Electronic Supplementary Material (ESI) for Analytical Methods.

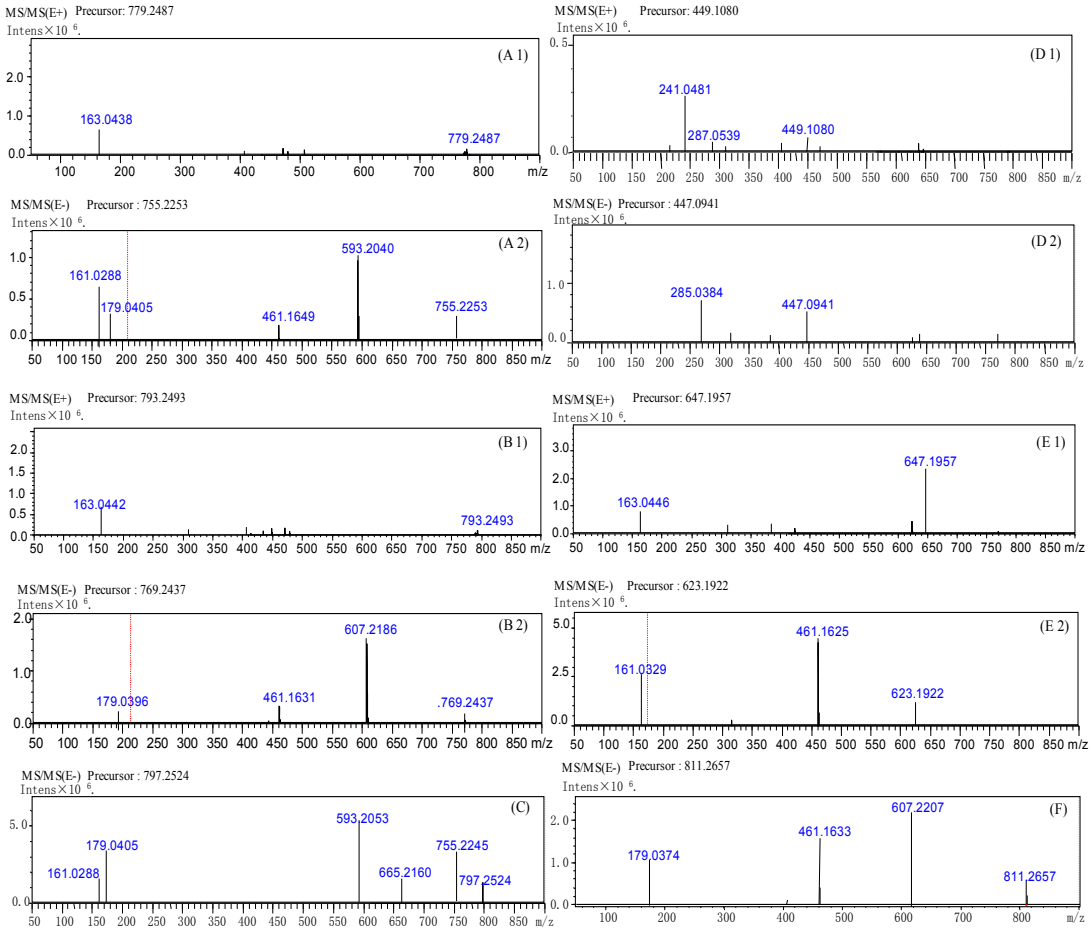
Supplemental Table A.1 Detail information of 11 batches of *Callicarpa kwangtungensis* chun. in China

Batch no.	Collect location	Collect time
1	Pingxiang City, Jiangxi Province, China	2013-10, annual
2	Pingxiang City, Jiangxi Province, China	2013-05, annual
3	Anyuan City, Jiangxi Province, China	2014-05, annual
4	Xiangdong City, Jiangxi Province, China	2012-10, annual
5	Tonggu City, Jiangxi Province, China	2012-11, biennial
6	Tonggu City, Jiangxi Province, China	2012-11, annual
7	Ganzhou City, Jiangxi Province, China	2013-05, annual
