Multi-detector Characterization of Grape Seed Extract to Enable *In Silico* Safety Assessment

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Figure S1. The stacked negative mode UHPLC-HRMS chromatograms of the GSE-1 extract, the extracted authentic grape seed (*Vitis vinifera)* material, the extracted authentic peanut skin (*Arachis* sp.) material (green trace), and the extracted authentic pine skin (*Piunus pinaster*) material (blue trace). The GSE-1 and authentic grape seed extracts were in agreement. There were no indications of adulteration in the GSE-1 extract when compared to the peanut skin and pine bark traces.

Figure S2. The stacked UHPLC-UV chromatograms of the GSE-1 extract, the extracted authentic grape seed (*Vitis vinifera)* material, the extracted authentic peanut skin (*Arachis* sp.) material (green trace), and the extracted authentic pine skin (*Piunus pinaster*) material (blue trace). The GSE-1 and authentic grape seed extracts were in agreement. There were no indications of adulteration in the GSE-1 extract when compared to the peanut skin and pine bark traces.

Figure S3. The narrow mass chromatograms for *m/z* 575.1189 (±5ppm) for GSE-1, authentic GSE, authentic peanut skins extract, authentic pine bark extract, and standards of proanthocyanidin A1 and A2 showed that GSE-1 and the authentic grape seed extract did not contain the key indicators of peanut skin and/or pine bark adulteration (proanthocyanidin A-type compounds).

Figure S4. (A) Overlay of the GSE-1 (black) and authentic GSE (red) CAD chromatograms from 18-30 minutes, highlighting an outlier in the GSE-1 sample. All other CAD peaks from the GSE-1 are accounted for in the authentic GSE. (B) The negative mode MS/MS spectrum at 23.3 min for the outlier in GSE-1 matched the MS/MS pattern for (C) 1-(3',4'-dihydroxyphenyl)-3-(2",4",6"-trihydroxyophenyl)propan-2-ol in literature.

Figure S5. A comparison of (A) the proposed structure for a degraded proanthocyanidin dimer based on MS/MS interpretation and (B) an isomer from literature with its reported MS/MS interpretation. Compared to Proanthocyanidin B1, the propose structure was missing a bond in the B'-ring, while the reported isomer was missing the bond in the B-ring. (C) The MS/MS spectrum of the proposed structure displayed similar types of fragmentation to the isomer in literature, but the differences in structure resulted in different observed masses. NOTE: RDA indicates where the fragment was generated via Retro Diels-Alder.

Figure S6. The CAD chromatogram of GSE-1 with each CAD peak labeled. The chromatogram was divided into three sections (0-17, 17-46, and 46-75 min) for clarity. The 39th peak is the broad peak ranging from about 18-50 min. The small peaks that are not labeled were below the threshold of toxicological concern.

Figure S7. Overlaid UHPLC-CAD chromatograms of the GSE-1 (black trace), GSE-1 treated with poly(vinylpolypyrrolidone) (PVPP) (green trace), GSE-1 filtered through a molecular weight cut-off

(MWCO) filter at 3000 Da (red trace), and the diluent blank (blue trace) showed the removal of the large chromatographic hump and supported its identity as tannins.

Figure S8. The overlaid chromatograms of GSE-1 filtered through a molecular weight cut-off (MWCO) filters at 3,000 Da (black traces), 10,000 Da (red traces), 30,000 Da (green traces), 50,000 Da (blue traces), and 100,000 Da (yellow traces). The top chromatograms represent the filtrate (passed through filter) and the bottom chromatograms represent the retentate (didn't pass through filter).

Figure S9. The retentate from the GSE after passing through a 30,000 MWCO filter was subjected to ESI-QTOF. With a collision energy (CE) of 10V, signals indicating high molecular weight tannin species was detected (top). As the CE was increased, fragments relating to sugars (*m/z* 162), catechin (*m/z* 288), and catechin-polymers (*m/z* 576, 864, etc.) were detected, further supporting the evidence for tannins.

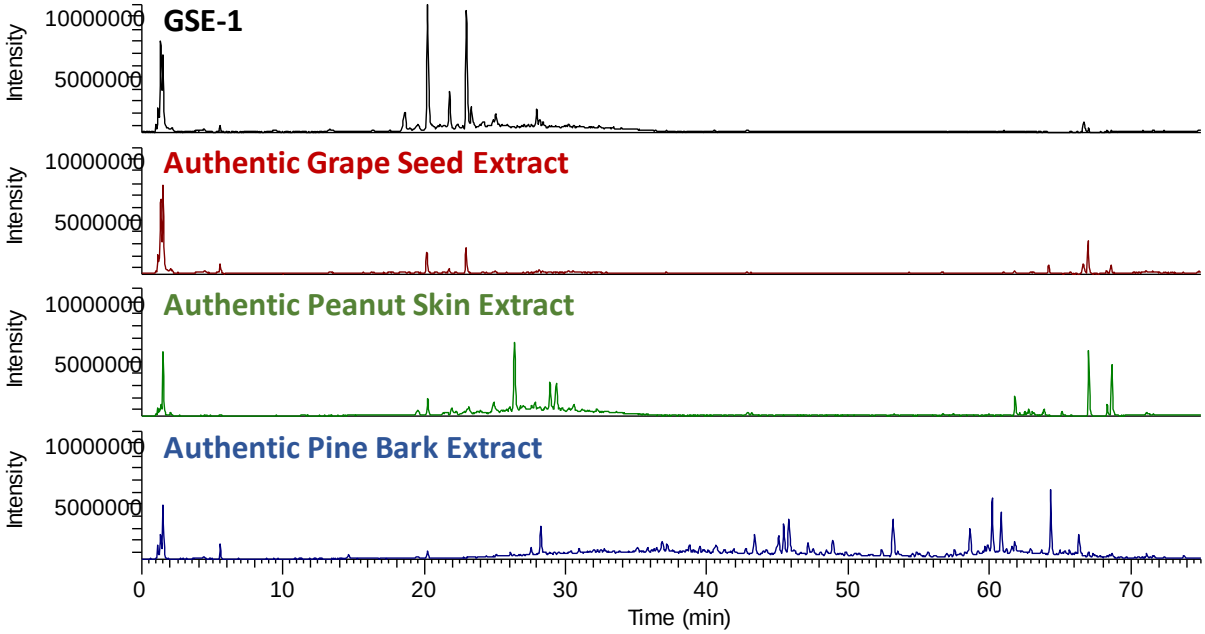
Figure S10. The calibration curves generated by area under the curve (AUC) from the CAD chromatograms for the four standards (top) compared to the isolated tannins (bottom). To the right of each are the averages all the calculated response factors (AUC/concentration) and their respective standard deviations.

Figure S11. (A) The CAD and (B) UV (280 nm) chromatographic profiles for the authenticated GSE voucher and the various extracts from different suppliers.

Table S1. Proposed identifications of components producing CAD peaks in the UHPLC-UV-CAD-HRMS/MS analysis of grape seed (*Vitis vinifera*) extract for GSE-1.

Table S2. Proposed identifications of components producing FID peaks in the GC-FID and GC-HRMS analysis of grape seed (*Vitis vinifera*) extract for GSE-1.

Supplemental Information



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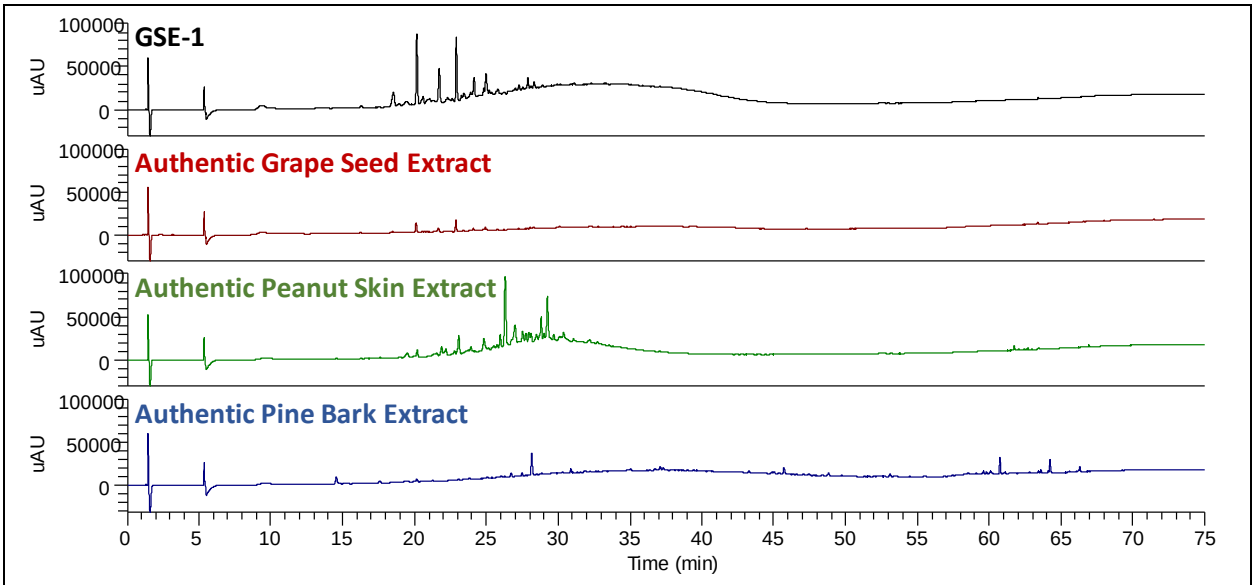

