Supplementary information

UPLC-QTOF-MS-based metabolomics and chemometrics studies of geographically diverse *C. torulosa* needles

Radhika Khanna [a*], Khushaboo Bhadoriya [a], Gaurav Pandey [a], V.K. Varshney [a*]

a Chemistry & Bioprospecting Division, Forest Research Institute, Dehradun 248006, India

a* khannaradhika113@gmail.com, vkvarshney1967@gmail.com, Chemistry & Bioprospecting Division, Forest Research Institute, Dehradun 248006, India

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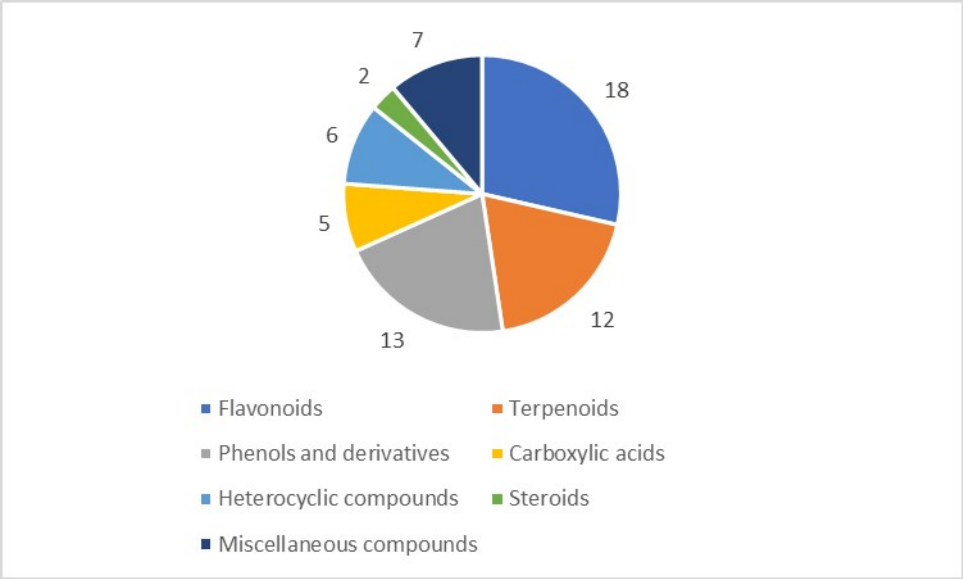


Figure1SI: Pie chart showing different classes of identified compounds

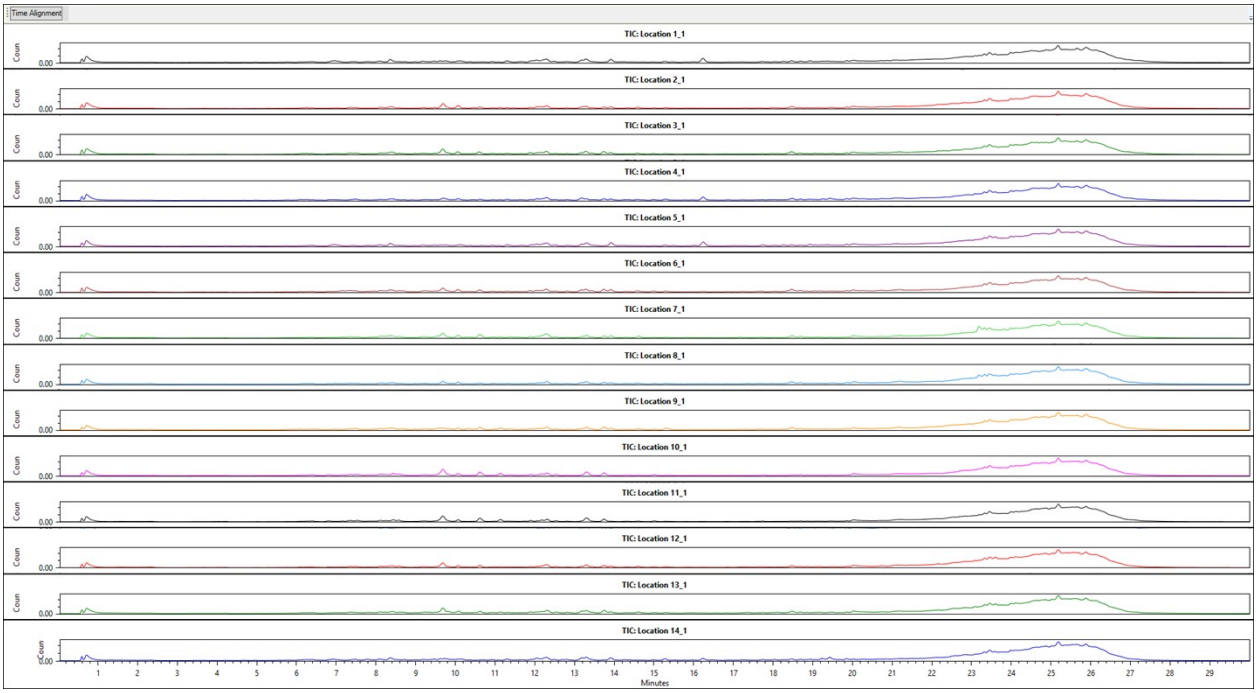


Figure 2 SI: Total Ion Chromatograms (TICs) of 25% aqueous methanol extracts of needles of *Cupressus torulosa* growing in 14 different geographical locations

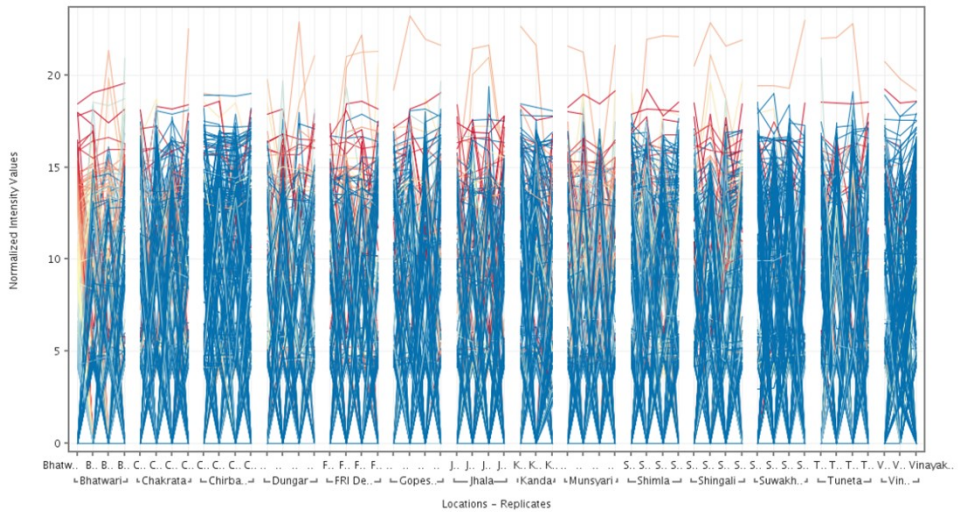


Figure 3SI: Profile plot representing intensity of detected ions across different geographical locations

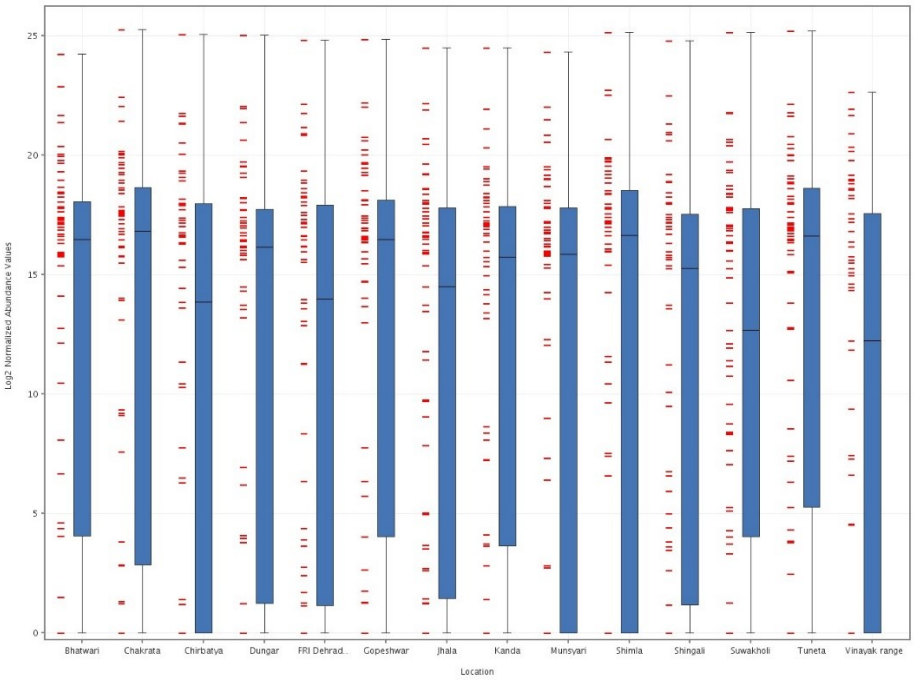


Figure 4SI: Box-whisker plot of identified compounds

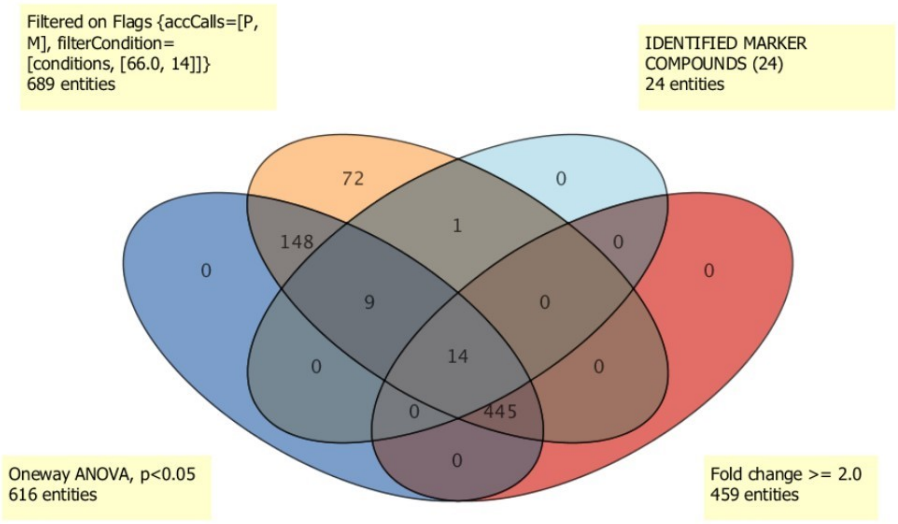


Figure 5SI: Vienn diagram representing marker compounds

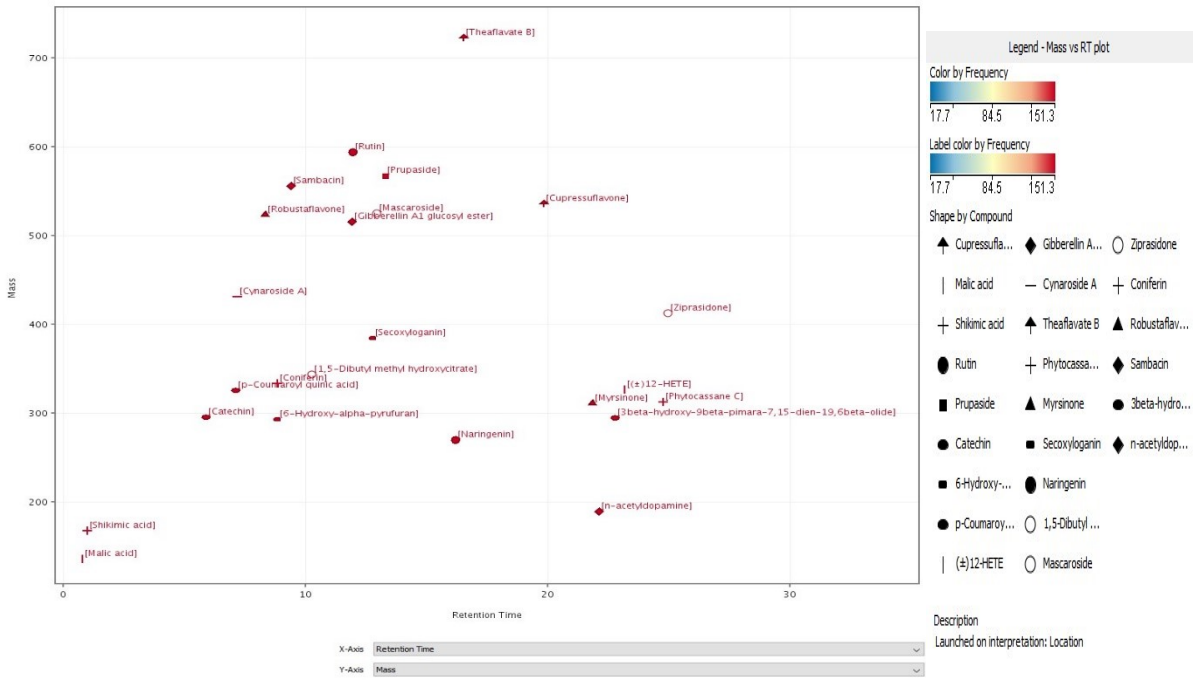


Figure 6SI: Mass v/s Retention Time (RT) plot of marker compounds

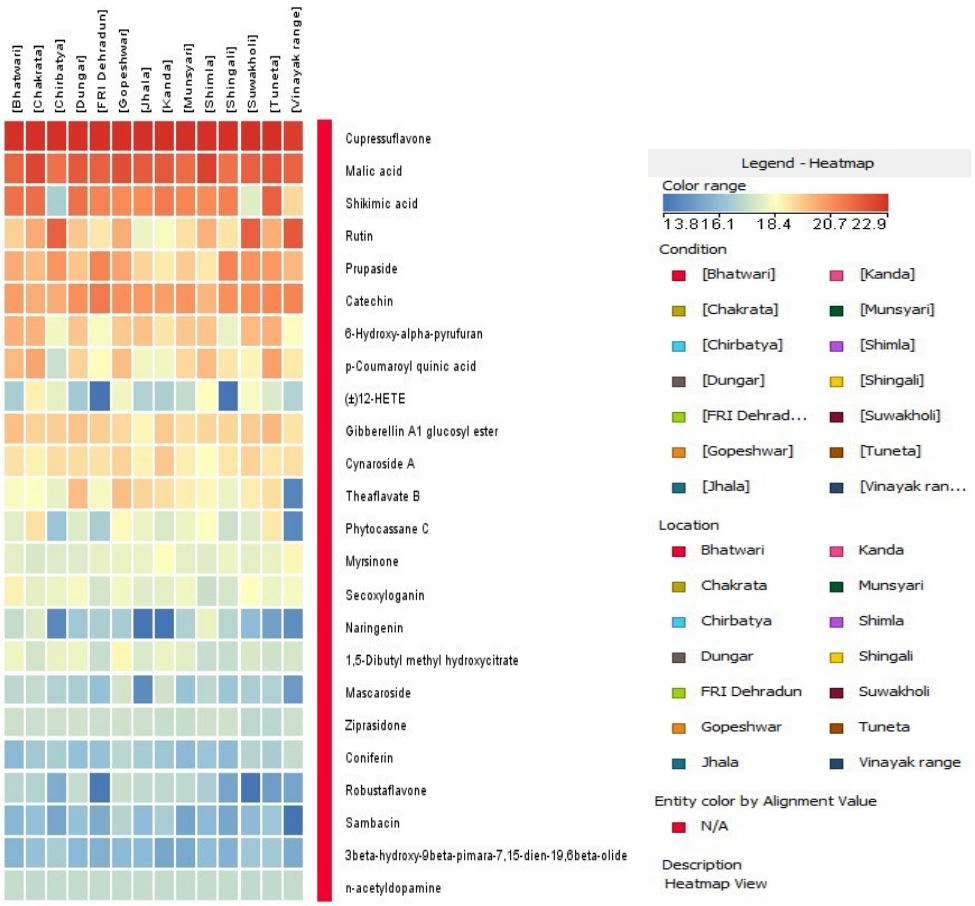


Figure 7SI: Heat map of marker compounds

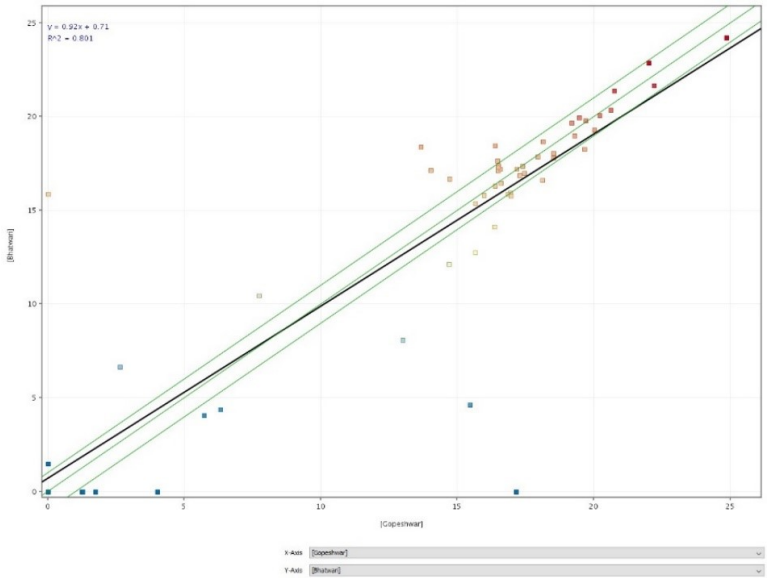


Figure 8SI: Scatter plot of Gopeshwar v/s Bhatwari

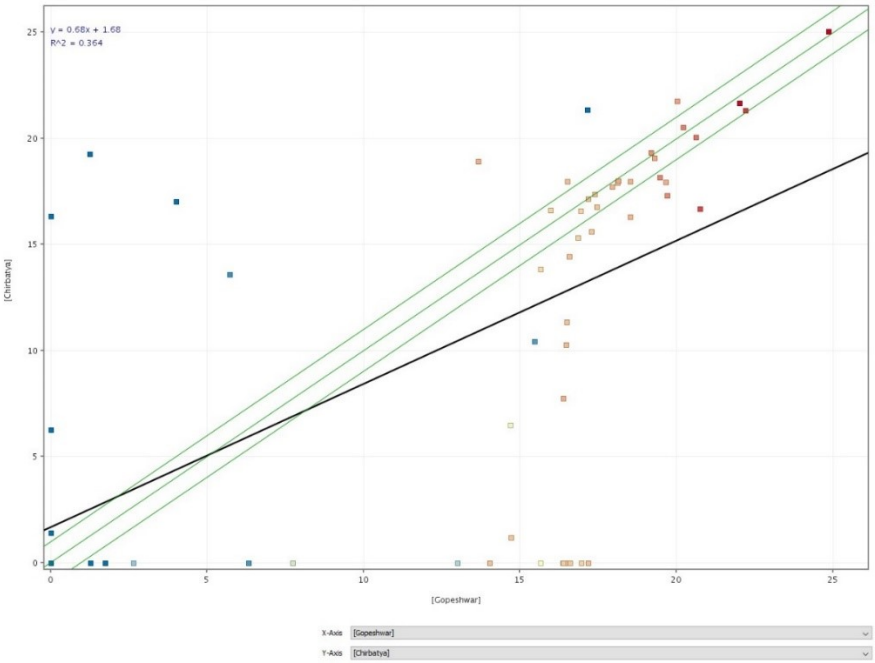


Figure 9SI: Scatter plot of Gopeshwar v/s Chirbatya

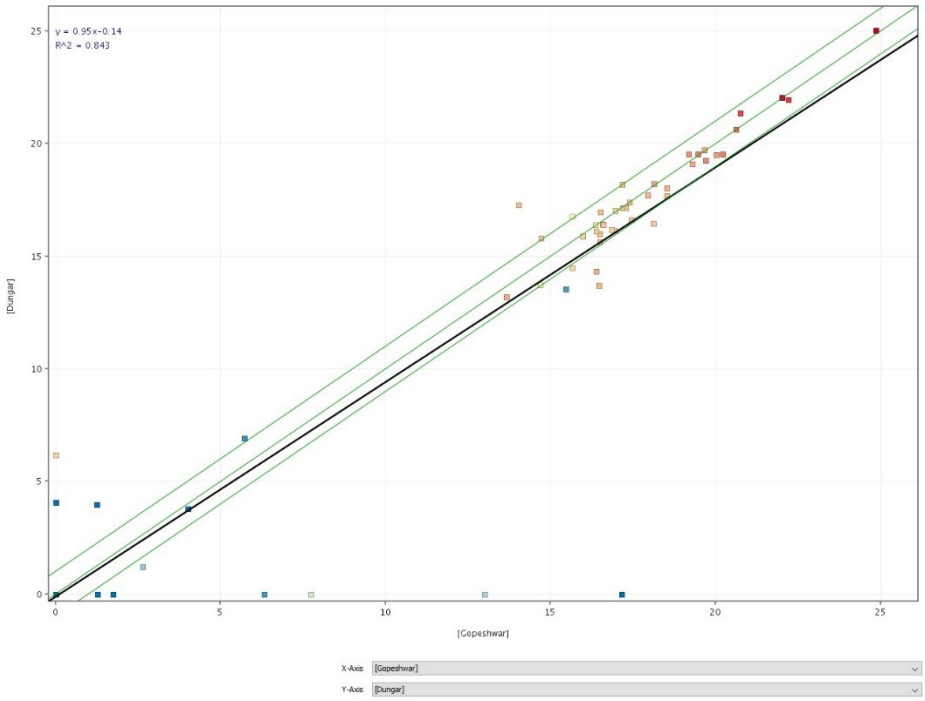


Figure 10SI: Scatter plot of Gopeshwar v/s Dungar

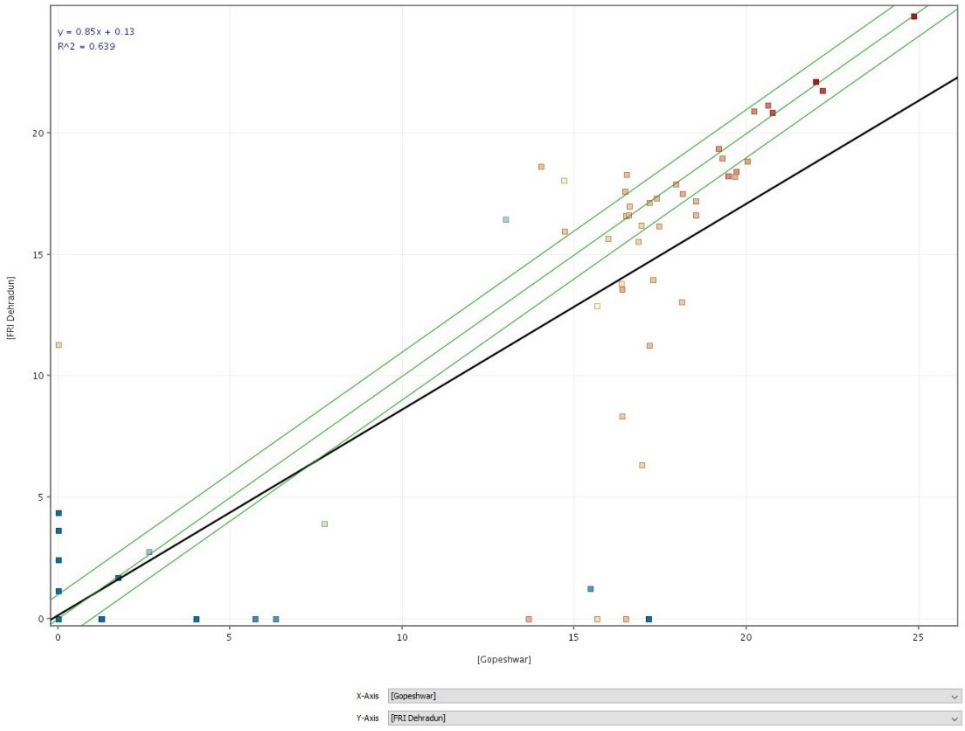


Figure 11SI: Scatter plot of Gopeshwar v/s FRI (Dehradun)

