-H-$C_3H_6O_3$]$^-$, 449.1040 [M-H-Glc]$^-$, 287.0540 [M-H-2Glc]$^-$, 193.0053 [M-H-B ring]$^-$, 181.0102 [^{1,2}A]$^-$, 153.0221 [^{1,2}A-CO]$^-$	4
B5	39.058	Carthamidin/Isocarthamidin -*O*-glucosyl-*O*-glucuronide	$C_{27}H_{30}O_{17}$	neg	625.1395	625.1410	-2.40	449.1058 [M-H-GluA]$^-$, 287.0519 [M-H-GluA-Glc]$^-$, 153.0174 [^{1,2}A-CO]$^-$, 139.0043 [^{1,3}A-CO]$^-$	4
B6	41.068	Carthamidin/Isocarthamidin	$C_{27}H_{32}O_{16}$	neg	611.1619	611.1617	0.33	521.1257 [M-H-$C_3H_6O_3$]$^-$,	4

		-*O*-glucosyl-*C*-glucoside						359.0700 [M-H-$C_3H_6O_3$-Glc-H]$^-$, 287.0462 [M-H-2Glc]$^-$, 225.0329 [M-H-2Glc-$2H_2O$-CO]$^-$, 193.0223 [M-H-Bring]$^-$, 181.0102 [^{1,2}A]$^-$, 153.0210 [^{1,2}A$^-$-CO]$^-$,119.5534 [^{1,3}B]$^-$	
B7	51.580	Carthamidin/Isocarthamidin -*O*-glucoside	$C_{21}H_{22}O_{11}$	neg	449.1090	449.1089	0.22	287.0533 [M-H-Glc]$^-$, 243.0624 [M-H-Glc-$2H_2O$-CO]$^-$, 193.0073 [M-H-B ring]$^-$, 181.0190 [^{1,2}A]$^-$, 167.0059 [^{1,3}A]$^-$,153.0210 [^{1,2}A-CO]$^-$, 139.0088 [^{1,3}A-CO]$^-$,	4
B8	59.558	Carthamidin/Isocarthamidin -*O*-glucoside	$C_{21}H_{22}O_{11}$	neg	449.1086	449.1089	-0.67	329.0432 [M-H-$C_4H_8O_4$]$^-$, 287.0491 [M-H-Glc]$^-$, 193.0044 [M-H-B ring]$^-$, 181.0153 [^{1,2}A]$^-$, 167.0467 [^{1,3}A]$^-$, 153.0253 [^{1,2}A-CO]$^-$,139.0088[^{1,3}A-CO]$^-$	4
B9	60.353	Carthamidin/Isocarthamidin -*O*-glucoside	$C_{21}H_{22}O_{11}$	neg	449.1082	449.1089	-1.56	287.0521 [M-H-Glc]$^-$, 233.0654, 181.0153 [^{1,2}A]$^-$, 193.0132 [M-H-B ring]$^-$, 153.0174 [^{1,2}A-CO]$^-$,	4
C1	16.537	6-Hydroxyquercetin	$C_{21}H_{20}O_{12}$	neg	463.0884	463.0882	0.43	317.0446 [M-H-Rha]$^-$, 146.9340 [^{0,3}B-H_2O]$^-$	5

		-3-*O*-rhamnoside							
C2	25.792	6-Hydroxyquercetin -3,6,7-*tri*-*O*-glucoside	$C_{33}H_{40}O_{23}$	neg	803.1869	803.1887	-2.24	641.1309 [M-H-Glc]$^-$, 479.0788 [M-H-2Glc]$^-$, 317.0258 [M-H-3Glc]$^-$	6
C3 [b]	48.302	Rutin	$C_{27}H_{30}O_{16}$	neg	609.1459	609.1461	-0.33	301.0290 [M-H-Rha-Glc]$^-$, 255.0265 [M-H-Rha-Glc-H_2O-CO]$^-$, 179.0278 [^{0,2}A]$^-$, 151.0039 [^{0,3}A]$^-$	5
C4 [b]	51.128	Quercetin-3-*O*-glucoside	$C_{21}H_{20}O_{12}$	neg	463.0883	463.0882	0.22	301.0322 [M-H-Glc]$^-$, 255.0297 [M-H-Glc-H_2O-CO]$^-$, 151.0023 [^{0,3}A]$^-$	5
C5	55.977	quercetin-*O*-methyl-*O*-glucosyl-*O*-rhamnoside	$C_{28}H_{32}O_{16}$	pos	625.1754	625.1763	-1.44	479.1100 [M+H-Rha]$^+$, 317.0616 [M+H-Glc-Rha]$^+$, 302.0407 [M+H-Glc-Rha-Me]$^+$, 286.8730 [M+H-Glc-Rha-CH_2O]$^+$, 149.0200 [^{1,3}B]$^+$, 121.0258 [^{0,2}A-CO_2]$^+$	7
D1	17.110	6-Hydroxykaemferol-8-*C*-glucosyl-*O*-glucoside	$C_{27}H_{30}O_{17}$	neg	625.1413	625.1410	0.48	505.0954 [M-H-$C_4H_8O_4$]$^-$, 355.0452 [M-H-$C_4H_8O_4$-$C_5H_{10}O_5$]$^-$, 343.0339 [M-H-$C_4H_8O_4$-Glc]$^-$, 299.0514 [M-H-$C_4H_8O_4$-Glc-CO_2]$^-$,	9, 10

								269.0435 [M-H-$C_4H_8O_4$-$C_5H_{10}O_5$-$C_3H_6O_4$]$^-$	
D2	21.088	Kaempferol-6,8-*di*-*C*-glucoside	$C_{27}H_{30}O_{16}$	neg	609.1455	609.1461	-0.98	489.0998 [M-H-$C_4H_8O_4$]$^-$,	
								459.0860 [M-H-$C_5H_{10}O_5$]$^-$,	
								339.0414 [M-H-$C_4H_8O_4$-$C_5H_{10}O_5$]$^-$,	
								311.0470 [M-H-$C_4H_8O_4$-$C_5H_{10}O_5$-CO]$^-$	
D3 [b]	28.983	6-Hydroxykaempferol	$C_{33}H_{40}O_{22}$	neg	787.1939	787.1938	0.13	625.1373 [M-H-Glc]$^-$,	
		-3,6,7-*tri*-*O*-glucoside						463.0850 [M-H-2Glc]$^-$,	
								301.0311 [M-H-3Glc]$^-$,	
								271.0135 [M-H-3Glc-CH_2OH]$^-$	
D4 [b]	29.252	6-Hydroxykaempferol-3,6-*di*	$C_{33}H_{38}O_{23}$	neg	801.1735	801.1731	0.50	625.1373 [M-H-GluA]$^-$,	
		-*O*-glucosyl-7-*O*-glucuronide						463.0848 [M-H-GluA-Glc]$^-$,	
								301.0313 [M-H-GluA-2Glc]$^-$,	
								271.0221 [M-H-GluA-2Glc -CH_2OH]$^-$,	
								225.0116 [M-H-GluA-2Glc -CH_2OH-H_2O-2CO]$^-$	
D5	29.645	6-Hydroxykaempferol-3-*O*	$C_{39}H_{50}O_{26}$	neg	933.2527	933.2517	1.07	771.1935 [M-H-Glc]$^-$, 609.1355 [M-H-2Glc]$^-$,	10
		-rutinosyl-6,7-*di*-*O*-glucoside						301.0338 [M-H-2Glc-Rha-GluA]$^-$, 155.0514	

D6	32.545	6-Hydroxykaemferol -3,7-*di*-*O*-glucoside	$C_{27}H_{30}O_{17}$	neg	625.1412	625.1410	0.32	463.0869 [M-H-Glc]$^-$, 301.0314 [M-H-2Glc]$^-$, 271.0369 [M-H-2Glc-CH_2O]$^-$	9, 10
D7	33.860	6-Hydroxykaempferol -3-*O*-glucosiyl-7-*O*-glucuronide	$C_{27}H_{28}O_{18}$	neg	639.1206	639.1203	0.47	463.0836 [M-H-GluA]$^-$, 301.0311 [M-H-GluA-Glc]$^-$, 255.0280 [M-H-GluA-Glc-H_2O-CO]$^-$, 245.0368 [M-H-GluA-Glc-CO-CO]$^-$, 179.0345 [^{0,2}A]$^-$	2
D8	33.960	Kaempferol-7-*O*-rhamnosyl -3-*O*-glucoside	$C_{27}H_{30}O_{15}$	neg	593.1511	593.1512	-0.17	447.1143 [M-H-Rha]$^-$, 285.0735 [M-H-Rha-Glc]$^-$, 135.0466 [^{0,2}A-CO]$^-$	8
D9	35.907	Kaemferol-3-*O*-glucosyl -7-*O*-glucuronide	$C_{27}H_{28}O_{17}$	neg	623.1251	623.1254	-0.48	533.1163 [M-H-$C_3H_6O_3$]$^-$, 447.0904 [M-H-GluA]$^-$, 285.0415 [M-H-Glc-GluA-Glc]$^-$, 255.0267 [M-H-2Glc-GluA-CH_2OH]$^-$, 227.0474 [M-H-2Glc-GluA -CH_2OH-CO]$^-$, 211.0366 [M-H-2Glc-GluA -2CO-H_2O]$^-$	2
D10	40.118	6-Hydroxykaempferol-3-*O* -rutinosyl-6-*O*-glucoside	$C_{33}H_{40}O_{21}$	neg	771.1984	771.1989	-0.65	609.1434 [M-H-Glc]$^-$, 463.0818 [M-H-Glc-Rha]$^-$, 301.0318 [M-H-2Glc-Rha]$^-$, 255.0261 [M-H-Glc-Rha-Glc-H_2O-CO]$^-$	10

D11 [b]	40.732	6-Hydroxykaempferol -6,7-*di*-*O*-glucoside	$C_{27}H_{30}O_{17}$	neg	625.1395	625.1410	-2.34	463.0849 $[M-H-Glc]^-$, 301.0301 $[M-H--2Glc]^-$, 271.0251 $[M-H-2Glc\ -CH_2OH]^-$, 255.0234 $[M-H-2Glc\ -H_2O-CO]^-$, 226.7479 $[M-H-2GluA\ -H_2O-2CO]^-$, 215.0531 $[M-H-2Glc\ -CH_2OH-2CO]^-$	
D12	41.813	Kaempferol-3,7-*di*-*O*-glucoside	$C_{27}H_{30}O_{16}$	pos	611.1604	611.1607	-0.05	449.1051 $[M-H-Glc]^+$, 287.0543 $[M-H-2Glc]^+$, 269.0136 $[M-H-2Glc-H_2O]^+$, 149.0219 $[^{0,3}B]^+$	2
D13	42.597	Kaemferol-7-*O*-glucosyl -3-*O*-glucuronide	$C_{27}H_{28}O_{17}$	pos	625.1384	625.1400	-2.56	463.0822 $[M+H-Glc]^+$, 287.0531 $[M+H-Glc-GluA]^+$, 165.0564 $[^{0,2}A]^+$, 121.0218 $[^{0,2}A-CO_2]^+$	2
D14 [b]	44.128	6-Hydroxykaempferol -3-*O*-rutinoside	$C_{27}H_{30}O_{16}$	pos	609.1606	609.1607	0.16	465.0993 $[M+H-Rha]^+$, 303.0471 $[M+H-Rha-Glc]^+$, 267.2995 $[M+H-Rha-Glc-H_2O-CO]^+$, 255.0126 $[M+H-Rha-Glc-H_2O-CH_2O]^+$, 153.0376 $[^{0,3}A]^+$	
D15 [b]	45.557	6-Hydroxykaemferol -3-*O*-glucoside	$C_{21}H_{20}O_{12}$	neg	463.0883	463.0882	0.22	301.0316 $[M-H-Glc]^-$, 255.0249 $[M-H-Glc-CH_2O]^-$ 183.0391 $[M-H-Glc-CH_2O-2CO-H_2O]^-$,	