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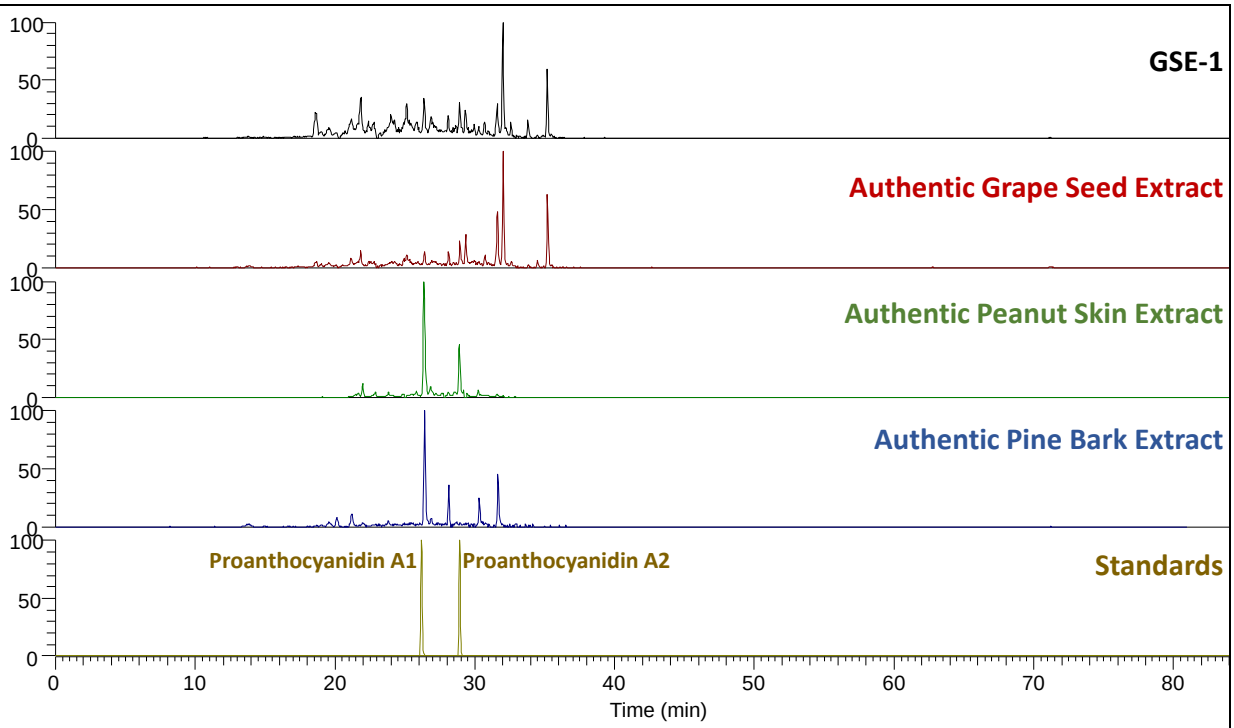

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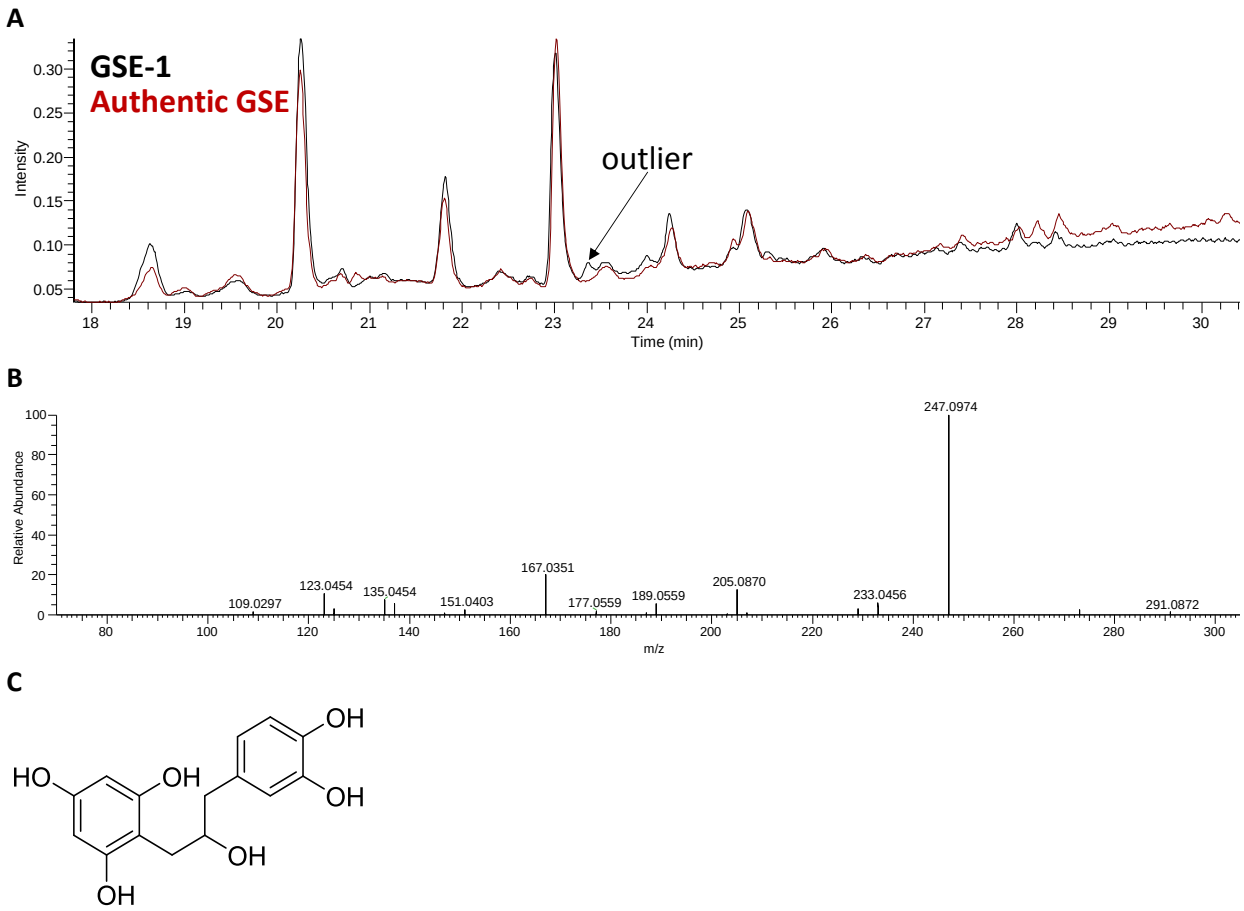

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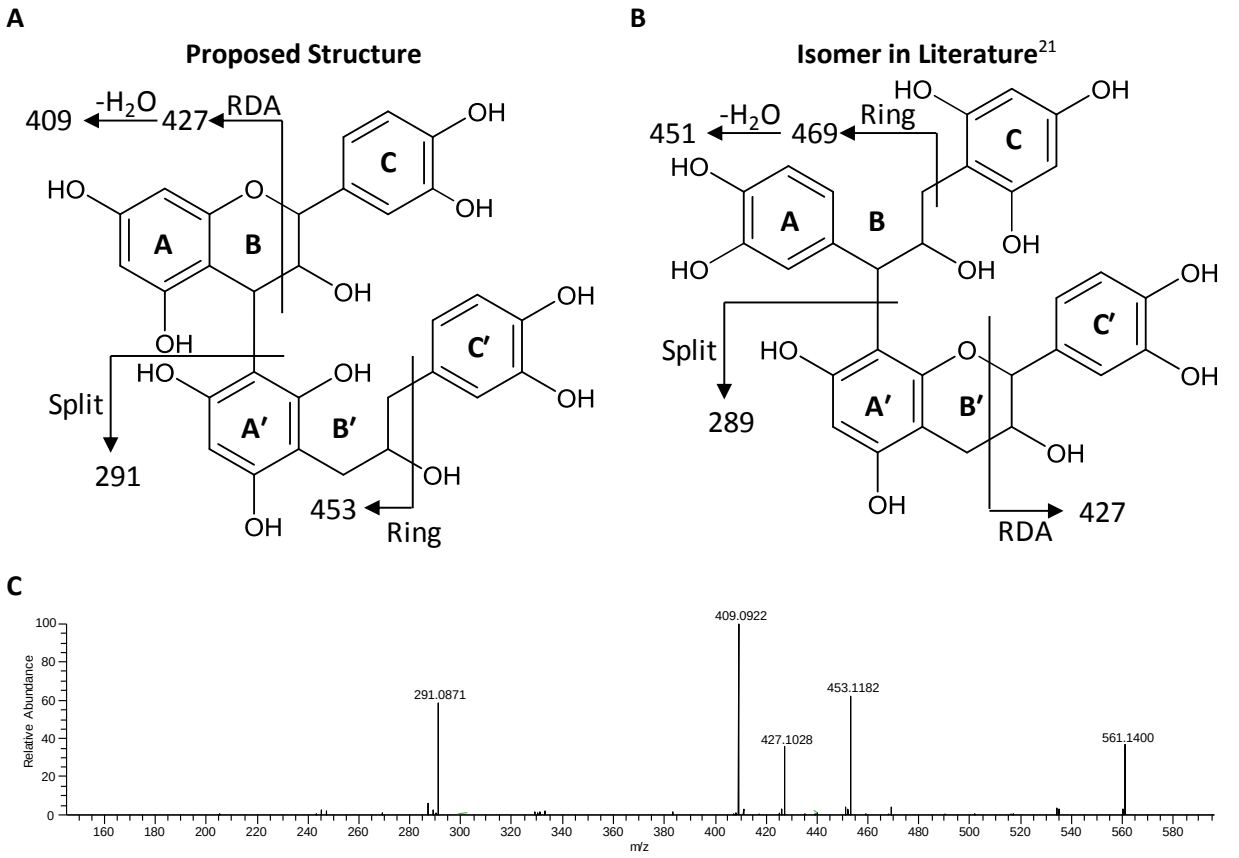

