Supplementary Material

Targeted and Suspect Screening of Phenolic Compounds in Plant-Based Milk Alternatives from the Greek Market

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Table S1. Chromatographic and mass spectral data of the phenolic compound standards. Compounds are grouped by structural class and listed in order of chromatographic retention time (R_t) within each group.

Analyte	R_t (min)	Chemical Formula	Elemental Composition	Theoretical Mass $[M-H]^-$	Measured Mass $[M-H]^-$	Mass error (ppm)
Phenylethanoids						
3-Hydroxytyrosol	7.32	$C_8H_{10}O_3$	$C_8H_9O_3^-$	153.0546	153.0546	0.00
Tyrosol	8.63	$C_8H_{10}O_2$	$C_8H_9O_2^-$	137.0597	137.0594	2.19
Phenolic Aldehyde						
Vanillin	9.32	$C_8H_8O_3$	$C_8H_7O_3^-$	151.0390	151.0388	1.32
Benzoic acid derivatives						
Gallic acid	4.66	$C_7H_6O_5$	$C_7H_5O_5^-$	169.0131	169.0134	-1.78
Protocatechuic acid	7.40	$C_7H_6O_4$	$C_7H_5O_4^-$	153.0188	153.0185	1.96
p-Hydroxybenzoic acid	8.19	$C_7H_6O_3$	$C_7H_5O_3^-$	137.0233	137.0232	0.73
Vanillic acid	8.51	$C_8H_8O_4$	$C_8H_7O_4^-$	167.0339	167.0340	-0.60
Syringic acid	8.53	$C_9H_{10}O_5$	$C_9H_9O_5^-$	197.0444	197.0448	-2.03
Homovanillic acid	8.63	$C_9H_{10}O_4$	$C_9H_9O_4^-$	181.0495	181.0496	-0.55
Cinnamic acid and derivatives						
Chlorogenic acid	7.35	$C_{16}H_{18}O_9$	$C_{16}H_{17}O_9^-$	353.0878	353.0882	-1.13
Caftaric acid	7.59	$C_{13}H_{11}O_9$	$C_{13}H_{11}O_9^-$	311.0409	311.0413	-1.29
Neochlorogenic acid	7.81	$C_{16}H_{18}O_9$	$C_{16}H_{17}O_9^-$	353.0878	353.0883	-1.42
trans-Coutaric acid	8.17	$C_{13}H_{12}O_8$	$C_{13}H_{11}O_8^-$	295.0459	295.0464	-1.69
Caffeic acid	8.47	$C_9H_8O_4$	$C_9H_7O_4^-$	179.0339	179.0341	-1.12
p-Coumaric acid	9.18	$C_9H_8O_3$	$C_9H_7O_3^-$	163.0390	163.0390	0.00
Sinapic acid	9.22	$C_{11}H_{12}O_5$	$C_{11}H_{11}O_5^-$	223.0612	223.0608	1.79
Ferulic acid	9.34	$C_{10}H_{10}O_4$	$C_{10}H_9O_4^-$	193.0495	193.0499	-2.07