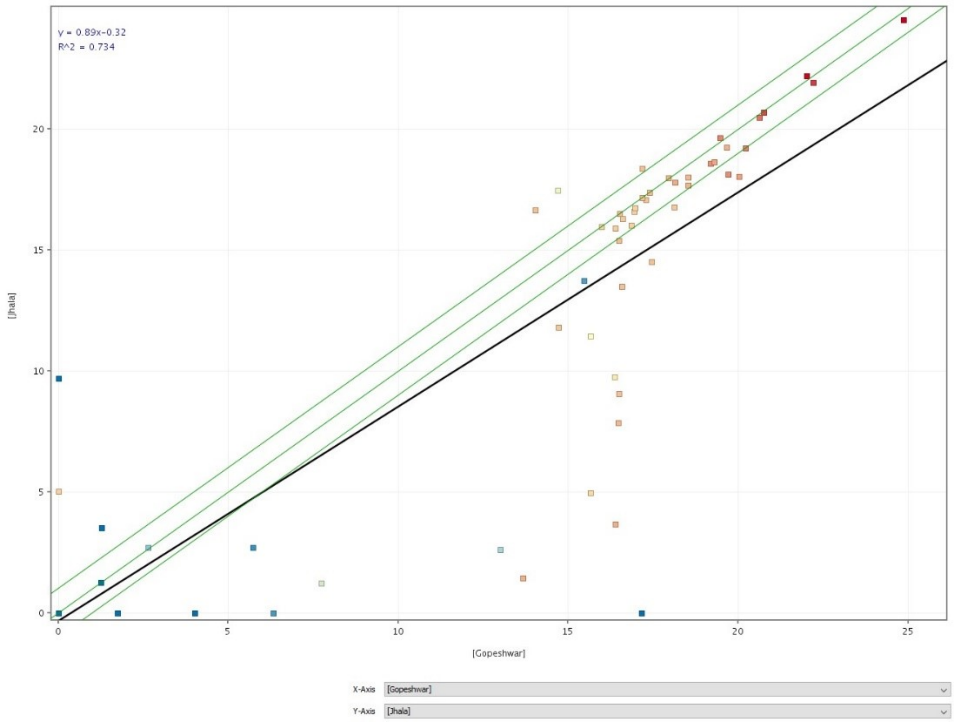


Figure 12SI: Scatter plot of Gopeshwar v/s Jhala

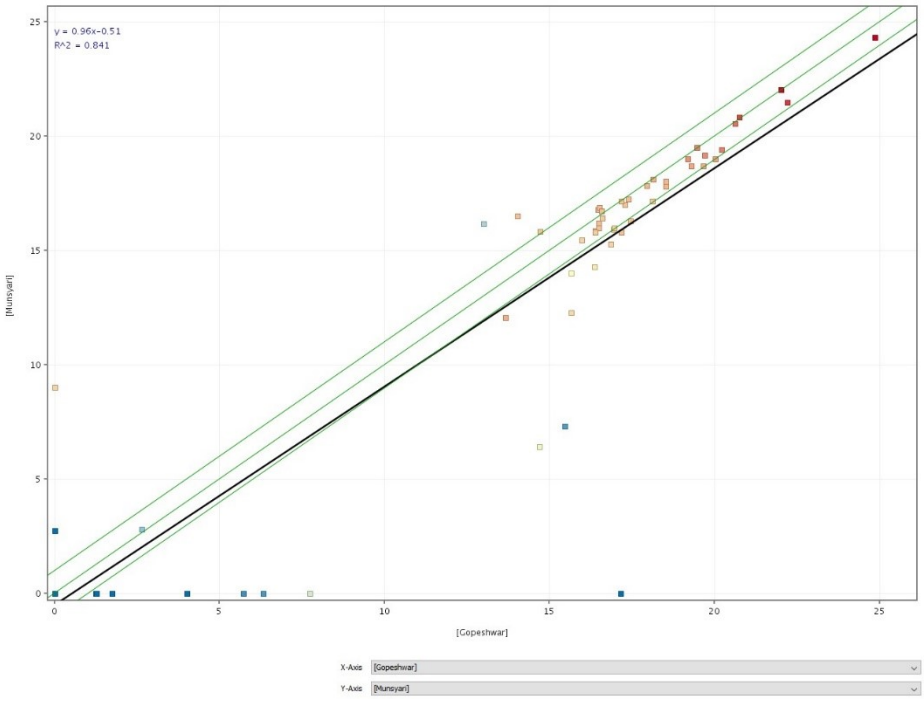


Figure 13SI: Scatter plot of Gopeshwar v/s Munsyari

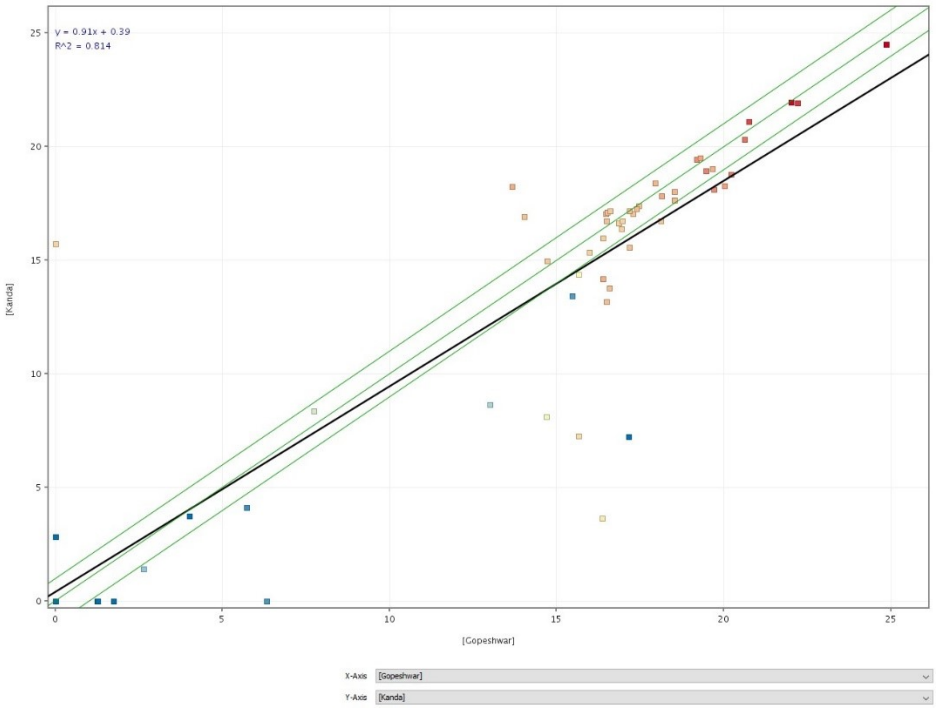


Figure 14SI: Scatter plot of Gopeshwar v/s Kanda

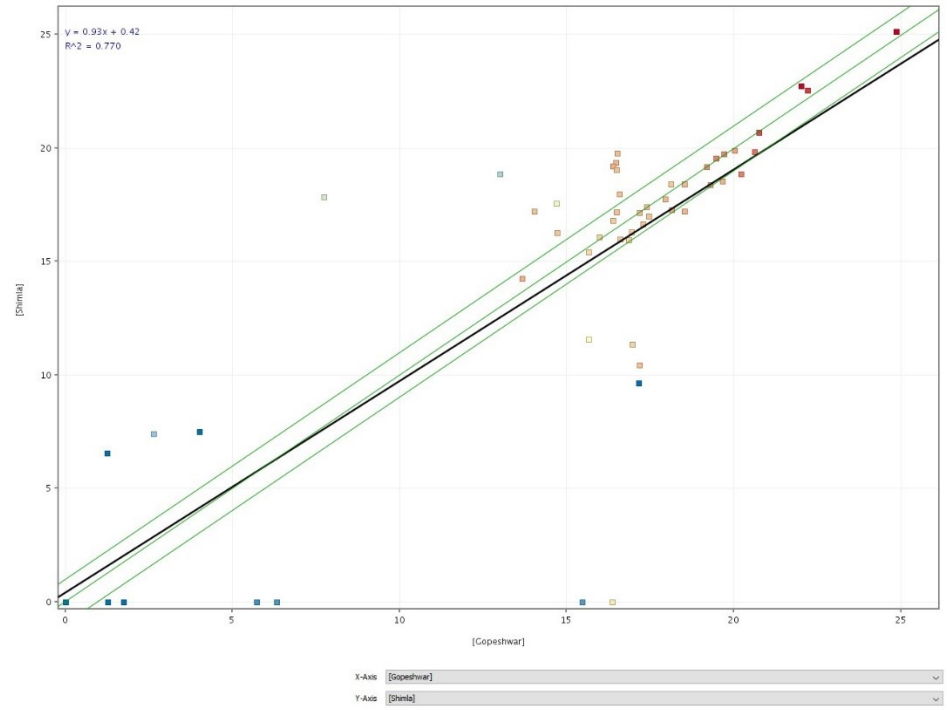


Figure 15SI: Scatter plot of Gopeshwar v/s Shimla

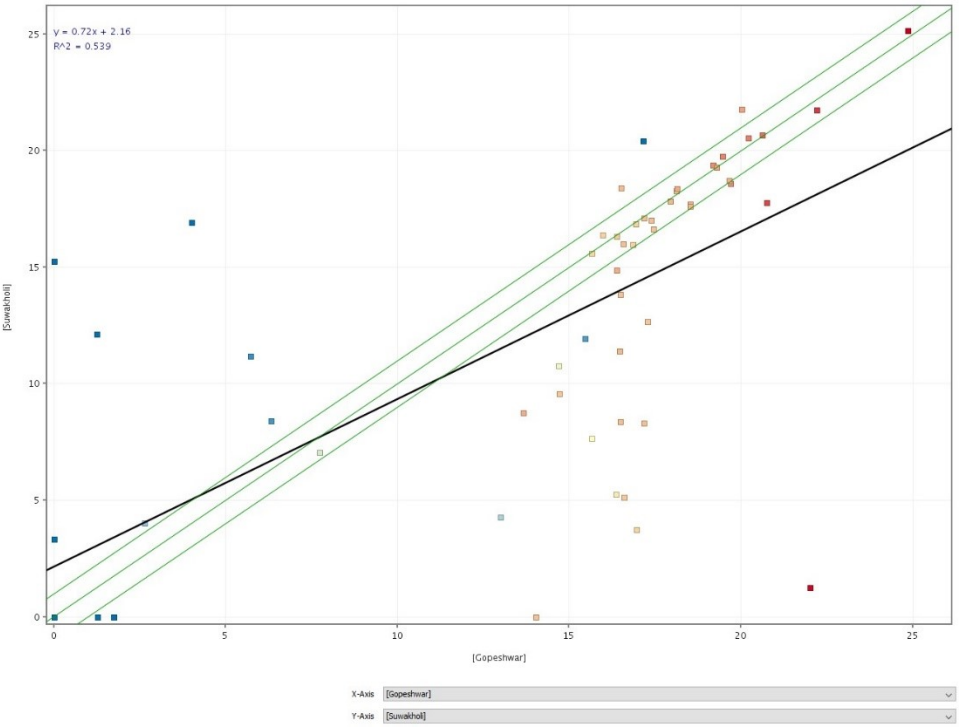


Figure 16SI: Scatter plot of Gopeshwar v/s Suwakholi

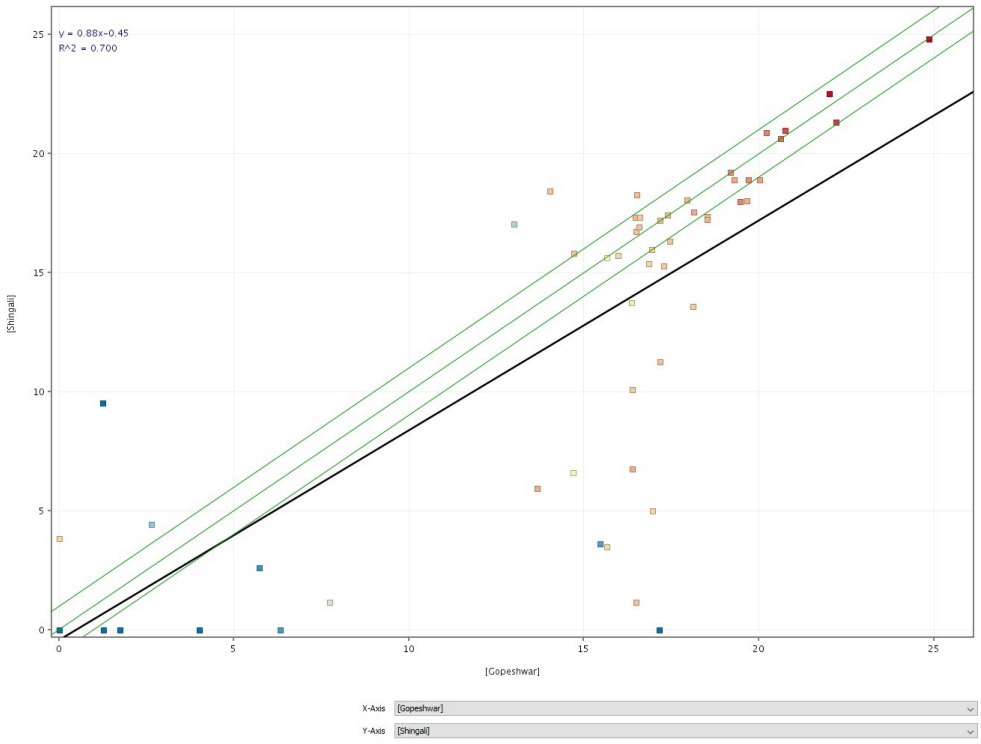


Figure 17SI: Scatter plot of Gopeshwar v/s Shingali

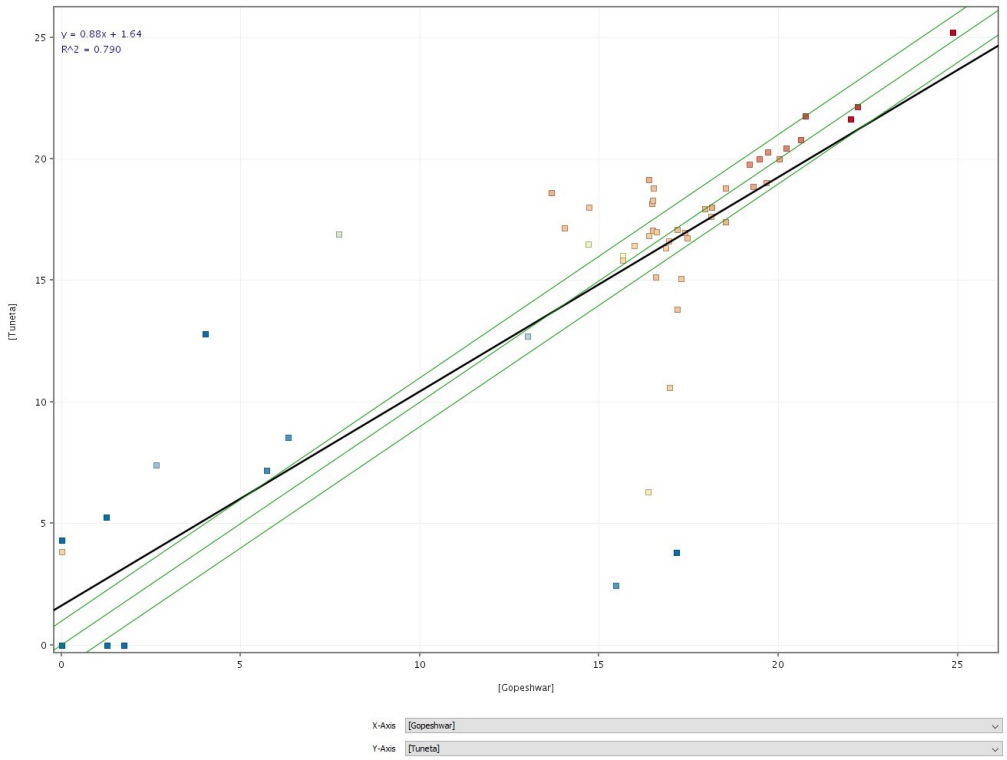


Figure 18SI: Scatter plot of Gopeshwar v/s Tuneta

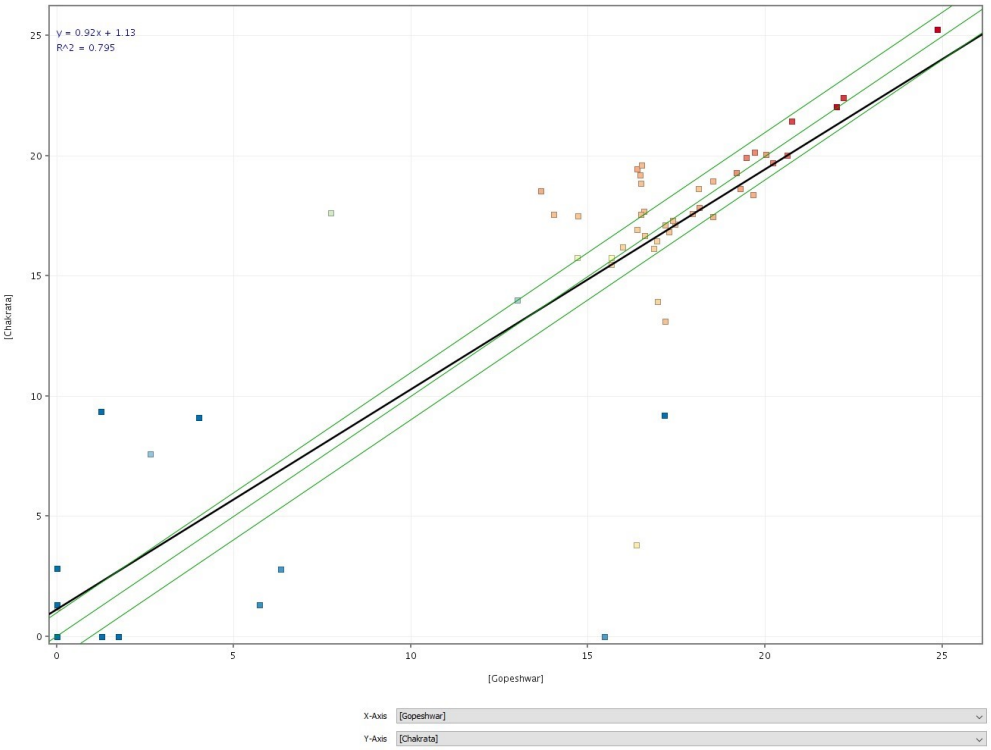


Figure 19SI: Scatter plot of Gopeshwar v/s Chakrata

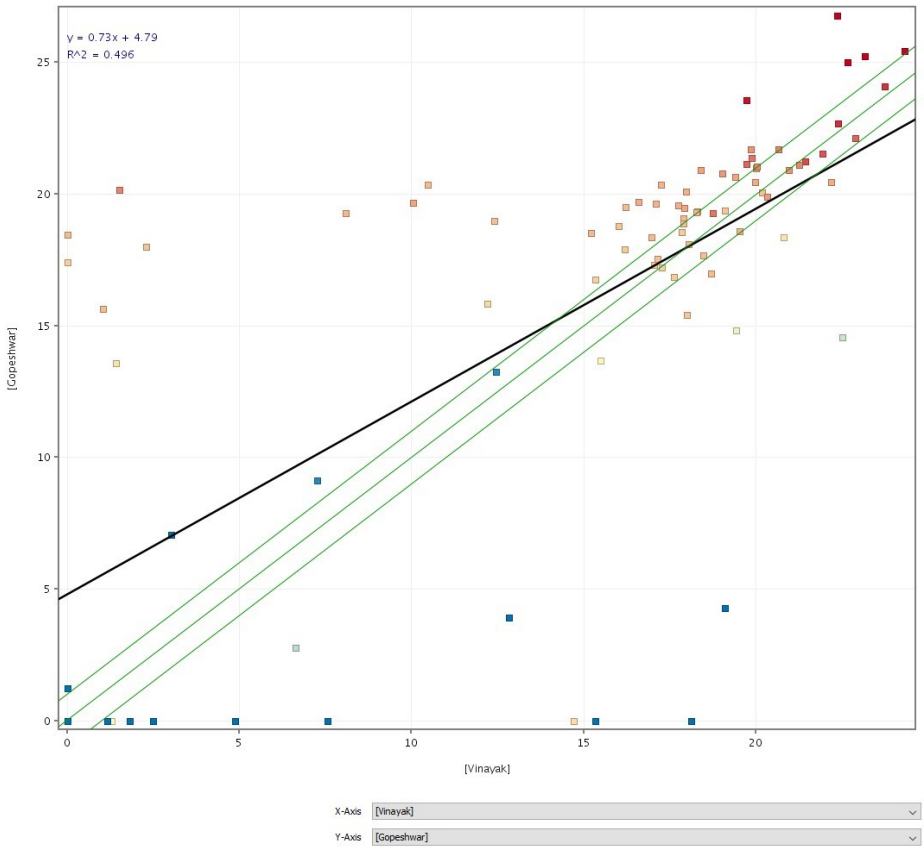


Figure 20SI: Scatter plot of Gopeshwar v/sVinayak

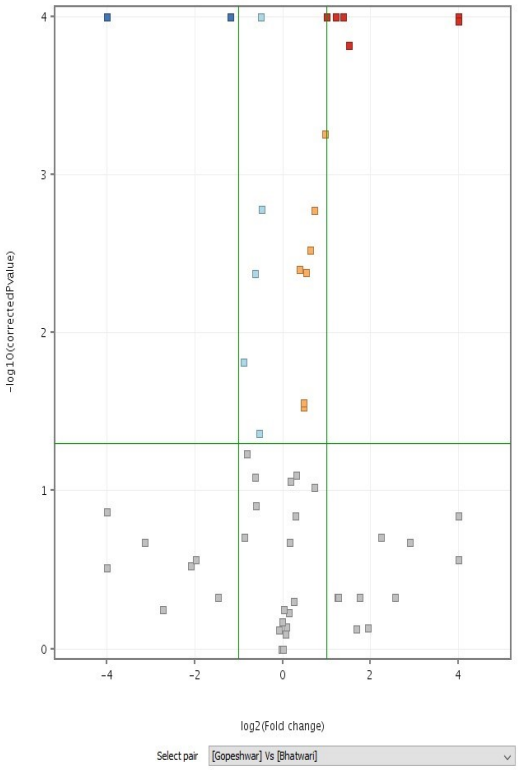


Figure 21SI: Volcano plot of Gopeshwar v/s Bhatwari

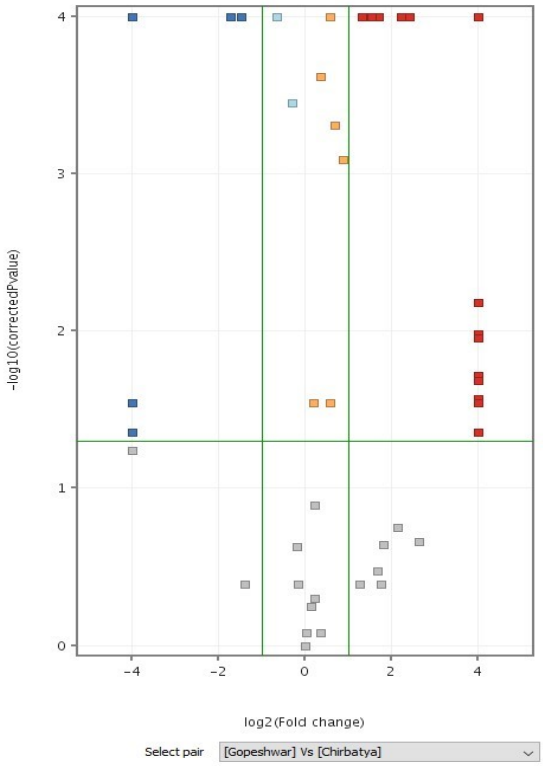