8	Kaili City,Guizhou Province, China	2012-10, annual
9	Guiyang,Guizhou Province, China	2014-09, annual
10	Guiyang,Guizhou Province, China	2012-10, annual
11	Anlong,Guizhou Province, China	2012-11, annual

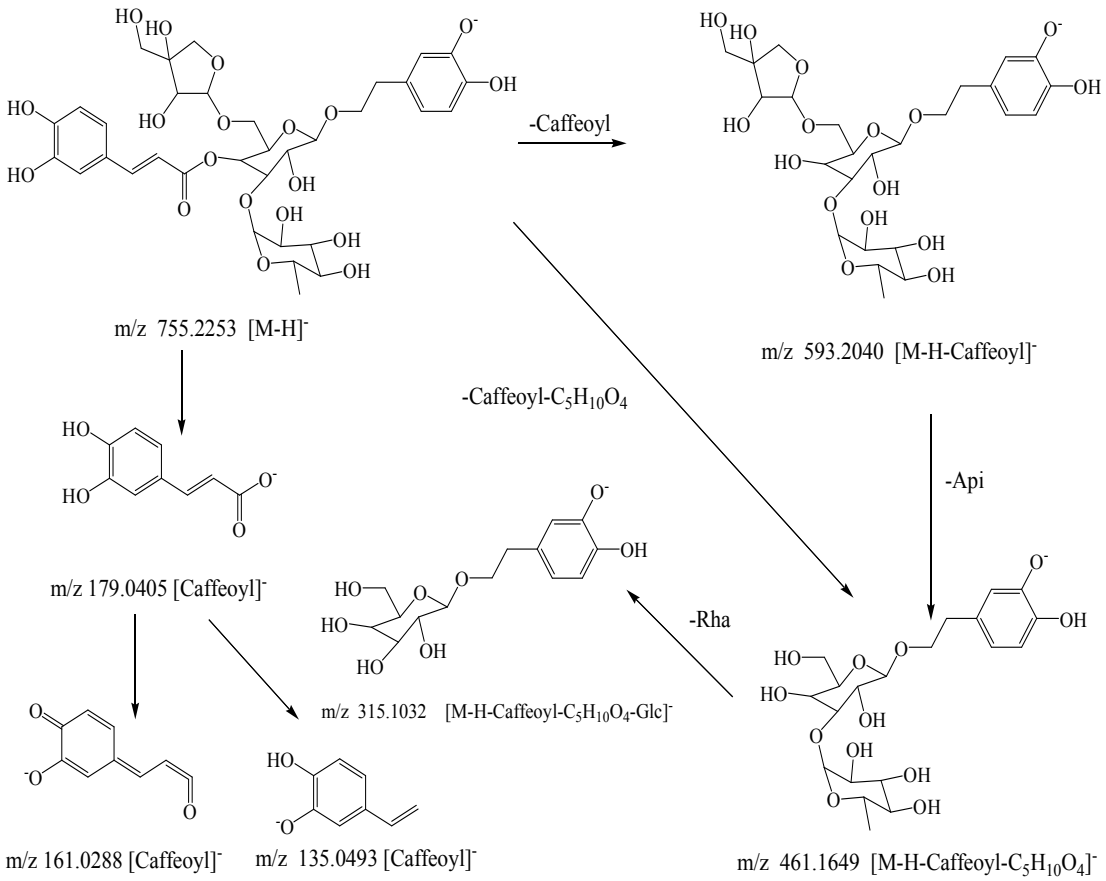
Supplemental Table A.2 Mass spectral and UV data of unknown compounds from *Callicarpa kwangtungensis* Chun

NO.[a]	RT(min)	UV λmax (nm)	MS^1	MS^2/MS^3 data	Molecular formula	Error (ppm)
1	4.820	328	643.1838 $[M+Na]^+$ 619.1827 $[M-H]^-$	569.6507、365.0822、 301.0867、152.0916	$C_{26}H_{36}O_{17}$	0.97
4	5.600	250、329	405.0269 $[M-H]^-$	191.0146、111.0047	$C_{15}H_{14}O_9$	8.64
7	8.658	253、276	475.1828 $[M-H]^-$	458.9120	$C_{21}H_{32}O_{12}$	1.47