trans-Cinnamic acid	11.80	$C_9H_8O_2$	$C_9H_7O_2^-$	147.0441	147.0438	2.04
Flavan-3-ols						
Epigallocatechin	7.50	$C_{15}H_{14}O_7$	$C_{15}H_{13}O_7^-$	305.0667	305.0671	-1.31
Catechin	7.93	$C_{15}H_{14}O_6$	$C_{15}H_{16}O_6^-$	289.0718	289.0721	-1.04
Epicatechin	8.28	$C_{15}H_{14}O_6$	$C_{15}H_{13}O_6^-$	289.0718	289.0721	-1.04
Epigallocatechin gallate	8.37	$C_{22}H_{18}O_{11}$	$C_{22}H_{17}O_{11}^-$	457.0776	457.0784	-1.75
Epicatechin gallate	8.96	$C_{22}H_{18}O_{10}$	$C_{22}H_{17}O_{10}^-$	441.0827	441.0833	-1.36
Procyanidins						
Procyanidin B1	7.49	$C_{30}H_{26}O_{12}$	$C_{30}H_{25}O_{12}^-$	577.1351	577.1367	-2.77
Procyanidin B2	7.99	$C_{30}H_{26}O_{12}$	$C_{30}H_{25}O_{12}^-$	577.1351	577.1365	-2.43
Flavonols						
Myricetin	9.79	$C_{15}H_{10}O_8$	$C_{15}H_9O_8^-$	317.0302	317.0304	-0.63
Quercetin	10.86	$C_{15}H_{10}O_7$	$C_{15}H_9O_7^-$	301.0354	301.0355	-0.33
Kaempferol	11.89	$C_{15}H_{10}O_6$	$C_{15}H_9O_6^-$	285.0405	285.0406	-0.35
Isorhamnetin	11.94	$C_{16}H_{12}O_7$	$C_{16}H_{11}O_7^-$	315.0510	315.0514	-1.27
Flavones						
Luteolin	10.70	$C_{15}H_{10}O_6$	$C_{15}H_9O_6^-$	285.0405	285.0406	-0.35
Apigenin	11.82	$C_{15}H_{10}O_5$	$C_{15}H_9O_5^-$	269.0455	269.0457	-0.74
Chrysin	13.05	$C_{15}H_{10}O_4$	$C_{15}H_9O_4^-$	253.0506	253.0507	-0.40
Flavonol glycosides						
Rutin	8.54	$C_{27}H_{30}O_{16}$	$C_{27}H_{29}O_{16}^-$	609.1461	609.1469	-1.31
Isoquercetin	8.77	$C_{21}H_{20}O_{12}$	$C_{21}H_{19}O_{12}^-$	463.0882	463.0894	-2.59

Astragalin	9.01	$C_{21}H_{20}O_{11}$	$C_{21}H_{19}O_{11}^-$	447.0933	447.0942	-2.01
Flavonol glycuronide						
Miquelianin	8.77	$C_{21}H_{18}O_{13}$	$C_{21}H_{17}O_{13}^-$	477.0674	477.0679	-1.05
Flavanones						
Naringenin	11.97	$C_{15}H_{12}O_5$	$C_{15}H_{11}O_5^-$	271.0612	271.0616	-1.48
Isoflavanones						
Daidzein	10.48	$C_{15}H_{10}O_4$	$C_{15}H_9O_4^-$	253.0506	253.0507	-0.40
Glycitein	10.50	$C_{16}H_{12}O_5$	$C_{16}H_{11}O_5^-$	283.0612	283.0615	-1.05
Genistein	11.93	$C_{15}H_{10}O_5$	$C_{15}H_9O_5^-$	269.0455	269.0459	-1.49
Formononetin	12.63	$C_{16}H_{12}O_4$	$C_{16}H_{11}O_4^-$	267.0663	267.0667	-1.50
Stilbenes						
Piceid	8.87	$C_{20}H_{22}O_8$	$C_{20}H_{21}O_8^-$	389.1242	389.1251	-2.31
trans-Resveratrol	10.39	$C_{14}H_{12}O_3$	$C_{14}H_{11}O_3^-$	227.0714	227.0711	1.32
Z-E-Viniferin	11.50	$C_{28}H_{22}O_6$	$C_{28}H_{21}O_6^-$	453.1344	453.1351	-1.54
Internal Standard						
Quercetin-d3 (IS)	10.80	$C_{15}H_7D_3O_7$	$C_{15}H_6D_3O_7^-$	304.0531	304.0545	-3.29

Table S2. Limits of detection (LODs, ng/mL) and limits of quantification (LOQs, ng/mL) of the phenolic compounds calculated based on the calibration curve. Compounds are grouped by structural class and listed in order of chromatographic retention time (R_t) within each group.