								151.0139 [^{1,3}A]$^-$	
D16	48.825	Kaempferol-7-*O*-rhamnosyl -3-*O*-glucoside	$C_{27}H_{30}O_{15}$	neg	593.1520	593.1512	1.35	447.0996 [M-H-Rha]$^-$, 285.0335 [M-H-Rha-Glc]$^-$	8
D17 [b]	55.218	Kaemferol-3-*O*-rutinoside	$C_{27}H_{30}O_{15}$	neg	593.1509	593.1512	-0.51	447.1167 [M-H-Rha]$^-$, 285.0377 [M-H-Rha-Glc]$^-$, 179.0408	
D18 [b]	58.617	Kaemferol-3-*O*-glucoside	$C_{21}H_{20}O_{11}$	neg	447.0936	447.0933	0.67	357.0652 [M-H-$C_3H_6O_4$]$^-$, 327.0515 [M-H-$C_4H_8O_5$]$^-$, 285.0363 [M-H-Glc]$^-$, 255.0295 [M-H-Glc-CH_2O]$^-$, 227.0326 [M-H-Glc-CH_2O-CO]$^-$, 211.0310 [M-H-Glc-2CO-H_2O]$^-$, 183.0544 [M-H-Glc-2CO-H_2O-CO]$^-$, 163.0080 [^{0,2}A]$^-$, 155.0553 [M-H-Glc-2CO-H_2O-CO]$^-$	
D19	59.433	6-Hydroxykaemferol-*O*-methyl -*O*-glucoside	$C_{22}H_{22}O_{12}$	neg	477.1039	477.1038	0.21	315.0513 [M-H-Glc]$^-$, 300.0245 [M-H-Glc-Me]$^-$, 271.0246 [M-H-Glc-C_2H_4O]$^-$, 255.0205 [M-H-Glc-Me-H_2O-CO]$^-$,	2

								179.0282 [^{0,2}A]$^-$,	
O1	24.560	4-*O*-Glucosylcinnamic acid	$C_{15}H_{18}O_8$	neg	325.0930	325.0929	0.31	163.0399 [M-H-Glc]$^-$, 119.0573 [M-H-Glc-CO_2]$^-$	11
O2	25.445	4-*O*-Glucosyl-phenyl propionic acid	$C_{15}H_{20}O_8$	neg	327.1091	327.1091	0.00	165.0542 [M-H-Glc]$^-$, 121.0617 [M-H-Glc-CO_2]$^-$	11
O3	39.373	4-*O*-Glucosylcinnamic acid isomer	$C_{15}H_{18}O_8$	neg	325.0928	325.0929	-0.30	163.0399 [M-H-Glc]$^-$, 119.0573 [M-H-Glc-CO_2]$^-$	11
U1	27.538	$C_{16}H_{16}O_7$-*O*-glucoside	$C_{22}H_{26}O_{12}$	pos	483.1517	483.1497	4.14	321.0322 [M+H-Glc]$^-$, 302.9044, 275.0962, 243.0726, 221.3209, 166.2562, 137.9331	
U2	30.180	$C_{16}H_{16}O_7$-*O*-glucoside	$C_{22}H_{26}O_{12}$	pos	483.1493	483.1497	-5.38	321.1039 [M+H-Glc]$^-$, 303.1022, 275.0892, 243.0732, 139.1145	

[a] A, B, C, D, O and U: corresponding to the different skeleton shown in Table 1.

[b] Identified with the reference compounds.

Table S2 Detailed LC/MS data for identification of the metabolites in rats after oral administration of kaempferol-3-*O*-rutinoside.

No.	t_R (min)	Identification	Formula	[M-H]$^-$			Major fragment ions	Detect in*	
				Meas. (Da)	Pred. (Da)	Error (ppm)		P	U
A1	23.540	Dihydrogalangin-*O*-sulfonate/α,2,4,6-tetrahydroxychalcone-*O*-sulfonate	$C_{15}H_{12}O_8S$	351.0171	351.0180	-2.56	333.0070 [M-H-H_2O]$^-$, 271.0528 [M-H-SO_3]$^-$, 253.0436 [M-H-SO_3-CO]$^-$, 225.0437 [M-H-SO_3-2CO]$^-$	-	+
A2	24.105	Dihydrokaempferol-*di*-*O*-glucuronide /α,2,4,4′,6-pentahydroxychalcone -*di*-*O*-glucuronide	$C_{27}H_{28}O_{18}$	639.1202	639.1203	-0.16	463.0764 [M-H-GluA]$^-$, 287.0547 [M-H-2GluA]$^-$ 259.0653 [M-H-2GluA-H_2O]$^-$, 243.0588	-	+
A3	34.765	Dihydrokaempferol-*O*-glucuronide /α,2,4,4′,6-pentahydroxychalcone -*O*-glucuronide	$C_{21}H_{20}O_{12}$	463.0881	463.0882	-0.22	287.0524 [M-H-GluA]$^-$, 259.0653 [M-H-GluA-H_2O]$^-$, 243.0588, 215.0709, 173.0621, 151.0094 [^{1,3}A]$^-$, 137.0254 [^{0,3}A]$^-$, 125.0269	+	-
A4	35.050	Dihydrokaempferol-*O*-sulfo -*O*-glucuronide	$C_{21}H_{20}O_{15}S$	543.0452	543.0450	0.37	463.0843 [M-H-SO_3]$^-$, 367.0065 [M-H-GluA]$^-$,	-	+

		/α,2,4,4′,6-pentahydroxychalcone -*O*-sulfo-*O*-glucuronide					287.0509 [M-H-GluA-SO_3]$^-$, 259.0590 [M-H-GluA-SO_3-H_2O]$^-$, 243.0690, 215.0704, 151.0060 [^{1,3}A]$^-$, 137.0254 [^{0,3}A]$^-$, 125.0256		
A5	37.785	Dihydrokaempferol-*O*-glucuronide/ α,2,4,4′,6-pentahydroxychalcone -*O*-glucuronide	$C_{21}H_{20}O_{12}$	463.0875	463.0882	-1.51	287.0526 [M-H-GluA]$^-$, 269.0428 [M-H-GluA-H_2O]$^-$, 259.0590 [M-H-GluA-CO]$^-$, 243.0604, 199.0778, 173.0656, 125.0263	-	+
A6	38.985	Dihydrokaempferol-*O*-glucuronide/ α,2,4,4′,6-pentahydroxychalcone -*O*-glucuronide	$C_{21}H_{20}O_{12}$	463.0872	463.0882	-0.21	287.0517 [M-H-GluA]$^-$, 269.0508 [M-H-GluA-H_2O]$^-$, 259.0603 [M-H-GluA-CO]$^-$, 243.0620, 201.0565, 173.0634, 151.0025 [^{1,3}A]$^-$, 125.0253	-	+
A7	40.707	Dihydrokaempferol-*O*-glucuronide/ α,2,4,4′,6-pentahydroxychalcone -*O*-glucuronide	$C_{21}H_{20}O_{12}$	463.0886	463.0882	0.86	287.0524 [M-H-GluA]$^-$, 259.0590 [M-H-GluA-CO]$^-$, 125.0271	-	+
A8	41.655	Dihydrogalangin-*di*-*O*-glucuronide/	$C_{27}H_{28}O_{17}$	623.1241	623.1254	-2.09	447.0878 [M-H-GluA]$^-$,	-	+

		α,2,4,6-tetrahydroxychalcone -*di*-*O*-glucuronide					271.0654 [M-H-2GluA]$^-$, 151.0094 [^{1,3}A]$^-$, 157.0094		
A9	45.965	Dihydrokaempferol-*O*-sulfonate/ α,2,4,4′,6-pentahydroxychalcone -*O*-sulfonate	$C_{15}H_{12}O_9S$	367.0129	367.0129	0.00	287.0531 [M-H-SO_3]$^-$, 259.0610 [M-H-SO_3-H_2O]$^-$, 243.0678, 215.0724, 173.0672, 165.0097, 151.0034 [^{1,3}A]$^-$, 125.0227	-	+
A10	49.120	Dihydrokaempferol-*O*-sulfonate/ α,2,4,4′,6-pentahydroxychalcone -*O*-sulfonate	$C_{15}H_{12}O_9S$	367.0134	367.0129	1.36	287.0531 [M-H-SO_3]$^-$, 259.0610 [M-H-SO_3-H_2O]$^-$, 243.0678, 165.0097, 125.0281	-	+
A11	54.945	Dihydrokaempferol-*O*-sulfonate/ α,2,4,4′,6-pentahydroxychalcone -*O*-sulfonate	$C_{15}H_{12}O_9S$	367.0134	367.0129	1.36	287.0531 [M-H-SO_3]$^-$, 259.0610 [M-H-SO_3-H_2O]$^-$, 243.0678, 215.0709, 173.0608, 165.0097, 151.0094 [^{1,3}A]$^-$, 125.0445	-	+
A12	68.730	Dihydrogalangin-*O*-sulfonate/ α,2,4,6-tetrahydroxychalcone -*O*-sulfonate	$C_{15}H_{12}O_8S$	351.0186	351.0180	1.71	271.0580 [M-H-SO_3]$^-$, 165.0225	-	+
A13	79.540	3,5-Dihydroxyflavanone-*O*-	$C_{21}H_{20}O_{10}$	431.0982	431.0983	-0.23	255.0642 [M-H-GluA]$^-$, 175.0259	-	+

		glucuronide/ α,2-dihydroxychalcone- *O*-glucuronide							
C1	52.630	Quercetin-*O*-glucuronide	$C_{21}H_{18}O_{13}$	477.0684	477.0674	2.10	301.0562 [M-H-GluA]$^-$, 273.0715 [M-H-GluA-CO]$^-$, 255.0603 [M-H-GluA-CO-H_2O]$^-$, 179.0132, 165.0172 [^{0,3}B]$^-$, 139.0429, 85.3560	-	+
C2	63.220	Quercetin-*O*-glucuronide	$C_{21}H_{18}O_{13}$	477.0684	477.0674	2.10	301.0291 [M-H-GluA]$^-$, 273.0382 [M-H-GluA-CO]$^-$, 245.0424 [M-H-GluA-2CO]$^-$, 151.0094 [^{1,3}A]$^-$	-	+
C3	65.395	Quercetin-*O*-methyl-*O*-glucuronide	$C_{22}H_{20}O_{13}$	491.0828	491.0831	-0.61	315.0466 [M-H-GluA]$^-$, 300.0328 [M-H-GluA-Me]$^-$, 271.0174, 255.0267	-	+
D1	36.575	Kaempferol-*di*-*O*-glucuronide	$C_{27}H_{26}O_{18}$	637.1048	637.1046	0.31	461.0659 [M-H-GluA]$^-$, 285.0391 [M-H-2GluA]$^-$, 267.0437 [M-H-2GluA-H_2O]$^-$, 257.0480 [M-H-2GluA-CO]$^-$, 243.0285,	-	+