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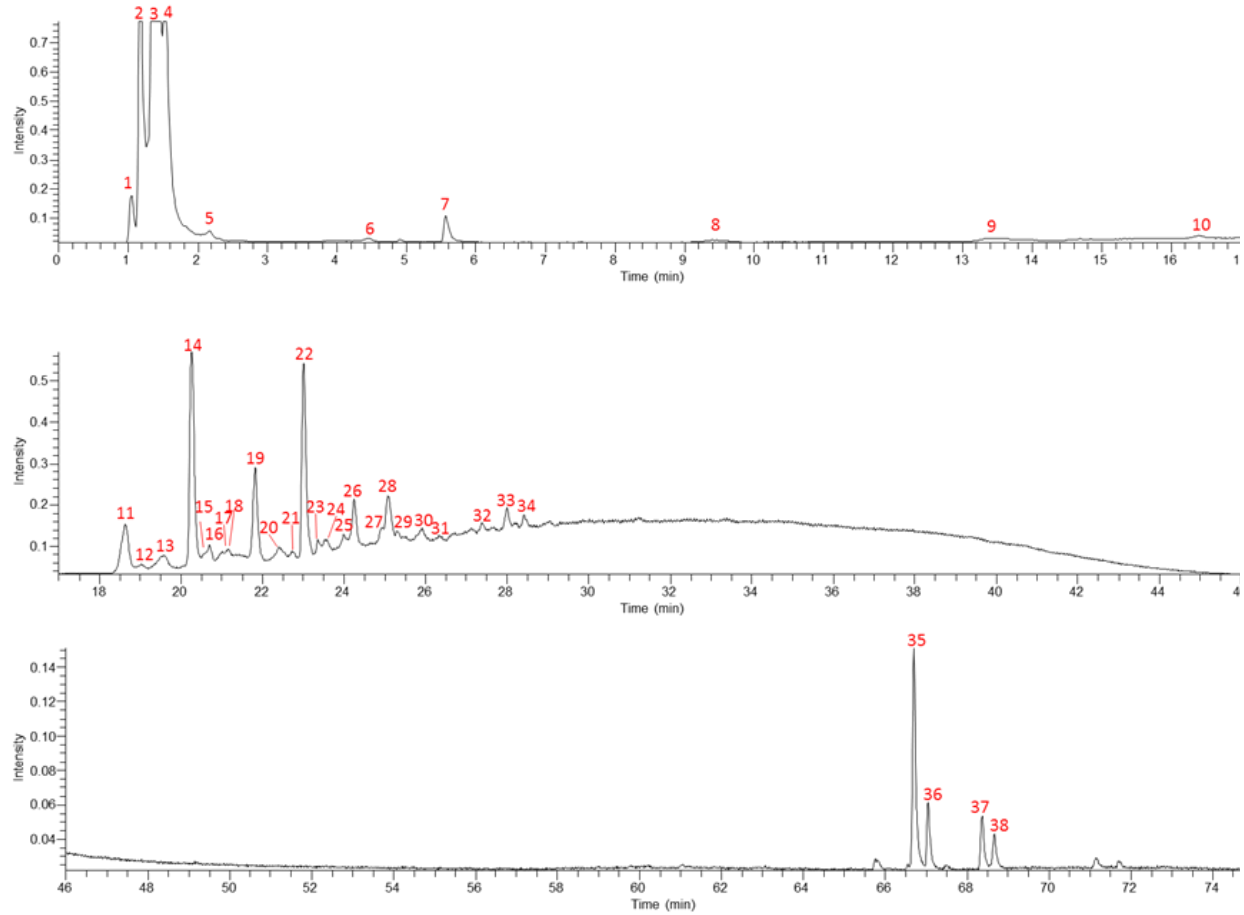

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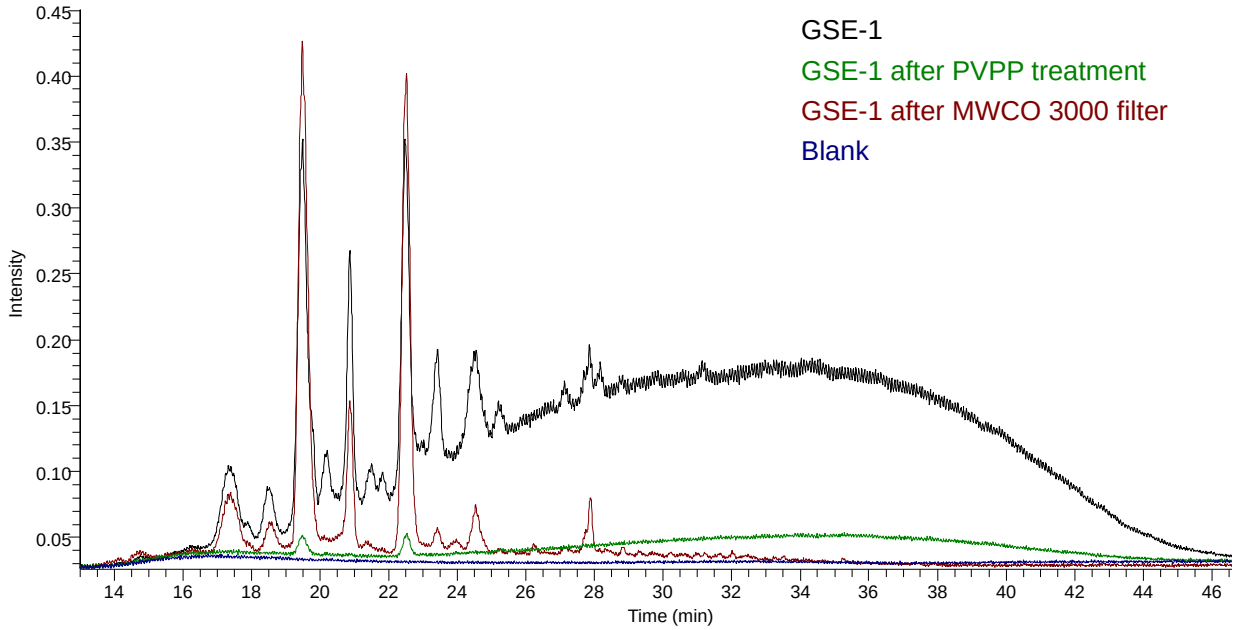

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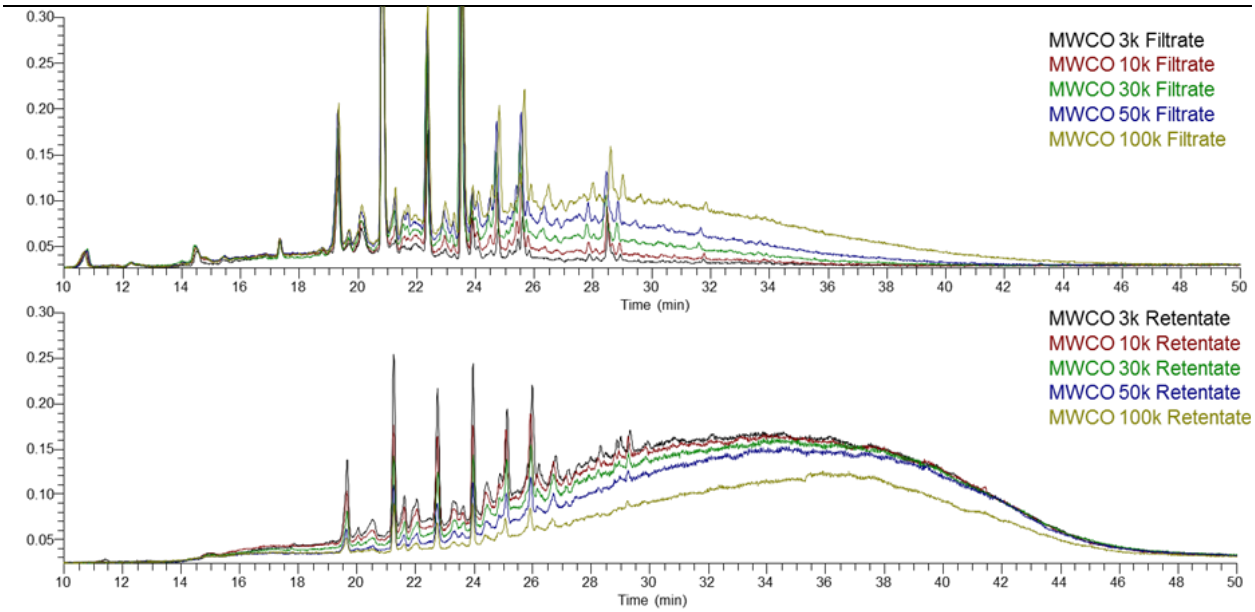

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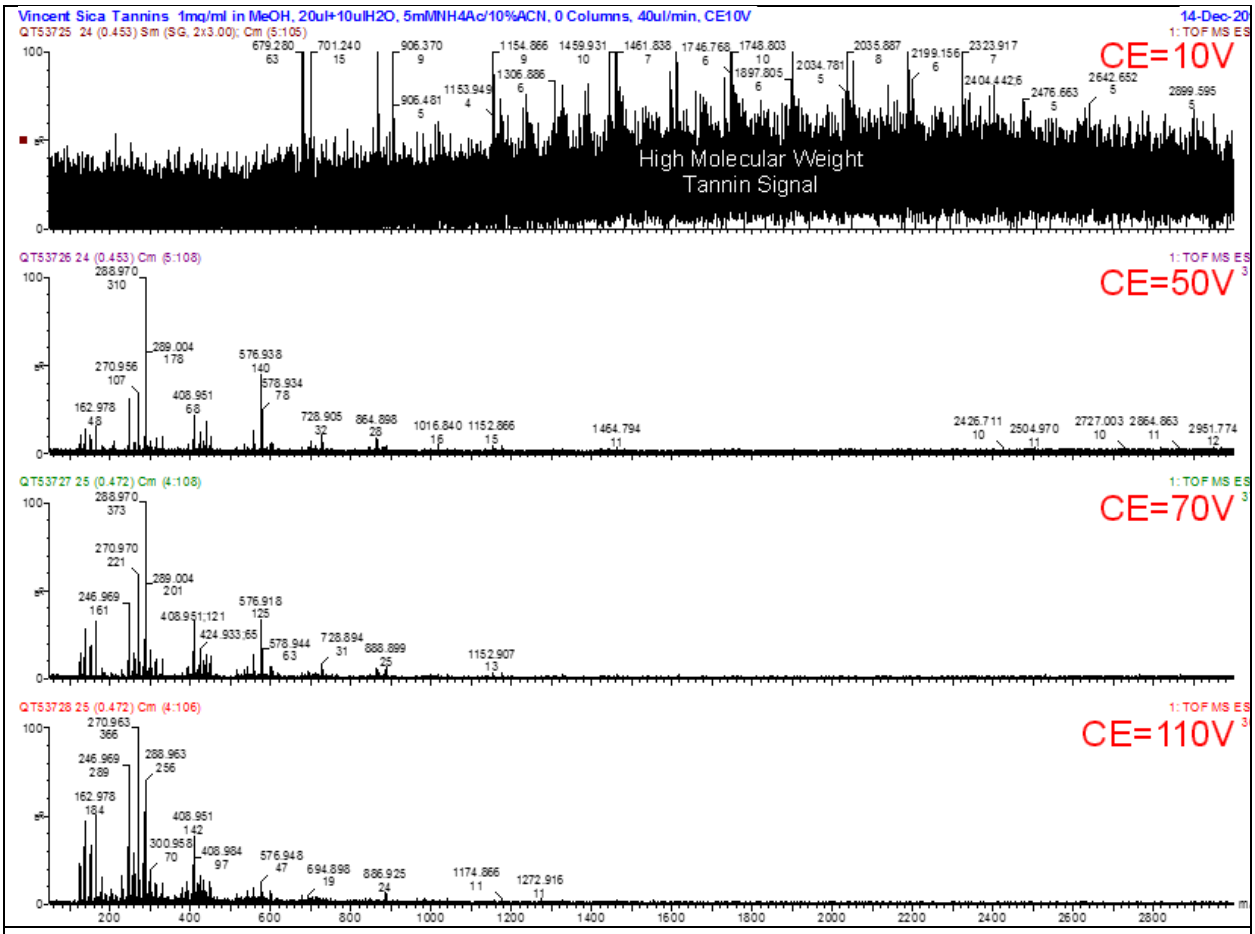