Analyte	LOD	LOQ
Phenylethanoids		
3-Hydroxytyrosol	0.82	2.71
Tyrosol	4.25	12.89
Phenolic Aldehyde		
Vanillin	1.98	6.01
Benzoic acid derivatives		
Gallic acid	2.75	8.32
Protocatechuic acid	3.72	11.28
p-Hydroxybenzoic acid	4.76	14.42
Vanillic acid	3.74	11.33
Syringic acid	2.35	7.12
Homovanillic acid	4.13	12.52
Cinnamic acid derivatives		
Chlorogenic acid	0.80	2.40
Caftaric acid	5.96	18.09
Neochlorogenic acid	0.55	1.68
trans-Coutaric acid	3.11	5.24
Caffeic acid	3.56	10.89
p-Coumaric acid	4.00	12.12
Sinapic acid	1.52	4.59
Ferulic acid	3.17	9.61
trans-Cinnamic acid	3.40	10.31
Flavan-3-ols		
Epigallocatechin	0.92	2.81
Catechin	0.27	0.81
Epicatechin	0.37	1.11
Epigallocatechin gallate	2.46	7.47
Epicatechin gallate	0.40	1.22

Analyte	LOD	LOQ
Procyanidins		
Procyanidin B1	1.21	3.99
Procyanidin B2	1.79	5.92
Flavonols		
Myricetin	4.36	13.22
Quercetin	0.91	2.71
Kaempferol	0.82	2.51
Isorhamnetin	1.01	3.07
Flavones		
Luteolin	2.16	6.41
Apigenin	1.20	3.64
Chrysin	3.42	10.32
Flavonol glycosides		
Rutin	0.51	1.53
Isoquercetin	0.42	1.27
Astragalin	2.97	9.02
Flavonol glycuronide		
Miquelianin	4.41	13.31
Flavanones		
Naringenin	2.03	6.01
Isoflavanones		
Daidzein	2.39	7.42
Glycitein	3.54	8.62
Genistein	2.55	7.71
Formononetin	3.89	11.77
Stilbenes		
Piceid	1.39	4.22
trans-Resveratrol	0.77	1.89
Z-E-Viniferin	2.73	8.27