							241.0606, 239.0406 [M-H-GluA-CO-H_2O]$^-$, 199.0366, 169.0660, 163.0086 [^{0,2}A]$^-$, 151.0094 [^{1,3}A]$^-$, 135.0117 [^{0,3}A]$^-$		
D2	36.885	Kaempferol-*di*-*O*-glucuronide	$C_{27}H_{26}O_{18}$	637.1004	637.1046	-6.59	461.0647 [M-H-GluA]$^-$, 285.0379 [M-H-2GluA]$^-$, 267.0278 [M-H-2GluA-H_2O]$^-$, 257.0506 [M-H-GluA-CO]$^-$, 239.0361 [M-H-2GluA-H_2O-CO]$^-$, 229.0471 [M-H-GluA-CO-CO]$^-$, 199.0380, 185.0649, 169.0658, 163.0053 [^{0,2}A]$^-$, 151.0074 [^{1,3}A]$^-$, 135.0104 [^{0,3}A]$^-$	-	+
D3	39.435	Kaempferol-3-*O*-glucosyl -*O*-glucuronide	$C_{27}H_{28}O_{17}$	623.1268	623.1254	2.25	447.0881 [M-H-GluA]$^-$, 285.0386 [M-H-GluA-Glc]$^-$, 267.0278 [M-H-GluA-Glc-H_2O]$^-$, 257.0428 [M-H-GluA-Glc-CO]$^-$, 241.0531, 239.0331 [M-H-GluA-Glc-H_2O-CO]$^-$, 229.0 460 [M-H-GluA-Glc-2CO]$^-$, 213.0567,	-	+

							197.0580, 195.0486, 163.0098 [^{0,2}A]$^-$		
D4	40.290	Kaempferol-*di*-*O*-glucuronide	$C_{27}H_{26}O_{18}$	637.1025	637.1046	-3.30	461.0642 [M-H-GluA]$^-$,	-	+
							285.0382 [M-H-2GluA]$^-$,		
							267.0278 [M-H-GluA-H_2O]$^-$,		
							257.0428 [M-H-GluA-CO]$^-$,		
							229.0534 [M-H-GluA-2CO]$^-$,		
							213.0567,195.0418,169.0587,		
							163.0036 [^{0,2}A]$^-$, 151.0054 [^{1,3}A]$^-$, 145.0318,		
							137.0254, 135.0101 [^{0,3}A]$^-$		
D5	41.805	Kaempferol-*di*-*O*-glucuronide	$C_{27}H_{26}O_{18}$	637.1048	637.1046	0.31	461.0651 [M-H-GluA]$^-$,	-	+
							285.0341 [M-H-2GluA]$^-$,		
							195.0486, 157.0094, 151.0054 [^{1,3}A]$^-$		
D6	42.825	Kaempferol-*di*-*O*-glucuronide	$C_{27}H_{26}O_{18}$	637.1048	637.1046	0.31	461.0673 [M-H-GluA]$^-$,	-	+
							285.0385 [M-H-2GluA]$^-$,		
							267.0278 [M-H-2GluA-H_2O]$^-$,		
							257.0428 [M-H-GluA-CO]$^-$, 239.0331,		
							229.0450, 213.0495, 197.0580,		

							163.0036 [^{0,2}A]$^-$, 151.0094 [^{1,3}A]$^-$		
D7	44.200	Kaempferol-*di*-*O*-glucuronide	$C_{27}H_{26}O_{18}$	637.1048	637.1046	0.31	461.0650 [M-H-GluA]$^-$,	-	+
							285.0378 [M-H-2GluA]$^-$		
							267.0278 [M-H-2GluA-H_2O]$^-$,		
							257.0428 [M-H-GluA-CO]$^-$,		
							239.0406 [M-H-GluA-CO-H_2O]$^-$,		
							229.0387, 195.0486, 169.0650, 163.0036 [^{0,3}A]$^-$,		
							151.0034 [^{1,3}A]$^-$		
D8	53.390	Kaempferol-3-*O*-glucosyl-*O*-sulfonate	$C_{21}H_{20}O_{14}S$	527.0501	527.0501	0.00	447.0876 [M-H-SO_3]$^-$,	-	+
							285.0414 [M-H-GluA-SO_3]$^-$, 255.0294		
D9	54.515	Kaempferol-*O*-sulfo-*O*-glucuronide	$C_{21}H_{18}O_{15}S$	541.0292	541.0293	-0.18	461.0654 [M-H-SO_3]$^-$,	-	+
							285.0371 [M-H-GluA-SO_3]$^-$,		
							267.0278 [M-H-GluA-SO_3-H_2O]$^-$,		
							257.0506 [M-H-GluA-SO_3-CO]$^-$,		
							241.0455, 229.0534 [M-H-GluA-SO_3-CO]$^-$,		
							197.0648, 169.0714, 163.0036 [^{0,2}A]$^-$		
D10	57.105	Kaempferol-3-*O*-rutinoside	$C_{27}H_{30}O_{15}$	593.1522	593.1513	1.52	285.0375 [M-H-GluA-Rha]$^-$,	-	+

							267.0278 [M-H-GluA-Rha-H_2O]$^-$, 257.0428 [M-H-GluA-Rha-CO]$^-$, 239.0331 [M-H-GluA-Rha-CO-H_2O]$^-$, 229.0534 [M-H-GluA-Rha-2CO]$^-$, 213.0567, 151.0022 [^{1,3}A]$^-$		
D11	59.055	Kaempferol-*O*-glucuronide	$C_{21}H_{18}O_{12}$	461.0728	461.0725	0.65	285.0383 [M-H-GluA]$^-$, 267.0267 [M-H-GluA-H_2O]$^-$, 257.0463 [M-H-GluA-CO]$^-$, 243.0285, 213.0567, 195.0425, 169.0650, 151.0046 [^{1,3}A]$^-$, 135.0112 [^{0,3}A]$^-$	+	+
D12	61.780	Kaempferol-*O*-glucuronide	$C_{21}H_{18}O_{12}$	461.0716	461.0725	-1.95	285.0385 [M-H-GluA]$^-$, 267.0301 [M-H-GluA-H_2O]$^-$, 257.0447 [M-H-GluA-CO]$^-$, 243.0285, 229.0534 [M-H-GluA-2CO]$^-$, 213.0403, 195.0418, 179.0442, 169.0659, 163.0063 [^{0,2}A]$^-$, 151.0064 [^{1,3}A]$^-$, 135.0169[^{0,3}A]$^-$,107.0109[^{0,3}A-CO]	-	+

D13	62.870	Kaempferol-*O*-sulfo-*O*-glucuronide	$C_{21}H_{18}O_{15}S$	541.0291	541.0293	-0.37	461.0663 $[M-H-SO_3]^-$, 285.0348 $[M-H-GluA-SO_3]^-$, 267.0278 $[M-H-GluA-SO_3-H_2O]^-$, 257.0412 $[M-H-GluA-SO_3-CO]^-$, 241.0531, 229.0522 $[M-H-GluA-2CO]^-$, 163.0036 $[^{0,2}A]^-$, 151.0094 $[^{1,3}A]^-$, 143.0036, 137.0254, 135.0123 $[^{0,3}A]^-$	+	+
D14	63.765	Kaempferol-*O*-glucuronide	$C_{21}H_{18}O_{12}$	461.0712	461.0725	-2.82	285.0387 $[M-H-GluA]^-$, 257.0439 $[M-H-GluA-H_2O]^-$, 243.0285, 229.0534 $[M-H-GluA-H_2O-CO]^-$, 213.0567, 199.0366, 169.0638, 163.0048 $[^{0,2}A]^-$, 151.0046 $[^{1,3}A]^-$, 135.0056 $[^{0,3}A]^-$, 107.0209 $[^{0,3}A-CO]^-$,	+	+
D15	67.395	Kaempferol-*O*-glucuronide	$C_{21}H_{18}O_{12}$	461.0719	461.0725	-1.74	285.0398 $[M-H-GluA]^-$, 151.0046 $[^{1,3}A]^-$	-	+
D16	71.885	Kaempferol-*O*-methyl-*O*-glucuronide	$C_{22}H_{20}O_{12}$	475.0835	475.0882	-9.89	299.0517 $[M-H-GluA]^-$, 284.0238 $[M-H-GluA-Me]^-$	-	+
D17	75.405	Kaempferol-*O*-methyl-*O*-glucuronide	$C_{22}H_{20}O_{12}$	475.0861	475.0882	-4.42	285.0385 $[M-H-GluA-Me]^-$, 284.0305,	-	+

							257.0458 [M-H-GluA-Me-H_2O]$^-$, 213.0567, 163.0114 [^{0,2}A]$^-$, 151.0084 [^{1,3}A]$^-$, 107.0209 [^{0,3}A-CO]$^-$		
O1	25.265	4-Sulfo-benzoic acid	$C_7H_6O_6S$	216.9812	216.9801	5.07	137.0264 [M-H-SO_3]$^-$, 93.0363 [M-H-SO_3-CO_2]$^-$	+	-
O2	47.985	4-Hydroxybenzoic acid-*O*-methyl-*O*-sulfonate	$C_8H_8O_6S$	230.9976	230.9969	3.03	151.0418 [M-H-SO_3]$^-$, 136.0249 [M-H-SO_3-Me]$^-$	+	-
O3	13.195	2,4,6-Trihydroxybenzoic acid -*O*-glucuronide	$C_{13}H_{14}O_{11}$	345.0454	345.0463	-2.61	169.0172 [M-H-GluA]$^-$, 151.0034 [M-H-GluA-H_2O]$^-$	-	+
O4	63.405	2,4,6-Trihydroxybenzoic acid -*O*-glucuronide	$C_{13}H_{14}O_{11}$	345.0469	345.0463	1.74	169.0172 [M-H-GluA]$^-$, 151.0034 [M-H-GluA-H_2O]$^-$	-	+

* Detect in: P, plasma; U, urine; +, detected; −, not detected.

Table S3 Detailed LC/MS data for identification of the metabolites in rats after oral administration of 6-hydroxykaempferol-3-*O*-rutinoside.