Figure 22SI: Volcano plot of Gopeshwar v/s Chirbatya

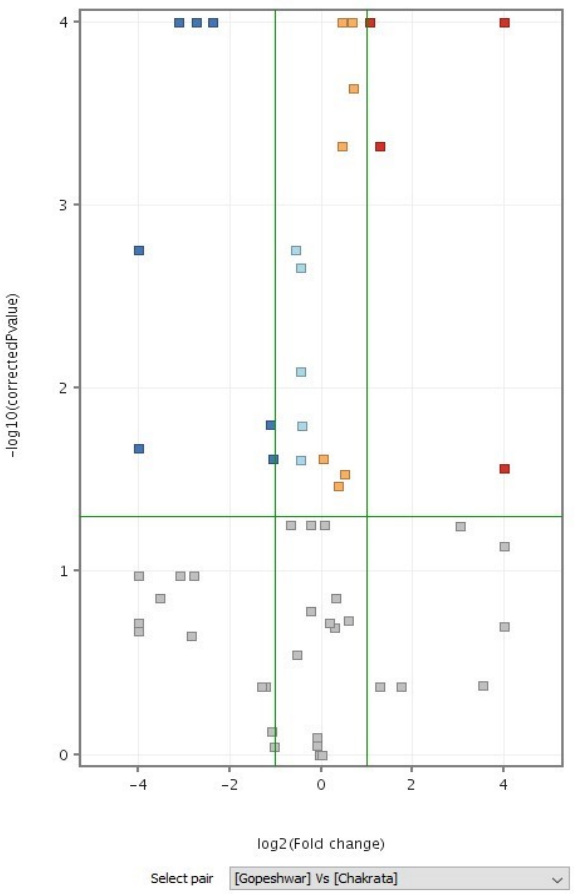


Figure 23SI: Volcano plot of Gopeshwar v/s Chakrata

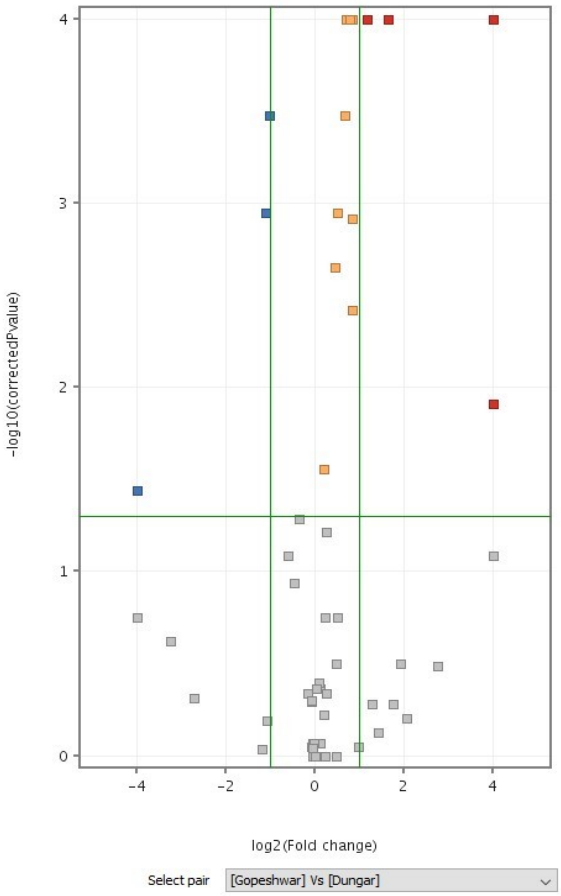


Figure 24SI: Volcano plot of Gopeshwar v/s Dungar

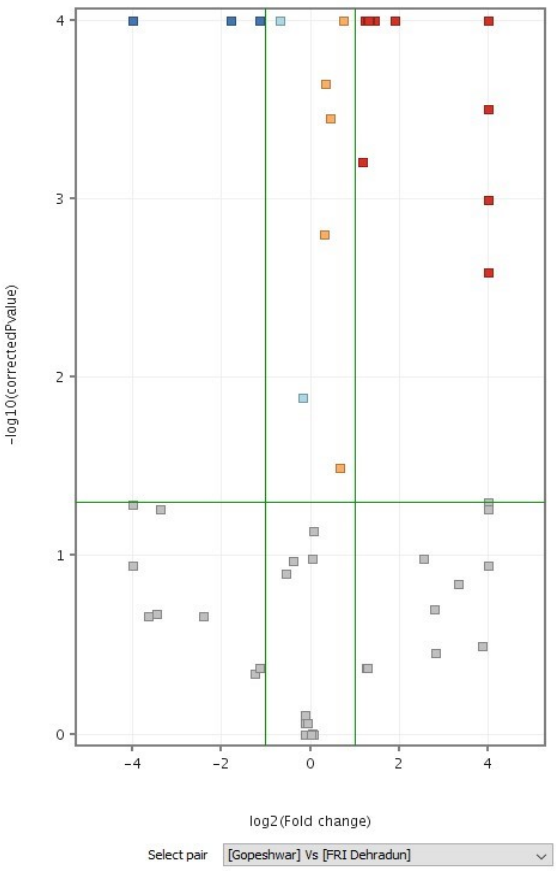


Figure 25SI: Volcano plot of Gopeshwar v/s FRI (Dehradun)`

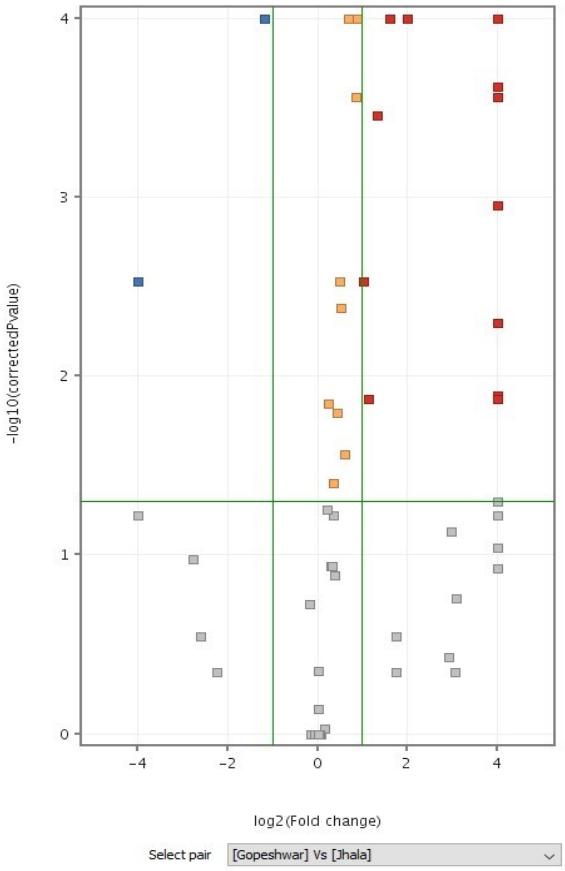


Figure 26SI: Volcano plot of Gopeshwar v/s Jhala

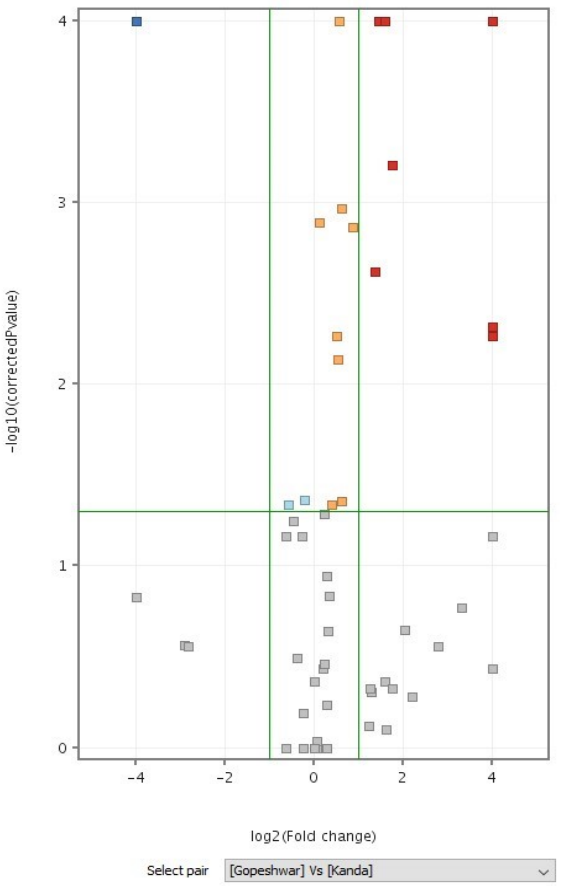


Figure 27SI: Volcano plot of Gopeshwar v/s Kanda

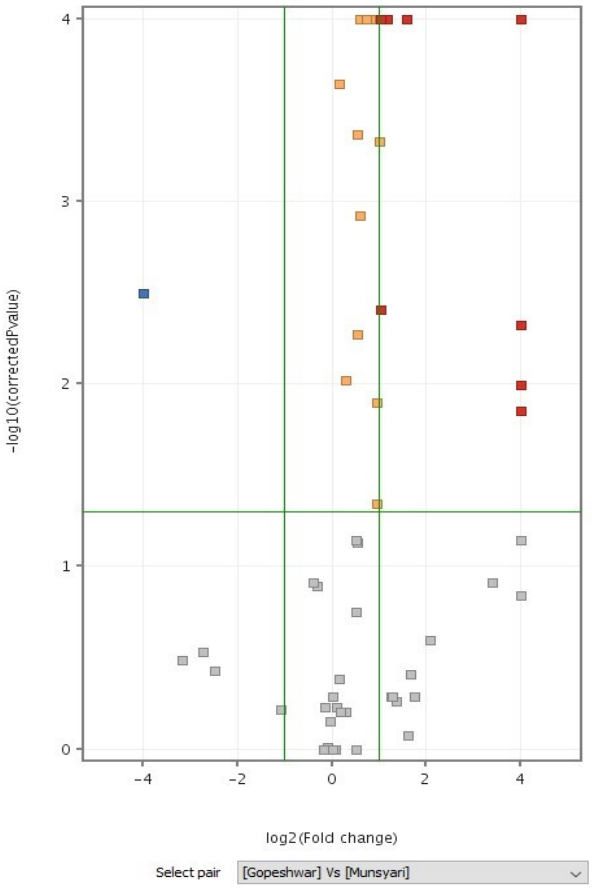
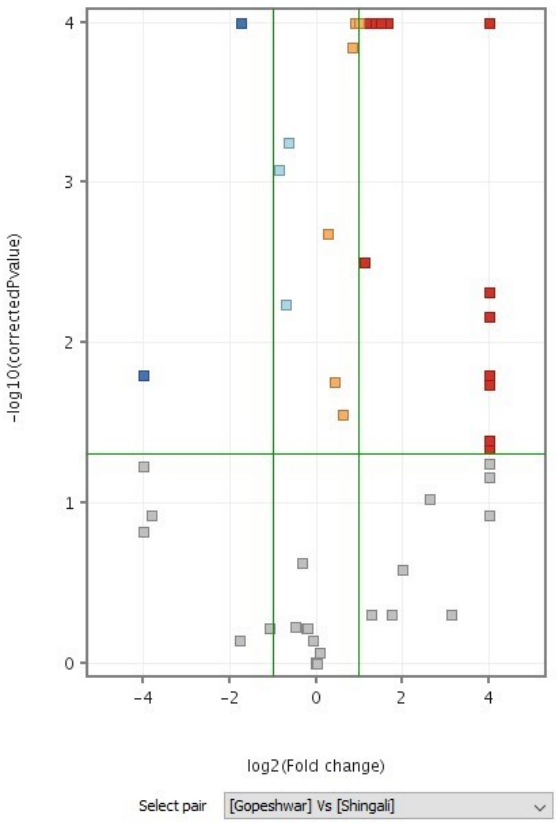


Figure 28SI: Volcano plot of Gopeshwar v/s Munsiyari



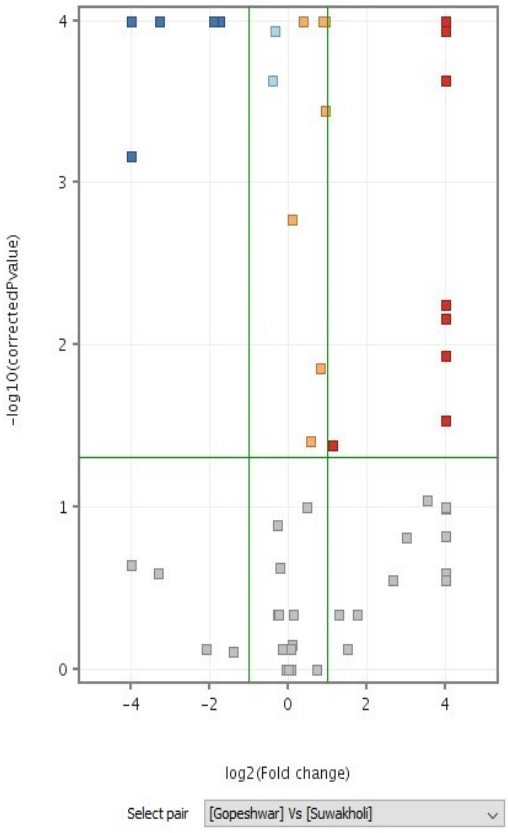
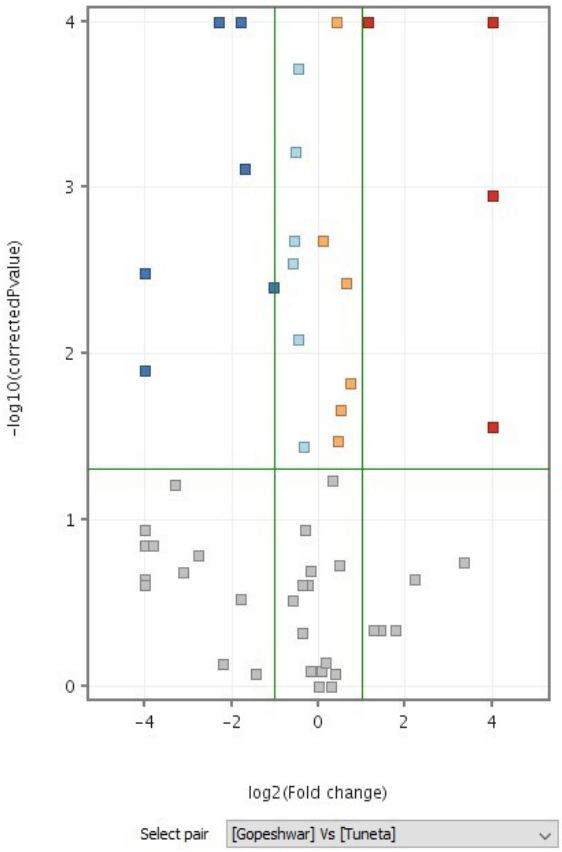


Figure 29SI: Volcano plot of Gopeshwar v/s Shingali **Figure 30SI: Volcano plot of Gopeshwar v/s Suwakholi**



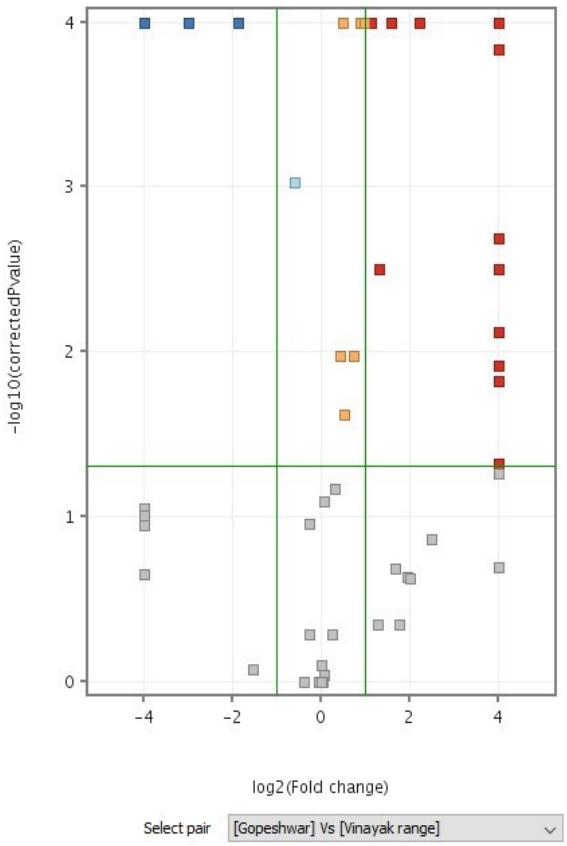


Figure 31SI: Volcano plot of Gopeshwar v/s Tuneta **Figure 32SI: Volcano plot of Gopeshwar v/s Vinayak**