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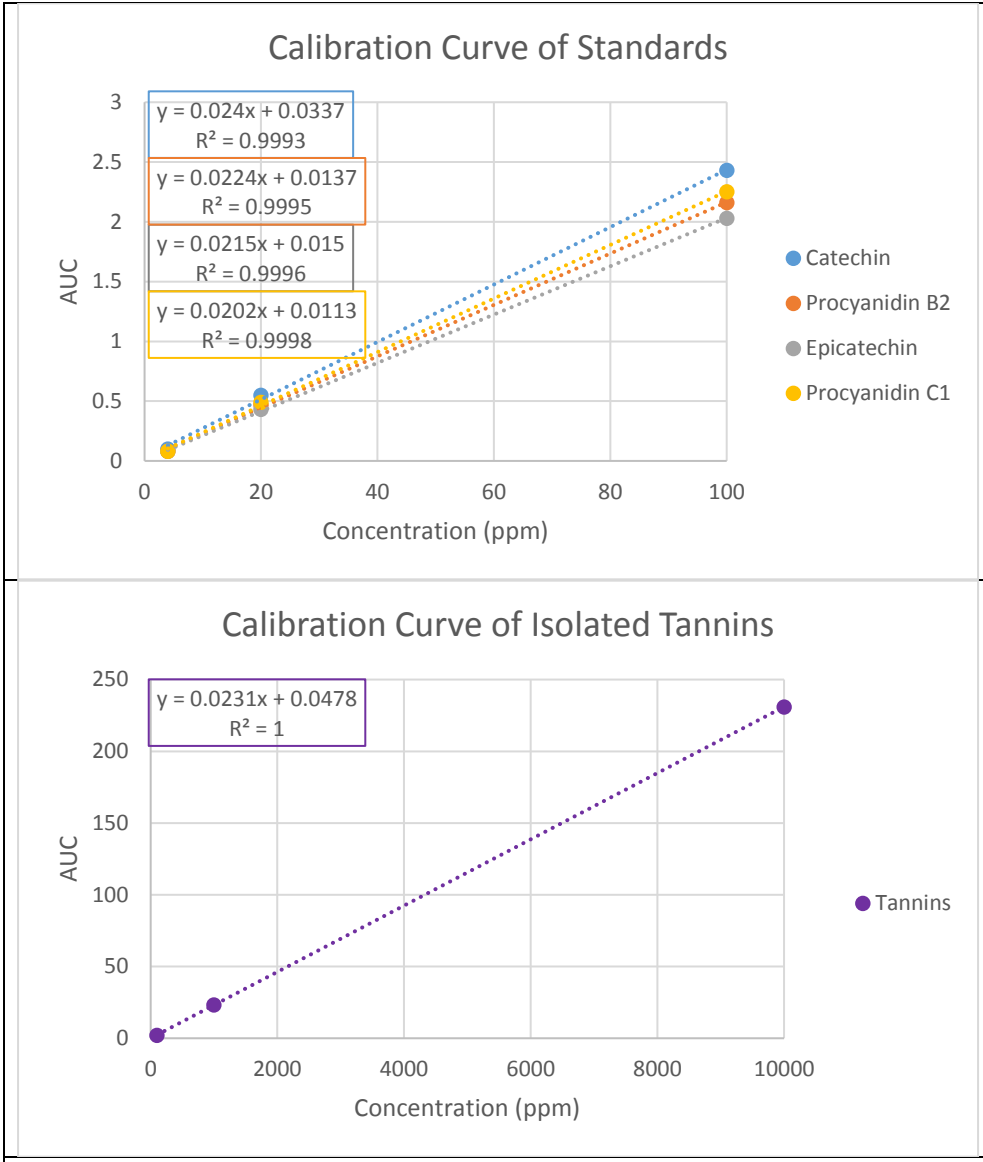


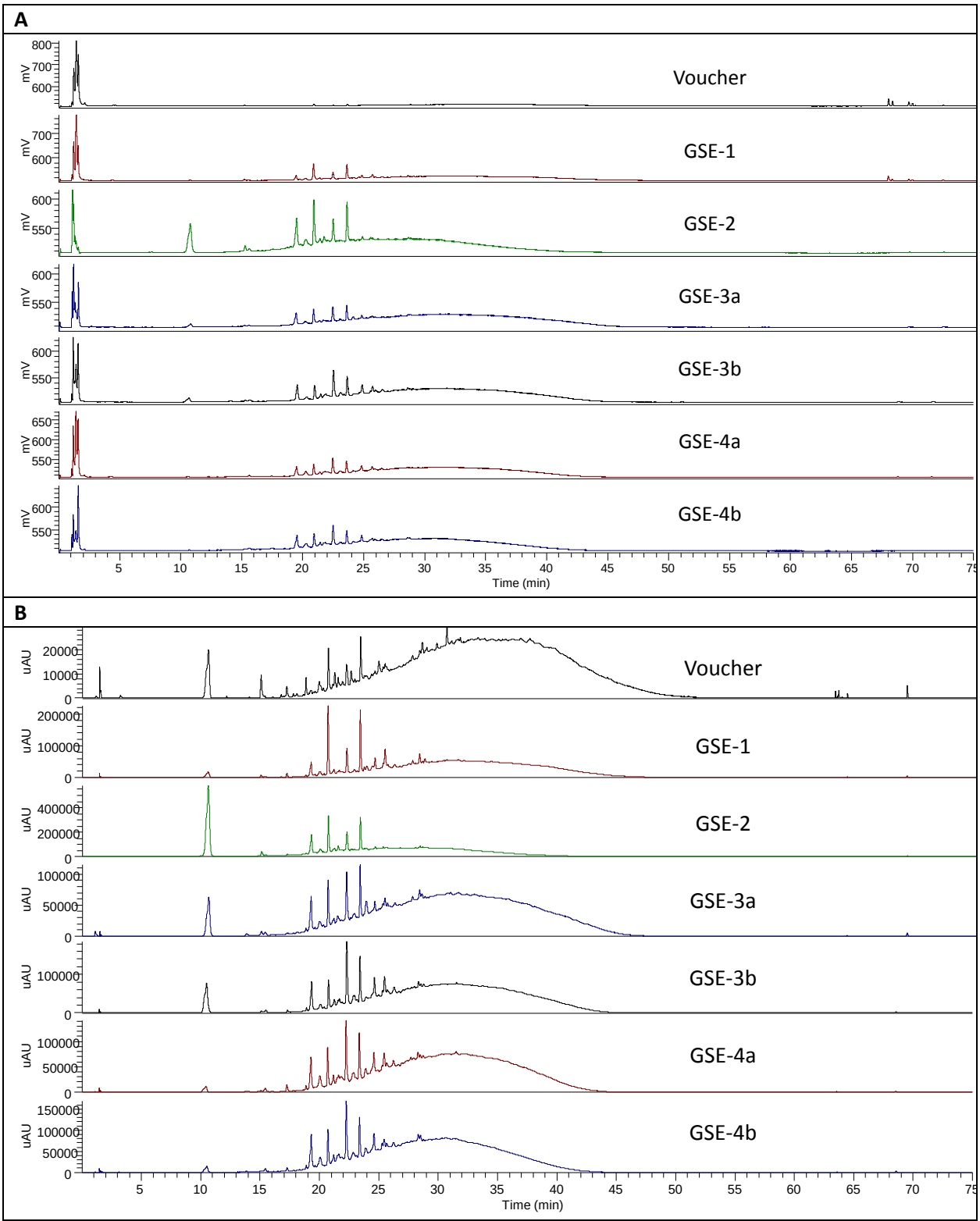
Average Response Factor (RF): 0.0226

Standard Deviation of Response Factor: 0.002

Average Response Factor: 0.0227

Standard Deviation of Response Factor: 0.001

Figure S10. The calibration curves generated by area under the curve (AUC) from the CAD chromatograms for the four standards (top) compared to the isolated tannins (bottom). To the right of each are the averages all the calculated response factors (AUC/concentration) and their respective standard deviations.