No.	t_R (min)	Identification	Formula	[M-H]$^-$			Major fragment ions	Detect in*	
				Meas. (Da)	Pred. (Da)	Error (ppm)		P	U
A1 [a]	24.070	Dihydrokaempferol-*di*-*O*-glucuronide/α,2,4,4′,6-pentahydroxychalcone-*di*-*O*-glucuronide	$C_{27}H_{28}O_{18}$	639.1197	639.1203	-0.94	463.0855 [M-H-GluA]$^-$, 287.0514 [M-H-2GluA]$^-$, 259.0666 [M-H-GluA-CO]$^-$	+	+
A2 [a]	34.605	Dihydrokaempferol-*O*-glucuronide/α,2,4,4′,6-pentahydroxychalcone-*O*-glucuronide	$C_{21}H_{20}O_{12}$	463.0883	463.0882	0.22	287.0564 [M-H-GluA]$^-$, 269.0505 [M-H-GluA-H_2O]$^-$, 259.0666 [M-H-GluA-CO]$^-$, 243.0681, 215.0635, 201.0545, 151.0051 [^{1,3}A]$^-$	-	+
A3 [a]	37.765	Dihydrokaempferol-*O*-glucuronide/α,2,4,4′,6-pentahydroxychalcone-*O*-glucuronide	$C_{21}H_{20}O_{12}$	463.0880	463.0882	-0.43	287.0558 [M-H-GluA]$^-$, 259.0621 [M-H-GluA-H_2O]$^-$, 150.9970 [^{1,3}A]$^-$, 125.0224	-	+
A4 [a]	38.680	Dihydrokaempferol-*O*-	$C_{21}H_{20}O_{12}$	463.0887	463.0882	1.08	287.0566 [M-H-GluA]$^-$,	-	+

		glucuronide/α,2,4,4′,6-pentahydroxychalcone-*O*-glucuronide					259.0625 [M-H-GluA-H_2O]$^-$, 243.0720, 215.0707, 173.0626, 151.0091 [^{1,3}A]$^-$, 125.0278		
A5 [a]	41.465	Dihydrogalangin-*di*-*O*-glucuronide/ α,2,4,6-Tetrahydroxychalcone -*di*-*O*-glucuronide	$C_{27}H_{28}O_{17}$	623.1258	623.1254	0.64	447.0934 [M-H-GluA]$^-$, 271.0617 [M-H-2GluA]$^-$, 151.0051 [^{1,3}A]$^-$	-	+
A6	41.665	Dihydrogalangin-*di*-*O*-glucuronide/ α,2,4,6-Tetrahydroxychalcone -*di*-*O*-glucuronide	$C_{27}H_{28}O_{17}$	623.1267	623.1254	2.09	447.0916 [M-H-GluA]$^-$, 271.0580 [M-H-2GluA]$^-$	-	+
A7 [a]	45.260	Dihydrokaempferol-*O* -glucuronide	$C_{21}H_{20}O_{12}$	463.0883	463.0882	0.22	287.0514 [M-H-GluA]$^-$, 259.0588 [M-H-GluA-CO]$^-$	-	+
A8	45.730	Dihydrokaempferol-*O*-sulfonate	$C_{15}H_{12}O_9S$	367.0126	367.0129	-0.82	287.0569 [M-H-GluA]$^-$, 259.0627 [M-H-GluA-CO]$^-$	-	+
A9 [a]	54.435	Dihydrogalangin-*O*-sulfonate/ α,2,4,4′,6-pentahydroxychalcone -*O*-sulfonate	$C_{15}H_{12}O_9S$	367.0124	367.0129	-1.36	287.0549 [M-H-SO_3]$^-$, 269.0505 [M-H-SO_3-H_2O]$^-$, 259.0628 [M-H-SO_3-CO]$^-$, 243.0647, 215.0707, 199.0775, 173.0621,	-	+

							165.0219, 151.0091 [^{1,3}A]$^-$,125.0270		
A10 [a]	59.115	Dihydrogalangin-*O*-sulfo-*O*-glucuronide/α,2,4,6-Tetrahydroxychalcone-*O*-sulfo-*O*-glucuronide	$C_{21}H_{20}O_{14}S$	527.0494	527.0501	-1.33	447.0996 [M-H-SO_3]$^-$, 351.0169 [M-H-GluA]$^-$, 271.0625 [M-H-GluA-SO_3]$^-$, 254.9798, 177.0187, 165.0219, 151.0080 [^{1,3}A]$^-$, 119.0532	-	+
A11	60.270	Dihydrogalangin-*O*-sulfo-*O*-glucuronide/α,2,4,6-Tetrahydroxychalcone-*O*-sulfo-*O*-glucuronide	$C_{21}H_{20}O_{14}S$	527.0508	527.0501	1.33	447.0908 [M-H-SO_3]$^-$, 351.0165 [M-H-GluA]$^-$, 271.0620 [M-H-GluA-SO_3]$^-$, 177.0187, 151.0085 [^{1,3}A]$^-$	-	+
D1	59.620	Kaempferol-*O*-sulfo-*O*–glucuronide	$C_{21}H_{18}O_{15}S$	541.0292	541.0293	-0.18	461.0540 [M-H-SO_3]$^-$, 364.9985 [M-H-GluA]$^-$, 285.0381 [M-H-GluA-SO_3]$^-$, 257.0433 [M-H-GluA-SO_3-H_2O]$^-$, 163.0036, 135.0123 [^{0,3}A]$^-$, 151.0094 [^{1,3}A]$^-$	+	-
D2[a]	64.695	Kaempferol-*O*-glucuronide	$C_{21}H_{18}O_{12}$	461.0725	461.0725	0.00	285.0783 [M-H-GluA]$^-$, 175.0257	-	+
E1	29.518	6-Hydroxykaempferol-*tri*-*O*-glucuronide	$C_{33}H_{34}O_{25}$	829.1303	829.1316	-1.57	653.0946 [M-H-GluA]$^-$, 477.0646 [M-H-2GluA]$^-$, 301.0341 [M-H-3GluA]$^-$, 205.2601	-	+

E2	38.095	6-Hydroxykaempferol-*O*-methyl -*di*-*O*-glucuronide	$C_{28}H_{28}O_{19}$	667.1155	667.1152	0.45	491.0822 [M-H-GluA]$^-$, 315.0489 [M-H-2GluA]$^-$, 300.0242 [M-H-2GluA-Me]$^-$	+	+
E3	40.750	6-Hydroxykaempferol -*di*-*O*-glucuronide	$C_{27}H_{26}O_{19}$	653.0994	653.0995	-0.15	477.0652 [M-H-GluA]$^-$, 301.0336 [M-H-2GluA]$^-$, 283.0242 [M-H-2GluA-CO]$^-$, 271.0331 [M-H-2GluA-CH_2O]$^-$, 255.0264 [M-H-GluA-H_2O-CO]$^-$, 245.0406, 229.0605, 211.0445, 201.0592	-	+
E4	41.425	6-Hydroxykaempferol -*di*-*O*-glucuronide	$C_{27}H_{26}O_{19}$	653.1012	653.0995	2.60	477.0616 [M-H-GluA]$^-$, 301.0373 [M-H-2GluA]$^-$, 283.0160 [M-H-2GluA-CO]$^-$, 255.0342 [M-H-GluA-H_2O-CO]$^-$,	-	+
E5	41.920	6-Hydroxykaempferol -*di*-*O*-glucuronide	$C_{27}H_{26}O_{19}$	653.1017	653.0995	3.37	477.0681 [M-H-GluA]$^-$, 301.0373 [M-H-2GluA]$^-$, 255.0342 [M-H-GluA-H_2O-CO]$^-$, 245.0497 [M-H-GluA-2CO]$^-$	-	+

E6	42.420	6-Hydroxykaempferol -*di*-*O*-glucuronide	$C_{27}H_{26}O_{19}$	653.1003	653.0995	1.22	477.0663 [M-H-GluA]$^-$, 301.0346 [M-H-2GluA]$^-$, 255.0342 [M-H-GluA-H_2O-CO]$^-$	-	+
E7	52.425	6-Hydroxykaempferol-*O*-glucuronide	$C_{21}H_{18}O_{13}$	477.0673	477.0674	-0.21	301.0469 [M-H-GluA]$^-$, 273.0838 [M-H-GluA-CO]$^-$, 255.0431 [M-H-GluA-H_2O-CO]$^-$, 245.0484 [M-H-GluA-2CO]$^-$, 229.0423, 179.0720 [^{0,2}A]$^-$, 165.0273, 139.0466, 133.0341 [^{1,3}B]$^-$, 131.0646 [^{0,3}B-CO]$^-$, 105.0369 [^{1,3}B-CO]$^-$	+	+
E8	61.735	6-Hydroxykaempferol-*O*–methyl -*O*-glucuronide	$C_{22}H_{20}O_{13}$	491.0829	491.0831	-0.41	315.0500 [M-H-GluA]$^-$, 300.0253 [M-H-GluA-Me]$^-$, 272.0325 [M-H-GluA-Me-CO]$^-$, 255.0264 [M-H-GluA-Me-CO-H_2O]$^-$	-	+
E9	65.110	6-Hydroxykaempferol-*O*–methyl -*O*-glucuronide	$C_{22}H_{20}O_{13}$	491.0837	491.0831	1.22	315.0546 [M-H-GluA]$^-$, 300.0321 [M-H-GluA-Me]$^-$, 272.0271 [M-H-GluA-Me-CO]$^-$	-	+

E10	65.340	6-Hydroxykaempferol-*O*-glucuronide	$C_{21}H_{18}O_{13}$	477.0663	477.0674	-2.31	301.0385 $[M-H-GluA]^-$, 283.0160 $[M-H-GluA-CO]^-$	-	+

[a] Identified by a comparison with the metabolites in rats after oral administration of kaempferol-3-*O*-rutinoside.

[*] Detect in: P, plasma; U, urine; +, detected; −, not detected.

Table S4 Detailed LC/MS data for identification of the metabolites in rats after oral administration of HSYA.

No.	t_R(min)	Identification	Formula	[M–H]⁻			Major fragment ions	Detectin*	
				Meas.(Da)	Pred.(Da)	Error (ppm)		P	U
A1[a]	33.980	HSYA	$C_{27}H_{32}O_{16}$	611.1605	611.1617	-1.96	491.1140 [M-H-$C_4H_8O_4$]⁻, 473.1056 [M-H-$C_4H_8O_4$-H_2O]⁻,403.1003, 325.0699, 283.0572 [M-H-$C_4H_8O_4$-CO-C_2H_2O]⁻, 259.0634, 243.0285, 195.0350, 125.0227	+	+
A2	43.870	2,4,6-Trihydroxychalcone -*O*-glucuronide	$C_{21}H_{20}O_{10}$	431.0984	431.0983	0.23	255.0656 [M-H-GluA]⁻, 149.0252	-	+
A3	46.705	2,4,4',5,6-Pentahydroxychalcone -*O*-methyl-*O*-glucuronide	$C_{22}H_{22}O_{12}$	477.1040	477.1038	0.42	301.0724 [M-H-GluA]⁻, 273.0737 [M-H-GluA-CO]⁻, 258.0578[M-H-GluA-CO-Me]⁻, 139.0438	-	+
A4	49.965	2,4,6-Trihydroxychalcone -*O*-glucuronide	$C_{21}H_{20}O_{10}$	431.0988	431.0983	1.16	255.0654[M-H-GluA]⁻, 175.0275, 149.0251, 135.0112, 97.8455	+	+
A5	52.720	2,4,4',5,6-Pentahydroxychalcone -*O*-methyl-*O*-glucuronide	$C_{22}H_{22}O_{12}$	477.1034	477.1038	-0.84	301.0683 [M-H-GluA]⁻, 273.0756, 258.0578 [M-H-GluA-CO-Me]⁻,	+	+

							240.0420, 179.0365, 139.0429		
A6	61.780	2,4,4',6-Tetrahydroxychalcone -*O*-glucuronide	$C_{21}H_{20}O_{11}$	447.0929	447.0933	0.89	271.0638 [M-H-GluA]$^-$, 175.0311, 151.0043 [^{0,3}A]$^-$	+	+
A7	63.695	2,4,4',6-Tetrahydroxychalcone -*O*-glucuronide	$C_{21}H_{20}O_{11}$	447.0927	447.0933	-1.34	271.0575 [M-H-GluA]$^-$, 151.0070 [^{0,3}A]$^-$, 171.0190	+	+
A8	69.020	2,4,6-Trihydroxychalcone -*O*-sulfonate	$C_{15}H_{12}O_7S$	335.0213	335.0230	-5.07	255.0646 [M-H-SO_3]$^-$,149.0294, 135.0104	-	+
A9	70.720	2,4,4',5,6-Pentahydroxychalcone-*O*-methyl-*O*-glucuronide	$C_{22}H_{22}O_{12}$	477.1030	477.1038	-1.68	301.0683 [M-H-GluA]$^-$	-	+
A10	49.965	2,4,6-Trihydroxychalcone -*O*-glucuronide	$C_{21}H_{20}O_{10}$	431.0988	431.0983	1.16	255.0645 [M-H-GluA]$^-$, 175.0256	-	+
A11	69.020	2,4,6-Trihydroxychalcone -*O*-sulfonate	$C_{15}H_{12}O_7S$	335.0224	335.0230	-5.07	255.0645[M-H-SO_3]$^-$,121.0342	-	+
O1	34.705	4-Sulfo-*O*-methyl-phenylacetic acid	$C_8H_8O_6S$	230.9967	230.9969	-0.87	151.0437 [M-H-SO_3]$^-$,136.0184 [M-H-SO_3-Me]$^-$, 117.0031	-	-
O2	37.350	4-Sulfo-phenylpropionic acid	$C_9H_{10}O_6S$	245.0125	245.0126	0.41	165.0580 [M-H-SO_3]$^-$,121.0693 [M-H-SO_3-CO_2]$^-$	+	-
O3	37.355	4-Sulfo-cinnamic acid	$C_9H_8O_6S$	242.9961	242.9969	-3.29	163.0402 [M-H-SO_3]$^-$,119.0527 [M-H-SO_3-CO_2]$^-$	+	+

[a] Identified by comparison with the reference compound.