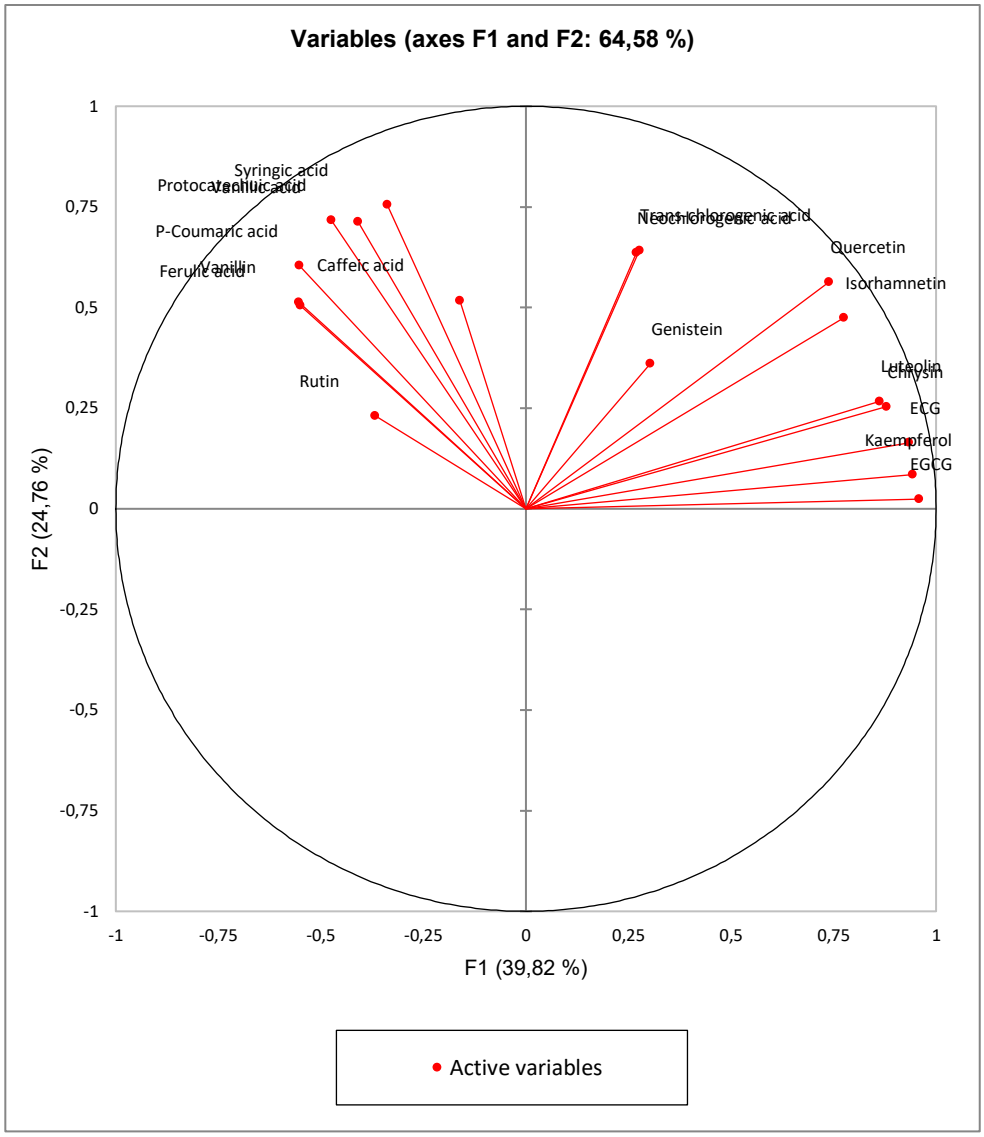


Figure S1. Principal component analysis: graph depicting the contribution of the variables.

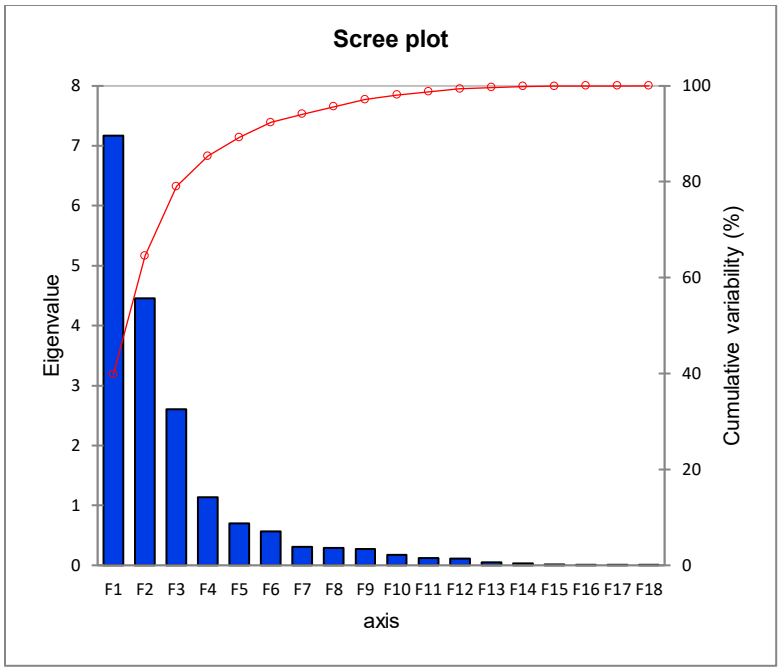


Figure S2. Principal component analysis: scree plot of phenolic compounds in PBMAs.