8	9.918	250、283、330	392.1140 $[M-H]^-$	383.1175	$C_{22}H_{19}NO_6$	4.08
9	10.208	250、283、330	392.1215$[M-H]^-$	383.1175、215.1670	$C_{14}H_{21}NO_9$	3.32
12	10.997	278、328	458.1434$[M-H]^-$	377.1100、179.0439	$C_{40}H_{54}O_{24}$	0.87
15	15.563	267、337	429.1684$[M-H]^-$	163.0594	$C_{20}H_{30}O_{10}$	-0.47
30	45.948	270、330	465.1430 $[M+Cl]^-$ 453.3422 $[M+Na]^+$	327.2526、237.3673		1.76
31	46.895	237、328	747.2442$[M+Na]^+$ 723.2369$[M-H]^-$	561.2108	$C_{41}H_{40}O_{12}$	-0.28
35	51.655	270	329.2297$[M-H]^-$ 353.2316$[M+Na]^+$	229.1413、211.1303	$C_{18}H_{34}O_5$	3.64

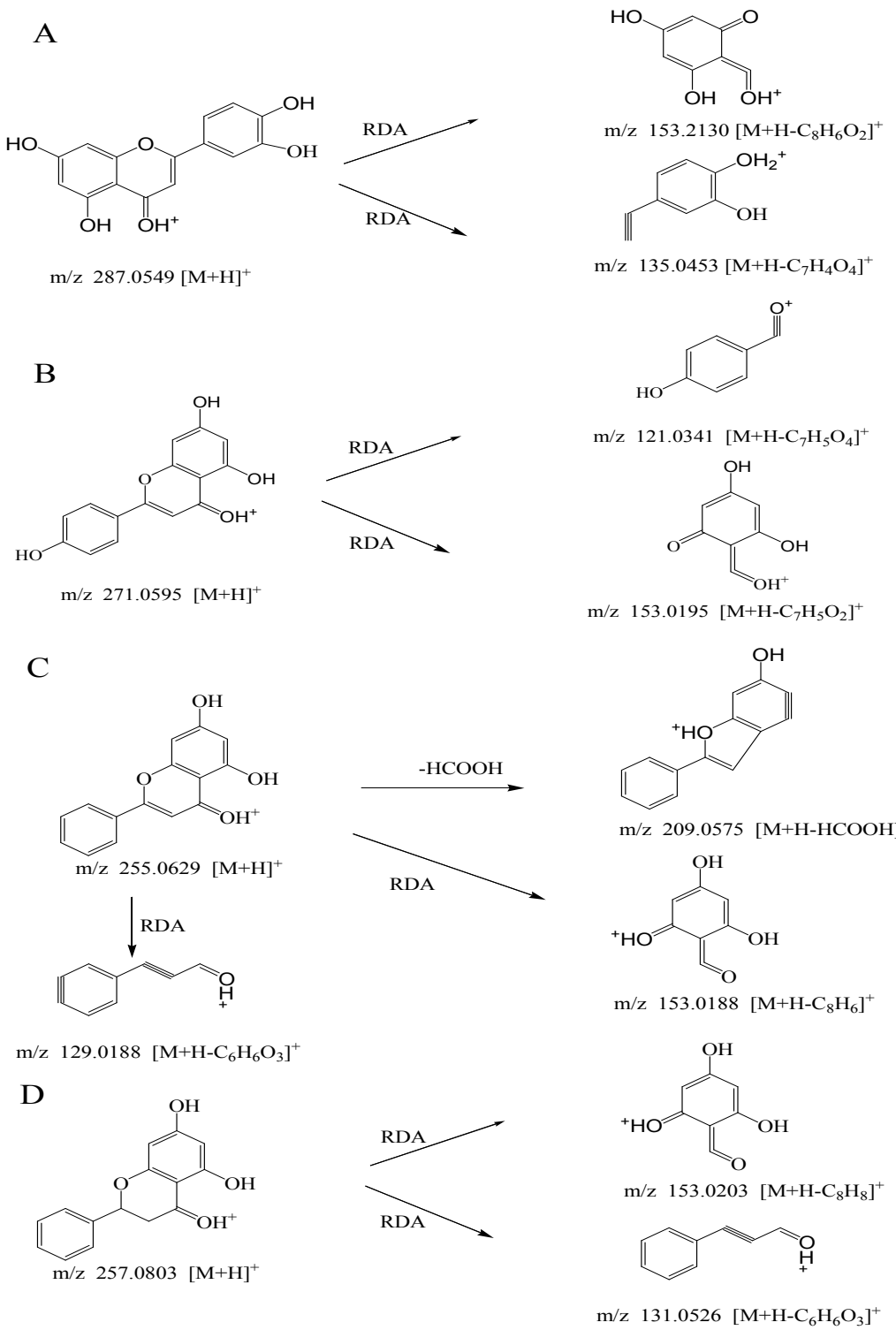
[a] The notation for analytes refer to Fig. 2.