[*] Detect in: P, plasma; U, urine; +, detected; −, not detected.

Table S5 Detailed LC/MS data for identification of the metabolites in rats after oral administration of ECT.

No.	t_R (min)	Identification	Major fragment ions
A1[b]	18.038	Isomer of HSYA	491.1179 $[M-H-C_4H_8O_4]^-$, 473.1048 $[M-H-C_4H_8O_4-H_2O]^-$, 403.0966 $[^{0,4}X-CO]^-$, 323.0927, 283.0500 $[M-H-C_4H_8O_4-CO-C_2H_2O]^-$
A2[b]	18.462	Isomer of HSYA	491.1218 $[M-H-C_4H_8O_4]^-$, 473.1090 $[M-H-C_4H_8O_4-H_2O]^-$, 355.0817, 283.0639 $[M-H-C_4H_8O_4-CO-C_2H_2O]^-$, 225.0400, 203.0738
A3[b]	28.163	5,6,7,4′-Tetrahydroxy-flavanonol-*O*-glucosyl-*C*-glucoside	507.1163 $[M-H-C_4H_8O_4]^-$, 356.0371 $[M-H-C_4H_8O_4-C_5H_{10}O_5]^-$
A4	30.850	Chalcone-2-*O*-glucuronide	223.0585 $[M-H-GluA]^-$
A5[a]	32.380	HSYA	491.1156 $[M-H-C_4H_8O_4]^-$, 473.1155 $[M-H-C_4H_8O_4-H_2O]^-$, 403.1156 $[^{0,4}X-CO]^-$, 375.0916, 325.0676 $[M-H-C_4H_8O_4-CO]^-$, 283.0599 $[M-H-C_4H_8O_4-COC_2H_2O]^-$, 257.0433, 227.0674, 167.0467
A6[b]	34.028	Isomer of HSYA	491.1124 $[M-H-C_4H_8O_4]^-$, 473.0996 $[M-H-C_4H_8O_4-H_2O]^-$, 403.0966 $[^{0,4}X-CO]^-$, 329.0530, 283.0599 $[M-H-C_4H_8O_4-CO-C_2H_2O]^-$, 223.0272, 219.0291, 121.2076
A7[c]	34.348	Dihydrokaempferol-*O*-glucuronide/α,2,4,4′,6-pentahydroxychalcone-*O*-glucuronide	287.0491 $[M-H-GluA]^-$, 259.0575 $[M-H-GluA-H_2O]^-$, 146.9340, 125.0216

A8	36.448	6-Hydroxykaempferolchalcone-*O*-methyl -*O*-glucuronide/3,5,6,7,4′-pentahydroxyflavanonol -*O*-methyl-*O*-glucuronide	317.0606 [M-H-GluA]$^-$, 289.0620 [M-H-GluA-CO]$^-$, 274.0399 [M-H-GluA-CO-Me]$^-$, 181.0179 [^{1,2}A]$^-$
A9	39.225	6-Hyrdoxykaempferolchalcone-*O*-glucuronide/3,5,6,7,4′-pentahydroxyflavanonol-*O*-glucuronide	303.0477 [M-H-GluA]$^-$, 285.0433 [M-H-GluA-H_2O]$^-$, 275.0560 [M-H-GluA-CO]$^-$, 259.0512, 217.0519, 203.0410,189.0735
A10[b]	40.907	Safflor yellow A	433.1066 [M-H-$C_4H_8O_4$]$^+$, 355.0755 [M+H-Glc-H_2O-2CH_2O]$^+$, 301.0683 [M+H-Glc-$C_5H_8O_4$]$^+$, 181.0213 [M+H-Glc-$C_5H_8O_4$-$C_4H_8O_4$]$^+$
A11[b]	47.698	Tinctormine	472.1055 [M-H-$C_4H_8O_4$]$^-$, 446.1277 [M-H-$C_3H_6O_3$-2CO]$^-$, 364.0774, 244.0235 [M-H-$C_4H_8O_4$-$C_3H_6O_3$-H_2O]$^-$, 218.0410, 216.0263
A12	48.017	2,4,6-Trihydroxychalcone-*O*-sulfo-*O*-glucuronide	431.0890 [M-H-SO_3]$^-$, 335.0192 [M-H-GluA]$^-$, 255.0641 [M-H-GluA-SO_3]$^-$, 149.0352, 135.0020
A13[e]	48.822	2,4,6-Trihydroxychalcone-*O*-glucuronide	255.0583 [M-H-GluA]$^-$, 175.0216, 150.0264
A14	55.105	6-Hyrdoxykaempferolchalcone-*O*-methyl -*O*-sulfonate/3,5,6,7,4′-Pentahydroxyflavanonol -*O*-methyl-*O*-sulfonate	317.0667, 302.0346 [M-H-SO_3-Me]$^-$, 289.0698 [M-H-SO_3-CO]$^-$, 274.0485 [M-H-SO_3-CO-Me]$^-$, 194.9916, 181.0102, 157.1020, 169.0107, 139.0088
A15[c]	55.435	Dihydrokaempferol-*O*-sulfonate/	287.0555 [M-H-SO_3]$^-$, 259.0628 [M-H-CO-SO_3]$^-$,

		α,2,4,6-Tetrahydroxychalcone-*O*-sulfonate	185.0586 [M-H-CO-SO_3-2CO-H_2O]$^-$, 181.0867 [^{1,2}A]$^-$
A16[b]	56.120	Anhydrosafflor yellow B	1025.2427 [M-H-H_2O]$^-$, 923.2152 [M-H-$C_4H_8O_4$]$^-$, 715.1555, 593.1389 [B ring]$^-$, 449.1022 [A ring]$^-$
A17	58.640	2,4,4',6-Tetrahydroxychalcone-*O*-glucuronide	271.0609 [M-H-GluA]$^-$, 177.0192
A18[e]	60.102	2,4,4',6-Tetrahydroxychalcone-*O*-glucuronide	271.0586 [M-H-GluA]$^-$, 177.0192
A19[e]	62.020	Dihydrogalangin-*O*-glucuronide/ α,2,4,6-Tetrahydroxychalcone-*O*-glucuronide	271.0637 [M-H-GluA]$^-$
A20	66.915	Dihydrogalangin-*O*-sulfo-*O*-glucuronide /α,2,4,6-Tetrahydroxychalcone-*O*-sulfo-*O*-glucuronide	351.0087 [M-H-GluA]$^-$, 271.0681 [M-H-GluA-SO_3]$^-$
A21[a]	69.027	Isosafflomin C	551.1737 [M-H-CO_2-H_2O]$^-$, 431.0966 [M-H-CO_2-H_2O-$C_4H_8O_4$]$^-$, 361.1003 [M-H-CO_2-H_2O-$C_4H_8O_4$-$C_3H_6O_3$]$^-$, 241.0497 [^{0,2}X-C_2H_2O-CO]$^-$, 182.0437
A22[a]	70.627	Safflomin C	551.1528 [M-H-CO_2-H_2O]$^-$, 425.1048, 361.0992 [M-H-CO_2-H_2O-$C_4H_8O_4$-$C_3H_6O_3$]$^-$, 241.0469 [^{0,2}X-C_2H_2O-CO]$^-$
B1[b]	37.820	Carthamidin/Isocarthamidin-*O*-glucoside	299.0550 [M-H-$C_5H_{10}O_5$]$^-$, 287.0485 [M-H-Glc]$^-$, 259.0817 [M-H-Glc-CO]$^-$, 153.0291 [^{1,2}A-CO]$^-$
B2	39.035	Carthamidin/Isocarthamidin-*O*-glucosyl -*O*-glucuronide	449.1024 [M-H-GluA]$^-$, 287.0513 [M-H-2GluA]$^-$, 193.0053 [M-H-B ring]$^-$, 181.0139 [^{1,2}A]$^-$, 153.0280 [^{1,2}A-CO]$^-$, 138.8860 [^{1,3}A-CO]$^-$

B3	39.307	Carthamidin/Isocarthamidin-*O*-glucosyl -*O*-glucuronide	449.1056 [M-H-GluA]$^-$, 287.0519 [M-H-2GluA]$^-$, 197.0599 [M-H-B ring]$^-$, 181.0102 [^{1,2}A]$^-$, 153.0143 [^{1,2}A-CO]$^-$
B4	39.448	Carthamidin/Isocarthamidin-*di*-*O*-glucuronide	463.0855 [M-H-GluA]$^-$, 287.0533 [M-H-2GluA]$^-$, 193.0220 [M-H-B ring]$^-$, 181.0166 [^{1,2}A]$^-$, 167.0014 [^{1,3}A]$^-$, 153.0221 [^{1,2}A-CO]$^-$
B5	39.978	Carthamidin/Isocarthamidin-*di*-*O*-glucuronide	463.0859 [M-H-GluA]$^-$, 343.0339 [M-H-$C_4H_8O_4$]$^-$, 287.0538 [M-H-2GluA]$^-$, 269.0500 [M-H-2GluA-H_2O]$^-$, 243.0618,193.0190 [M-H-B ring]$^-$, 181.0149 [^{1,2}A]$^-$,167.0009 [^{1,3}A]$^-$, 153.0280 [^{1,2}A-CO]$^-$, 138.6740 [^{1,3}A-CO]$^-$
B6	40.795	Carthamidin/Isocarthamidin-*O*-glucosyl-*C*-glucoside	521.1278 [M-H-$C_4H_8O_4$]$^-$, 449.1143, 313.0685, 287.0515, 193.0132 [M-H-B ring]$^-$, 181.1568 [^{1,2}A]$^-$
B7	44.242	Carthamidin/Isocarthamidin-*O*-glucosyl -*O*-glucuronide	449.1031 [M-H-GluA]$^-$, 359.0721 [M-H-$C_3H_6O_3$]$^-$, 287.0533 [M-H-GluA-Glc]$^-$, 193.0000 [M-H-B ring]$^-$, 181.0138 [^{1,2}A]$^-$
B8	44.367	Carthamidin/Isocarthamidin-*di*-*O*-glucuronide	463.0855 [M-H-GluA]$^-$, 373.0586, 317.0509, 287.0533 [M-H-2GluA]$^-$, 193.0198 [M-H-B ring]$^-$, 181.0149 [^{1,2}A]$^-$, 167.0026 [^{1,3}A]$^-$, 153.0221 [^{1,2}A-CO]$^-$, 139.0021 [^{1,3}A-CO]$^-$
B9	48.467	Carthamidin/Isocarthamidin-*O*-glucuronide	287.0530 [M-H-GluA]$^-$, 193.0517 [M-H-B ring]$^-$, 181.0102 [^{1,2}A]$^-$, 153.0162 [^{1,2}A-CO]$^-$
B10	49.357	Carthamidin/Isocarthamidin	269.1460 [M-H-H_2O]$^-$, 225.1465, 193.0073 [M-H-B ring]$^-$, 153.0973 [^{1,2}A-CO]$^-$, 139.0423 [^{1,3}A-CO]$^-$

