

## **Supplementary Information**

### **Metabolomic-based strategy for fingerprinting *Sambucus nigra* L. berries volatile terpenoids and norisoprenoids: influence of ripening and cultivar**

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**Table S1 Monoterpene, sesquiterpenic and norisoprenoid metabolites detected in ‘Sabugueira’ elderberries (*S. nigra* L.) during ripening, from the harvesting season of 2013. The harvesting date in light gray corresponds to the ripe stage.**

Peak number	<sup>1</sup> t <sub>R</sub> <sup>a</sup> (s)	<sup>2</sup> t <sub>R</sub> <sup>a</sup> (s)	Compound	RI <sub>lit</sub> <sup>b</sup>	RI <sub>calc</sub> <sup>c</sup>	GC Peak Area (x10 <sup>6</sup> ) <sup>d</sup> and RSD (%)									
						2 <sup>nd</sup> Aug	8 <sup>th</sup> Aug	Harvesting date	21 <sup>st</sup> Aug	28 <sup>th</sup> Aug					
<i>Monoterpene compounds</i>															
<i>Hydrocarbon-type</i>															
1	312	0.430	α-Pinene	941	938	5.99 (7.3)	1.08 (2.1)	14.15 (13.6)	24.02 (13.4)	2.36 (2.1)					
2	330	0.490	Verbenene	967	957	-	-	-	-	0.08 <sup>f</sup>					
3	342	0.401	Camphepane	960	961	-	0.20 (10.7)	0.07 <sup>f</sup>	0.64 (11.2)	-					
4	348	0.470	β-Pinenene	987	975	13.54 (22.3)	2.83 (9.7)	3.45 (2.8)	14.93 (25.1)	1.37 (19.6)					
5	360	0.500	Myrcene	1008	988	2.17 (15.7)	2.62 (12.3)	1.60 (2.5)	6.82 (3.3)	0.43 (9.0)					
6	378	0.447	β-Phellandrene	1035	1008	0.58 (10.1)	0.85 (16.4)	0.32 (27.9)	1.72 (12.1)	0.13 (10.8)					
7	396	0.500	Limonene <sup>h</sup>	1035	1027	126.90 (17.9)	118.78 (28.9)	81.98 (10.1)	11.65 (4.1)	26.20 (2.0)					
8	396	0.570	p-Cymene <sup>h</sup>	1039	1027	26.23 (12.3)	16.48 (27.5)	14.56 (28.2)	46.62 (11.2)	6.47 (22.7)					
9	426	0.590	1,3,8-p-Menthatriene	1121	1060	12.02 (9.2)	10.11 (17.3)	7.09 (16.5)	24.86 (9.6)	4.83 (16.3)					
10	456	0.530	Terpinolene	1097	1094	1.48 (20.1)	0.90 (20.2)	0.46 (29.3)	2.34 (1.8)	0.20 (8.6)					
11	456	0.620	p-Cymenene	1090	1094	1.37 (22.8)	1.18 (5.2)	0.46 (24.0)	2.58 (19.5)	-					
12	582	0.620	m/z 93, 43, 77	-	1237	-	0.42 (22.9)	-	0.10 (3.5)	-					
						<b>Subtotal (GC Peak Area)</b>	<b>190.27</b>	<b>155.15</b>	<b>124.09</b>	<b>136.27</b>					
						<b>Subtotal (%)<sup>g</sup></b>	<b>60.6</b>	<b>52.8</b>	<b>79.8</b>	<b>66.5</b>					
						<b>Subtotal (Number of Compounds)</b>	<b>9</b>	<b>11</b>	<b>10</b>	<b>11</b>					
										<b>9</b>					
<i>Oxygen containing</i>															
13	438	0.640	Linalool oxide isomer (furanoid) <sup>h,i</sup>	1078	1074	1.94 (25.4)	-	-	0.53 (4.4)	-					
14	438	0.730	Dihydromyrcenol	1076	1074	1.05 (4.4)	-	-	1.47 (28.7)	1.39 (26.2)					
15	456	0.720	Linalool oxide isomer (furanoid) <sup>h,i</sup>	1097	1094	0.17 (11.9)	-	-	0.14 (9.3)	-					
16	462	0.820	Linalool <sup>h</sup>	1108	1101	16.03 (26.1)	8.62 (6.6)	2.72 (5.8)	8.10 (16.0)	15.13 (12.2)					