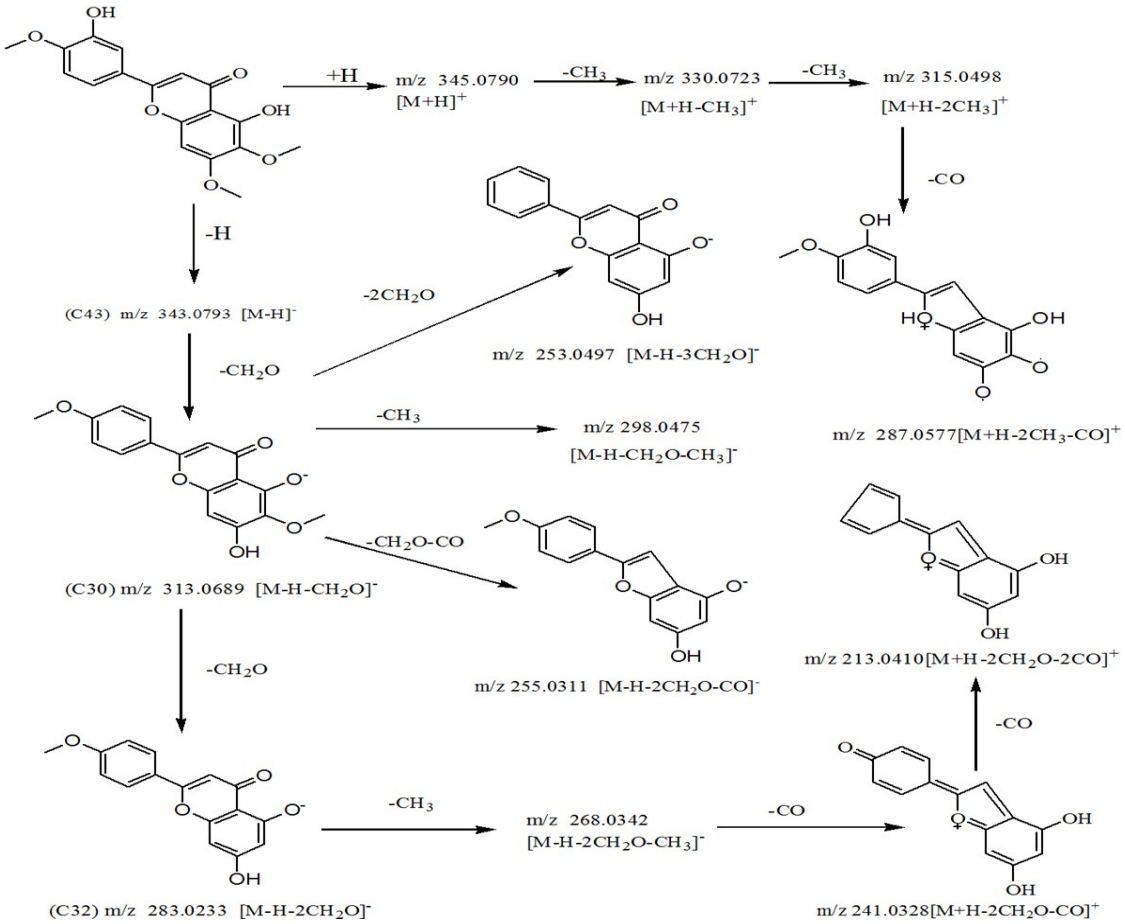
Supplemental Fig. A1 The MS^2 spectra of (A1) forsythoside B, (B1) poliumoside, (D1) luteolin-7-*O*-β-glucoside, (E1) verbascoside in positive ion mode and (A2) forsythoside B, (B2) poliumoside, (C) 2'-acetyl forsythoside