B11	50.032	Carthamidin/Isocarthamidin-*O*-methyl -*O*-glucuronide	301.0691[M-H-GluA]$^-$, 286.0481 [M-H-GluA0-Me]$^-$, 199.0322
B12	51.900	Carthamidin/Isocarthamidin-*O*-glucuronide	317.0517, 287.0555 [M-H-GluA]$^-$, 193.0132 [M-H-B ring]$^-$, 181.0102 [^{1,2}A]$^-$, 167.0140 [^{1,3}A]$^-$, 153.0170 [^{1,2}A-CO]$^-$
B13	52.133	Carthamidin/Isocarthamidin-*O*-sulfo-*O*-glucuronide	463.0867 [M-H-SO_3]$^-$, 367.0003 [M-H-GluA]$^-$, 287.0529 [M-H-GluA-SO_3]$^-$, 193.0263 [M-H-B ring]$^-$
B14	52.625	Carthamidin/Isocarthamidin-*O*-sulfo-*O*-glucuronide	463.0840 [M-H-SO_3]$^-$, 367.0032 [M-H-GluA]$^-$, 287.0435 [M-H-GluA-SO_3]$^-$, 254.9785, 139.0199 [^{1,3}A-CO]$^-$
B15	58.837	Carthamidin/Isocarthamidin-*O*-glucuronide	287.0475 [M-H-GluA]$^-$, 239.1330
B16	58.845	Carthamidin/Isocarthamidin-*O*-methyl-*O*-sulfo -*O*-glucuronide	477.0624 [M-H-SO_3]$^-$, 380.0858 [M-H-GluA]$^-$, 301.0300 [M-H-SO_3-GluA]$^-$, 286.0336 [M-H-SO_3-GluA-Me]$^-$, 271.0135 [M-H-SO_3-GluA-CH_2OH]$^-$, 181.0102[^{1,2}A]$^-$
B17	59.108	Carthamidin/Isocarthamidin-*O*-methyl -*O*-glucuronide	301.0707 [M-H-GluA]$^-$, 286.0737 [M-H-GluA-Me]$^-$, 255.0296, 181.0102 [^{1,2}A]$^-$, 179.0028, 175.0216
B18	62.053	Carthamidin/Isocarthamidin-*O*-methyl-*O*-sulfo -*O*-glucuronide	477.0578 [M-H-SO_3]$^-$, 381.0216 [M-H-GluA]$^-$, 301.0652 [M-H-SO_3-GluA]$^-$, 286.0336 [M-H-GluA-Me]$^-$, 267.0373 [M-H-SO_3-GluA-Me-OH]$^-$
B19	62.823	Carthamidin/Isocarthamidin-*O*-methyl -*O*-glucuronide	301.0652 [M-H-GluA]$^-$, 286.0496 [M-H-SO_3-GluA-Me]$^-$, 267.0373 [M-H-SO_3-GluA-Me-OH]$^-$

B20	75.695	Carthamidin/Isocarthamidin-*O*-sulfonate	287.0567 [M-H-SO_3]$^-$, 181.0134 [^{1,2}A]$^-$, 153.0268 [^{1,2}A-CO]$^-$
B21	81.830	Carthamidin/Isocarthamidin-*O*-sulfonate	287.0575 [M-H-SO_3]$^-$, 139.0013 [^{1,3}A-CO]$^-$
B22	83.280	Carthamidin/Isocarthamidin-*O*-methyl-*O*-sulfonate	301.0695 [M-H-GluA]$^-$, 286.0481 [M-H-SO_3-GluA-Me]$^-$, 225.0542, 193.0263 [M-H-B ring]$^-$, 181.0102 [^{1,2}A]$^-$, 166.9977 [^{1,3}A]$^-$
C1	16.997	6-Hydroxyquercetin-3-*O*-rhamnoside	317.0530 [M-H-Rha]$^-$, 245.0410, 187.0348, 155.0011, 143.0515
C2	20.063	6-Hydroxyquercetin-7-*O*-glucuronide/ 6-Hydroxyquercetin-4′-*O*-glucuronide	317.1076 [M-H-GluA]$^-$,299.1053 [M-H-GluA-CO]$^-$, 269.0968, 239.0816, 227.0814, 209.0710, 183.0550, 155.2323, 129.0452
D1[b]	33.853	Kaempferol-7-*O*-rhamnosyl-3-*O*-glucoside	447.1096 [M-H-Rha]$^-$
D2	34.367	Kaempferol-*di*-*O*-glucuronide	461.0714 [M-H-GluA]$^-$, 285.0396 [M-H-2GluA]$^-$, 239.0304 [M-H-2GluA-H_2O-CO]$^-$, 155.0436
D3[c]	36.242	Kaempferol-*di*-*O*-glucuronide	461.0690 [M-H-GluA]$^-$, 285.0373 [M-H-2GluA]$^-$, 257.0585 [M-H-2GluA-H_2O]$^-$, 239.0304 [M-H-2GluA-H_2O-CO]$^-$, 227.0332, 211.0356, 195.0445, 151.0023 [^{1,3}A]$^-$
D4	42.597	Kaempferol-3-*O*-glucosyl-*O*-glucuronide	447.0888 [M-H-GluA]$^-$, 285.0730 [M-H-GluA-Glc]$^-$, 239.0304 [M-H-GluA-Glc-CO-H_2O]$^-$, 215.0392
D5[c]	42.975	Kaempferol-*di*-*O*-glucuronide	461.0729 [M-H-GluA]$^-$, 385.0420, 285.0411 [M-H-2GluA]$^-$, 239.0304 [M-H-2GluA-H_2O-CO]$^-$, 195.0366, 185.0634, 123.0179, 121.0304 [^{0,2}B]$^-$
D6	43.598	Kaempferol-*di*-*O*-glucuronide	461.0668 [M-H-GluA]$^-$, 351.0427, 285.0380 [M-H-2GluA]$^-$,

			239.0304 [M-H-2GluA-H_2O-CO]$^-$, 130.9129 [^{0,3}B-H_2O]$^-$
D7[c]	44.005	Kaempferol-*di*-*O*-glucuronide	461.0690 [M-H-GluA]$^-$, 285.0373 [M-H-2GluA]$^-$, 239.0304 [M-H-2GluA-H_2O-CO]$^-$
D8	51.505	Kaempferol-7-*O*-glucuronide /Kaempferol-4′-*O*-glucuronide	285.0403 [M-H-GluA]$^-$, 267.0219 [M-H-GluA-H_2O]$^-$, 239.0377 [M-H-GluA-H_2O-CO]$^-$, 227.0973, 223.1122, 215.0531, 211.0448, 199.0456, 195.0443
D9[c]	58.845	Kaempferol-*O*-sulfo-*O*-glucuronide	461.0778 [M-H-SO_3]$^-$, 365.000 [M-H-GluA]$^-$, 285.0383 [M-H-GluA-SO_3]$^-$, 257.0433 [M-H-GluA-SO_3-H_2O]$^-$, 213.0581, 151.0023 [^{1,3}A]$^-$
D10	59.582	Kaempferol-*O*-sulfo-*O*-glucuronide	461.0689 [M-SO_3]$^-$, 364.9941 [M-H-GluA]$^-$, 285.0407 [M-H-GluA-SO_3]$^-$, 254.9800, 211.0393
D11[c]	59.707	Kaempferol-7-*O*-glucuronide /Kaempferol-4′-*O*-glucuronide	285.0385[M-H-GluA]$^-$, 257.0399 [M-H-GluA-SO_3-H_2O]$^-$, 243.0243, 239.0377, 229.0781, 167.0528, 163.0045 [^{0,2}A]$^-$, 135.0075 [^{0,3}A]$^-$
D12[c]	61.635	Kaempferol-7-*O*-glucuronide /Kaempferol-4′-*O*-glucuronide	285.0381 [M-H-GluA]$^-$, 169.0722, 143.0438
D13[c]	63.307	Kaempferol-*O*-sulfo-*O*-glucuronide	461.0427 [M-H-SO_3]$^-$, 364.9920 [M-H-GluA]$^-$, 285.0383 [M-H-GluA-SO_3]$^-$, 257.0433 [M-H-GluA-SO_3-H_2O]$^-$, 243.0292, 239.0304, 211.0035, 151.0023 [^{1,3}A]$^-$
D14	64.753	Kaempferol-*O*-methyl-*O*-sulfo-*O*-glucuronide	378.0594 [M-H-GluA]$^-$, 299.0536 [M-H-GluA-SO_3]$^-$, 284.0255 [M-H-GluA-SO_3-Me]$^-$, 254.9766, 211.0310
D15	65.437	Kaempferol-*O*-methyl-*O*-glucuronide	299.0555 [M-H-GluA]$^-$

D16	67.657	Kaempferol-*O*-glucuronide	285.0380 [M-H-GluA]$^-$, 241.0403, 175.0342
D17	78.613	Kaempferol-*O*-methyl-*O*-glucuronide	299.0574 [M-H-GluA]$^-$, 284.0352 [M-H-GluA-Me]$^-$, 219.0851
E1	17.110	6-Hydroxykaempferol-8-*C*-glucosyl-*O*-glucoside	505.0945 [M-H-$C_4H_8O_4$]$^-$, 355.0380 [M-H-$C_4H_8O_4$-$C_5H_{10}O_5$]$^-$, 299.0468, 225.0542,
E2[d]	29.662	6-Hydroxykaempferol-*tri*-*O*-glucuronide	653.0975 [M-H-GluA]$^-$, 477.0654 [M-H-2GluA]$^-$, 301.0321 [M-H-3GluA]$^-$,
E3	34.005	6-Hydroxykaempferol-*di*-*O*-glucuronide	477.0647 [M-H-GluA]$^-$, 301.0304 [M-H-GluA]$^-$, 255.0280 [M-H-GluA-H_2O-CO]$^-$, 245.0559 [M-H-GluA-2CO]$^-$, 199.0322, 187.0348, 173.0229, 151.0419 [^{0,3}A]$^-$
E4[d]	37.628	6-Hydroxykaempferol-*O*-methyl-*O*-glucuronide	491.0778 [M-H-GluA]$^-$, 315.0473 [M-H-GluA]$^-$, 300.0237 [M-H-2GluA-Me]$^-$, 255.0264 [M-H-2GluA-Me-H_2O-CO]$^-$, 243.0292, 197.0200 ,182.9904, 120.5205[^{0,2}B]$^-$
E5	38.580	6-Hydroxykaempferol-*O*-methyl-*O*-glucuronide /Quercetin-*O*-methyl-*O*-glucuronide	491.0778 [M-H-GluA]$^-$, 315.0473 [M-H-2GluA]$^-$, 300.0237 [M-H-2GluA-Me]$^-$, 271.0216, 255.0293
E6	40.212	6-Hydroxykaempferol-*O*-glucosyl-*O*-glucuronide /Quercetin-*O*-glucosyl-*O*-glucuronide	463.0770 [M-H-GluA]$^-$, 301.0333 [M-H-GluA-Glc]$^-$, 255.0280 [M-H-GluA-Glc-CO-H_2O]$^-$, 183.0416
E7[d]	40.442	6-Hydroxykaempferol-*O*-glucuronide	477.0650 [M-H-GluA]$^-$, 371.0312, 301.0309 [M-H-2GluA]$^-$, 283.0173 [M-H-2GluA-CO]$^-$, 255.0366 [M-H-2GluA-CO-H_2O]$^-$, 183.0672, 178.9978[^{0,2}A]$^-$, 151.0375 [^{0,2}A-CO]$^-$
E8[d]	41.082	6-Hydroxykaempferol-*O*-glucuronide	477.0647 [M-H-GluA]$^-$, 301.0304 [M-H-2GluA]$^-$, 271.0187 [M-H-2GluA-CH_2O]$^-$, 255.0280 [M-H-2GluA-CO-H_2O]$^-$, 183.0501, 169.0353, 151.0023 [^{0,2}A-CO]$^-$