For the suspect screening of phenolic compounds, tentative identification was based on their exact masses, MS/MS fragmentation patterns and the presence of diagnostic fragment ions, previously reported in literature for avenanthramides [2,3], and isoflavones [4].

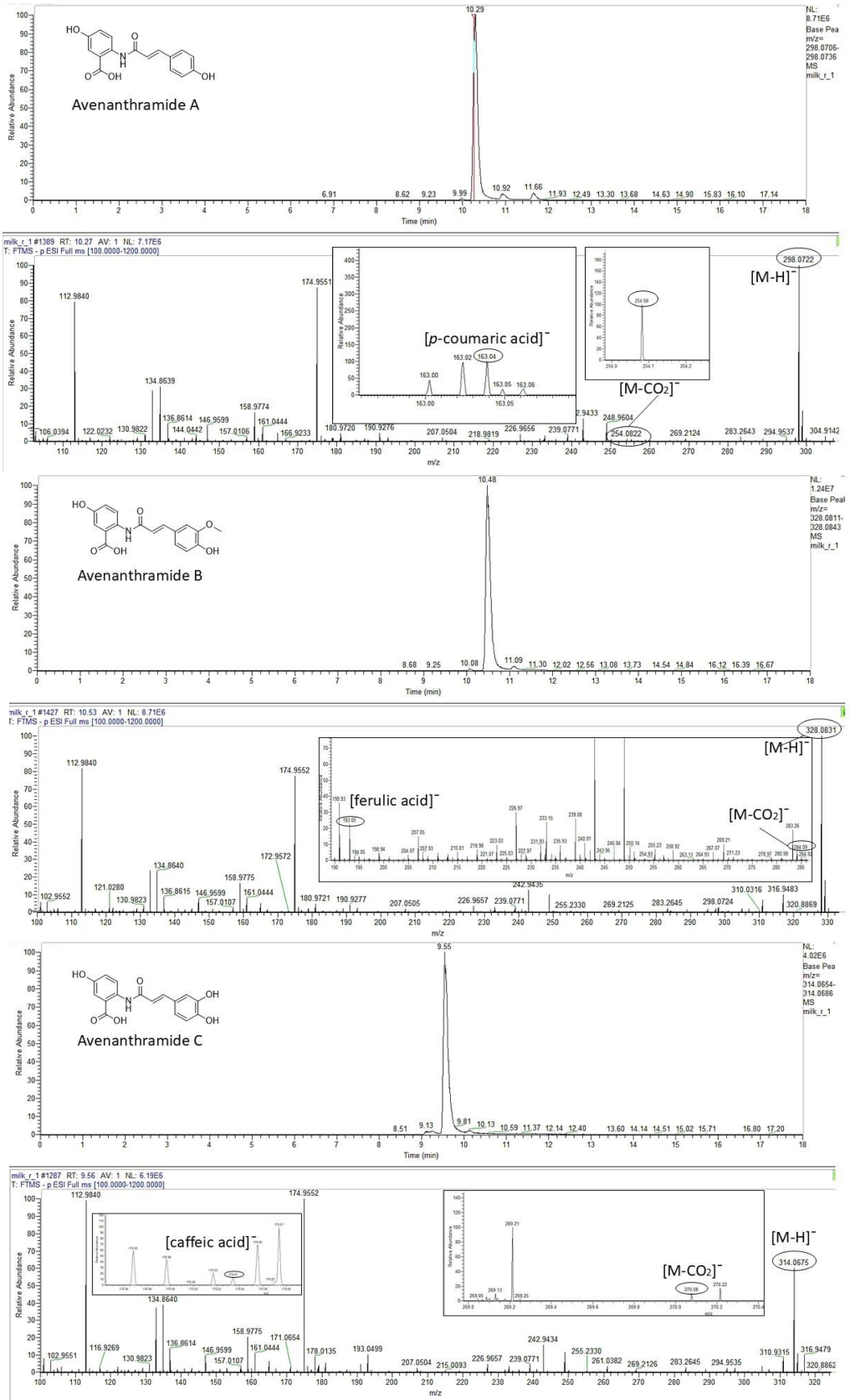
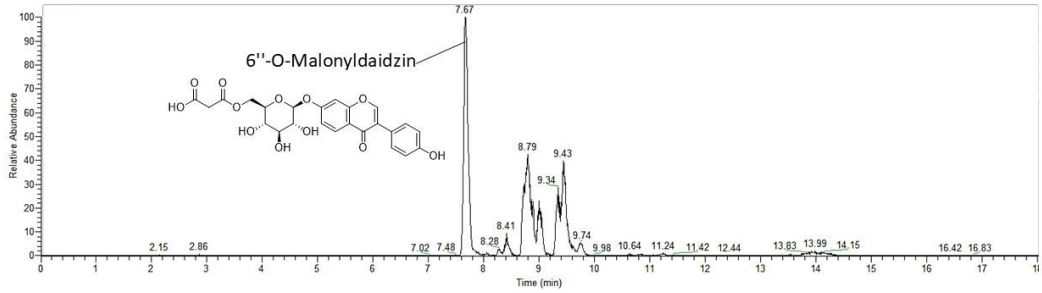
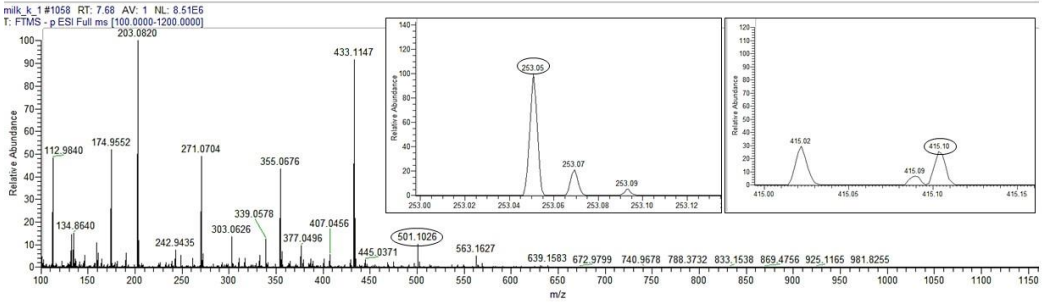
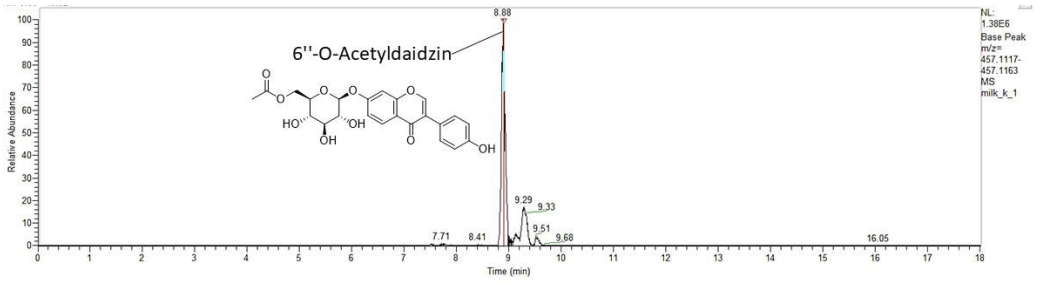
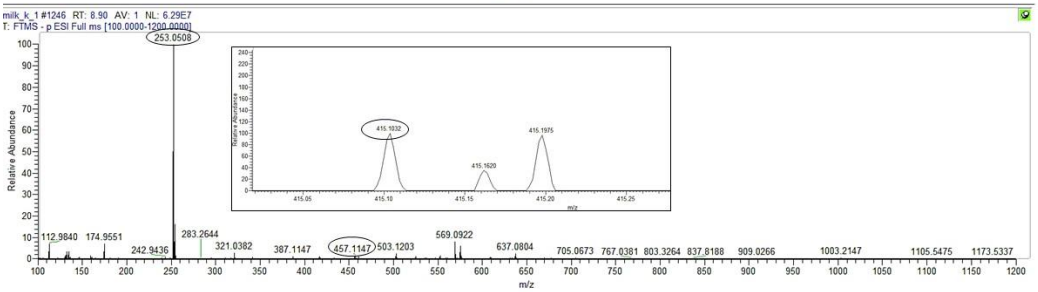