B, (D2) luteolin-7-*O*-β-glucoside, (E2) verbascoside, (F) 2'-acetyl poliumoside in negative ion mode.



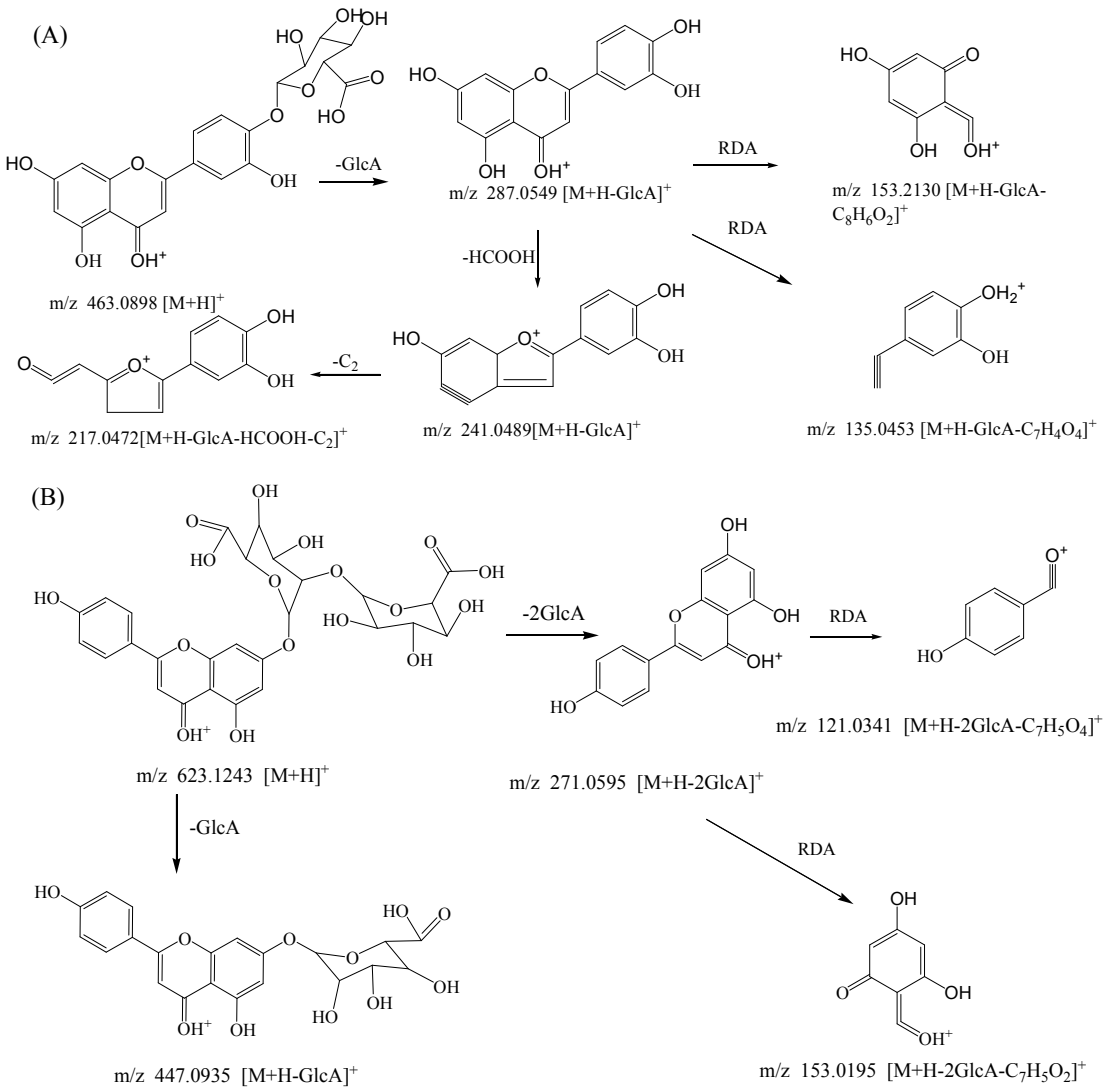
Supplemental Fig. A2 Proposed fragmentation pathway for forsythoside B.



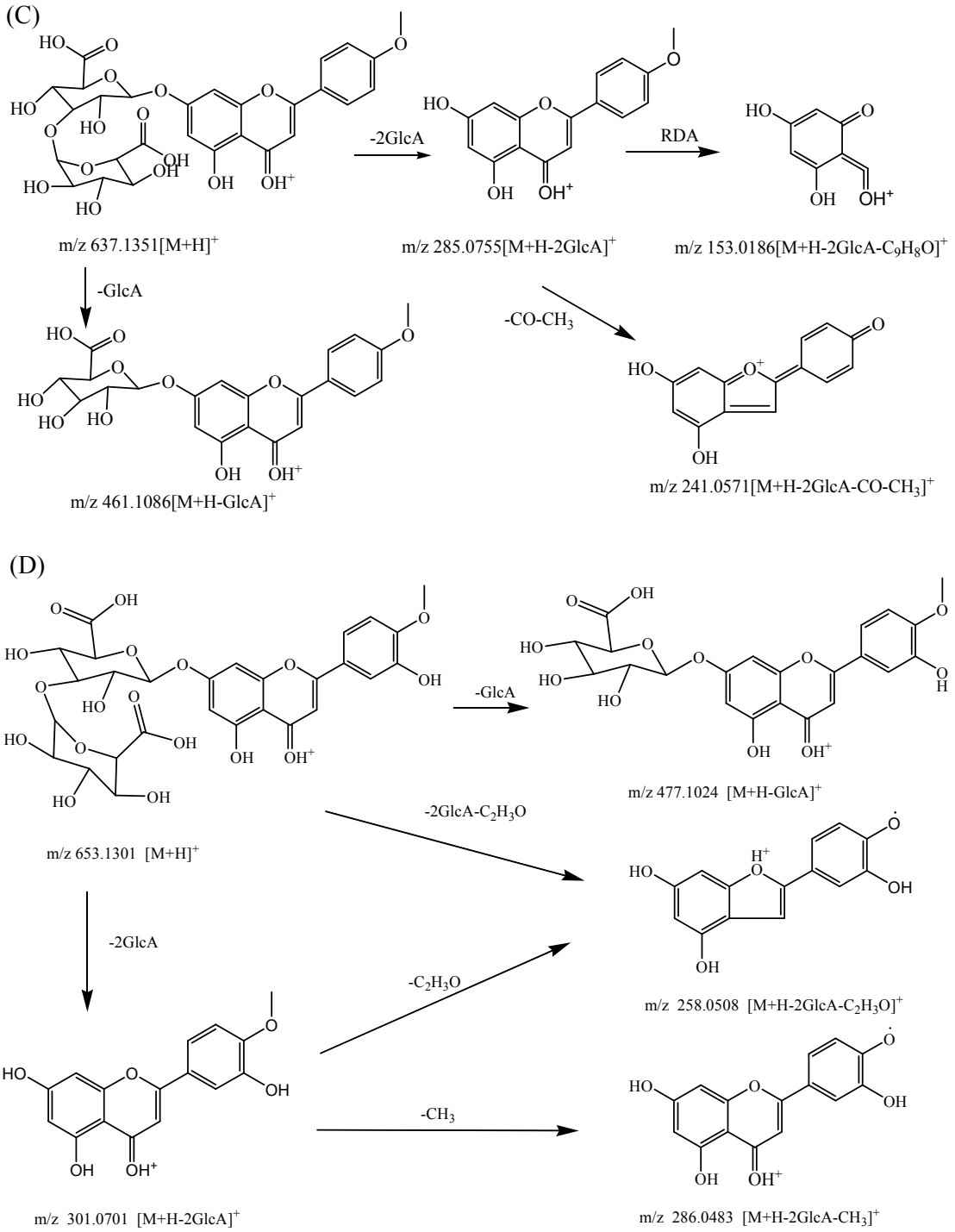
Supplemental Fig. A3 Proposed fragmentation pathways