E9[d]	41.612	6-Hydroxykaempferol-*O*-glucuronide	477.0679 [M-H-GluA]$^-$, 301.0360 [M-H-2GluA]$^-$, 245.0707 [M-H-2GluA-2CO]$^-$, 187.0607, 163.0080, 157.0901, 153.0104, 145.0689
E10[d]	42.060	6-Hydroxykaempferol-*O*-glucuronide	477.0667 [M-H-GluA]$^-$, 301.0318 [M-H-2GluA]$^-$, 283.0227 [M-H-2GluA-CO]$^-$, 255.0308 [M-H-2GluA-CO-H_2O]$^-$, 253.0056 [M-H-2GluA-CH_2O]$^-$, 227.0332 [M-H-2GluA-CH_2O-CO]$^-$, 211.0998, 201.0546, 131.0538 [^{0,3}B-H_2O]$^-$
E11	45.318	6-Hydroxykaempferol-*di*-*O*-glucuronide	477.0647 [M-H-GluA]$^-$, 301.0304 [M-H-GluA]$^-$, 255.0280 [M-H-GluA-H_2O-CO]$^-$, 183.0501, 179.0018 [^{0,2}A]$^-$, 153.0028
E12	47.340	6-Hydroxykaempferol-*di*-*O*-glucuronide	477.0620 [M-H-GluA]$^-$, 301.0338 [M-H-2GluA]$^-$, 178.9902 [^{0,2}A]$^-$
E13[d]	51.203	6-Hydroxykaempferol-*O*-glucuronide	301.0469 [M-H-GluA]$^-$, 255.0431 [M-H-GluA-H_2O-CO]$^-$, 207.1206, 181.0166
E14	55.315	6-Hydroxykaempferol-*O*-methyl-*O*-glucuronide /Quercetin-*O*-methyl-*O*-glucuronide	315.0482 [M-H-GluA]$^-$, 300.0254 [M-H-GluA-Me]$^-$, 271.0251 [M-H-GluA-Me-CH_2O]$^-$, 255.0280 [M-H-GluA-Me-H_2O-CO]$^-$, 243.0292 [M-H-GluA-Me-CH_2O-CO]$^-$
E15	60.060	6-Hydroxykaempferol-*O*-methyl-*O*-glucuronide /Quercetin-*O*-methyl-*O*-glucuronide	315.0477 [M-H-GluA]$^-$, 300.0200 [M-H-GluA-Me]$^-$, 272.0288 [M-H-GluA-Me-CO]$^-$, 255.0261 [M-H-GluA-Me-H_2O-CO]$^-$, 254.0223 [M-H-GluA-Me-CO-H_2O]$^-$, 243.0336 [M-H-GluA-Me-CO-H_2O]$^-$, 169.0353, 121.0263 [^{0,2}B]$^-$
E16 [d]	63.253	6-Hydroxykaempferol-*O*-methyl-*O*-glucuronide	315.0497 [M-H-GluA]$^-$, 300.0254 [M-H-GluA-Me]$^-$, 271.0251 [M-H-GluA-Me-CO]$^-$, 255.0366 [M-H-GluA-H_2O-CO]$^-$, 183.0416, 171.0357
E17	63.697	6-Hydroxykaempferol-*O*-glucuronide	301.0330 [M-H-GluA]$^-$, 283.0227 [M-H-GluA-CO]$^-$, 255.0431 [M-H-GluA-CO-H_2O]$^-$,

		/Quercetin-*O*-glucuronide	217.0630, 135.0185 $[^{0,2}A\text{-}CO_2]^-$
E18	64.535	6-Hydroxykaempferol-*O*-methyl-*O*-sulfo -*O*-glucuronide/Quercetin-*O*-methyl-*O*-sulfo -*O*-glucuronide	315.0487 $[M\text{-}H\text{-}GluA\text{-}SO_3]^-$, 300.0301 $[M\text{-}H\text{-}GluA\text{-}SO_3\text{-}Me]^-$, 242.0264 $[M\text{-}H\text{-}GluA\text{-}SO_3\text{-}Me\text{-}CH_2O\text{-}H_2O]^-$
E19[d]	66.115	6-Hydroxykaempferol-*O*-glucuronide	301.0682 $[M\text{-}H\text{-}GluA]^-$
G1	40.722	3,5-Dihydroxyflavone-*O*-sulfo-*O*-glucuronide	333.0035 $[M\text{-}H\text{-}GluA]^-$, 253.0463 $[M\text{-}H\text{-}GluA\text{-}SO_3]^-$, 211.0310, 133.0233, 117.0384
G2	41.765	3,5-Dihydroxyflavone-*O*-glucuronide	255.0629$[M+H\text{-}GluA]^+$, 227.0884 $[M+H\text{-}GluA\text{-}CO]^+$, 199.0749 $[M+H\text{-}GluA\text{-}2CO]^+$, 181.0590 $[M+H\text{-}GluA\text{-}2CO\text{-}H_2O]^+$, 153.0678$[^{1,3}A]^+$, 137.0194 $[^{0,3}A]^+$
G3	43.157	3,5-Dihydroxyflavone-*O*-sulfo-*O*-glucuronide	333.0059 $[M\text{-}H\text{-}GluA]^-$,253.0480$[M\text{-}H\text{-}GluA\text{-}SO_3]^-$, 211.0379, 223.0414, 197.0599, 161.0312
G4	71.392	3,5-Dihydroxyflavone-*O*-sulfonate	253.0479 $[M\text{-}H\text{-}SO_3]^-$, 195.0379
G5	78.873	3,5-Dihydroxyflavone-*O*-glucuronide	253.0468 $[M\text{-}H\text{-}GluA]^-$, 225.0542 $[M\text{-}H\text{-}GluA\text{-}CO]^-$
G6	42.385	Galangin-*O*-methyl-*O*-sulfo-*O*-glucuronide	363.0160 $[M\text{-}H\text{-}GluA]^-$, 283.0596 $[M\text{-}H\text{-}GluA\text{-}SO_3]^-$, 268.0373 $[M\text{-}H\text{-}GluA\text{-}SO_3\text{-}Me]^-$, 251.0363, 239.0241, 224.0467
G7	43.827	Galangin-*O*-methyl-*O*-glucuronide	285.0737 $[M+H\text{-}GluA]^+$, 270.0498 $[M+H\text{-}GluA\text{-}Me]^+$, 257.0884 $[M+H\text{-}GluA\text{-}CO]^+$, 242.0489 $[M+H\text{-}GluA\text{-}CO\text{-}Me]^+$, 225.0690, 213.0600, 169.0639 $[^{0,2}A\text{-}CO]^-$, 167.0338
G8	49.222	Galangin-*O*-sulfo-*O*-glucuronide	348.9983 $[M\text{-}H\text{-}GluA]^-$, 269.03999 $[M\text{-}H\text{-}GluA\text{-}SO_3]^-$,

			227.0332 [M-H-GluA-SO_3]$^-$, 149.0537
G9	52.408	Galangin-*O*-sulfo-*O*-glucuronide	348.9979 [M-H-GluA]$^-$, 269.0429 [M-H-GluA-SO_3]$^-$, 241.0477 [M-H-GluA-SO_3-H_2O]$^-$, 227.0343, 225.0400, 199.0456, 169.0599, 155.0553
G10	53.384	Galangin-*O*-methyl-*O*-sulfo-*O*-glucuronide	348.9986 [M-H-GluA]$^-$, 269.0431 [M-H-GluA-SO_3]$^-$, 227.0373, 199.0189, 169.0772, 159.0426
G11	55.817	Galangin-*O*-glucuronide	271.0589 [M+H-GluA]$^+$, 253.0506 [M+H-GluA-H_2O]$^+$, 243.0684 [M+H-GluA-CO]$^+$, 197.0626 [M+H-GluA-CO-CO-H_2O]$^+$, 169.0762 [M+H-GluA-CO-CO-2H_2O]$^+$, 153.0154 [^{1,3}A]$^+$
G12	56.152	Galangin-*O*-methyl-*O*-sulfo-*O*-glucuronide	349.0031 [M-H-GluA]$^-$, 269.0448 [M-H-GluA-SO_3]$^-$
G13	62.278	Galangin-*O*-glucuronide	269.0444 [M-H-GluA]$^-$
G14	72.393	Galangin-*O*-methyl-*O*-sulfonate	283.0608 [M-H-SO_3]$^-$, 268.0354 [M-H-SO_3-Me]$^-$
H1	31.538	Dihydrochalcone-2-*O*-glucuronide	225.0827 [M-H-GluA]$^-$,175.0216
H2	54.687	2,6-Dihydroxydihydrochalcone-*O*-sulfo -*O*-glucuronide	321.0415 [M-H-GluA]$^-$, 241.0829 [M-H-GluA-SO_3]$^-$, 135.0466, 121.0308
H3	58.415	2,6-Dihydroxydihydrochalcone-*O*-sulfo -*O*-glucuronide	321.0421 [M-H-GluA]$^-$, 241.0900 [M-H-GluA-SO_3]$^-$, 200.9798, 147.0718, 135.0466, 119.0527
H4	65.322	α,2,4,6-Tetrahydroxydihydrochalcone	273.0708 [M-H-GluA]$^-$, 167.0381