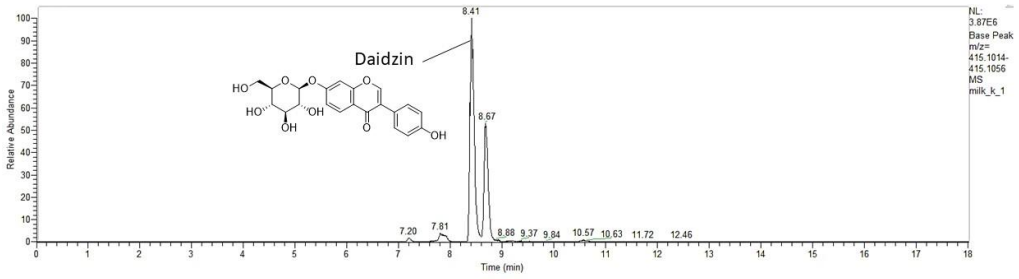
Figure S3. Chromatographic data, extracted ion chromatogram and mass spectra of avenanthramides identified in oat-based milk samples using Orbitrap mass spectrometer.

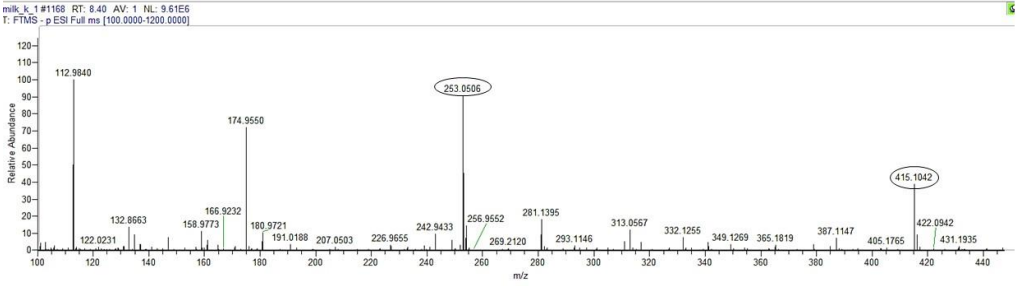

6''-O-Malonyldaidzin
Relative Abundance
Time (min)


milk_k_1 #1058 RT: 7.68 AV: 1 NL: 8.51E6
T: FTMS - p ESI Full ms [100.0000-1200.0000]
Relative Abundance
m/z


6''-O-Acetyldaidzin
NL: 1.38E6 Base Peak m/z= 457.1117-457.1163 MS milk_k_1
Relative Abundance
Time (min)


milk_k_1 #1246 RT: 8.90 AV: 1 NL: 6.29E7
T: FTMS - p ESI Full ms [100.0000-1200.0000]
Relative Abundance
m/z


Daidzin
NL: 3.87E6 Base Peak m/z= 415.1014-415.1056 MS milk_k_1
Relative Abundance
Time (min)


milk_k_1 #1168 RT: 8.40 AV: 1 NL: 9.61E6
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Relative Abundance
m/z