for luteolin (A, C32), apigenin (B, C33), chrysin (C, C39) and 5,7-dihydroxy-2-phenylchroman-4-one (D, C40).



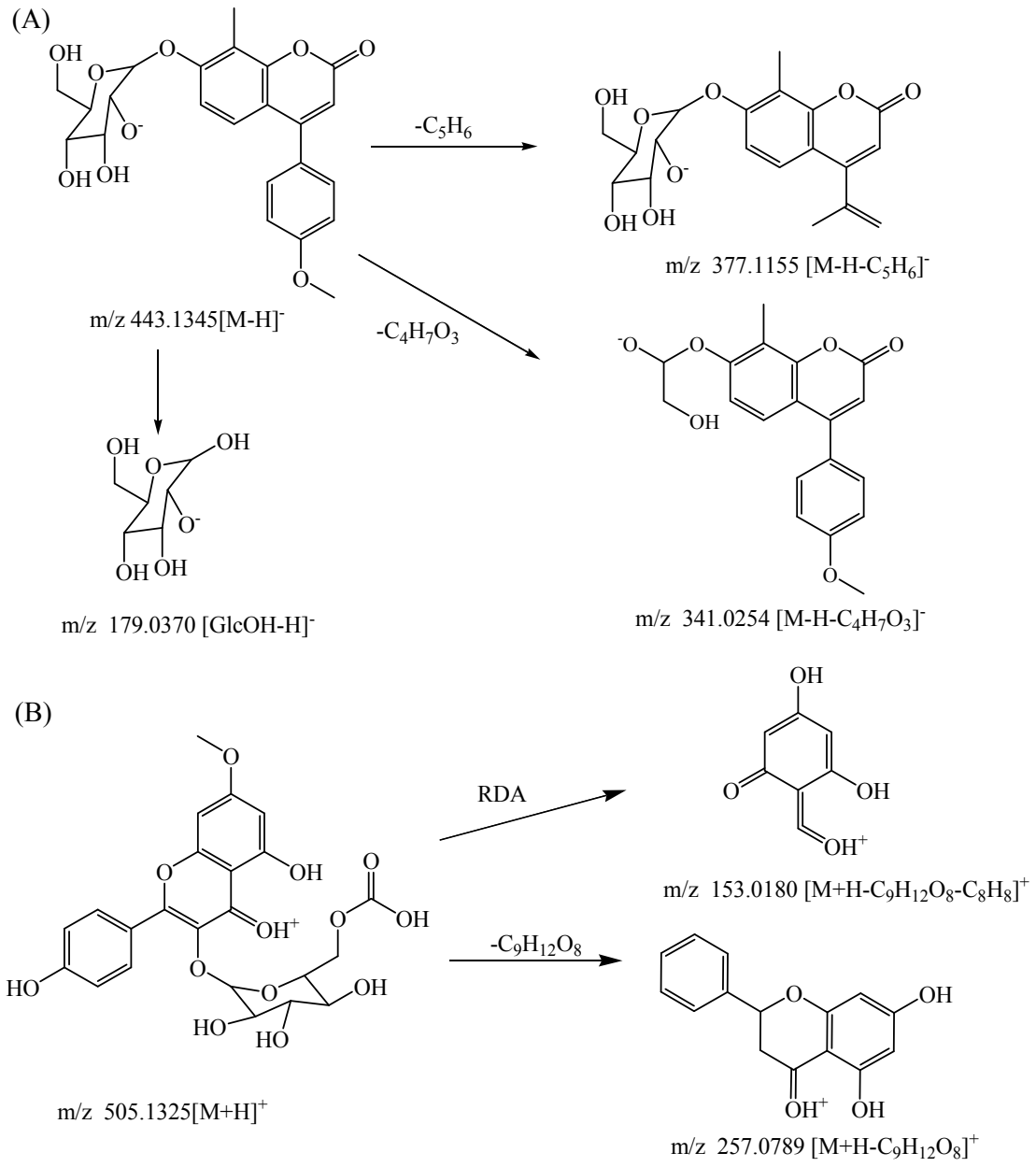
Supplemental Fig. A4 Proposed fragmentation pathway for 5,7-dihydroxy-2- (3-hydroxy-4-methoxy-phenyl) - 6, 7- dimethoxy-chromone (C43).