		-*O*-glucuronide	
H5	70.435	α,2,4,6-Tetrahydroxy dihydrochalcone -*O*-glucuronide	273.0752 [M-H-GluA]$^-$
H6	70.908	α,2,6-Trihydroxydihydrochalcone-*O*-sulfo -*O*-glucuronide	337.0359 [M-H-GluA]$^-$, 257.0840 [M-H-GluA-SO_3]$^-$, 241.1506, 205.0342
H7	71.960	α,2,6-Trihydroxydihydrochalcone-*O*-glucuronide	257.0802 [M-H-GluA]$^-$, 175.0248
H8	72.445	α,2,6-Trihydroxydihydrochalcone-*O*-glucuronide	257.0840 [M-H-GluA]$^-$
H9	74.168	α,2,6-Trihydroxydihydrochalcone-*O*-sulfo -*O*-glucuronide	433.1123 [M-H-SO_3]$^-$, 337.0341 [M-H-GluA]$^-$, 257.0802 [M-H-GluA-SO_3]$^-$, 213.0995, 135.0295, 119.1211, 109.0357
H10	78.283	α,2,6-Trihydroxydihydrochalcone-*O*-sulfo -*O*-glucuronide	433.0946 [M-H-SO_3]$^-$, 337.0393 [M-H-GluA]$^-$, 257.0892 [M-H-GluA-SO_3]$^-$
H11	83.343	α,2,4,4′,6-Pentahydroxydihydrochalcone -*O*-glucuronide	369.0724 [M-H-GluA]$^-$, 289.0679 [M-H-GluA-SO_3]$^-$, 183.0339, 165.0212
O1	20.355	(3-*O*-Sulfo-phenyl)-acetic acid	151.0372 [M-H-SO_3]$^-$, 107.0513 [M-H-CO_2]$^-$
O2	22.667	3-hydroxyphenylacetic acid-*O*-glucuronide	167.0411 [M-H-GluA]$^-$, 135.0491
O3	23.002	3,4-Dihydroxyphenylacetic acid	163.0424 [M-H-H_2O]$^-$, 135.0471 [M-H-GluA-CO]$^-$, 119.0532 [M-H-CO_2]$^-$
O4	37.110	4-hydroxyphenylacetic acid-*O*-glucuronide	167.1079 [M-H-GluA]$^-$

O5	39.882	4-Hydroxyphenyl propionic acid	147.0412 $[M-H]^-$, 103.1104 $[M-H-CO_2]^-$
O6[c]	49.665	(4-*O*-Sulfo-phenyl)-acetic acid isomer	151.0411 $[M-H-SO_3]^-$
O7	23.368	2,3,4,6-Tetrahydroxybenzoic acid-*O*-glucuronide	185.1101 $[M-H-GluA]^-$, 167.0956 $[M-H-GluA-H_2O]^-$
O8	31.947	2,3,4,6-Tetrahydroxybenzoic acid-*O*-glucuronide	185.1284 $[M-H-GluA]^-$, 167.1201 $[M-H-GluA-H_2O]^-$, 157.0229 $[M-H-GluA-CO]^-$
O9	35.433	2,3,4,6-Tetrahydroxybenzoic acid-*O*-glucuronide	185.1217 $[M-H-GluA]^-$,175.0175
O10	68.097	2,3,4,6-*O*-Methyl-tetrahydroxybenzoic acid	184.0940 $[M-H-Me]^-$, 155.1129 $[M-H-CO_2]^-$, 137.0095 $[M-H-CO_2-H_2O]^-$
O11	21.087	2,4,6-Trihydroxybenzoic acid -*di*-*O*-methyl-*O*-glucuronide	197.0433 $[M-H-GluA]^-$, 182.0181 $[M-H-GluA-Me]^-$
O12	26.322	2,4,6-Trihydroxybenzoic acid-*O*-methyl -*O*-sulfonate	219.0011 $[M-H-CO_2]^-$, 183.0274 $[M-H-SO_3]^-$, 168.0057 $[M-H-SO_3-Me]^-$, 139.0446 $[M-H-SO_3-CO_2]^-$
O13	31.585	2,4,6-Trihydroxybenzoic acid-*di*-*O*-methyl -*O*-sulfonate	247.1207 $[M-H-2Me]^-$, 197.0451 $[M-H-SO_3]^-$, 153.0602 $[M-H-SO_3-CO_2]^-$, 135.0515 $[M-H-SO_3-CO_2-H_2O]^-$, 125.0683 $[M-H-SO_3-CO_2-CO]^-$
O14	31.598	2,4,6-Trihydroxybenzoic acid-*di*-*O*-methyl -*O*-glucuronide	343.1377 $[M-H-2Me]^-$, 197.0907 $[M-H-GluA]^-$, 179.0662, 157.0249, 153.0924 $[M-H-GluA-CO_2]^-$
O15	47.453	2,4,6-Trihydroxybenzoic acid-*di*-*O*-methyl -*O*-sulfonate	197.0812 $[M-H-SO_3]^-$, 182.0593 $[M-H-SO_3-Me]^-$, 167.0222 $[M-H-SO_3-2Me]^-$, 153.0602 $[M-H-SO_3-CO_2]^-$
O16	14.627	4-Hydroxybenzoic acid–*O*-glucoside	299.0792, 137.0233 $[M-H-GluA]^-$

O17	27.912	3,4-Dihydroxybenzoic acid-*O*-methyl -*O*-sulfonate	202.9995 $[M-H-CO_2]^-$, 167.0376 $[M-H-SO_3]^-$, 152.0164 $[M-H-SO_3-Me]^-$, 123.0494 $[M-H-SO_3-CO_2]^-$, 108.0294 $[M-H-SO_3-CO_2-Me]^-$
O18	21.940	4-Hydroxyphenylpropionic acid-*di*-*O*-methyl -*O*-glucuronide	195.0630 $[M-H-GluA]^-$
O19	28.478	4-Hydroxyphenylpropionic acid-*O*-glucoside	163.0429 $[M-H-Glc]^-$, 119.0577 $[M-H-Glc-CO_2]^-$
O20	34.342	4-Hydroxyphenylpropionic acid-*O*-glucuronide	165.0943 $[M-H-GluA]^-$
O21	34.912	4-Hydroxyphenylpropionic acid-*di*-*O*-methyl -*O*-glucuronide	195.0710 $[M-H-GluA]^-$, 180.0031 $[M-H-GluA-Me]^-$
O22[e]	34.915	4-Hydroxyphenylpropionic acid-*O*-sulfonate	165.0581 $[M-H-SO_3]^-$, 121.0640 $[M-H-CO_2]^-$
O23	35.660	4-Hydroxyphenylpropionic acid-*O*-sulfonate	165.0603 $[M-H-SO_3]^-$, 121.0721 $[M-H-CO_2]^-$
O24	37.050	4-Hydroxyphenylpropionic acid-*O*-glucuronide	165.0538 $[M-H-GluA]^-$, 147.0189 $[M-H-GluA-H_2O]^-$, 135.0515
O25	38.160	4-Hydroxyphenylpropionic acid-*O*-sulfonate	165.0593 $[M-H-SO_3]^-$
O26	80.512	4-Hydroxyphenylpropionic acid-*O*-sulfonate	165.0565 $[M-H-SO_3]^-$, 135.0442
O27	28.298	Benzene-1,2,3,5-tetraol-*tri*-*O*-methyl-*O*-sulfonate	183.0619 $[M-H-SO_3]^-$, 168.0436 $[M-H-SO_3-Me]^-$, 153.0221 $[M-H-SO_3-2Me]^-$
O28	37.653	4-Coumaric acid	119.0579 $[M-H-CO_2]^-$
O29[e]	38.163	4-Sulfo-coumaric acid	199.0042 $[M-H-CO_2]^-$, 163.0383 $[M-H-SO_3]^-$, 135.0295 $[M-H-SO_3-CO]^-$, 119.0511 $[M-H-SO_3-CO_2]^-$

O30	39.987	4-Sulfo-coumaric acid isomer	199.0122 [M-H-CO_2]$^-$, 163.0392, 119.0530 [M-H-SO_3-CO_2]$^-$, 107.0464
O31	40.262	4-Sulfo-coumaric acid isomer	199.0122 [M-H-CO_2]$^-$, 163.0407 [M-H-SO_3], 119.0555 [M-H-SO_3-CO_2]$^-$, 107.0464
O32	23.650	Phloroglucinol-*O*-sulfonate	125.0216 [M-H-SO_3]$^-$
O33	35.707	Phloroglucinol-*di*-*O*-methyl-*O*-glucuronide	153.0572 [M-H-GluA]$^-$
O34	40.675	Phloroglucinol-*di*-*O*-methyl-*O*-glucuronide	153.0615 [M-H-GluA]$^-$, 138.0537 [M-H-GluA-Me]$^-$, 123.0208 [M-H-GluA-2Me]$^-$
O35	49.237	Phloroglucinol-*O*-methyl-*O*-sulfonate	139.0405 [M-H-SO_3]$^-$
O36	49.657	Phloroglucinol-*di*-*O*-methyl-*O*-sulfonate	153.0565 [M-H-SO_3]$^-$, 138.0322 [M-H-SO_3-Me]$^-$, 123.0809 [M-H-SO_3-2Me]$^-$
U1	17.972	$C_{15}H_{16}O_4$-*O*-glucuronide	259.1065 [M-H-GluA]$^-$, 175.0216
U2	19.493	$C_{16}H_{14}O_9$-*di*-*O*-glucuronide	525.0844 [M-H-GluA]$^-$, 507.0711, 349.0517 [M-H-2GluA]$^-$, 331.0411, 299.0227, 271.0213, 255.0280, 239.0304, 187.0399, 178.9902,
U3	23.445	$C_{16}H_{14}O_9$-*di*-*O*-glucuronide	525.0833 [M-H-GluA]$^-$, 507.0711, 349.0642, 331.0411, 299.0195, 285.0176, 271.0213, 239.0597, 187.0399
U4	24.028	$C_{16}H_{14}O_9$-*di*-*O*-glucuronide	525.0844 [M-H-GluA]$^-$, 507.0790,465.0774, 349.0495 [M-H-2GluA]$^-$, 331.0444, 299.0140, 271.0135, 254.2876, 243.0292
U5	24.960	$C_{16}H_{14}O_9$-*di*-*O*-glucuronide	525.0877 [M-H-GluA]$^-$, 475.0458, 331.0503, 299.0182
U6	26.363	$C_{16}H_{14}O_9$-*di*-*O*-glucuronide	525.0856 [M-H-GluA]$^-$, 507.0743, 475.0467, 349.0559, 331.0429, 231.0747, 183.0416, 139.0088

U7	27.538	$C_{16}H_{16}O_7$-*O*-glucoside	465.1334, 345.1097, 321.1057 $[M+H\text{-}GluA]^+$, 243.0726
U8	30.180	$C_{16}H_{16}O_7$-*O*-glucoside	465.1229, 363.1064, 321.1049 $[M+H\text{-}GluA]^+$, 243.0652, 174.0552
U9	30.513	$C_{16}H_{14}O_8$-*O*-glucuronide	333.0592 $[M\text{-}H\text{-}GluA]^-$, 315.0471 $[M\text{-}H\text{-}GluA\text{-}H_2O]^-$, 255.0280
U10	31.818	$C_{16}H_{14}O_8$-*O*-glucuronide	333.0592 $[M\text{-}H\text{-}GluA]^-$, 315.0471 $[M\text{-}H\text{-}GluA\text{-}H_2O]^-$
U11	36.227	$C_{16}H_{14}O_9$-*O*-glucuronide	507.0757 $[M\text{-}H\text{-}H_2O]^-$, 349.0495 $[M\text{-}H\text{-}GluA]^-$, 331.0462, 299.0189, 193.9859
U12	53.570	$C_{15}H_{16}O_3$-*O*-glucuronide	243.0661 $[M\text{-}H\text{-}GluA]^-$
U13	68.383	$C_{15}H_{16}O_7$-*O*-glucuronide	307.0679 $[M\text{-}H\text{-}GluA]^-$, 263.0829, 233.0724

[a] Identified by comparison with the reference compounds.

[b] Identified by comparison with ECT.

[c] Identified by comparison with the metabolites in rats after oral administration of kaempferol-3-*O*-rutinoside.

[d] Identified by comparison with the metabolites in rats after oral administration of 6-hydroxykaempferol-3-*O*-rutinoside.

[e] Identified by comparison with the metabolites in rats after oral administration of HSYA.