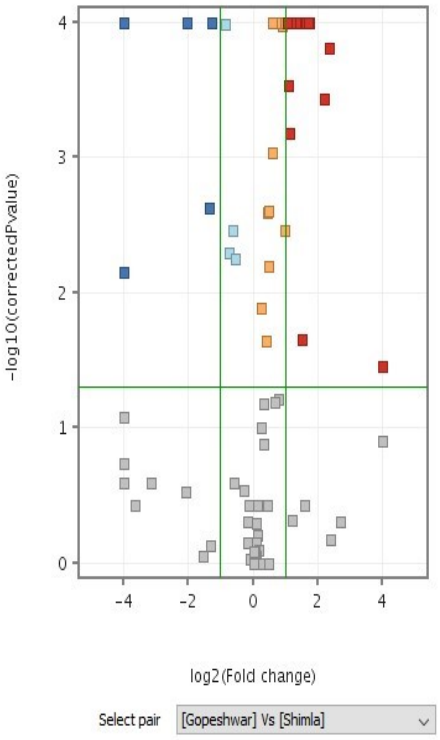


Figure 33SI: Volcano plot of Gopeshwar v/s Shimla

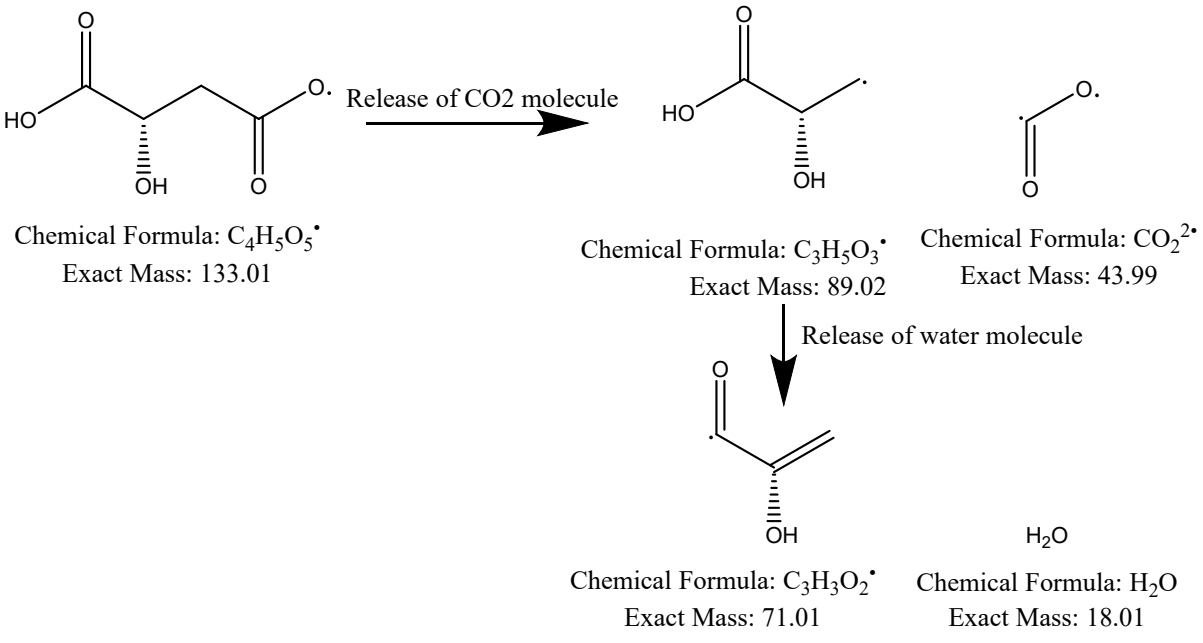


Figure 34SI: Fragmentation pathway of Malic acid

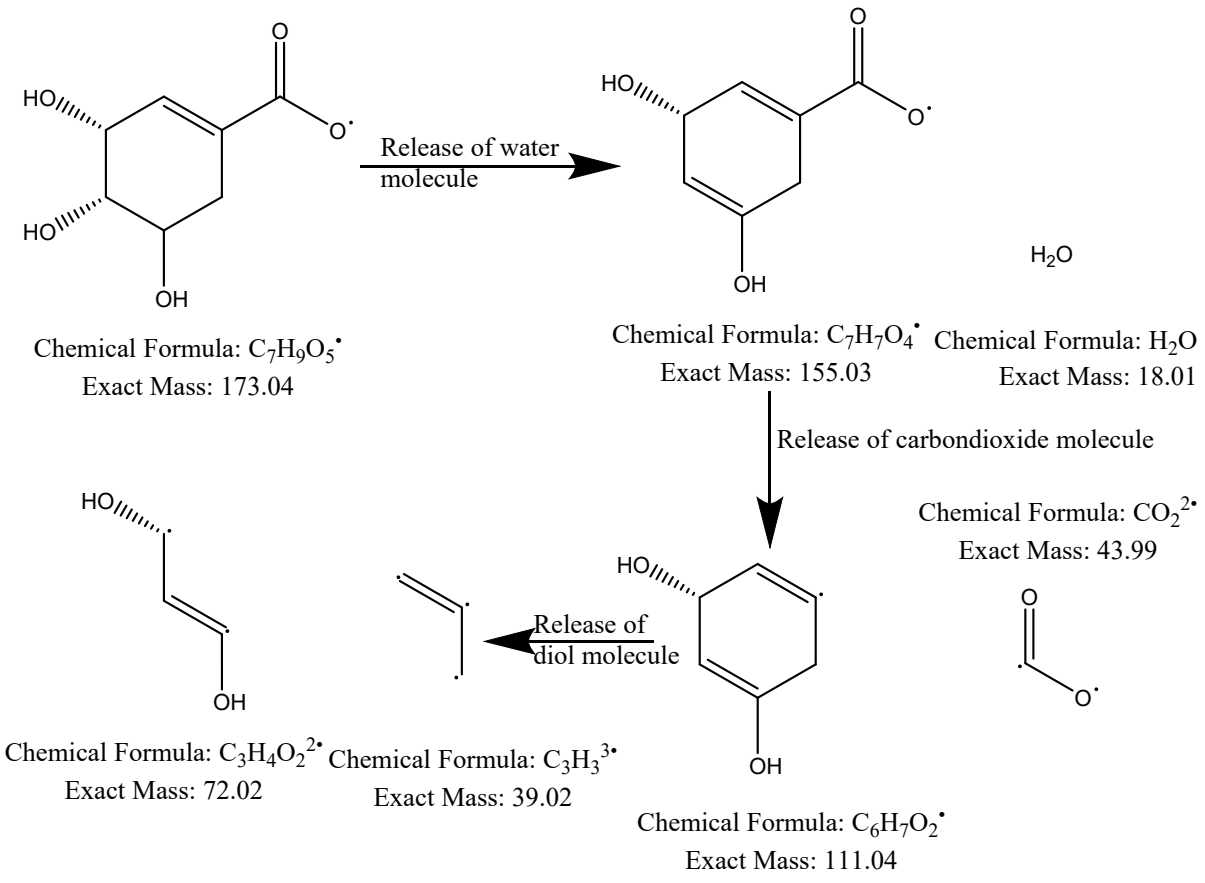


Figure 35SI: Fragmentation pathway of Shikimic acid

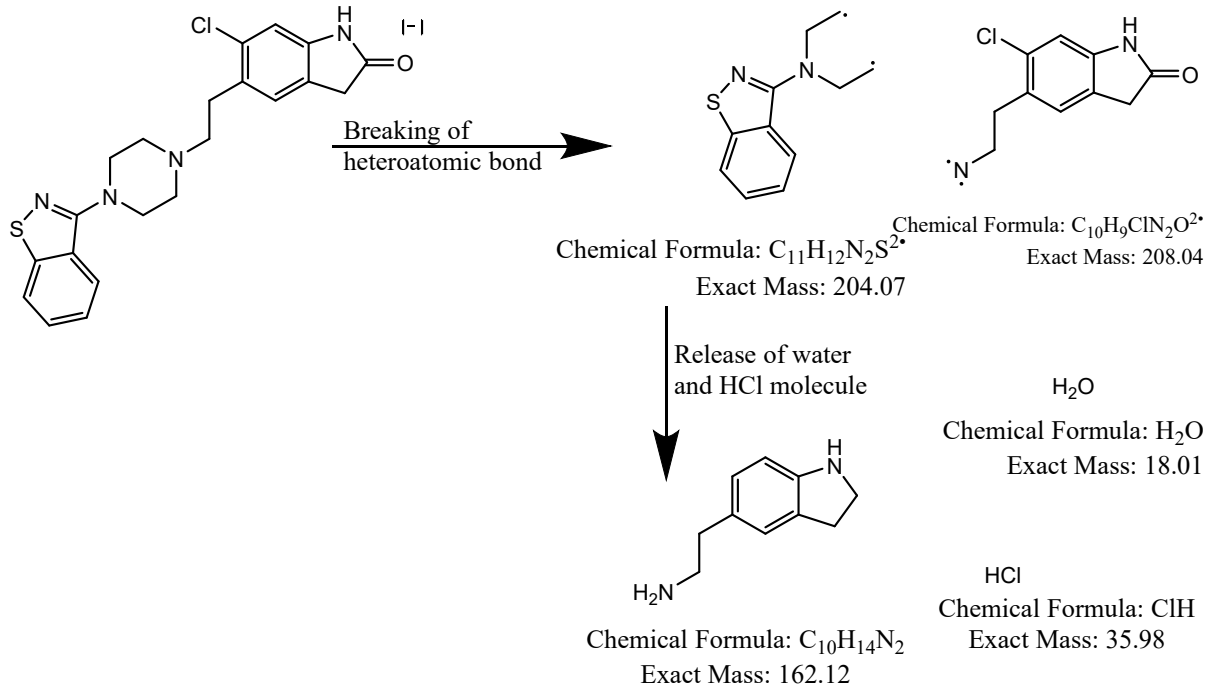
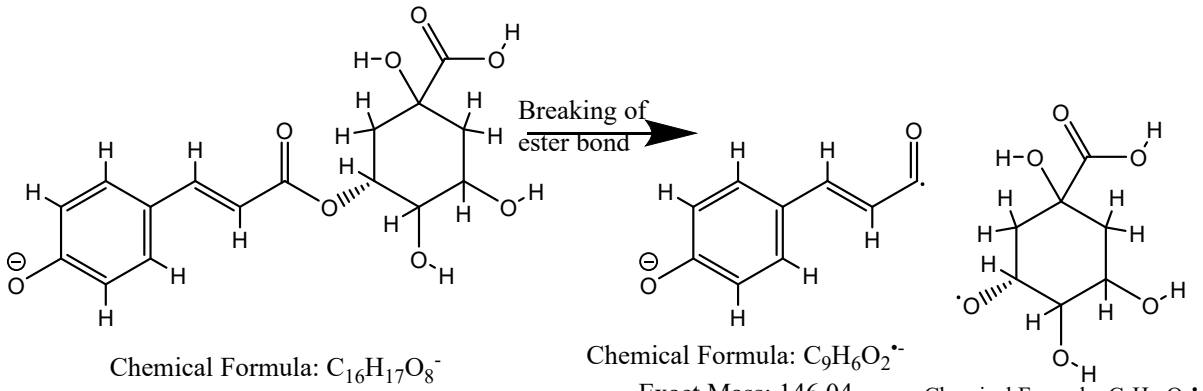
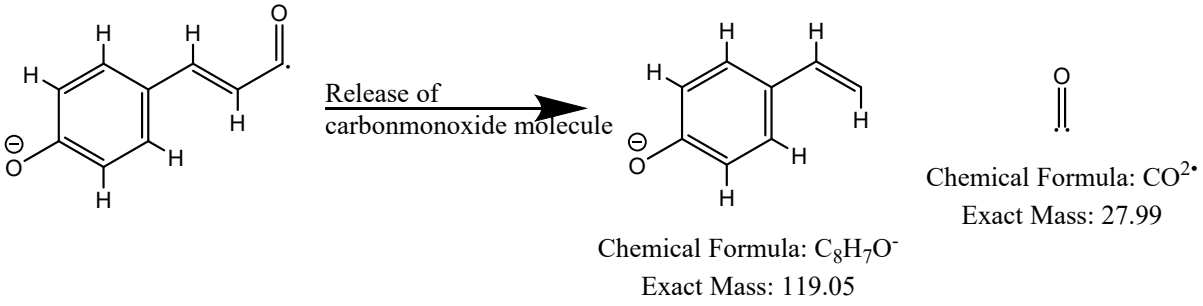