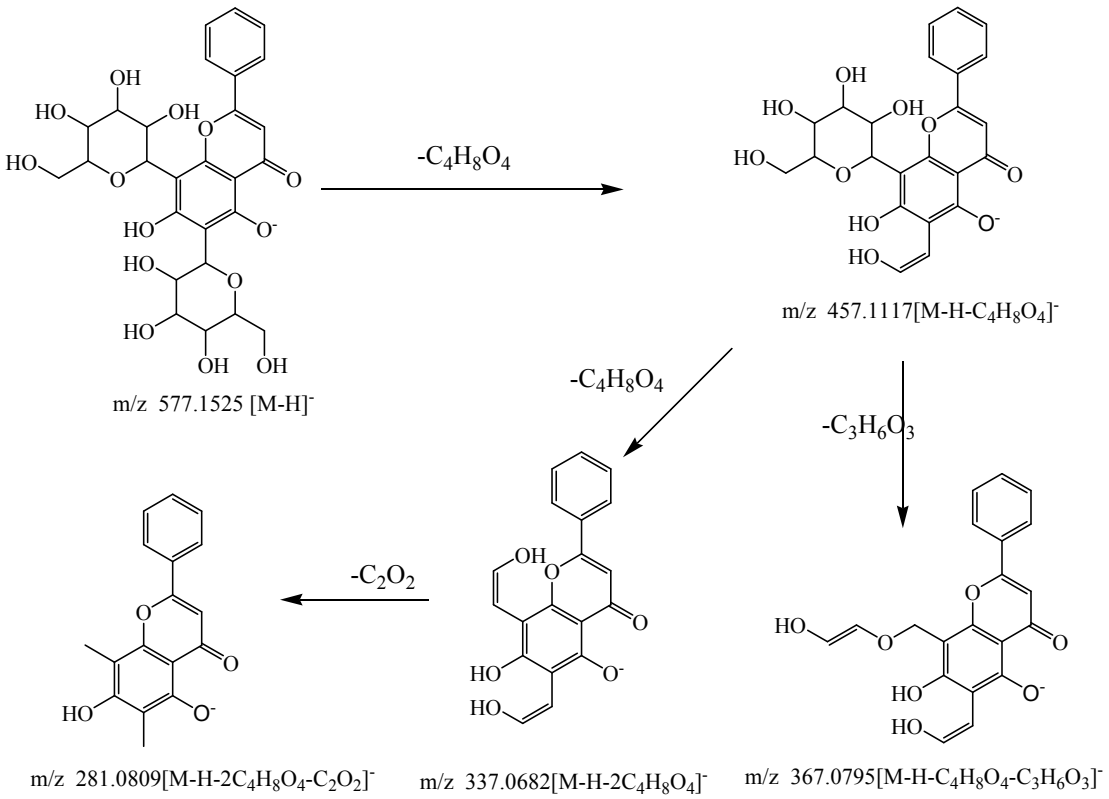
Supplemental Fig. A5 Proposed fragmentation pathways for Luteolin-3'-O-β-glucuronide (A, C26) and Apigenin-7-O-diglycuronides (B, C22).