17	468	0.950	Hotrienol	1122	1108	3.06 (28.5)	-	0.45 (5.2)	1.21 (4.5)	1.12 (6.1)					
18	474	0.510	Rose oxide	1117	1114	1.09 (16.9)	2.55 (9.1)	-	0.51 (13.5)	0.15 (18.3)					
19	480	0.870	Fenchol	1118	1121	-	-	-	0.34 (22.9)	-					
20	492	0.510	Rose oxide isomer	1130	1131	-	1.57 (22.1)	-	0.12 (11.4)	-					
21	498	0.600	Artemisia alcohol	1083	1141	0.50 (23.4)	-	0.74 (9.1)	-	0.70 (10.9)					
22	504	0.740	Camphor	1147	1148	-	-	-	-	0.04 <sup>f</sup>					
23	510	0.650	Citronellal <sup>h</sup>	1159	1154	0.17 (24.6)	-	-	-	0.60 (20.6)					
24	516	0.990	Hotrienol isomer	1122	1162	20.27 (4.3)	0.52 (5.0)	-	3.13 (6.1)	8.46 (14.6)					
25	522	0.690	Pinocarvone	1164	1167	0.09 (20.5)	0.10 (7.3)	0.51 (20.0)	1.42 (6.8)	0.45 (28.0)					
26	528	0.850	Menthol <sup>h</sup>	1173	1174	-	-	0.10 (1.2)	0.10 (9.7)	-					
27	528	0.990	Borneol <sup>h</sup>	1172	1174	1.71 (18.9)	-	-	0.96 (13.2)	-					
28	528	1.070	Epoxylinalool	1173	1175	19.50 (12.3)	4.49 (23.8)	1.38 (5.1)	1.67 (28.7)	1.38 (27.5)					
29	534	0.787	Terpinen-4-ol	1181	1181	0.46 (6.9)	0.88 (1.9)	0.26 (19.9)	0.98 (21.6)	-					
30	540	1.380	p-Cymen-8-ol	1203	1188	0.40 (23.4)	-	-	0.57 (15.8)	-					
31	546	0.500	3(10)-Caren-2-ol	1211	1194	0.26 (29.3)	0.43 (1.1)	0.25 (11.1)	-	0.27 (20.4)					
32	546	0.920	α-Terpineol <sup>h</sup>	1206	1194	1.01 (1.4)	1.00 (28.8)	0.48 (17.8)	2.21 (13.5)	0.29 (16.7)					
33	576	0.950	β-Citronellol <sup>h</sup>	1237	1230	0.40 (21.3)	-	-	0.33 (14.0)	1.77 (22.2)					
34	576	1.050	trans-Geraniol <sup>h</sup>	1235	1230	0.08 <sup>f</sup>	-	-	0.62 (2.8)	-					
35	588	0.750	m/z 59, 68, 43	-	1244	-	-	-	0.05 <sup>f</sup>	0.04 <sup>f</sup>					
36	588	0.800	Citral isomer <sup>h,i</sup>	1241	1244	0.72 (13.5)	1.11 (26.7)	0.64 (17.6)	1.65 (2.5)	0.23 (22.1)					
37	588	0.910	Carvone <sup>h</sup>	1245	1244	-	0.21 <sup>e</sup> (0.4)	-	0.19 (11.6)	-					
38	600	1.070	Nerol <sup>h</sup>	1242	1258	2.57 (23.3)	0.29 (4.3)	-	0.77 (13.3)	1.23 (14.7)					
39	612	0.820	Citral isomer <sup>h,i</sup>	1287	1272	1.95 (8.8)	1.12 (25.6)	1.48 (24.9)	2.03 (17.7)	1.97 (22.7)					
40	684	0.600	β-Terpinyl acetate	-	1357	0.84 (28.6)	1.08 (2.4)	0.20 (21.2)	4.84 (18.4)	0.55 (21.9)					
41	702	0.607	Geranyl acetate	1383	1385	1.32 (19.9)	1.31 (29.5)	0.48 (9.7)	1.62 (17.2)	0.18 (31.1)					
42	714	0.680	10-(Acetyl methyl)-3-carene	1380	1401	1.61 (26.1)	8.74 (6.8)	0.13 (4.0)	4.10 (12.0)	0.11 (24.0)					
						<b>Subtotal (GC Peak Area)</b>	<b>77.12</b>	<b>33.67</b>	<b>9.75</b>	<b>39.26</b>					
						<b>Subtotal (%)</b>	<b>24.6</b>	<b>11.5</b>	<b>6.3</b>	<b>19.2</b>					
						<b>Subtotal (Number of Compounds)</b>	<b>24</b>	<b>16</b>	<b>14</b>	<b>26</b>					
										<b>20</b>					
<i>Nosioprenoids</i>															
43	402	0.620	2,2,6-Trimethyl-cyclohexanone	1051	1034	1.13 (23.7)	2.60 (13.2)	0.48 (10.3)	-	1.44 (1.6)					