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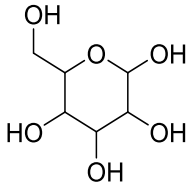
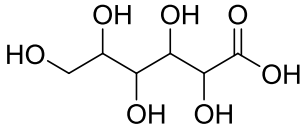
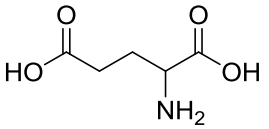
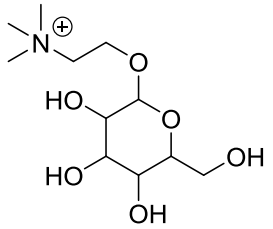
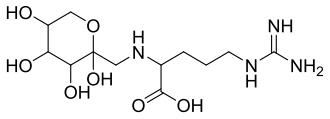
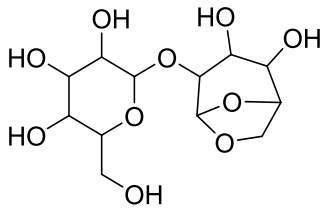
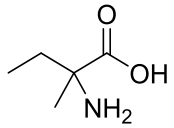
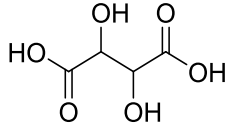
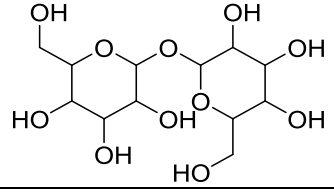
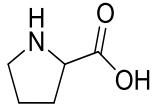
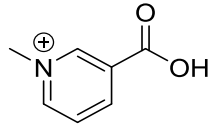
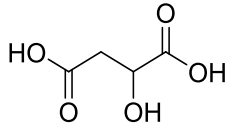
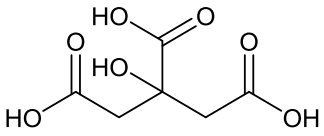
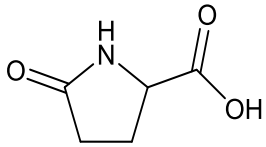
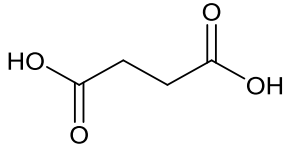
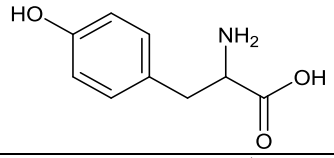
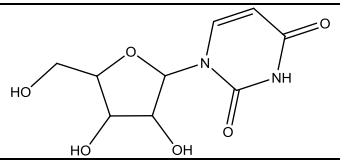
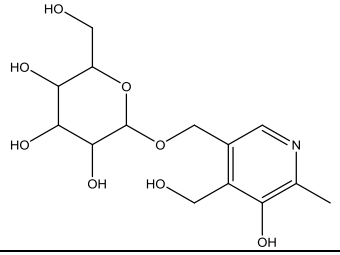
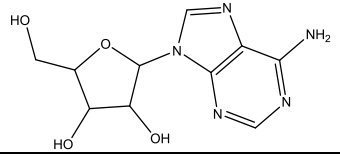
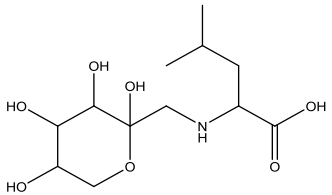
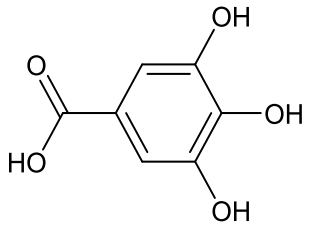
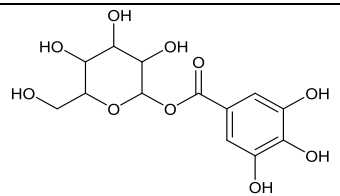
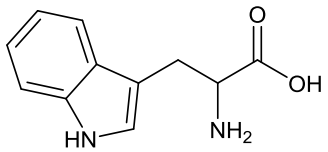
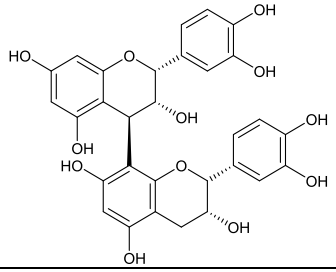
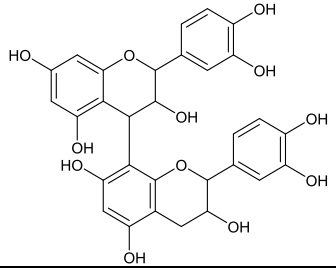
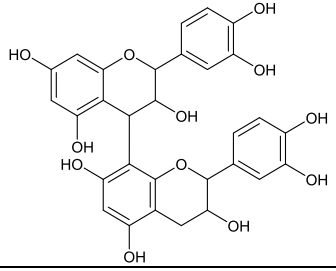
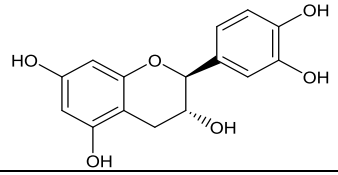
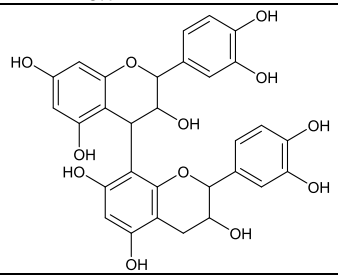
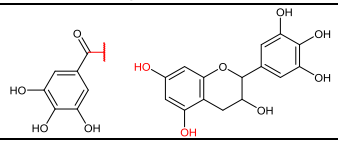
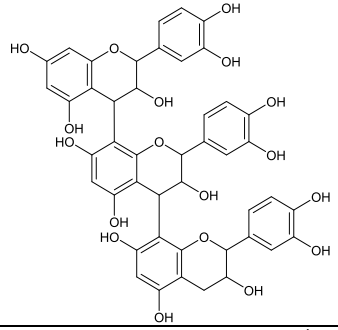
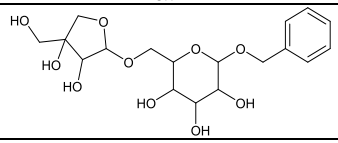
CAD Peak	RT (min)	Exp. *m/z* -, top +, bottom	Mass Acc. (ppm) -, top +, bottom	Proposed ID Molecular Formula	Structure	High Resolution Fragments [1] (*m/z* intensity)
1a	1.04	158.9781 110.0084	3.441 -3.153	Magnesium salts	Mg^{2+}	
1b		174.9566 125.9859	2.788 -2.430	Calcium salts	Ca^{2+}	
2a	1.18	112.9858 190.9117	1.712 -1.381	Sodium salts	Na^{+}	
2b		128.9598 122.9243	1.832 -1.949	Potassium salts	K^{+}	
3a	1.37	179.0555 203.0524	-2.576 -1.178	Monosaccharide $C_6H_{12}O_6$		Negative 59.0139 (100), 71.0139 (42), 89.0243 (39), 101.0245 (7), 113.0243 (6)
3b		195.0502 219.0263 [6]	-3.927 -0.477	Gluconic Acid $C_6H_{12}O_7$		Negative 111.0089 (14), 129.0195 (98), 159.0301 (100), 177.0407 (12), 195.0510 (43)
3c		146.0456 148.0602	-3.435 -1.178	Glutamic Acid $C_5H_9NO_4$		Positive 84.0444 (3), 102.0550 (14), 130.0500 (100)
3d		N/A 266.1594	N/A -1.255	Choline hexoside $C_{11}H_{23}NO_6$		Positive 104.1070 (53), 266.1602 (100) MS^3 60.0806 (100)
3e		N/A 337.1712	N/A -1.796	Arginyl fructose $C_{12}H_{24}N_4O_7$		Positive 173.1402 (34), 175.1193 (54), 217.1301 (35), 257.1614 (100), 260.1133 (27), 283.1407 (), 301.1512 (18), 319.1617 (90)

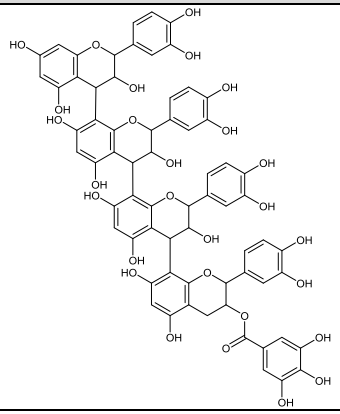
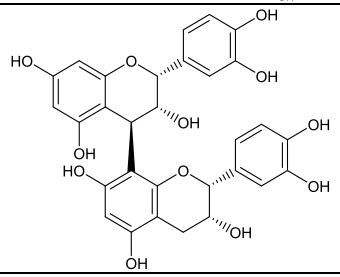
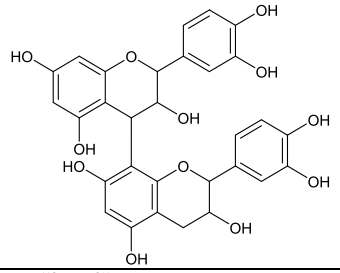
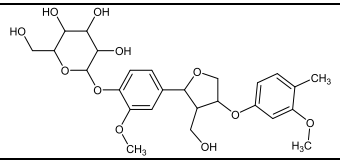
CAD Peak	RT (min)	Exp. *m/z* -, top +, bottom	Mass Acc. (ppm) -, top +, bottom	Proposed ID Molecular Formula	Structure	High Resolution Fragments [1] (*m/z* intensity)
3f		N/A 325.1122	N/A -1.917	Cellobiosan $C_{12}H_{20}O_{10}$		Positive 145.0497 (11), 253.0712 (14), 271.0824 (19), 289.0910 (24), 306.1184 (100), 307.1151 (94)
3g		N/A 118.0860	N/A -2.923	Isovaline $C_5H_{11}NO_2$		Positive 72.0807 (100), 101.0598 (15)
4a	1.53	149.0087 N/A	-3.028 N/A	Tartaric Acid $C_4H_6O_6$		Negative 59.0140 (65), 87.0089 (100). 103.0038 (95), 130.9988 (42), 149.0094 (17)
4b		341.1073 365.1052 [6]	-4.880 -0.582	Disaccharide $C_{12}H_{22}O_{11}$		Negative 89.0246 (18), 113.0246 (23), 119.0352 (14), 143.0353 (26), 161.0459 (26), 179.0563 (100)
4c		N/A 116.0703	N/A -2.456	Proline $C_5H_9NO_2$		Positive 70.0651 (100)
4d		N/A 138.0546	N/A -2.644	N-methylnicotinate $C_7H_7NO_2$		Positive 94.0649 (100)
5a	2.17	133.0139 157.0107 [6]	-2.380 -0.092	Malic Acid $C_4H_6O_5$		Negative 115.30037 (100)
5b		N/A 306.9972	N/A N/A	Unidentified		Positive 172.9760 (4), 244.9968 (7), 270.9764 (8), 288.9866 (100)

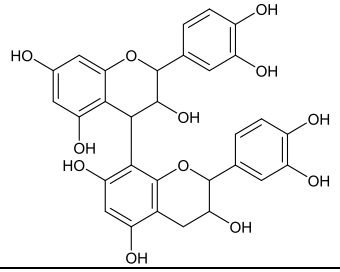
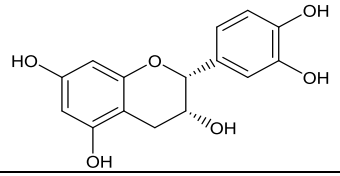
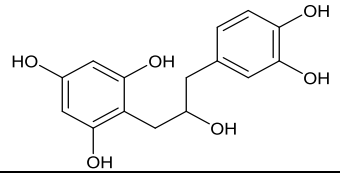
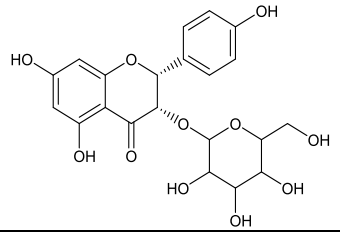
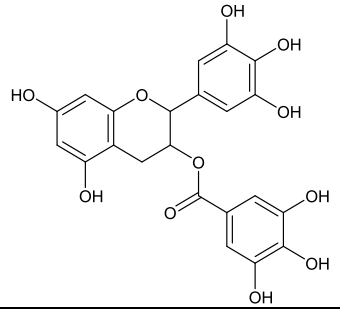
CAD Peak	RT (min)	Exp. *m/z* -, top +, bottom	Mass Acc. (ppm) -, top +, bottom	Proposed ID Molecular Formula	Structure	High Resolution Fragments [1] (*m/z* intensity)
6a	4.46	191.0192 215.0162 [6]	-2.857 0.122	Citric Acid $C_6H_8O_7$		Negative 111.0089 (100), 173.0092 (13) Positive 169.0110 (56), 197.0059 (100)
6b		128.0355 130.0498	1.747 0.122	Pyroglutamic Acid $C_6H_8O_7$		Positive 84.0444 (100)
7a	5.56	117.0189 N/A	-2.922 N/A	Succinic Acid $C_4H_6O_4$		Negative 73.0296 (100), 99.0088 (53)
7b		180.0659 182.0807	-3.812 -2.470	Tyrosine $C_9H_{11}NO_3$		Positive 136.0758 (23),165.0547 (100)
7c		243.0611 N/A	-4.770 N/A	Uridine $C_9H_{12}N_2O_6$		Negative 110.0249 (12), 140.0355 (4), 152.0356 (9), 174.9561 (6), 200.0566 (100)
7d		N/A 332.1329	N/A -3.171	Glucopyranosyl pyridoxine $C_{14}H_{21}NO_8$		Positive 152.0708 (6), 170.0813 (7), 314.1236 (100)
7e		N/A 268.1032	N/A -2.684	Adenosine $C_{10}H_{14}N_5O_4$		Positive 136.0618 (100)