Figure 36SI: Fragmentation pathway of Ziprasidone





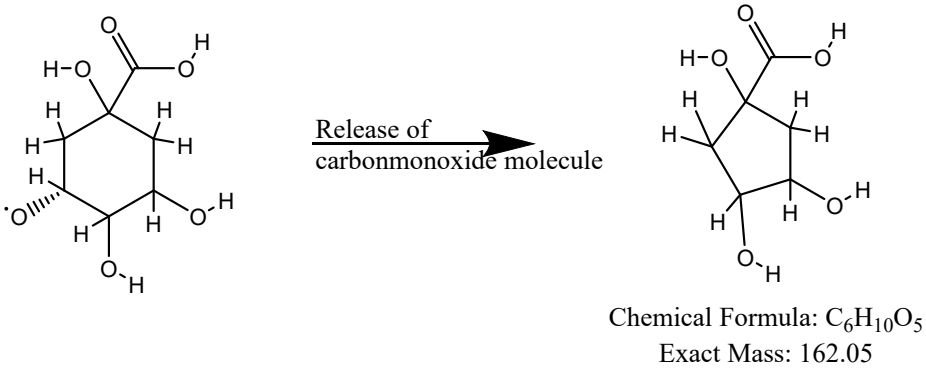


Figure 37SI: Fragmentation pathway of p-Coumaroyl quinic acid

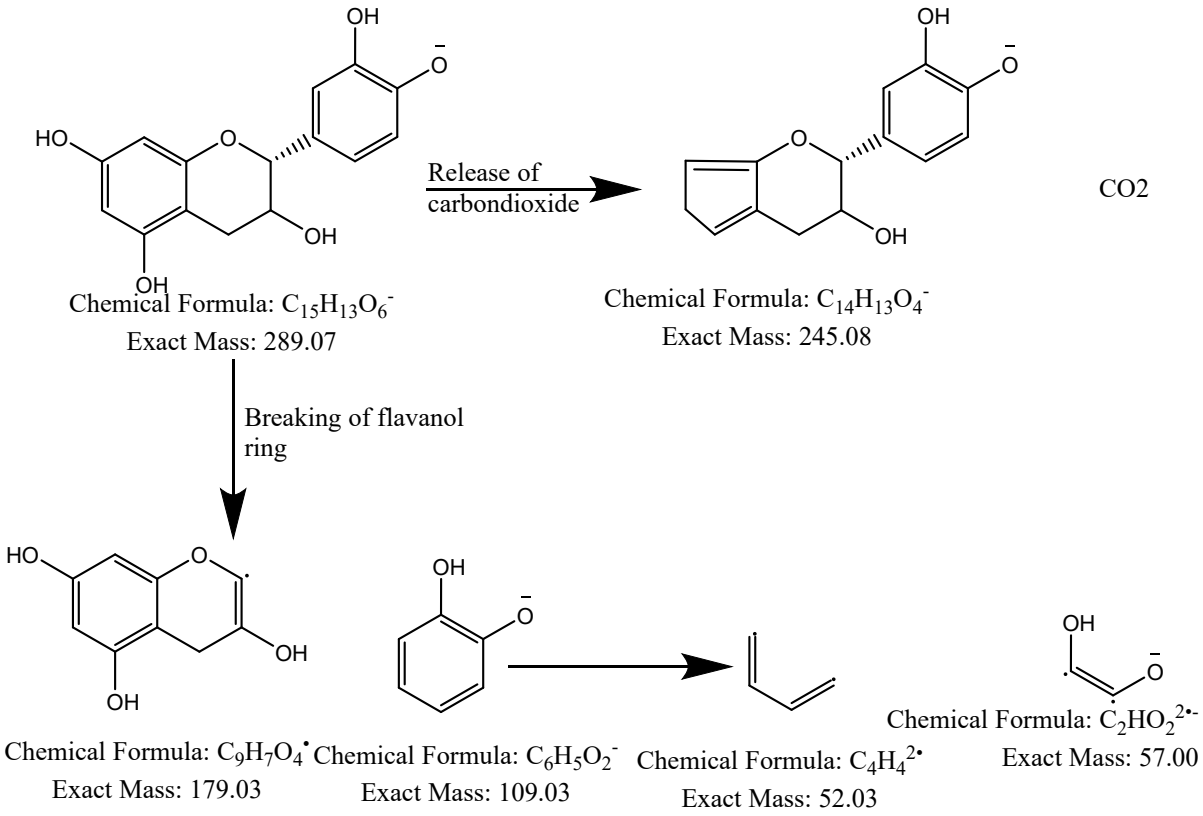


Figure 38SI: Fragmentation pathway of Catechin

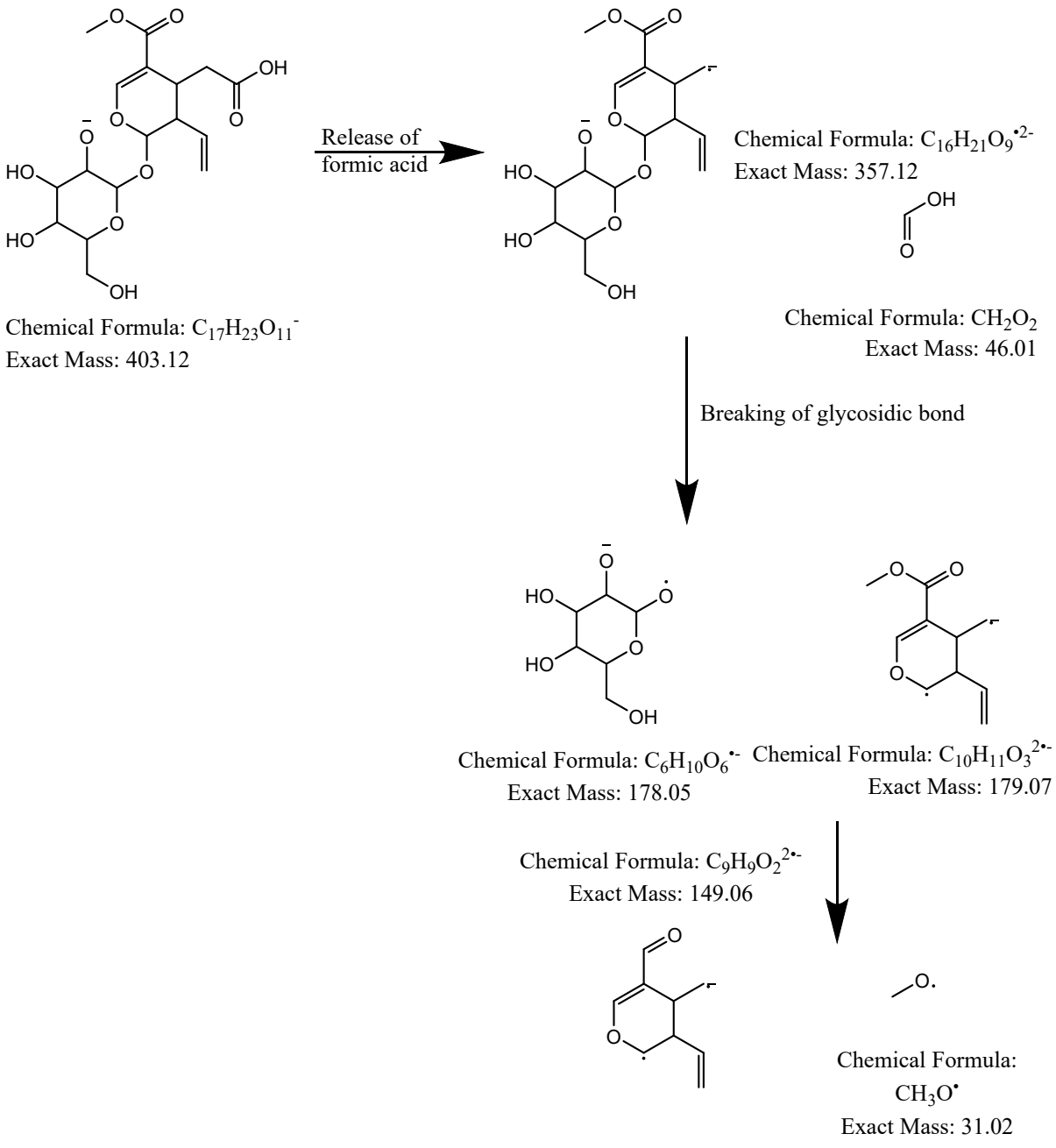


Figure 39SI: Fragmentation pattern of Secoxyloganin

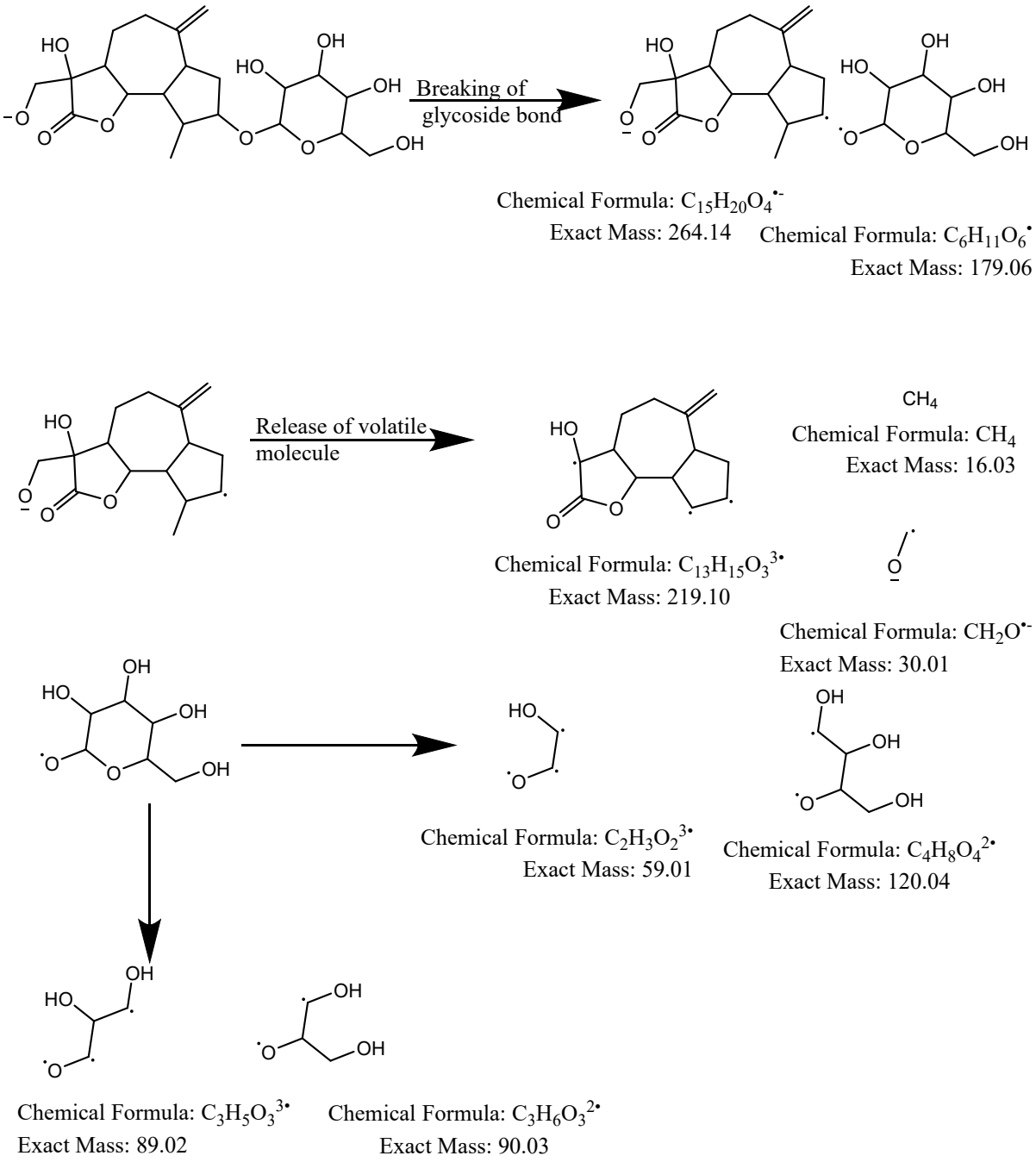


Figure 40SI: Fragmentation pathway of Cynaroside A

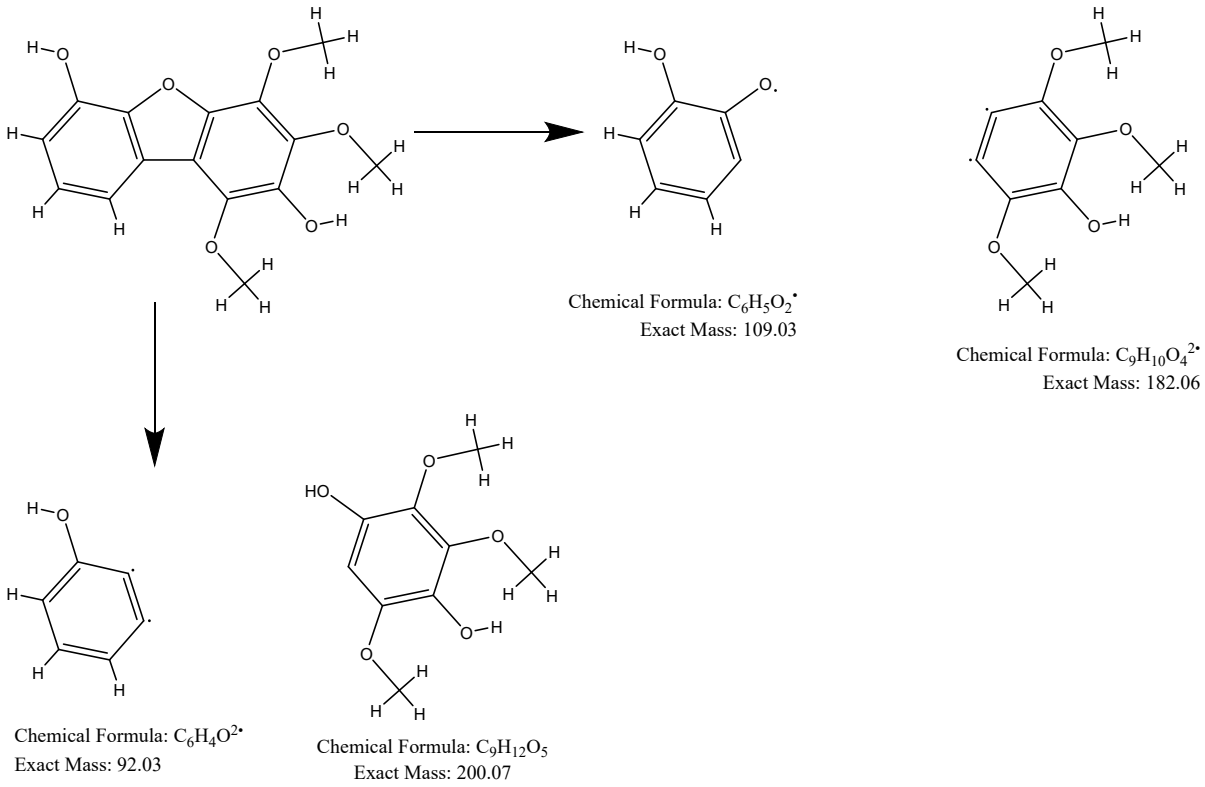


Figure 41SI: Fragmentation pathway of 6-Hydroxy-alpha-pyrufuran

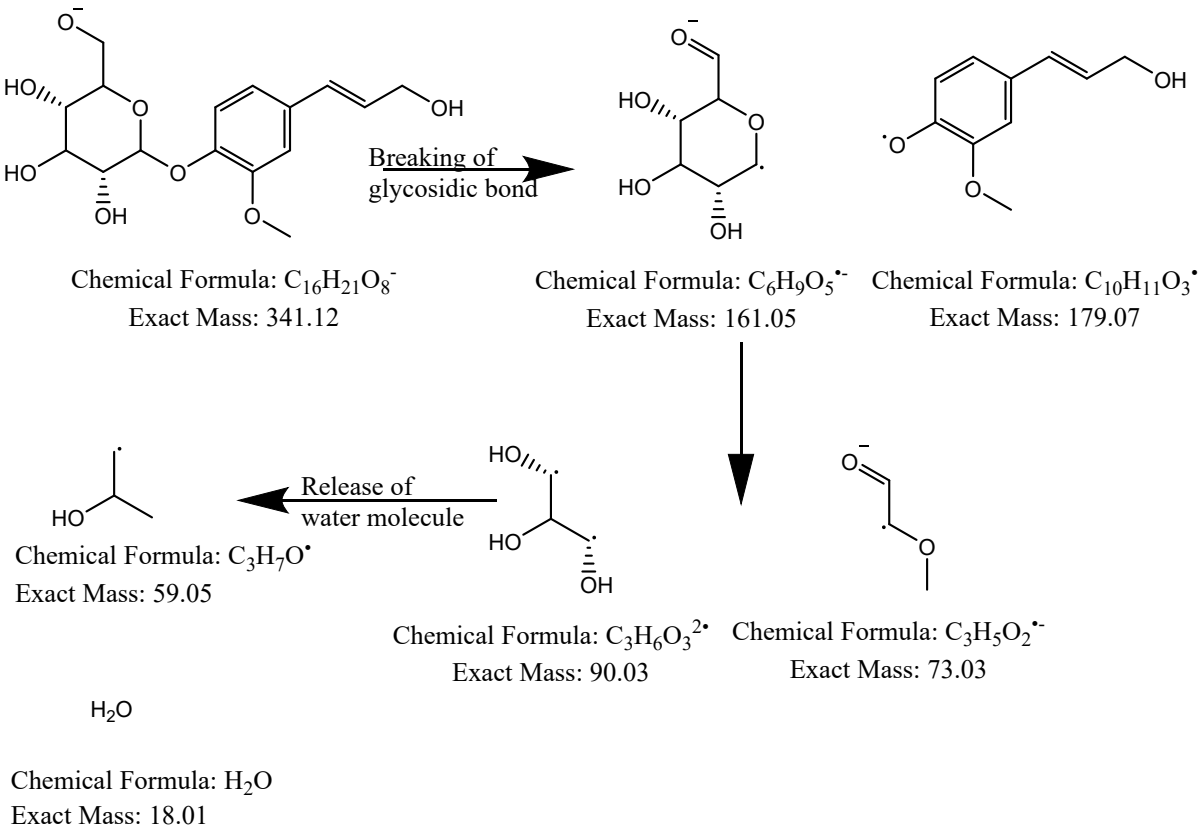


Figure 42SI: Fragmentation pathway of Coniferin

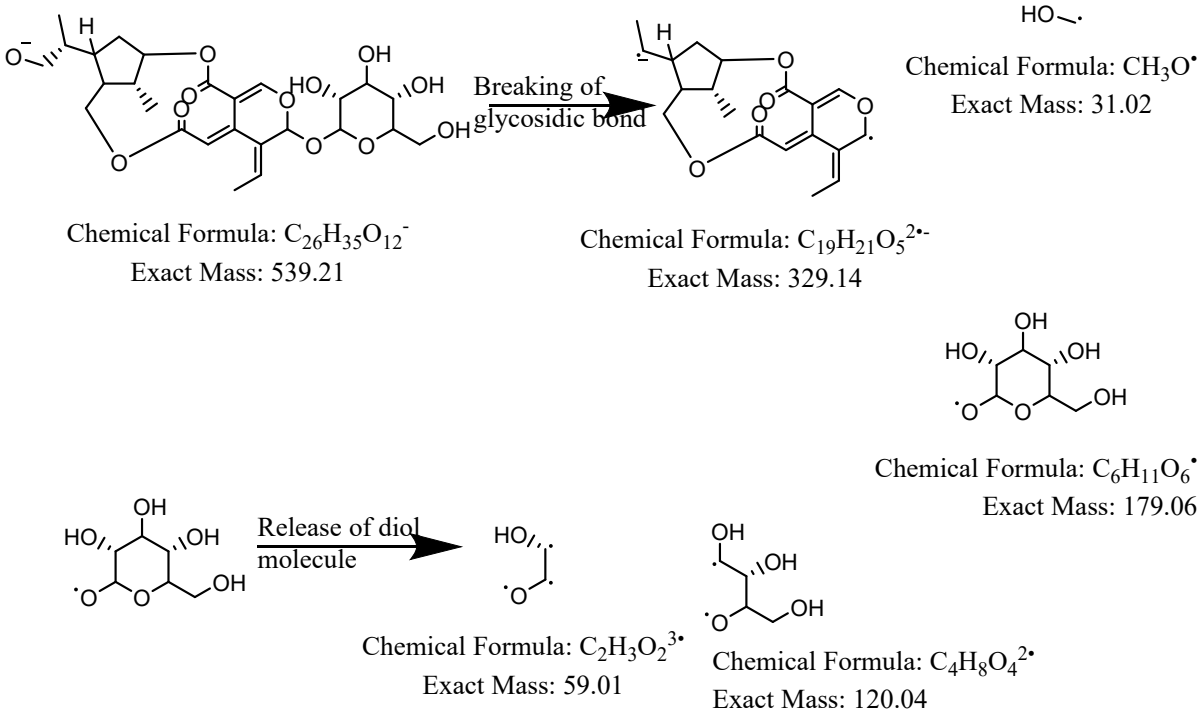


Figure 43SI: Fragmentation pathway of Sambacin

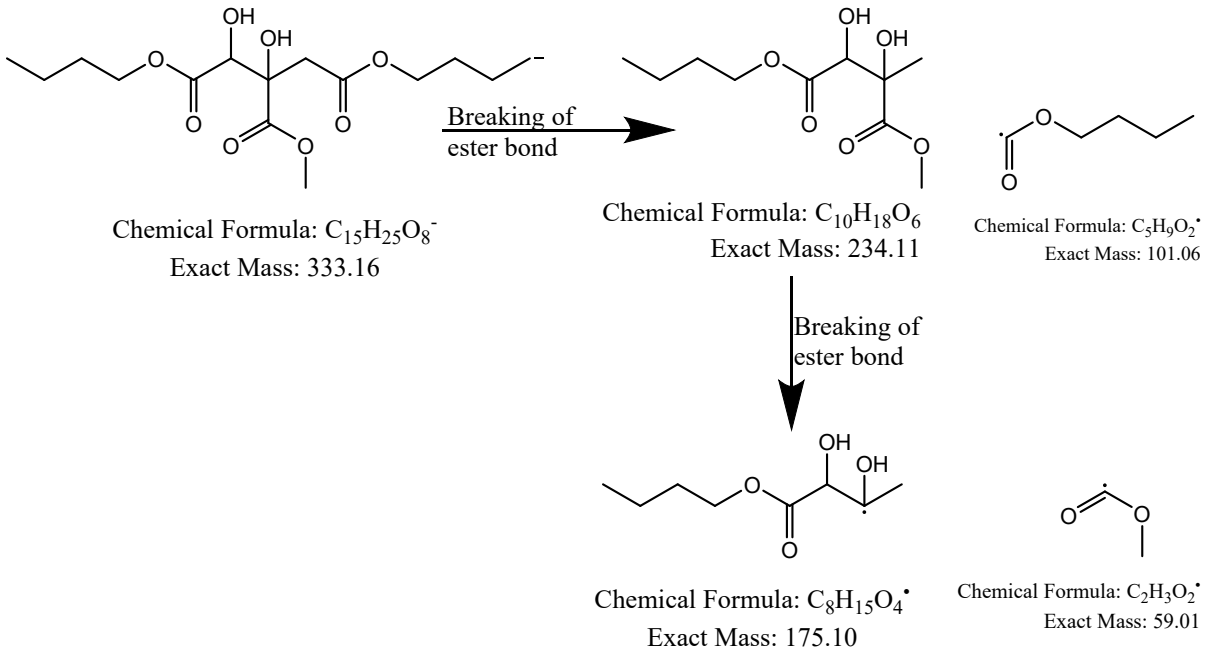


Figure 44SI: Fragmentation pathway of 1,5-Dibutyl methyl hydroxy citrate

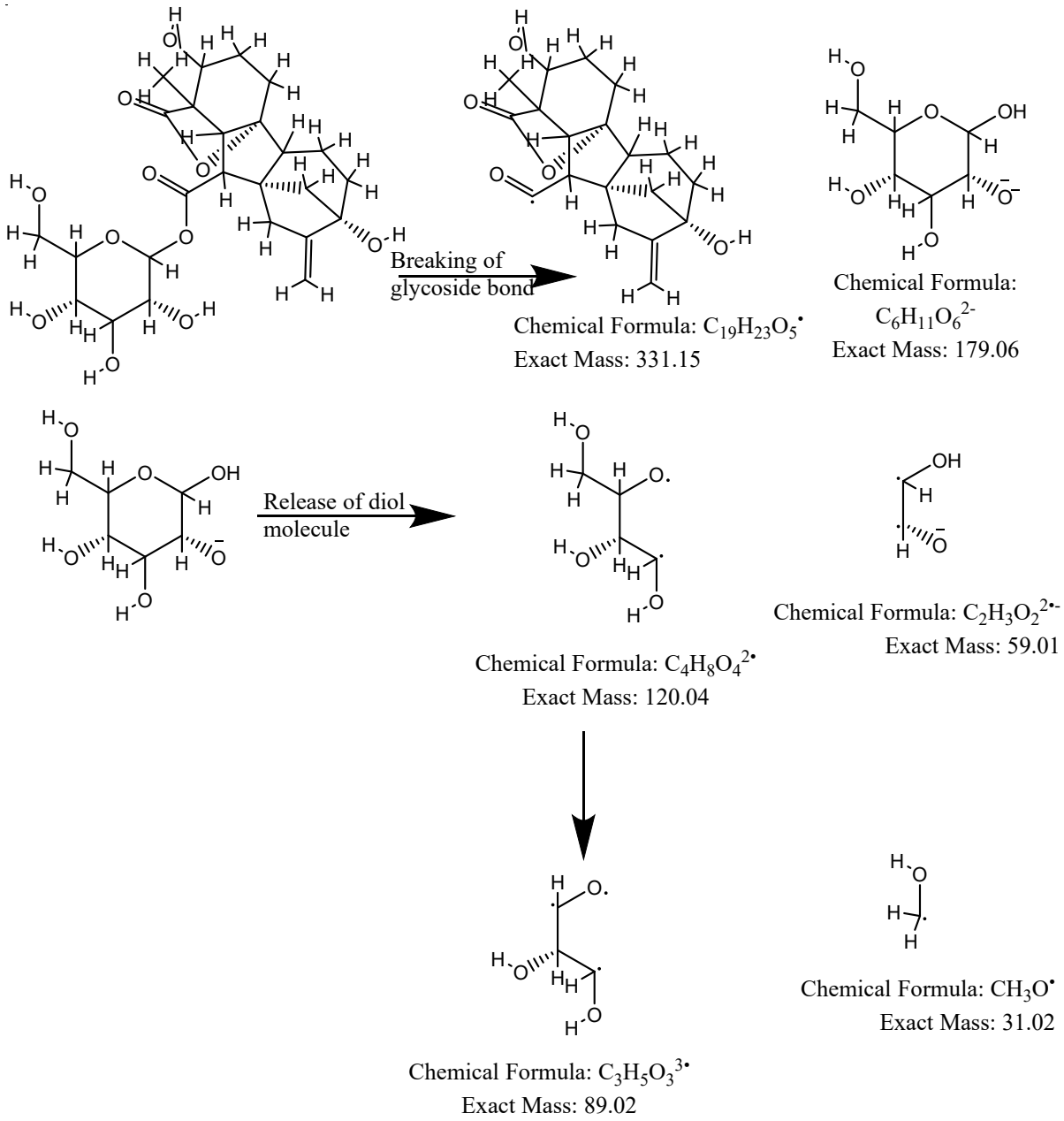


Figure 45SI: Fragmentation pathway of Gibberellin A1 glucosyl ester

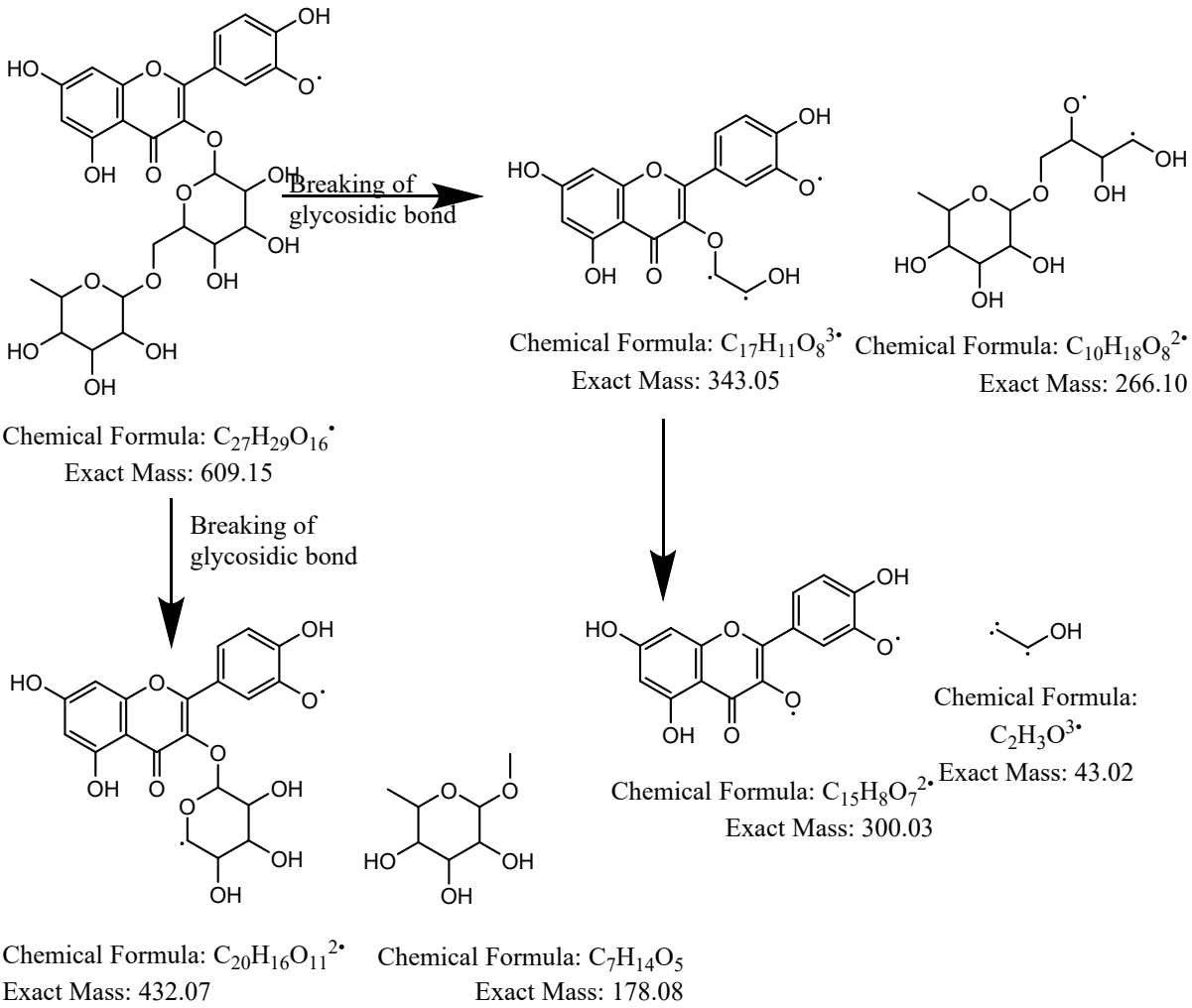


Figure 46SI: Fragmentation pathway of Rutin

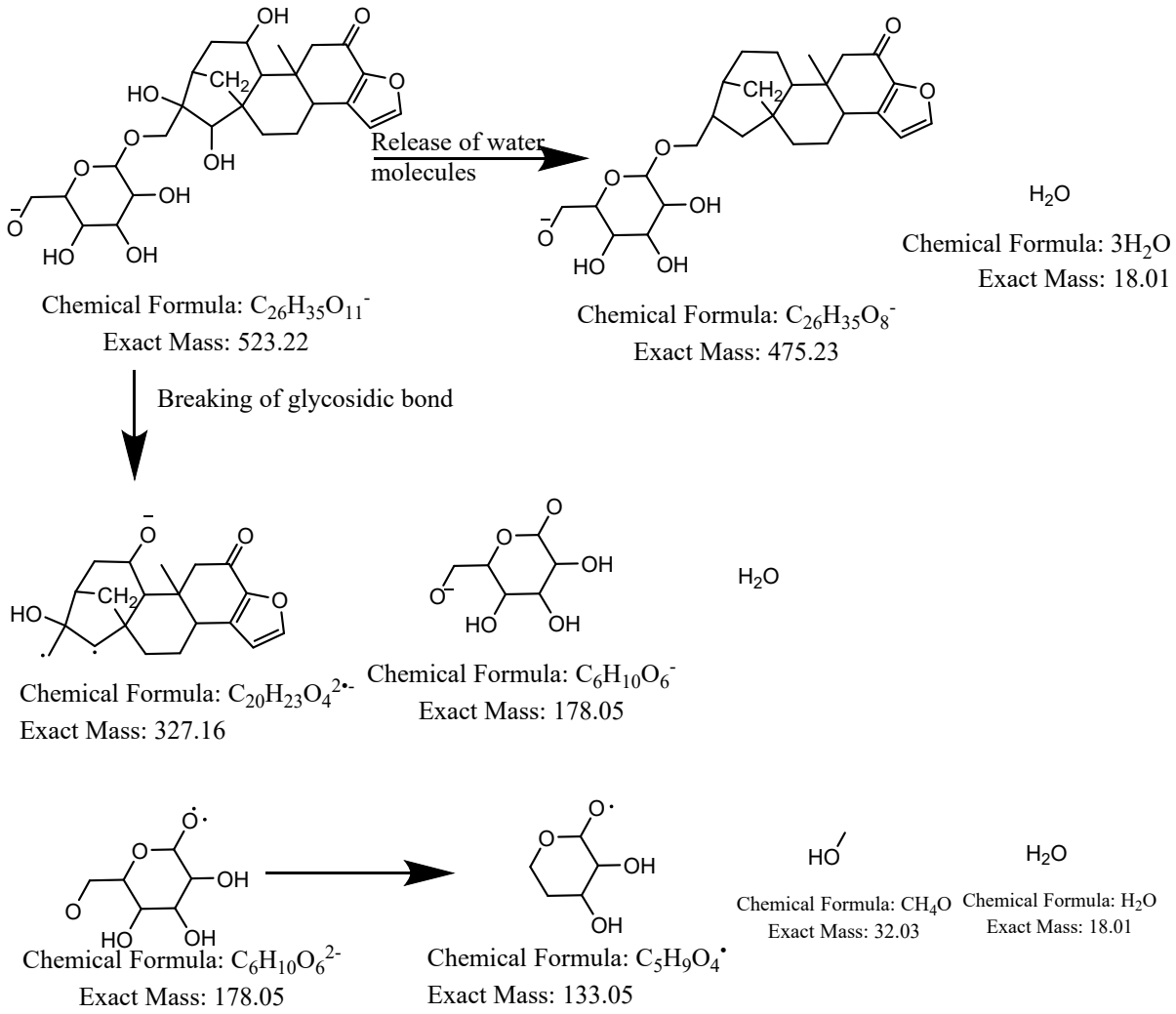


Figure 47SI: Fragmentation pathway of Mascaroside

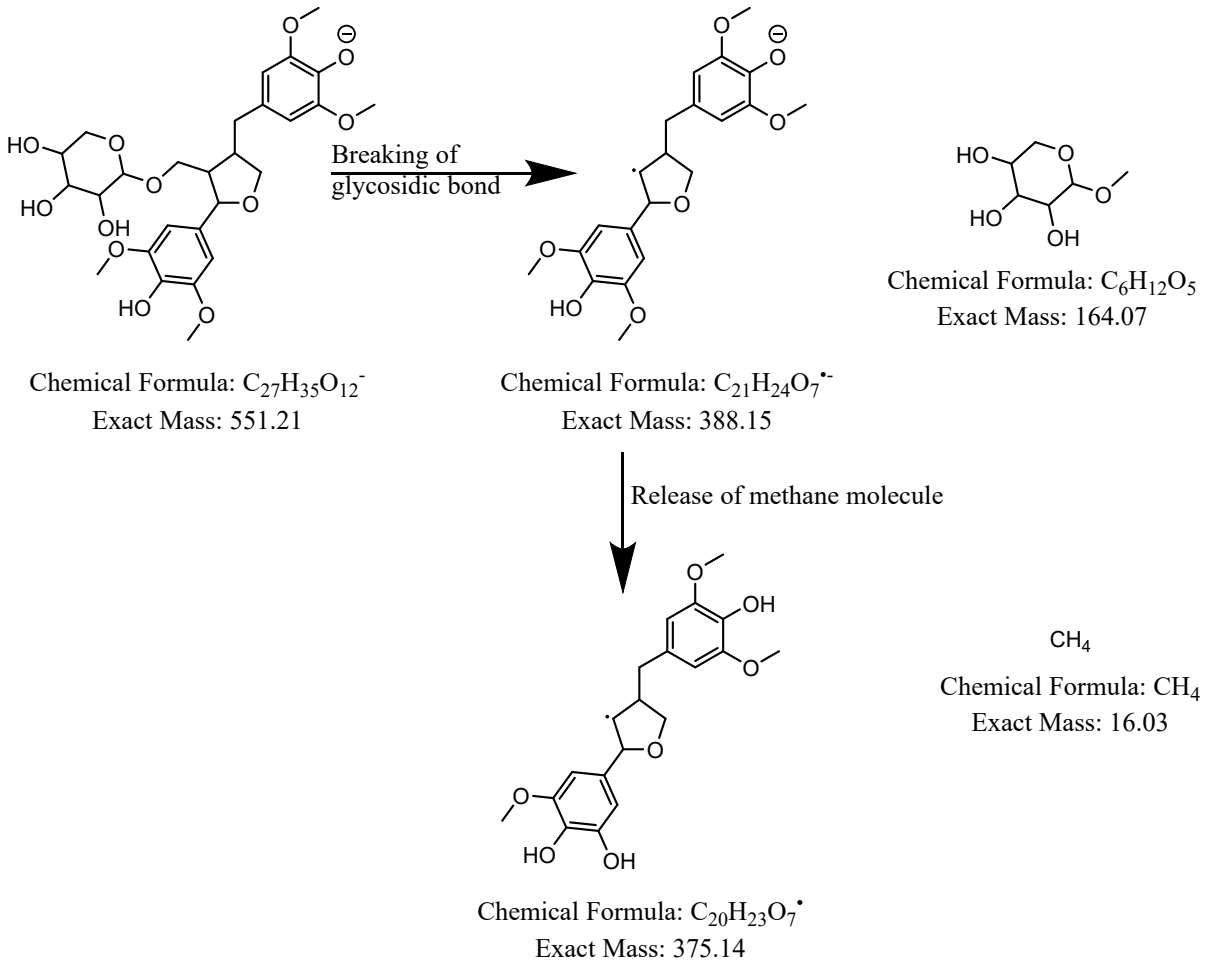


Figure 48SI: Fragmentation pathway of Prupaside

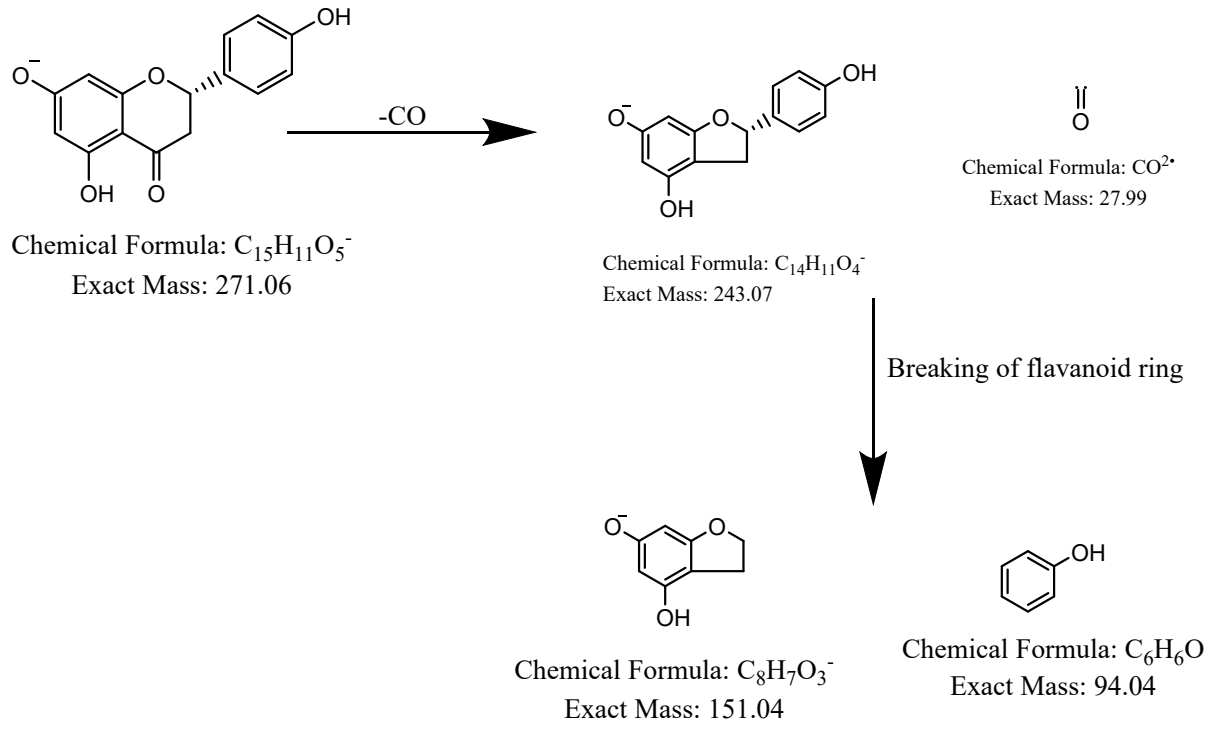


Figure 49SI: Fragmentation pathway of Naringenin

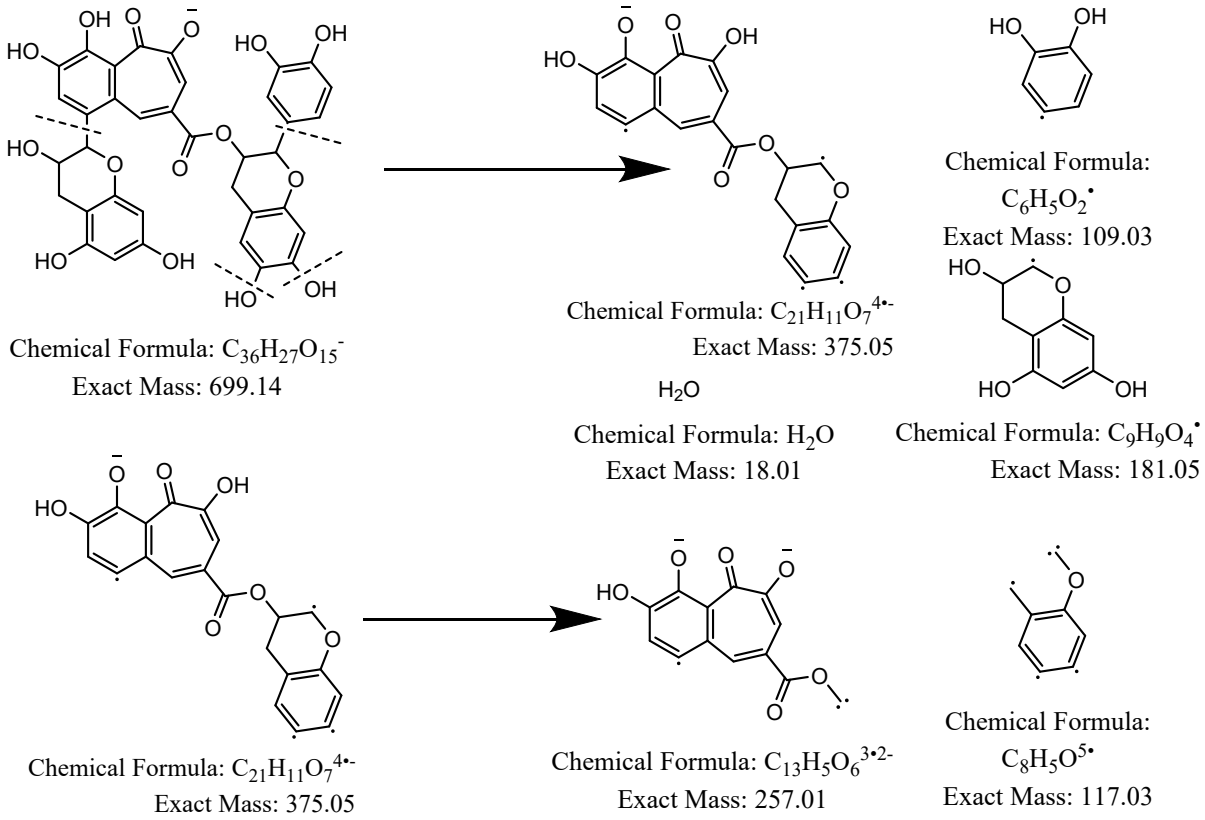


Figure 50SI: Fragmentation pathway of Theaflavate B

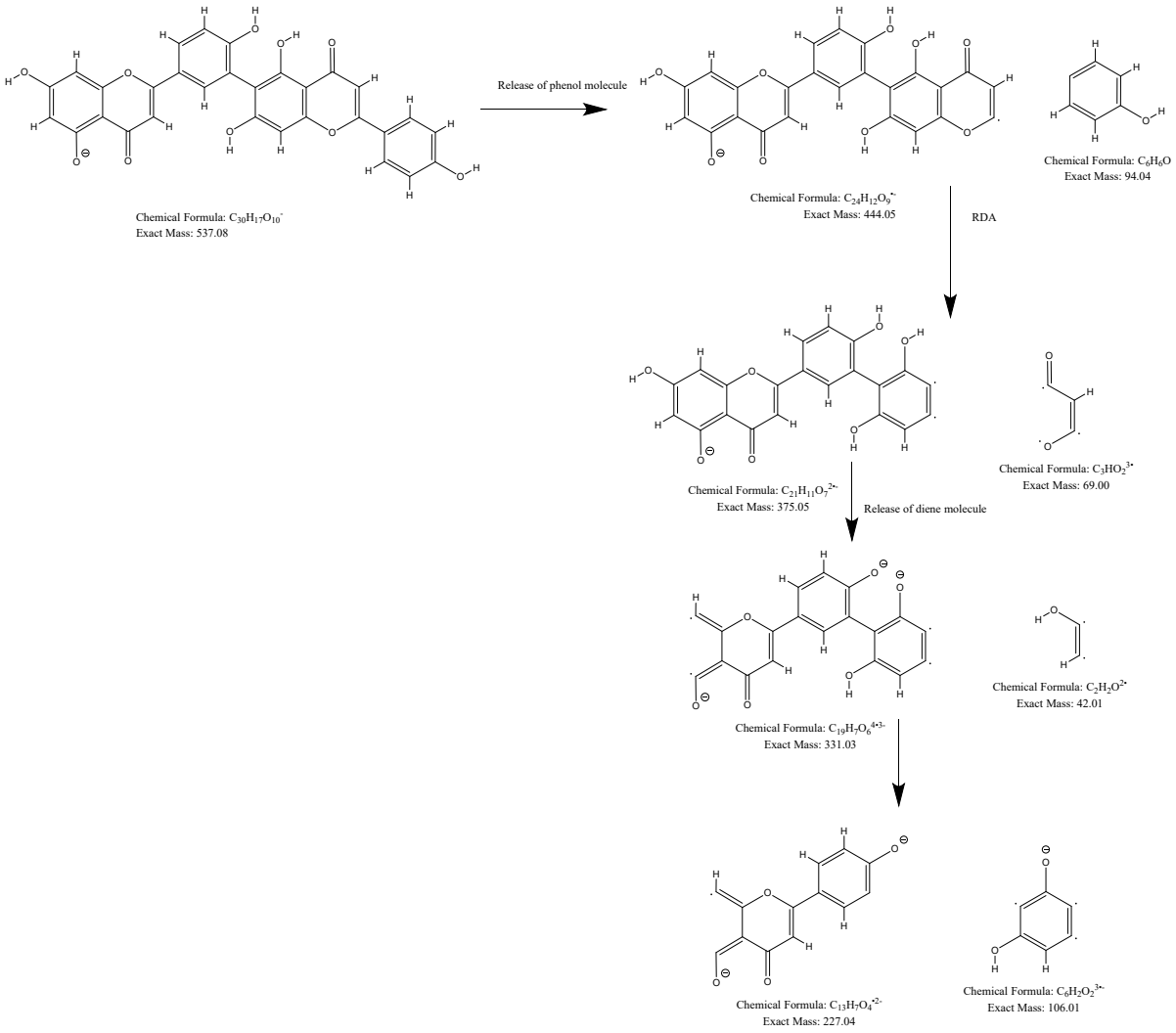


Figure 51SI: Fragmentation pathway of Robustaflavone

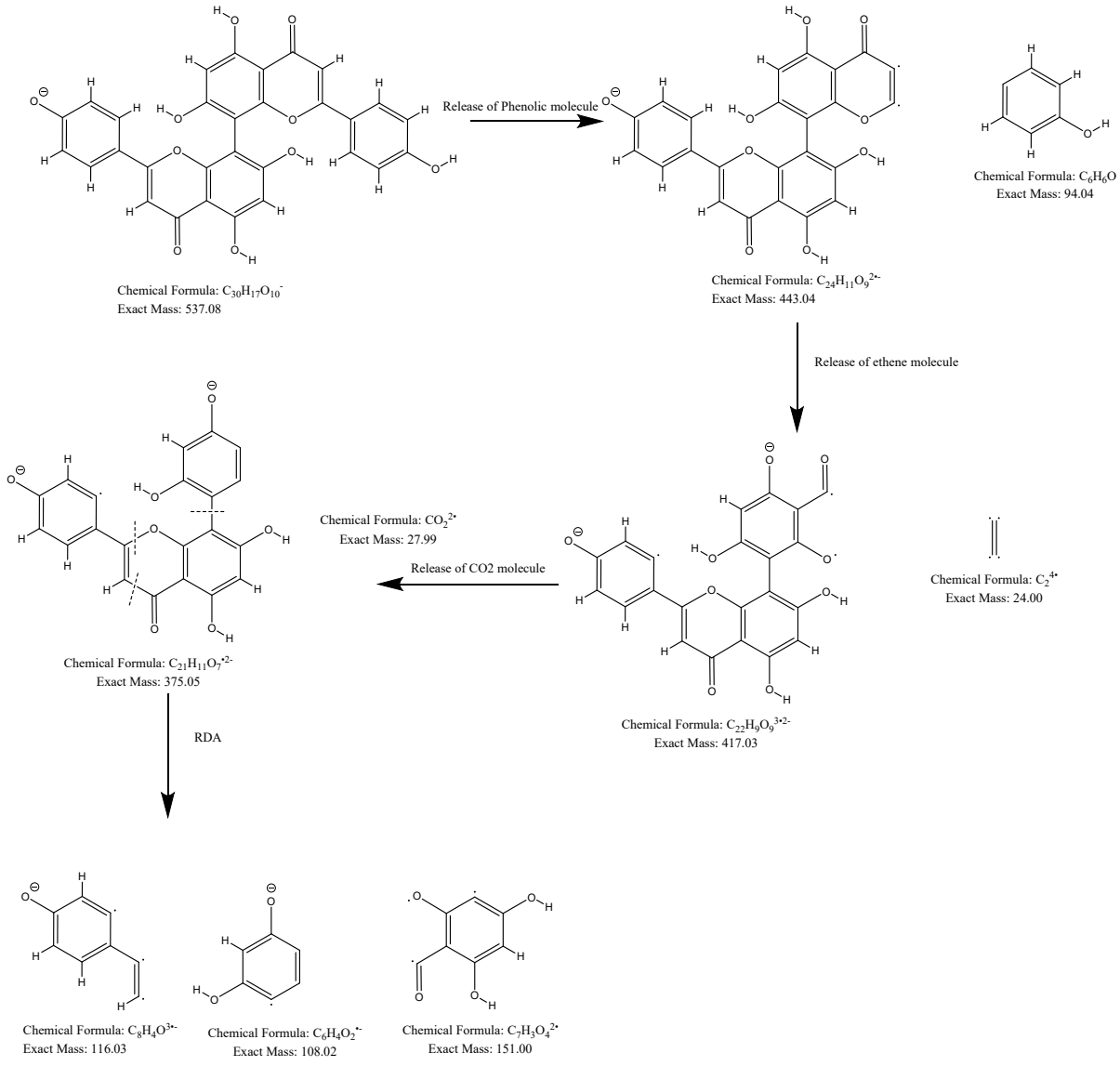


Figure 52SI: Fragmentation pathway of Cupressuflavone

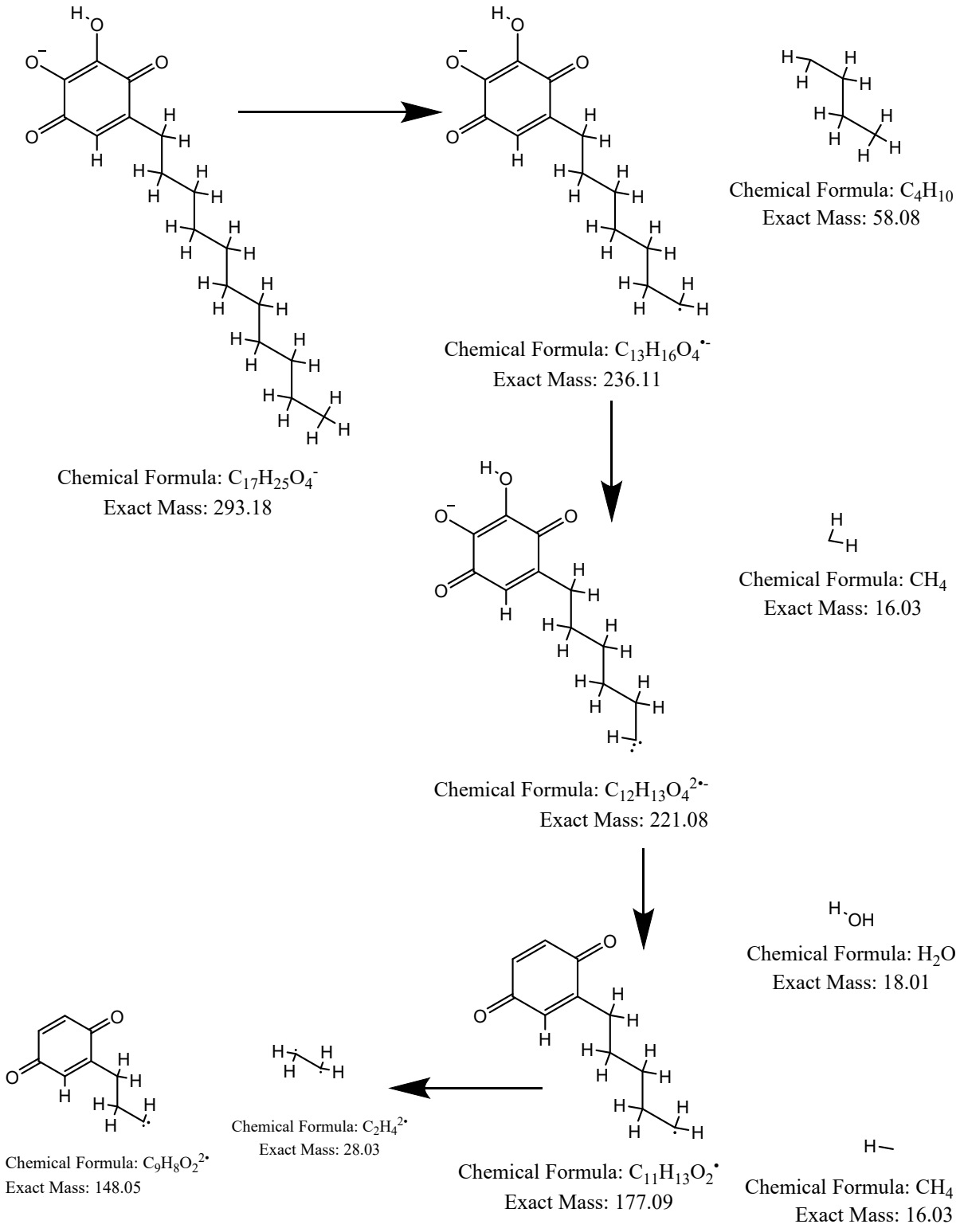


Figure 53SI: Fragmentation pathway of Myrsinone

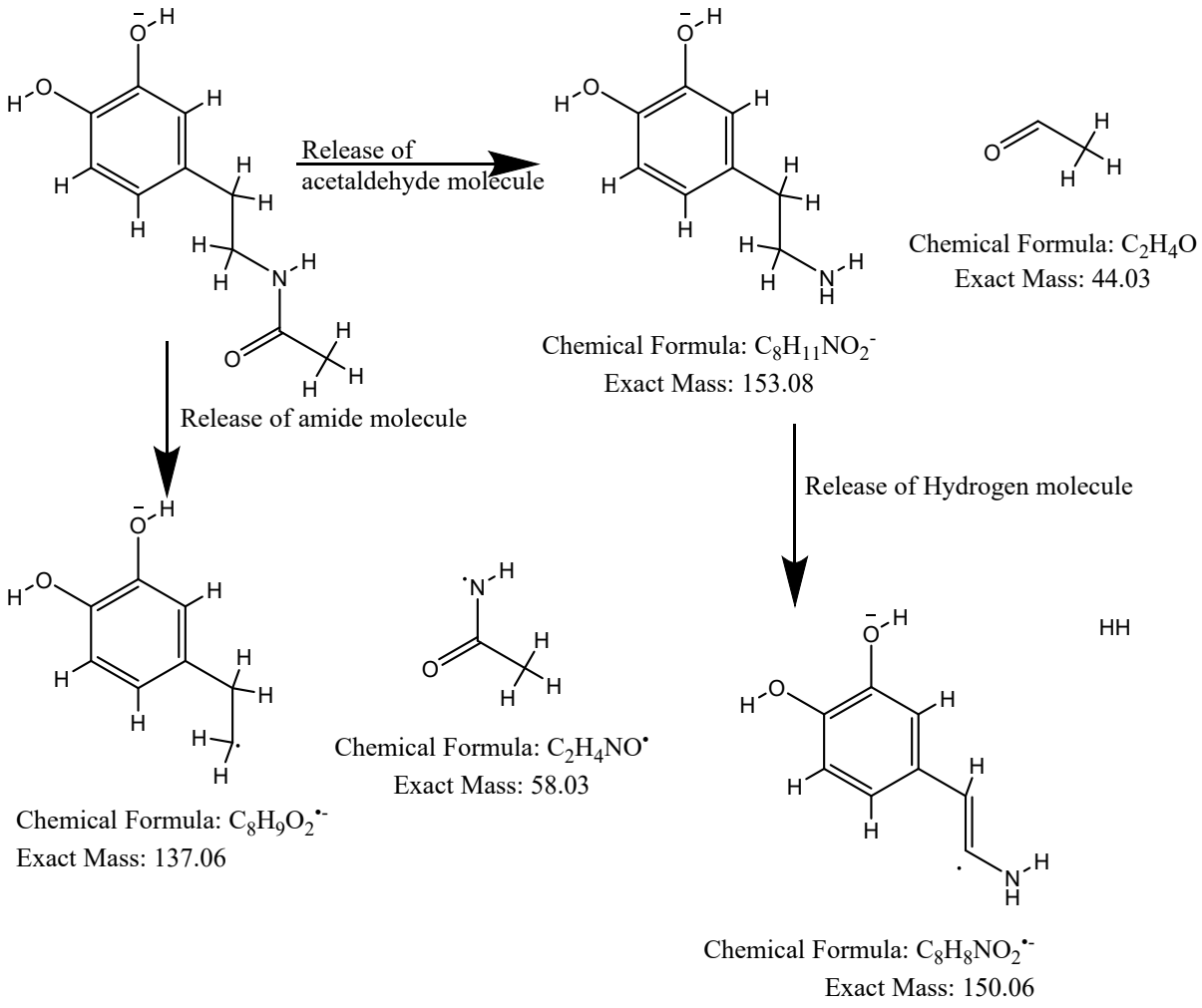


Figure 54SI: Fragmentation pathway of n-acetyldopamine

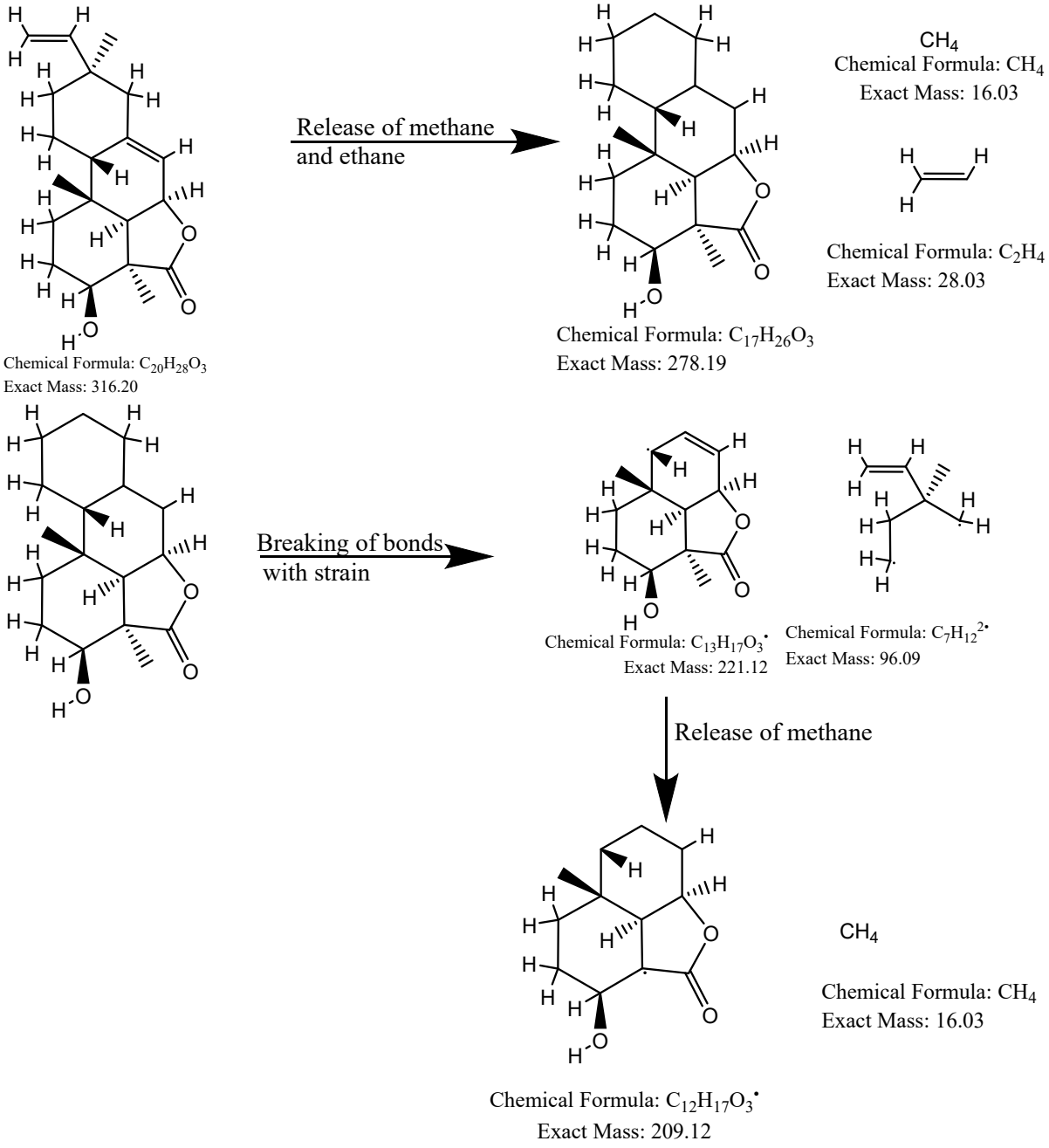