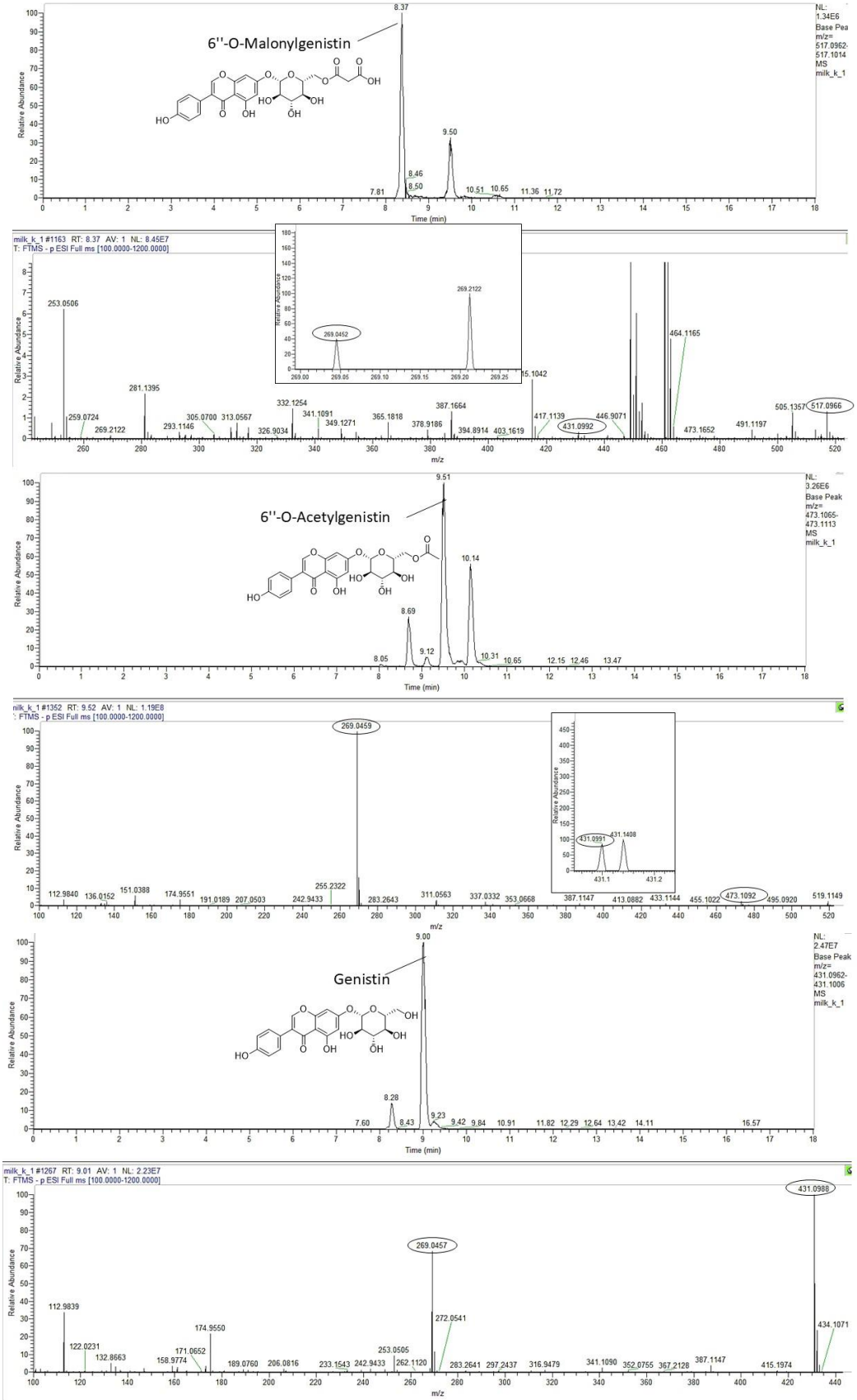


Figure S4. Chromatographic data, extracted ion chromatogram and mass spectra of isoflavones identified in soy-based milk samples using Orbitrap mass spectrometer.

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