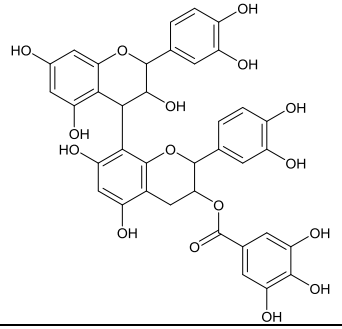
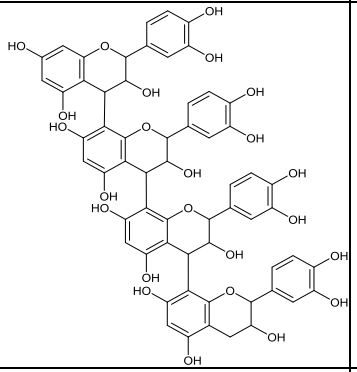
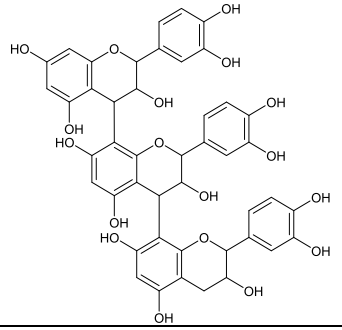
CAD Peak	RT (min)	Exp. *m/z* -, top +, bottom	Mass Acc. (ppm) -, top +, bottom	Proposed ID Molecular Formula	Structure	High Resolution Fragments [1] (*m/z* intensity)
7f		N/A 294.1537	N/A -3.972	Leucine-Fructose $C_{12}H_{23}NO_7$		Positive 276.1445 (100) MS^3 132.1021 (12), 230.1390 (44), 248.1495 (26), 258.1339 (100)
7g		251.0760 N/A	-4.782 N/A	Unidentified $C_9H_{16}O_8$		Negative 151.0612 (100), 204.9751 (6), 232.0472 (7)
7h		253.0916 N/A	-4.705 N/A	Unidentified $C_9H_{18}O_8$		Negative 207.0874 (100)
7i		289.0663 N/A	-4.873 N/A	Unidentified $C_{10}H_{14}O_8N_2$		Negative 174.9561 (55), 188.9494 (97), 221.0669 (100), 243.0623 (75), 271.0947 (23)
7j		N/A 229.1541	N/A -2.440	Unidentified $C_{11}H_{21}N_2O_3$		Positive 70.0648 (5), 124.0754 (8), 142.0867 (100), 170.0813 (8), 211.1444 (3)
7k		N/A 241.1541	N/A -2.318	Unidentified $C_{12}H_{21}N_2O_3$		Positive 84.0807 (6), 128.1071 (24), 144.1022 (15), 194.0814 (29), 196.0970 (100), 213.1601 (5)
7l		N/A 314.0909	N/A -4.658	Unidentified $C_{19}H_{12}N_3O_2$		Positive 97.0284 (8), 136.0620 (100), 143.0165 (4), 161.0269 (3), 179.0376 (8), 296.0817 (92)
8	9.46	169.0137 171.0288	-3.234 -0.057	Gallic acid $C_7H_6O_5$		Negative 125.0245 (100), 169.0143 (25)
9a	13.39	331.0655 333.0815	-4.863 -0.520	Glucogallin $C_{13}H_{16}O_{10}$		Negative 169.0142 (100) MS^3 125.0246 (100)

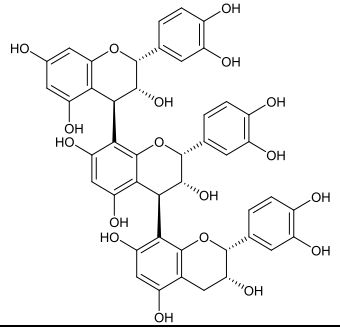
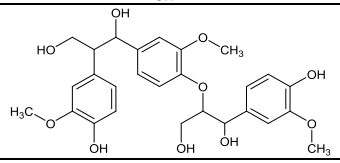
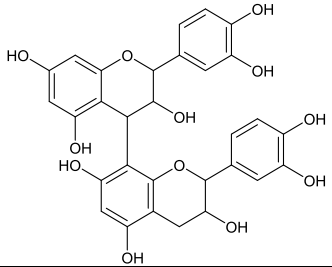
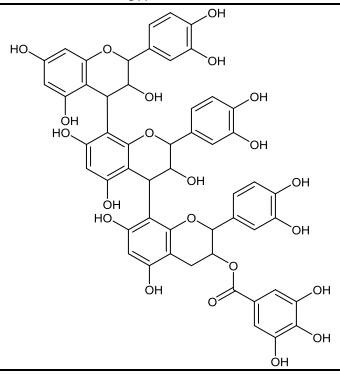
CAD Peak	RT (min)	Exp. *m/z* -, top +, bottom	Mass Acc. (ppm) -, top +, bottom	Proposed ID Molecular Formula	Structure	High Resolution Fragments [1] (*m/z* intensity)
9b		N/A 206.5312 [5]	N/A N/A	Unidentified		Positive 186.0182 (42), 195.0235 (100), 204.0289 (25)
10	16.39	203.0818 205.0969	-3.698 -1.337	Tryptophan $C_{11}H_{12}N_2O_2$		Negative 116.0507 (32), 142.0663 (11), 159.0930 (100), 186.056 (12) Positive 188.0706 (100)
11	18.62	577.1350 579.1482	-0.293 -2.543	Procyanidin B1 $C_{30}H_{26}O_{12}$		Negative 289.0719 (40), 407.0774 (76), 408.0805 (14), 425.0875 (100), 451.1033 (42), 559.1244 (10)
12	19.02	577.1347 579.1485	-0.848 -2.077	Procyanidin B $C_{30}H_{26}O_{12}$		Negative 269.0455 (17), 289.0719 (24), 407.0774 (40), 425.0875 (100), 439.1030 (42), 451.1033 (21), 533.1451 (21), 559.1244 (23)
13	19.57	577.1346 579.1479	-0.865 -3.130	Procyanidin B $C_{30}H_{26}O_{12}$		Negative 289.0719 (40), 407.0774 (76), 408.0805 (14), 425.0875 (100), 451.1033 (42), 559.1244 (10)

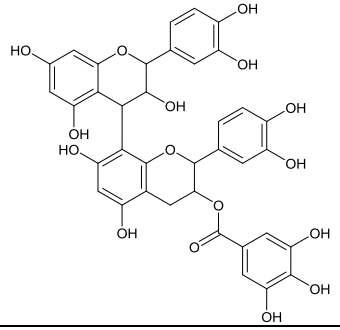
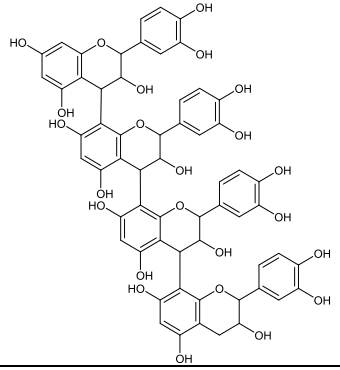
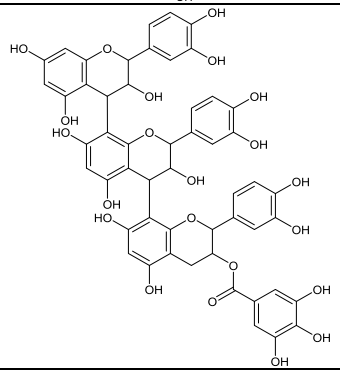
CAD Peak	RT (min)	Exp. *m/z* -, top +, bottom	Mass Acc. (ppm) -, top +, bottom	Proposed ID Molecular Formula	Structure	High Resolution Fragments [1] (*m/z* intensity)
14	20.25	289.0710 291.0855	-2.530 -2.867	Catechin $C_{15}H_{14}O_6$		Negative 179.0351 (15), 205.0505 (34), 245.0816 (100)
15a	20.57	577.1346 579.1479	-0.917 -3.026	Procyanidin B $C_{30}H_{26}O_{12}$		Negative 289.0719 (40), 407.0774 (76), 408.0805 (14), 425.0875 (100), 451.1033 (42), 559.1244 (10)
15b		457.0776 459.0912	-0.076 -3.633	Gallocatechin Gallate isomer $C_{22}H_{18}O_{11}$		Negative 166.9990 (15), 289.0718 (100), 413.0877 (17)
15c		N/A 201.5167 [5]	N/A N/A	Unknown		
16	20.69	865.1965 867.2111	-2.320 -2.272	Procyanidin C $C_{45}H_{38}O_{18}$		Negative 287.0569 (24), 407.0776 (38), 425.0890 (24), 543.0941 (20), 577.1364 (63), 587.1206 (24), 695.1427 (100), 713.1527 (31), 739.1671 (41), 847.1898 (14), 867.2060 (53)
17	21.01	401.1453 425.1408 [6]	0.049 -2.301	Benzyl alcohol $C_{18}H_{26}O_{10}$		Negative 161.0454 (12), 269.1026 (100)