Figure 55SI: Fragmentation pathway of 3-beta-hydroxy-9-beta-primara-7,15-diene-19,6 beta-o-lide

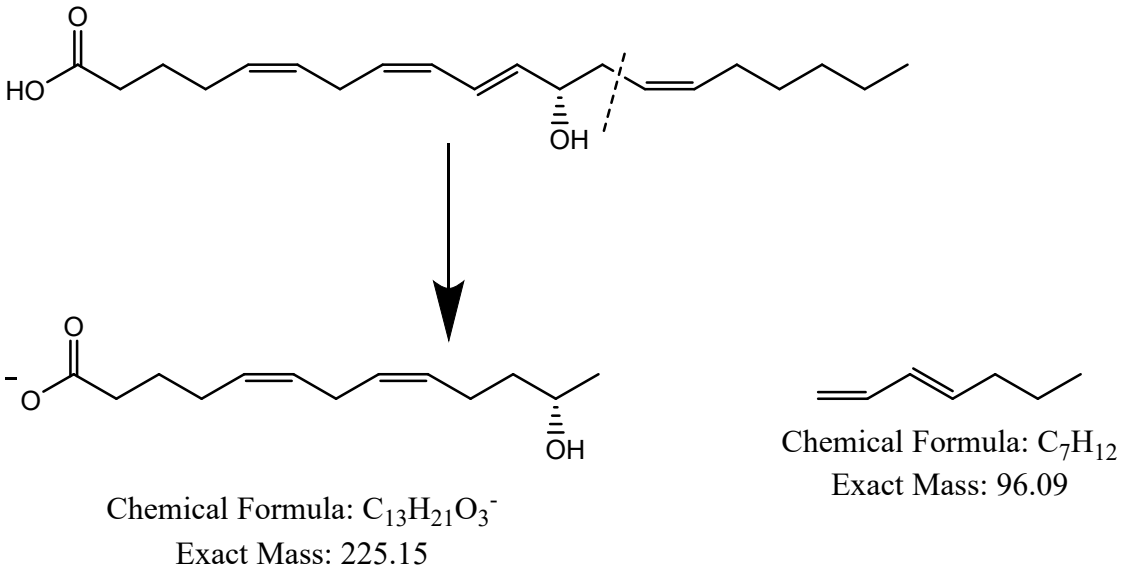


Figure 56SI: Fragmentationpattern of (±)12-Hydroxy-5,8,10,14-eicosatetraenoic acid

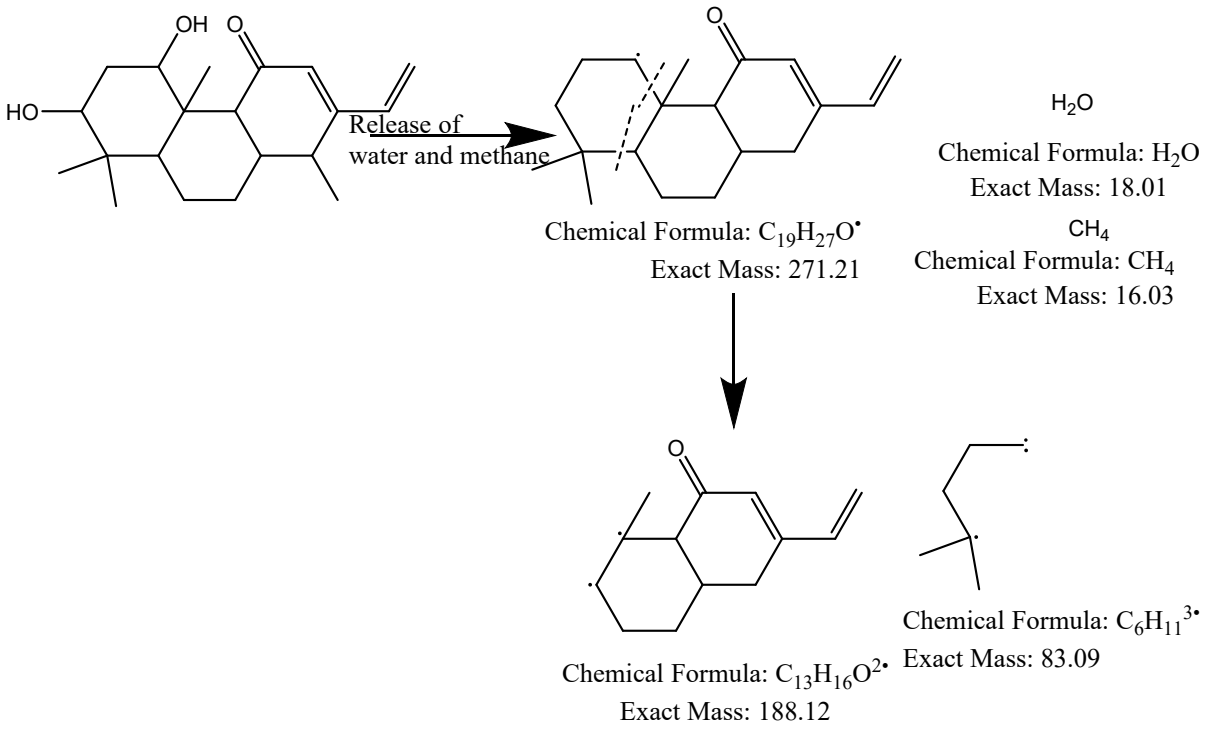
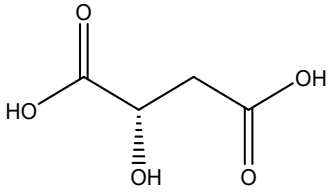
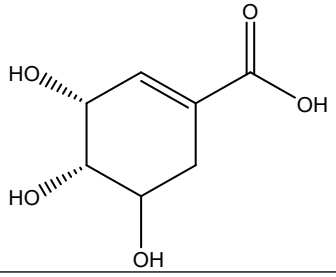
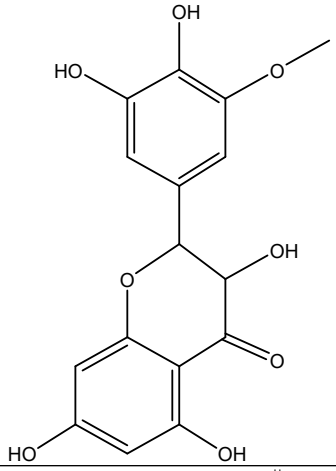
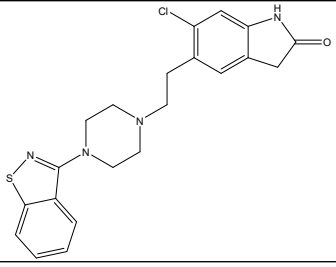


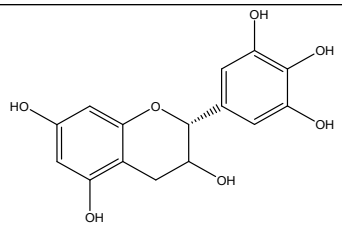
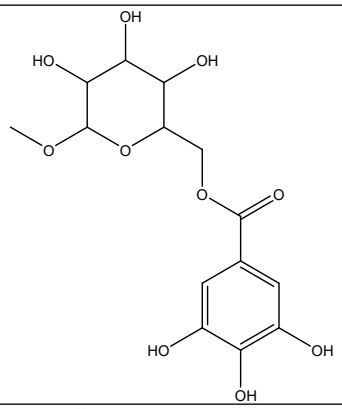
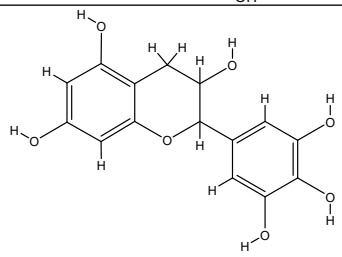
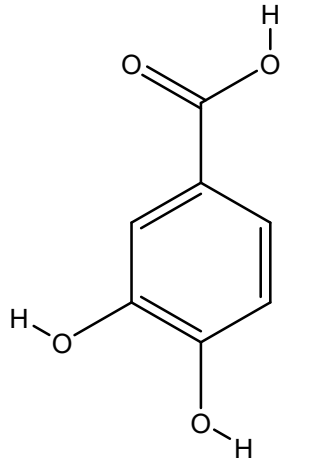
Figure 57SI: Fragmentation pathway of Phytocassane C

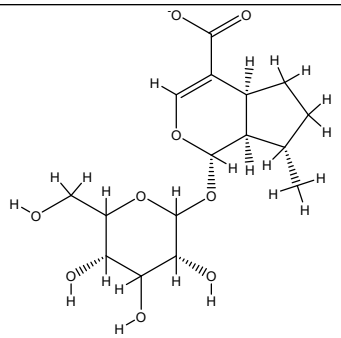
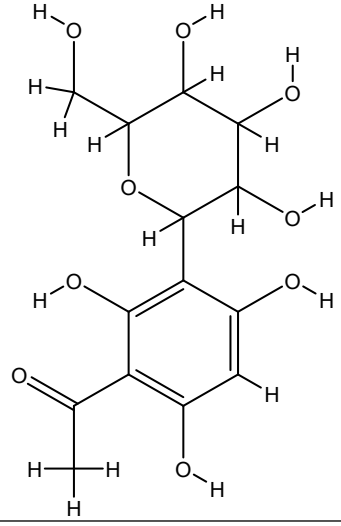
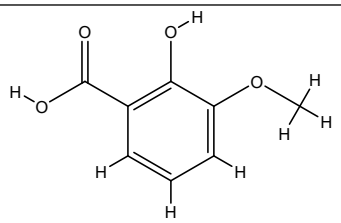
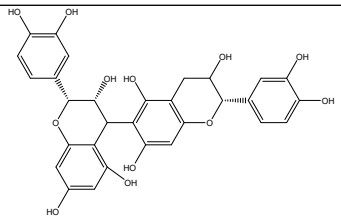
Table 1SI: *Cupressus torulosa* locations and their geographical coordinates

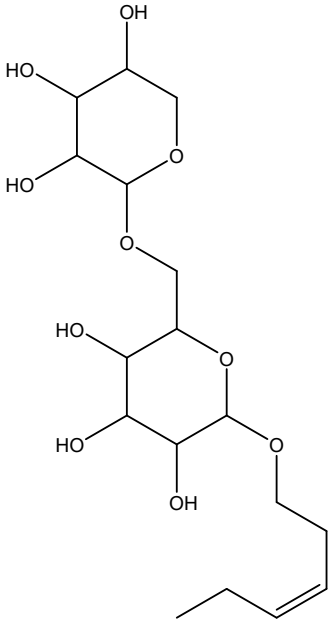
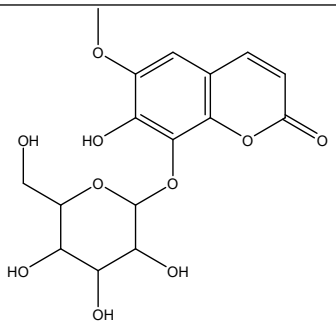
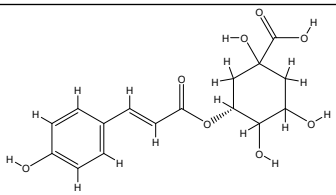
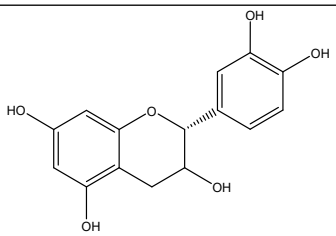
S.No	Location	Latitude	Longitude	Altitude (meter)
1	Suwakholi	78°10’21.06” E	30°26’43.58” N	2145
2	Tuneta	78°11’37.01” E	30°26’41.29” N	2350
3	Chakrata	77°51’51” E	30°44’20” N	2560
4	Shimla	77°18’56” E	31°11’53” N	2172
5	Chirbatya	78°50’18.32” E	30°22’40.12” N	2259
6	Gopeshwar	79°19’07.44” E	30°25’00.12” N	1648
7	Dungar	79°06’17.22” E	30°29’56.76” N	1502
8	Bhatwari	78°34’59” E	30°45’49” N	1418
9	Jhala	78°43’50” E	31°1’48” N	2487
10	FRI Dehradun	78°0’4.3” E	30°20’30.4” N	693
11	Shingali (nearOogla)	80°18’26.9” E	29°44’1.2” N	1561
12	Munsyari	80°13’50.9” E	30°3’48.3” N	2408 m
13	Kanda (Bageshwar)	79°53’2.2” E	29°49’43.1” N	1753 m
14	Vinayak (Nainarange) Nainital	79°24’51.9” E	29°27’18.9” N	2193 m

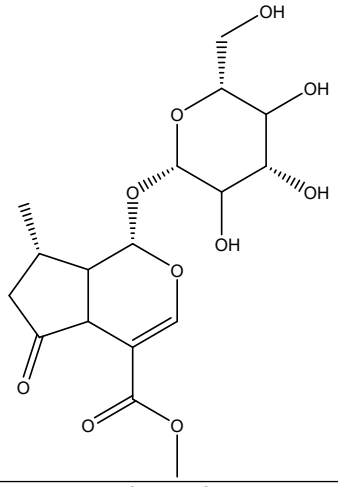