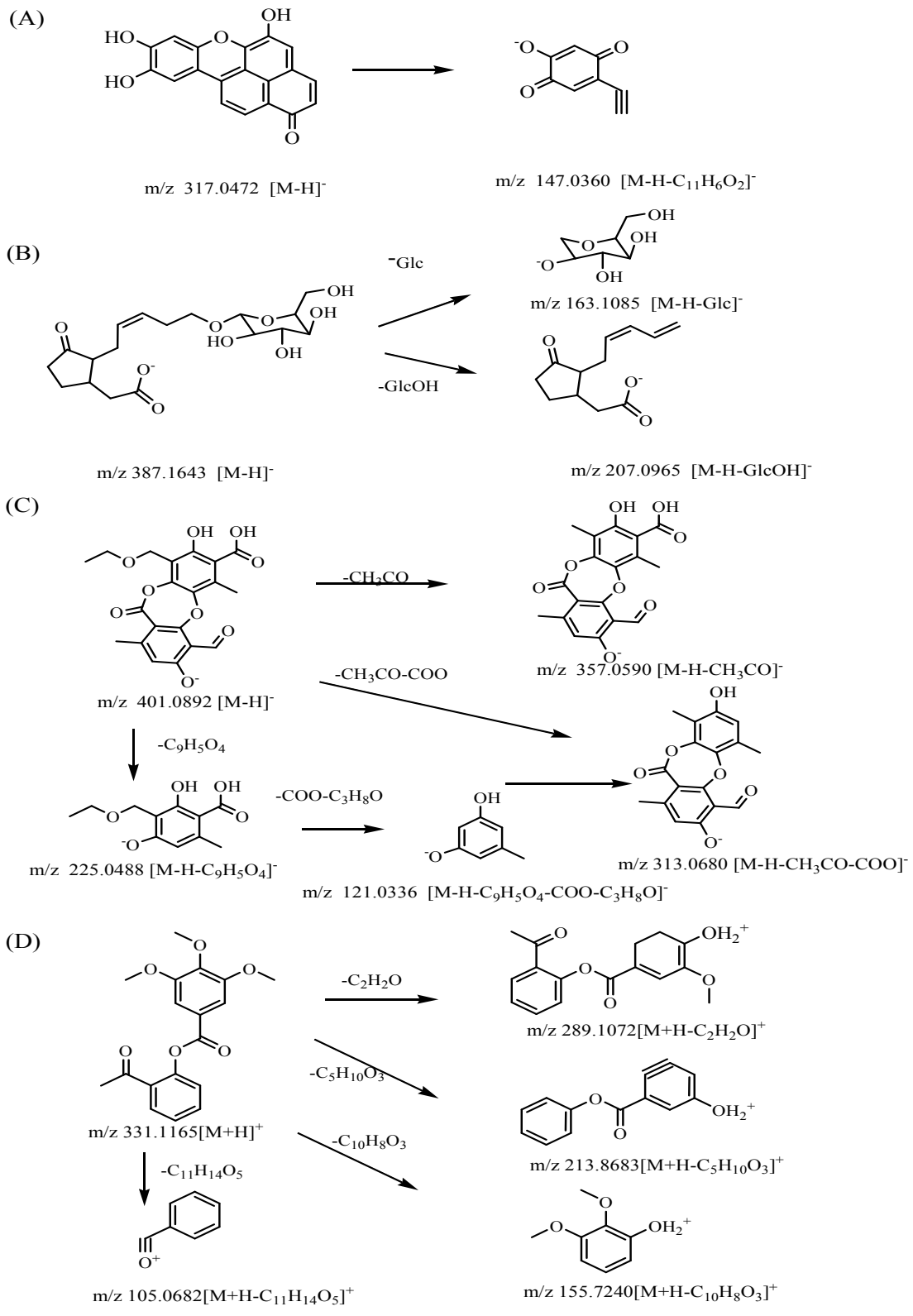
Supplemental Fig. A6 Proposed fragmentation pathways for Acacetin-7-O-diglycuronides (C, C34) and Diosmetin-7-O-diglycuronides (D,C25).



Supplemental Fig. A7 Proposed fragmentation pathways for 4-(4-methoxyphenyl)-8-methyl-7-(3,4,5-trihydroxy-6-(hydroxymethyl)-tetrahydro-2H-pyran-2-ylo xy)-2H-chromen-2-one (A, C16) and Neocomplanoside (B, C37).



Supplemental Fig. A8 Proposed fragmentation pathway for Chrysin-6,8-two-C-glycosides (C13).



Supplemental Fig. A9 Proposed fragmentation pathways for 5,8,9-trihydroxy-1H-naphtho[2,1,8-mna]xanthen-1-one (A), tuberonic acid glucoside (B), cetraric acid (C) and 2-acetylphenyl 3,4,5-trimethoxybenzoate (D).