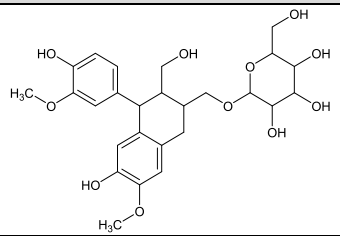
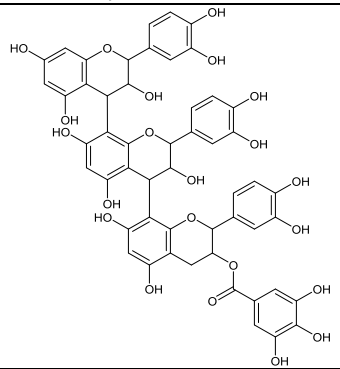
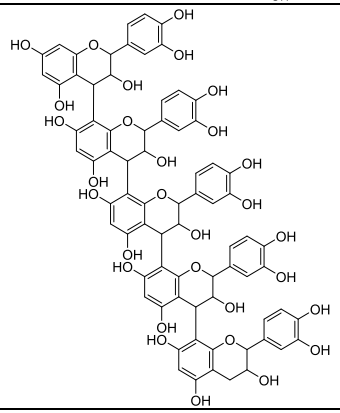
CAD Peak	RT (min)	Exp. *m/z* -, top +, bottom	Mass Acc. (ppm) -, top +, bottom	Proposed ID Molecular Formula	Structure	High Resolution Fragments [1] (*m/z* intensity)
18	21.14	652.1323 [5] N/A	-0.803 N/A	Galloylated Procyanidin (tetramer)		Negative 289.0722 (43), 303.0516 (16), 407.0780 (8), 491.0976 (11), 567.1045 (23), 576.1116 (93), 727.1305 (44), 853.1628 (13), 1015.1936 (54), 1179.2414 (13)
19	21.82	577.1350 579.1485	-0.207 -2.111	Procyanidin B2 $C_{30}H_{26}O_{12}$		Negative 289.0719 (40), 407.0774 (76), 408.0805 (14), 425.0875 (100), 451.1033 (42), 559.1244 (10)
20a	22.39	577.1344 579.1486	-1.229 -1.973	Procyanidin B $C_{30}H_{26}O_{12}$		Negative 269.0455 (17), 289.0719 (24), 407.0774 (40), 425.0875 (100), 439.1030 (42), 451.1033 (21), 533.1451 (21), 559.1244 (23)
20b		521.2028 545.1978 [6]	-0.144 -2.903	Lariciresinol Glucoside analogue $C_{26}H_{34}O_{11}$		Negative 359.1492 (100)
20c		N/A 219.1010	N/A -2.468	$C_{13}H_{14}O_3$		Positive 131.0858 (3), 159.0804 (14), 189.0911 (100), 191.1069 (16), 201.0913 (32)

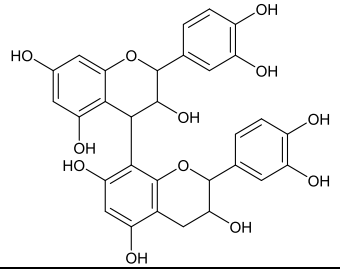
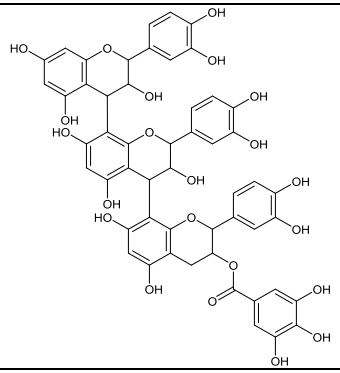
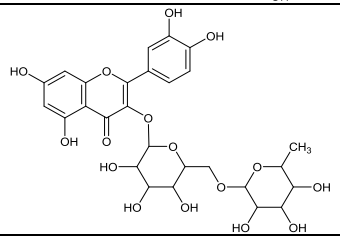
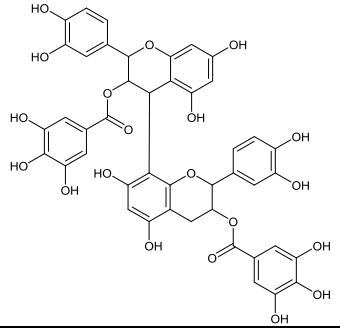
CAD Peak	RT (min)	Exp. *m/z* -, top +, bottom	Mass Acc. (ppm) -, top +, bottom	Proposed ID Molecular Formula	Structure	High Resolution Fragments [1] (*m/z* intensity)
21	22.73	577.1341 579.1487	-1.801 -1.766	Procyanidin B $C_{30}H_{26}O_{12}$		Negative 269.0455 (17), 289.0719 (24), 407.0774 (40), 425.0875 (100), 439.1030 (42), 451.1033 (21), 533.1451 (21), 559.1244 (23)
22	23.02	289.0714 291.0857	-1.389 -2.180	Epicatechin $C_{15}H_{14}O_6$		Negative 179.0351 (15), 205.0505 (34), 245.0816 (100)
23a	23.36	291.0873 293.1014	-0.211 -1.995	1-(3',4'-dihydroxy-phenyl)-3-(2",4",6"-trihydroxyophenyl) propan-2-ol $C_{15}H_{16}O_6$		Negative 123.0454 (10), 167.0351 (20), 205.0870 (13), 247.0974 (100), 291.0871 (13)
23b		449.1088 473.1045 [6]	-0.344 -1.929	Dihydrokaempferol 3-O-ß-D-glucoside $C_{21}H_{22}O_{11}$		Negative 259.0614 (35), 269.0458 (27), 287.0560 (100)
24a	23.54	457.0777 459.0912	0.078 -2.239	Epigallocatechin Gallate $C_{22}H_{18}O_{11}$		Negative 169.0143 (100), 287.0559 (11), 305.0663 (34), 331.0454 (56)

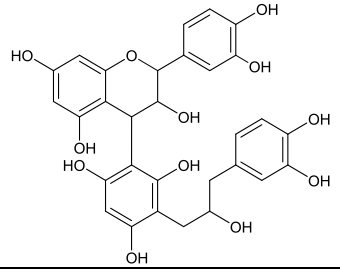
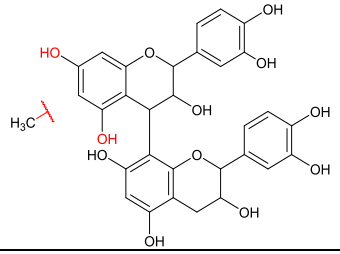
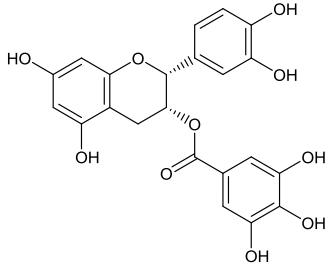
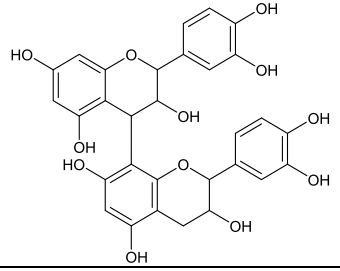
CAD Peak	RT (min)	Exp. *m/z* -, top +, bottom	Mass Acc. (ppm) -, top +, bottom	Proposed ID Molecular Formula	Structure	High Resolution Fragments [1] (*m/z* intensity)
24b		729.1448 731.1596	-1.725 -1.438	Galloylated Procyanidin (dimer) $C_{37}H_{30}O_{16}$		Negative 407.0783 (34), 425.0890 (25), 559.1271 (37), 577.1355 (100)
24c		576.1269 [5] 1155.2740	-0.684 -2.102	Procyanidin (tetramer) $C_{60}H_{50}O_{24}$		Negative 287.0561 (24), 289.0715 (40), 449.0869 (15), 491.0986 (76), 500.1021 (100), 567.1210 (17), 701.1504 (11), 739.1631 (16), 863.1813 (47), 1027.2266 (33)
25	23.99	865.1970 867.2120	-1.765 -1.211	Procyanidin C $C_{45}H_{38}O_{18}$		Negative 287.0569 (24), 407.0776 (38), 425.0890 (24), 543.0941 (20), 577.1364 (63), 587.1206 (24), 695.1427 (100), 713.1527 (31), 739.1671 (41), 847.1898 (14), 867.2060 (53)

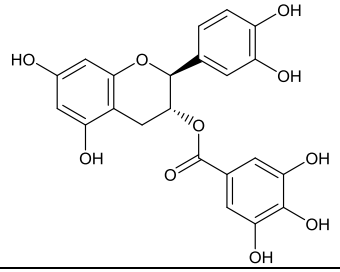
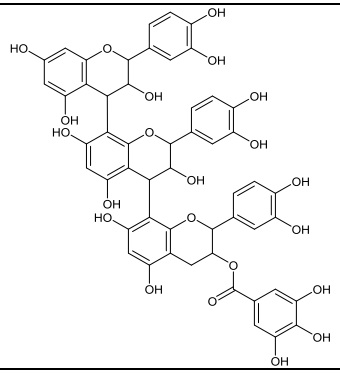
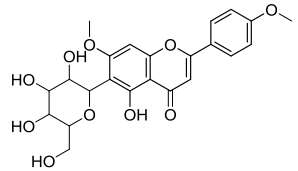
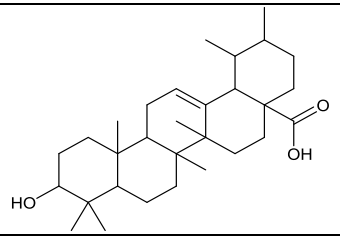
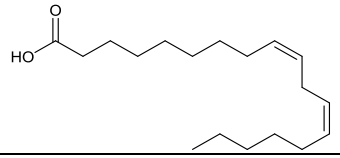
CAD Peak	RT (min)	Exp. *m/z* -, top +, bottom	Mass Acc. (ppm) -, top +, bottom	Proposed ID Molecular Formula	Structure	High Resolution Fragments [1] (*m/z* intensity)
26a	24.24	865.1968 867.2114	-1.962 -1.996	Procyanidin C1 $C_{45}H_{38}O_{18}$		Negative 287.0569 (24), 407.0776 (38), 425.0890 (24), 543.0941 (20), 577.1364 (63), 587.1206 (24), 695.1427 (100), 713.1527 (31), 739.1671 (41), 847.1898 (14), 867.2060 (53)
26b		515.1920 539.1871 [6]	-0.505 -3.150	Leptolepisol D $C_{27}H_{32}O_{10}$		Negative 195.0664 (18), 271.0972 (100), 319.1184 (51), 467.1702 (64)
27a	24.94	577.1349 579.1483	-0.432 -2.387	Procyanidin B $C_{30}H_{26}O_{12}$		Negative 289.0719 (40), 407.0774 (76), 408.0805 (14), 425.0875 (100), 451.1033 (42), 559.1244 (10
27b		508.1011 [5] 1019.2260	-0.117 1.865	Galloylated Procyanidin (trimer) $C_{52}H_{42}O_{22}$		Negative 287.0562 (21), 423.0721 (100), 441.0822 (41), 575.1195 (23), 603.1149 (16), 729.1450 (36), 847.1861 (16), 891.1776 (52)