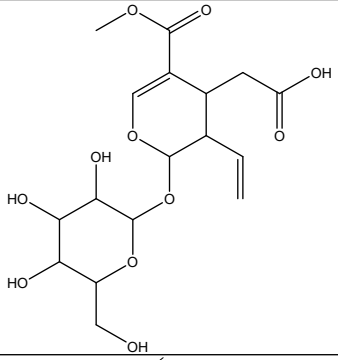
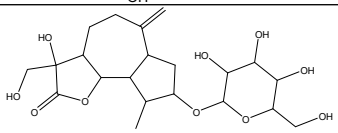
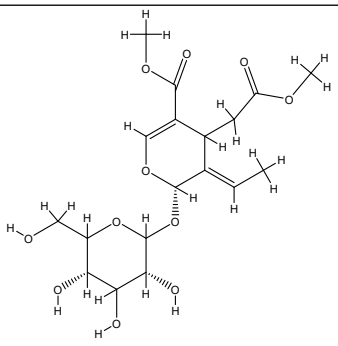
Table 2SI: Compounds identified in 25% aqueous methanol extracts of needles of *Cupressus torulosa* across 14 different geographical locations

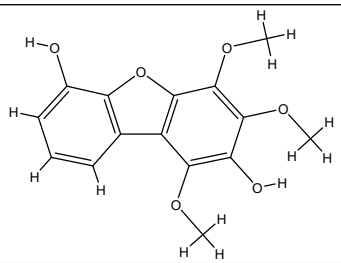
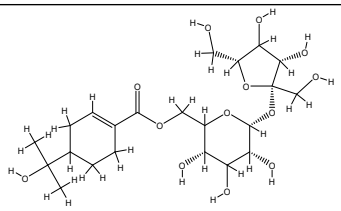
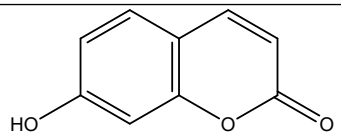
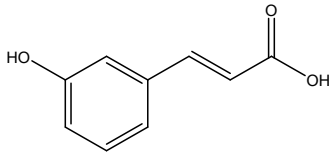
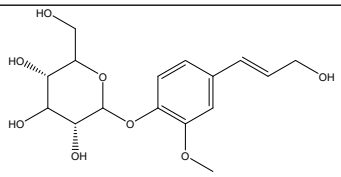
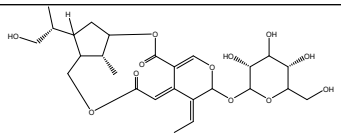
S. No	RT	Compound name	Molecular formula	$[M-H]^-$ m/z	Observed mass	Reference mass	Mass fragments	Identification score	Class of compound	Molecular Structure
1	0.802	Malic acid*	$C_4H_6O_5$	133.0142	134.0208	134.0209	115.0034, 89.0245, 71.0133	98.88	Dicarboxylic acid	
2	0.819	Shikimic acid*	$C_7H_{10}O_5$	173.0455	174.0519	174.0528	155.0353, 111.0443, 72.9934	94.57	Cyclohexanecarboxylic acid	
3	0.850	Hovenitin I	$C_{16}H_{14}O_8$	334.0689	334.0689	334.0685	217.0511, 173.0445, 159.0091, 71.0136	95.65	Flavanol (Catechin)	
4	2.873	Ziprasidone*	$C_{21}H_{21}ClN_4OS$	411.1063	412.1135	412.11245	411.1059, 208.9613, 162.9549	97.20	Heterocyclic compound	

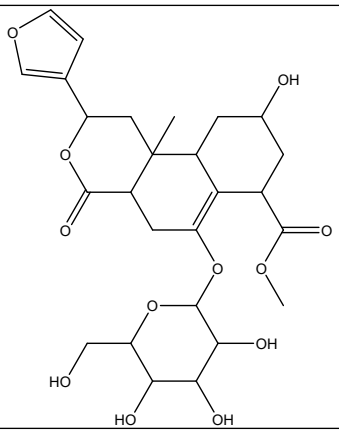
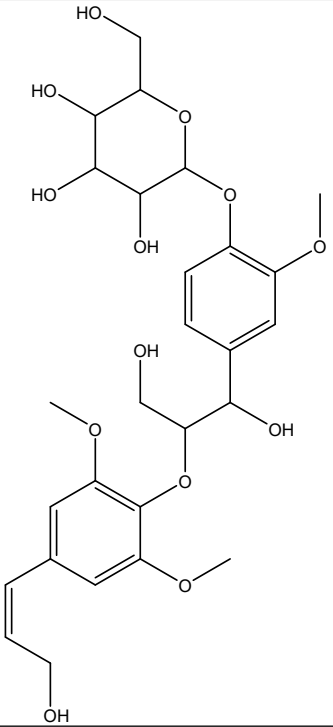
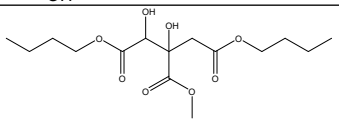
5	3.219	Gallocatechin	$C_{15}H_{14}O_7$	305.0666	306.0739	306.0739	125.0244, 179.0351, 261.0766, 305.0666, 83.0138, 167.0350, 219.0666	92.81	Flavanol	
6	3.274	Methyl 6-O-galloyl-beta-D-glucopyranoside	$C_{14}H_{18}O_{10}$	345.0825	346.0903	346.0899	59.0137, 345.0825, 285.8515	98.57	Phenolic Ester	
7	3.287	Epigallocatechin	$C_{15}H_{14}O_7$	305.0667	306.0720	306.0721	261.0754, 179.0341, 125.0256, 77.0375	95.63	Flavonoid (Catechin)	
8	3.803	3,4-Dihydroxybenzoic acid	$C_7H_6O_4$	153.0231	154.0257	154.0253	109.0294, 65.0035	95.66	Aromatic carboxylic acid	