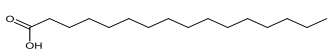
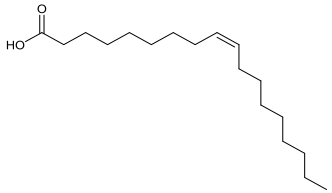
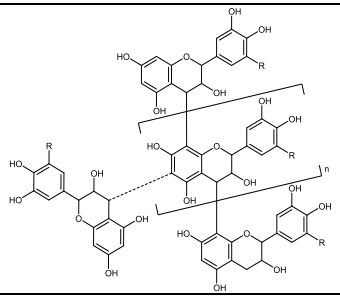
CAD Peak	RT (min)	Exp. *m/z* -, top +, bottom	Mass Acc. (ppm) -, top +, bottom	Proposed ID Molecular Formula	Structure	High Resolution Fragments [1] (*m/z* intensity)
28a	25.07	729.1451 731.1588	-1.341 -2.532	Galloylated Procyanidin (dimer) $C_{37}H_{30}O_{16}$		Negative 289.0721 (30), 407.0775 (100), 441.0830 (39), 451.1035 (52), 559.0978 (30), 577.1410 (43), 603.1148 (47), 731.1519 (33)
28b		576.1270 [5] 1155.2772	-0.511 0.642	Procyanidin (tetramer) $C_{60}H_{50}O_{24}$		Negative 287.0569 (33), 289.0720 (100), 407.0773 (57), 425.0876 (70), 451.1038 (50), 491.0986 (38), 500.1041 (62), 559.1296 (17), 863.1825 (56)
29a	25.30	508.1010 [5] 1019.2204	-0.157 -3.580	Galloylated Procyanidin (trimer) $C_{52}H_{42}O_{22}$		Negative 289.0716 (39), 303.0511 (100), 423.0713 (16),432.0923 (51), 577.1347 (30), 695.1393 (52), 713.1497 (40), 727.1293 (30)

CAD Peak	RT (min)	Exp. *m/z* -, top +, bottom	Mass Acc. (ppm) -, top +, bottom	Proposed ID Molecular Formula	Structure	High Resolution Fragments [1] (*m/z* intensity)
29b		521.2027 545.1981 [6]	-0.182 -2.335	Lariciresinol Glucosides analogue $C_{26}H_{34}O_{11}$		Negative 359.1489 (100)
30a	25.91	508.1007 [5] 1019.2219	-0.767 -2.148	Galloylated Procyanidin (trimer) $C_{52}H_{42}O_{22}$		Negative 289.0716 (39), 303.0511 (100), 423.0713 (16),432.0923 (51), 577.1347 (30), 695.1393 (52), 713.1497 (40), 727.1293 (30)
30b		720.1577 [5] N/A	-1.829 N/A	Procyanidin (pentamer) $C_{75}H_{62}O_{30}$		Negative 289.0722 (52), 407.0778 (22), 559.1128 (25), 577.1348 (78), 635.6320 (100), 863.1835 (61), 865.1957 (51), 1153.2533 (33), 1316.2962 (28)

CAD Peak	RT (min)	Exp. *m/z* -, top +, bottom	Mass Acc. (ppm) -, top +, bottom	Proposed ID Molecular Formula	Structure	High Resolution Fragments [1] (*m/z* intensity)
31	26.32	577.1347 579.1481	-0.848 -2.715	Procyanidin B $C_{30}H_{26}O_{12}$		Negative 269.0455 (17), 289.0719 (24), 407.0774 (40), 425.0875 (100), 439.1030 (42), 451.1033 (21), 533.1451 (21), 559.1244 (23)
32a	27.37	508.1008 [5] 1019.2223	-0.649 -1.726	Galloylated Procyanidin (trimer) $C_{52}H_{42}O_{22}$		Negative 289.0716 (39), 303.0511 (100), 423.0713 (16),432.0923 (51), 577.1347 (30), 695.1393 (52), 713.1497 (40), 727.1293 (30)
32b		609.1455 611.1591	-1.031 -2.620	Rutin $C_{27}H_{30}O_{16}$		Negative 301.0349 (100), 343.0453 (7) Positive 303.0500 (100), 465.1027 (29)
32c		881.1556 883.1705	-1.653 -1.302	Digalloylated Procyanidin (dimer) $C_{44}H_{34}O_{20}$		Negative 407.0778 (22), 441.0830 (6), 559.1328 (14), 603.1153 (6), 711.1359 (23), 729.1461 (100)

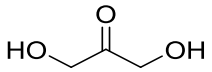
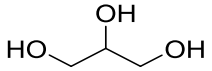
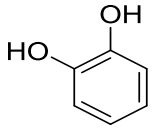
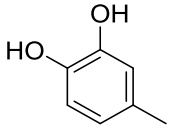
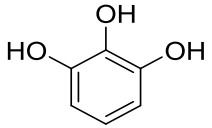
CAD Peak	RT (min)	Exp. *m/z* -, top +, bottom	Mass Acc. (ppm) -, top +, bottom	Proposed ID Molecular Formula	Structure	High Resolution Fragments [1] (*m/z* intensity)
32d		579.1505 581.1642	-0.448 -2.018	2-(3,4-dihydroxy-phenyl)-4-(3-(3-(3,4-dihydroxyphenyl)-2-hydroxypropyl)-2,4,6-trihydroxylphenyl) chromane-3,5,7-triol $C_{30}H_{28}O_{12}$		Negative 287.0562 (5), 291.0871 (58), 409.0922 (100), 427.1028 (34), 453.1182 (59), 561.1400 (34)
32e		591.1507 593.1643	-0.202 -1.758	Procyanidin B-type analogue $C_{31}H_{28}O_{12}$		Negative 215.0716 (20), 257.0822 (9), 289.0720 (74), 301.0720 (81), 439.1037 (100), 547.1598 (14)
33a	28.00	441.0826 443.0961	-0.272 -2.625	Epicatechin gallate $C_{22}H_{18}O_{10}$		Negative 169.0144 (17), 271.0609 (10), 289.0713 (100), 331.0454 (14)
33b		577.1347 579.1481	-0.831 -2.750	Procyanidin B $C_{30}H_{26}O_{12}$		Negative 289.0719 (40), 407.0774 (76), 408.0805 (14), 425.0875 (100), 451.1033 (42), 559.1244 (10

CAD Peak	RT (min)	Exp. *m/z* -, top +, bottom	Mass Acc. (ppm) -, top +, bottom	Proposed ID Molecular Formula	Structure	High Resolution Fragments [1] (*m/z* intensity)
34a	28.41	441.0826 443.0959	-0.227 -3.054	Catechin gallate $C_{22}H_{18}O_{10}$		Negative 169.0144 (17), 271.0609 (10), 289.0713 (100), 331.0454 (14)
34b		508.1008 [5] 1019.227	-0.531 -1.304	Galloylated Procyanidin (trimer) $C_{52}H_{42}O_{22}$		Negative 287.0561 (18), 413.0878 (14), 423.0720 (33), 432.0775 (100), 499.0954 (10), 575.1191 (22), 729.1450 (40), 891.1760 (47)
34c		459.1267 461.1428	-3.993 -3.043	Embigenin $C_{23}H_{24}O_{10}$		Positive 323.0907 (4), 341.1022 (23), 365.1027 (11), 395.1131 (27), 407.1127 (8), 425.1236 (28), 443.1341 (100)
35	66.70	455.3526 457.3665	-1.139 -2.475	Ursolic Acid $C_{30}H_{48}O_3$		Negative 407.3318 (100) Positive 393.3510 (7), 411.3625 (100), 439.3576 (69)
36	67.04	279.2329 281.2470	-0.048 -1.873	Linoleic Acid $C_{18}H_{32}O_2$		Negative 261.2222 (100)

CAD Peak	RT (min)	Exp. *m/z* -, top +, bottom	Mass Acc. (ppm) -, top +, bottom	Proposed ID Molecular Formula	Structure	High Resolution Fragments [1] (*m/z* intensity)
37	68.37	255.2332 257.2470	0.809 -1.931	Palmitic Acid $C_{16}H_{32}O_2$		Negative 237.2222 (100)
38	68.66	281.2488 283.2626	0.627 -1.860	Oleic Acid $C_{18}H_{34}O_2$		Negative 263.2378 (100) Positive 185.1538 (6), 199.1696 (8), 213.1852 (8), 227.2011 (6), 247.2423 (26), 265.2528 (100)
39	15-45	-	-	Tannins		

(1) High resolution MS/MS experiments were performed using CID with a NCE of 30.

Table S2. Proposed identifications of components producing FID peaks in the GC-FID and GC-HRMS analysis of grape seed (*Vitis vinifera*) extract for GSE-1.

Peak #	Kovats Retention Index	Exp. *m/z* [1] Mass Accuracy (ppm)	ID Molecular Formula	Structure	High Resolution Fragments [2] (*m/z*)
1	732	87.0441 (-0.006)	*Unidentified* $C_4H_6O_2$		61.0284, 43.0178, 33.0335 45.0335, 42.0099
2	894	91.0390 (0.192)	Dihydroxyacetone $C_3H_6O_3$		42.0098, 43.0177, 31.0179, 33.0335
3	966	91.0390 (0.039)	Glycerol $C_3H_8O_3$		61.0284, 43.0177, 44.0257
4	1188	111.0441 (0.216)	Catechol $C_6H_6O_2$		110.0362, 81.0335, 82.0413, 63.0229, 64.0308, 92.0257
5	1284	125.0597 (-0.288)	4-methyl catechol $C_7H_8O_2$		124.0519, 78.0464, 43.0178, 95.0492, 106.0414, 107.0492
6	1362	127.0390 (-0.084)	1,2,3-benzenetriol $C_6H_6O_3$		126.0310, 108.0205, 80.0256, 97.0284, 50.0151, 39.0227
7	1593	153.0543 (-1.768)	*Unidentified* $C_8H_8O_3$		123.0440, 152.0468, 77.0389 105.0336, 95.0492
8	1801	165.0544 (-1.579)	*Unidentified* $C_9H_8O_3$		136.0520, 164.0468, 89.0386, 107.0492, 43.0177, 79.0543

(1) Experimental *m/z* was acquired by chemical ionization (CI) on a high resolution mass spectrometer. The values indicate $[M+H]^+$.

(2) Fragmentation was acquired by electron ionization (EI) on a high resolution mass spectrometer.