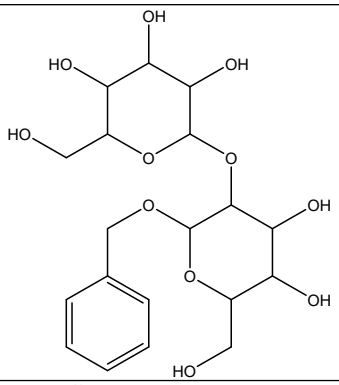
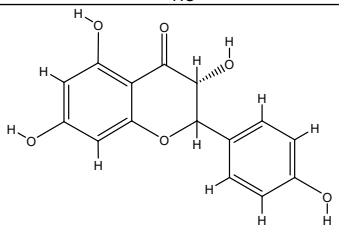
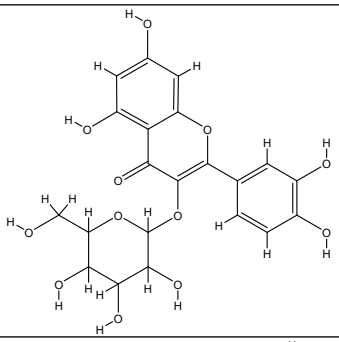
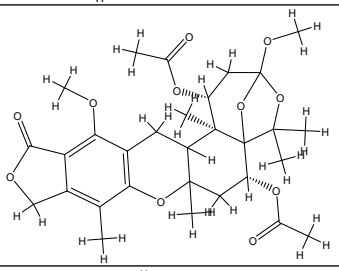
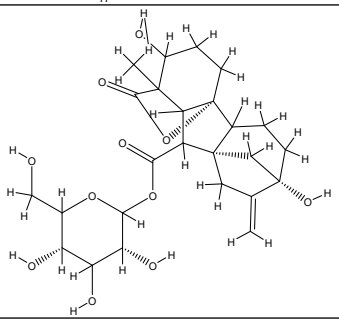
9	4.354	7-deoxyloganate	$C_{16}H_{24}O_9$	359.1345	360.1418	360.1420	89.0243, 179.0706 59.0139, 168.0530 359.1345	97.21	Terpene (Iridoid glycoside)	
10	4.827	3'-Glucosyl-2',4',6'-trihydroxyacetophenone	$C_{14}H_{18}O_9$	329.0876	330.0949	330.0950	328.9188, 198.9130, 59.0135	96.44	Phenolic glycoside	
11	4.941	3-Methoxysalicylic acid	$C_8H_8O_4$	167.0349	168.0421	168.0422	167.0349, 123.0448, 108.0211, 65.0220, 152.0118	95.45	Carboxylic acid	
12	5.312; 6.992	Procyanidin B5	$C_{30}H_{26}O_{12}$	577.1349	578.1422	578.1424	577.1349, 425.0879, 451.1041, 289.0717, 125.0246, 245.0816,	96.54	Flavonoid (Anthocyanidin)	

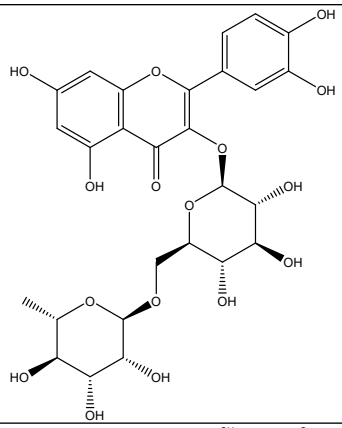
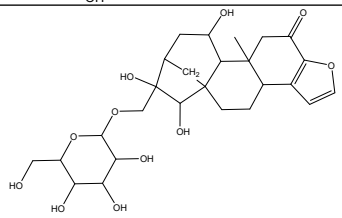
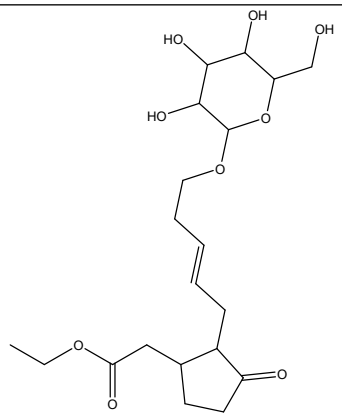
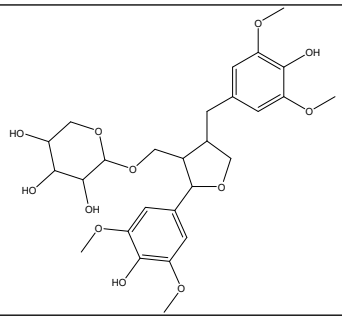
							83.0129			
13	5.549	cis-3-Hexenyl b-primeveroside	$C_{17}H_{30}O_{10}$	393.1765	394.1838	394.1838	393.1765, 161.0450, 163.8716, 101.0246, 119.0506, 59.0137	97.52	O-acyl carbohydrate	
14	6.068	Fraxin	$C_{16}H_{18}O_{10}$	369.0829	370.0901	370.0899	161.0245, 119.0536 369.0830, 133.0576	96.41	Coumarin glycoside	
15	6.211	p-Coumaroyl quinic acid*	$C_{16}H_{18}O_8$	337.0932	338.1004	338.1001	337.0932, 191.0562, 163.0402, 119.0459	95.65	Phenolic acid ester	
16	6.263	Catechin*	$C_{15}H_{14}O_6$	289.0718	290.0773	290.0790	245.0807, 203.0701, 179.0342, 109.0292, 57.0345	95.34	Flavonoid (Flavan-3-ol)	

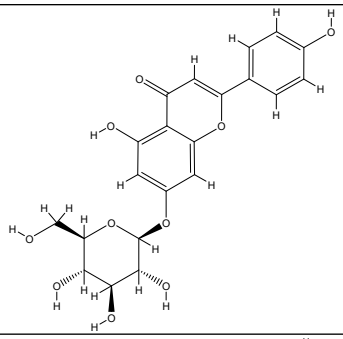
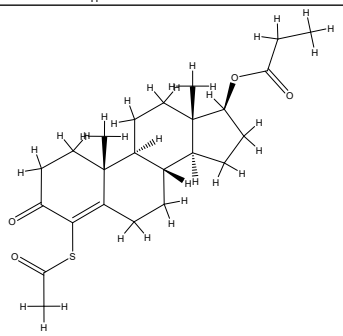
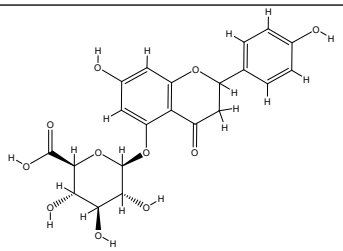
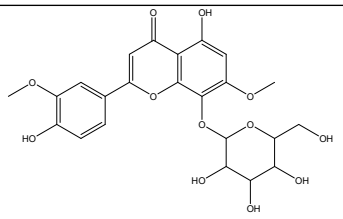
17	6.697	Verbenalin	$C_{17}H_{24}O_{10}$	387.1297	388.1370	388.1370	387.1297, 207.0673 181.0869, 123.0454 59.0135, 89.0241	94.63	Iridoid glycoside	
18	6.913	Secoxyloganin*	$C_{17}H_{24}O_{11}$	403.1226	404.1299	404.1318	357.1186, 179.0528, 149.0463	98.91	Terpene (Iridoid glycoside)	
19	7.124	Cynaroside A*	$C_{21}H_{32}O_{10}$	443.1920	444.1992	444.1995	443.1920, 237.0738 219.8699, 179.0561 131.0331, 89.0247 59.0134	93.42	Sesquiterpene glycoside	
20	7.428	Oleoside dimethyl ester	$C_{18}H_{26}O_{11}$	417.1400	418.1476	418.1475	417.1400, 297.0965 209.0820, 179.0351 161.0448,	95.62	Terpene glycoside	

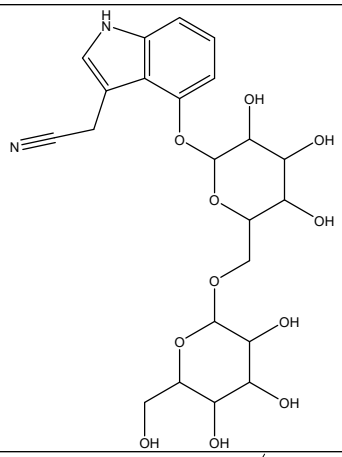
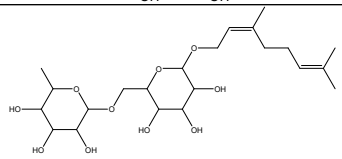
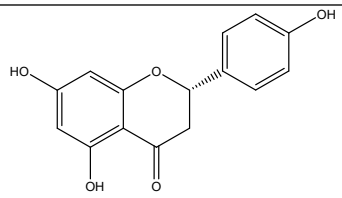
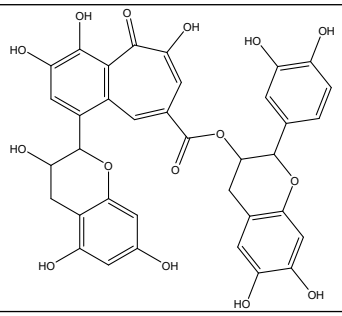
							89.0243			
21	8.217	6-Hydroxy-alpha-pyrufuran*	$C_{15}H_{14}O_6$	289.0717	290.0790	290.0790	289.0715, 201.0555 109.0296	94.71	Heterocyclic compound	
22	8.407	6-O-Oleuropeoylsucrose	$C_{22}H_{36}O_{13}$	507.2077	508.2154	508.2155	507.2076, 345.1357 209.9557, 256.0737 161.0460, 131.0359	97.82	Alicyclic disaccharide	
23	8.898	Umbelliferone	$C_9H_6O_3$	161.0244	162.0305	162.0304	133.0288, 77.0392	95.21	Coumarin	
24	8.932	m-Coumaric acid	$C_9H_8O_3$	163.0393	164.0465	164.04734	119.0494, 93.0335	96.11	Phenolic acid (Hydroxycinnamic acid)	
25	9.353	Coniferin*	$C_{16}H_{22}O_8$	341.1239	342.1313	342.1314	341.1239, 161.0602 59.0133, 73.0285	93.14	Phenolic acid glycoside	
26	9.568	Sambacin*	$C_{26}H_{36}O_{12}$	539.2137	540.2209	540.2206	539.2132 329.1390 195.0	92.10	Phenolic glycoside	

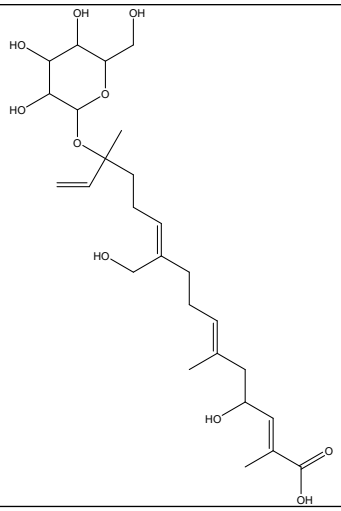
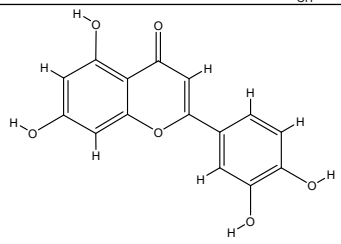
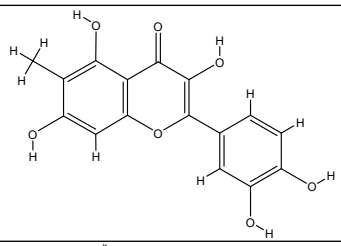
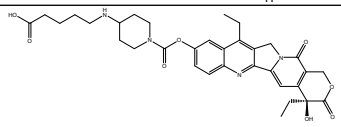
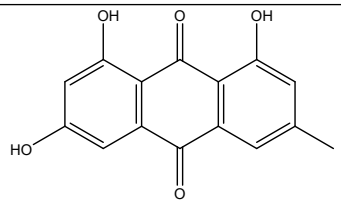
							662 59.01 37			
27	10. 121	Diosbul binosid e F	$C_{26}H_{34}O_{12}$	537. 1983	538.2 055	538.2 050	537.1 983, 491.1 924 315.1 239, 345.1 344 161.0 457	92.38	Terpen e glycosi de	
28	10. 231	Citrusin B	$C_{27}H_{36}O_{13}$	567. 2092	568.2 158	568.2 155	567.2 093, 429.4 083 211.0 626, 181.0 849 135.0 446, 165.0 571 89.02 62, 58.81 92	92.87	Phenol (Lignan glycosi de)	
29	10. 357	1,5- Dibutyl methyl hydrox ycitrate *	$C_{15}H_{26}O_8$	333. 1553	334.1 626	334.1 627	333.1 554, 234.8 990 175.1 022, 101.0 240 59.01 35	91.39	Aliphat ic ester	

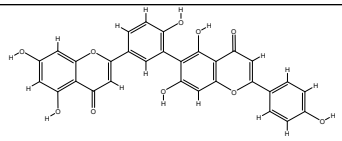
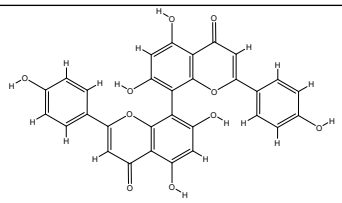
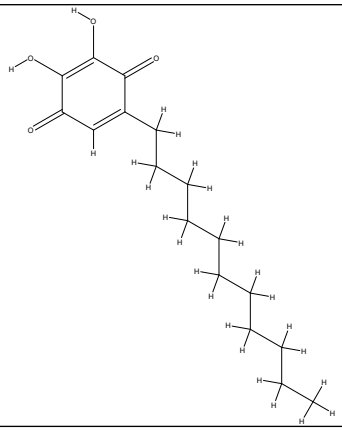
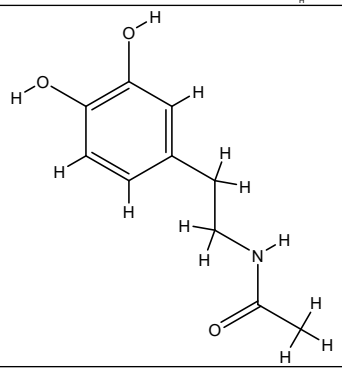
30	11.176	Zizybeoside I	$C_{19}H_{28}O_{11}$	431.1558	432.1631	432.1631	431.1558, 145.9314 89.0244, 59.0138	95.19	Phenolic glycoside	
31	11.615	Aromadendrin	$C_{15}H_{12}O_6$	287.0562	288.0635	288.2501	287.0562, 151.0029, 125.0245, 83.0138, 194.9717	98.78	Flavan-3-ol	
32	11.716	Hyperoside	$C_{21}H_{20}O_{12}$	463.0882	464.0955	464.4123	463.0888, 465.097, 271.0256	96.19	Flavonol glycoside	
33	11.775	Austalide C	$C_{30}H_{38}O_{11}$	573.2341	574.2414	574.2414	463.0888, 465.0972 271.0256	97.18	Heterocyclic compound	
34	12.337	Gibberellin A1 glucosyl ester*	$C_{25}H_{34}O_{11}$	509.2034	510.2106	510.2101	509.2031, 179.0715, 59.0137, 89.0244	94.18	Diterpene glycoside	

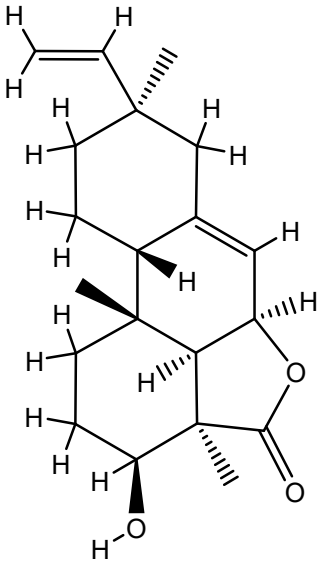
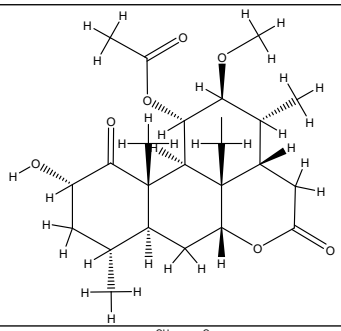
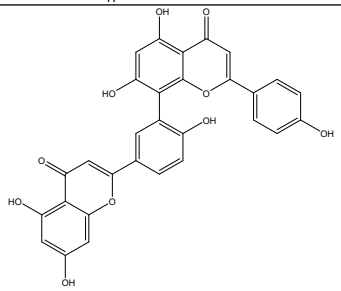
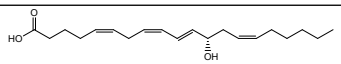
35	12.457	Rutin*	$C_{27}H_{30}O_{16}$	609.1431	610.1504	610.1533	343.0045, 300.0262, 271.0238, 178.9976	95.16	Flavonoid (Flavonol)	
36	12.594	Mascaroside*	$C_{26}H_{36}O_{11}$	523.2242	524.2262	524.2257	475.1940, 327.1593, 165.0560, 133.0271	98.45	Heterocyclic compound	
37	12.742	Ethyl 7-epi-12-hydroxyjasmonate glucoside	$C_{20}H_{32}O_9$	415.1975	416.2048	416.2046	415.1975, 369.1942, 235.7253, 209.0821, 161.0457, 179.0561, 89.0241, 59.0136	96.71	Carboxylic acid glycoside	
38	13.451	Prupaside*	$C_{27}H_{36}O_{12}$	551.2142	552.2213	552.2206	551.2141, 375.9805 165.0566, 101.0238	92.10	Lignan glycoside	

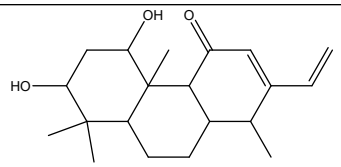
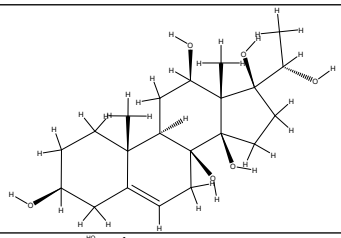
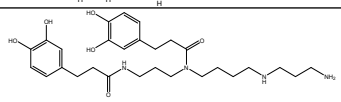
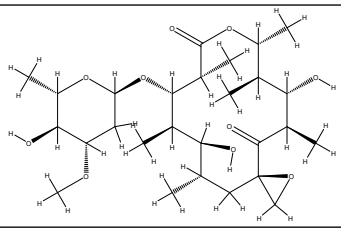
39	13.555	Apigenin 7-glucoside	$C_{21}H_{20}O_{10}$	431.1029	432.1029	432.1028	268.0363, 240.0409, 177.9781, 121.0293	92.19	Flavanone glucoside	
40	13.685	17beta-Hydroxy-4-mercaptoandrost-4-en-3- one 4-acetate 17-propionate	$C_{24}H_{34}O_4S$	417.2106	418.2181	418.2171	371.2065, 230.2044, 209.1532, 161.0444, 101.0245	96.10	Steroid ester	
41	14.174	Naringenin 5-O-glucuronide	$C_{21}H_{20}O_{11}$	447.0933	448.1005	448.1005	447.0931, 255.0297 151.0041, 59.0139 89.0241	95.19	Flavanone glucoside	
42	14.284	3',7-Dimethoxy-4',5,**8**-trihydroxyflavone 8-glucoside	$C_{23}H_{24}O_{12}$	491.1192	492.1264	492.1267	491.1192, 313.0344 285.0401	92.18	Flavone glycoside	

43	15.196	Cappariloside B	$C_{22}H_{28}N_2O_{11}$	495.1638	496.1692	496.1693	495.1627, 89.0246 101.0243, 71.0142	98.17	Heterocyclic compound	
44	16.458	Nerylrhamnosyl-glucoside	$C_{22}H_{38}O_{10}$	461.2394	462.2466	462.2464	461.2394, 59.0137 101.0244, 71.0138 161.0454	97.68	Terpene glycoside	
45	16.459	Naringenin*	$C_{15}H_{12}O_5$	271.0612	272.0668	272.0684	243.9003, 151.0035, 94.9251, 65.0032	95.16	Flavonoid	
46	16.842	Theaflavate B*	$C_{36}H_{28}O_{15}$	699.1357	700.1429	700.1428	537.0806, 375.0491, 257.0093, 137.0236	94.13	Flavonoid (Flavan-3-ol)	

47	16.851	Capsianoside V	$C_{26}H_{42}O_{10}$	513.2701	514.2773	514.2777	513.2700, 469.2483 179.0583, 161.0445 59.0140, 71.0133	97.28	Terpene glycoside	
48	17.581	Luteolin	$C_{15}H_{10}O_6$	285.0405	286.0461	286.0462	257.0436, 249.0184, 199.0381, 151.0023, 133.0281, 107.0129	98.14	Flavanoid (Flavone)	
49	17.983	Pinoquercetin	$C_{16}H_{12}O_7$	315.0497	316.0570	316.0571	300.0260, 272.0319, 148.0147	92.38	Flavanoid (Flavone)	
50	18.970	APC	$C_{33}H_{38}N_4O_8$	617.2614	618.2686 1	618.2689	617.2614, 587.2532	94.52	Heterocyclic compound	
51	18.973	Emodin	$C_{15}H_{10}O_5$	269.0455	270.0511	270.0528	225.0537, 149.0239, 117.0342, 65.0027	96.67	Anthraquinone	

52	19.934	Robustaflavone*	$C_{30}H_{18}O_{10}$	537.0833	538.0905	538.5	444.0530, 375.051, 331.0613, 117.0345	95.18	Biflavonoid	
53	20.084	Cupressuflavone*	$C_{30}H_{18}O_{10}$	537.0836	538.0908	538.0913	537.0825, 443.0407, 417.0314, 375.0512, 151.0034	97.18	Biflavonoid	
54	21.369	Myrsinone*	$C_{17}H_{26}O_4$	293.1759	294.1832	294.1831	236.1049, 221.1540, 177.0930, 148.0535, 96.9584	95.09	Quinone	
55	21.580	n-acetyldopamine*	$C_{10}H_{13}NO_3$	194.0822	195.0894	195.0895	194.0825, 150.9773 153.1286, 58.6112	94.16	Carboxamide	

56	21.702	3-beta-hydroxy-9-beta-primara-7,15-diene-19,6 beta-o-lide*	$C_{20}H_{28}O_3$	315.0214	316.4011	316.4012	278.0210 209.1129 117.0987	93.98	Terpene (Diterpenoid)	
57	21.973	Picrasin C	$C_{23}H_{34}O_7$	421.2245	422.2316	422.232	315.2047, 227.1292, 129.0199, 80.9646	97.45	Terpene (Iridoid)	
58	22.045	Amentoflavone	$C_{30}H_{18}O_{10}$	537.0828	538.0905	538.0899	537.0833, 443.0406 375.0512, 417.0615 117.0346	96.39	Biflavonoid	
59	23.073	(±)12-Hydroxy-5,8,10,14-eicosatetraenoic acid (HETE)*	$C_{20}H_{32}O_3$	319.2281	320.2354	320.2351	319.2279, 225.2876 96.9603	96.28	Eicosanoid	

60	24.171	Phytocassane C*	$C_{20}H_{30}O_3$	317.2124	318.2197	318.2194	317.2122, 271.2062, 83.0501	97.17	Terpene (Diterpenoid)	
61	25.078	Sarcostin	$C_{21}H_{34}O_6$	381.2296	382.2369	382.235	313.2144, 146.8670, 96.9595	93.19	Steroid (Corticosteroid)	
62	27.034	Kukoamine D	$C_{28}H_{42}N_4O_6$	529.3026	530.3097	530.3091	264.7739, 198.0158, 96.9593	92.20	Phenol (Catechol)	
63	27.601	L-Oleandrosyl-oleandolide	$C_{27}H_{46}O_{10}$	529.3026	530.3095	530.3092	471.2638, 195.747, 96.9595	91.05	Macrolide	

***Marker compound**