44	504	1.080	Ketoisoporphone	1171	1148	0.32 (12.4)	0.18 (27.5)	0.15 (16.5)	-	0.06 (11.1)
45	552	0.830	Safranal	1241	1201	-	-	2.07 (22.8)	-	-
46	570	0.670	$\beta$ -Cyclocitral	1261	1222	1.24 (27.3)	2.90 (27.1)	0.54 (21.7)	0.47 (17.2)	0.45 (1.2)
47	636	0.570	Dihydroedulan	1289	1300	22.09 (20.8)	56.02 (10.0)	1.37 (19.6)	3.66 (7.6)	2.67 (14.9)
48	654	0.500	Theaspirane	1308	1322	0.27 (6.5)	0.25 (17.9)	-	0.15 (3.9)	-
49	708	0.760	Damascenone	1379	1393	0.38 (17.0)	-	-	0.16 (7.3)	0.32 (20.8)
50	738	0.740	$\alpha$ -Ionone	1422	1432	0.17 (21.3)	-	0.07 (2.3)	-	-
51	744	0.950	Megastigma-3,5-dien-9-ol	1430	1440	0.10 (20.3)	0.32 (17.9)	-	0.23 (4.9)	-
52	750	0.850	$\beta$ -Ionon-5,6-epoxide	1428	1447	0.34 (28.8)	0.11 (12.1)	0.04 <sup>f</sup>	-	-
53	756	0.700	Geranyl acetone <sup>h</sup>	1454	1455	3.20 (16.6)	2.91 (29.0)	3.20 (15.5)	1.52 (6.7)	1.95 (22.6)
54	780	0.680	$\alpha$ -Methyl ionone	1486	1486	0.19 (23.8)	0.18 (11.5)	0.07 (7.1)	-	-
55	780	0.780	$\beta$ -Ionone <sup>h</sup>	1481	1487	0.26 (13.7)	0.64 (3.7)	0.26 (12.1)	-	-
56	900	0.970	Methyl dihydrojasmonate	1650	1660	0.09 <sup>f</sup>	-	-	-	-
<b>Subtotal (GC Peak Area)</b>				<b>29.74</b>		<b>66.10</b>		<b>8.15</b>		<b>6.20</b>
<b>Subtotal (%)</b>				<b>9.5</b>		<b>22.5</b>		<b>5.2</b>		<b>3.0</b>
<b>Subtotal (Number of Compounds)</b>				<b>13</b>		<b>10</b>		<b>10</b>		<b>6</b>
<b>Sesquiterpenic compounds</b>										
<i>Hydrocarbon-type</i>										
57	678	0.490	$\beta$ -Cubebene	1387	1354	0.26 (16.4)	0.22 (29.1)	0.21 (16.0)	0.10 (0.7)	0.10 (2.3)
58	702	0.500	$\alpha$ -Copaene <sup>h</sup>	1375	1385	-	1.12 (6.3)	0.80 (14.6)	0.78 (22.8)	0.23 (6.3)
59	708	0.510	$\beta$ -Bourbonene	1379	1393	-	-	-	-	-
60	714	0.540	$\beta$ -Elemene	1380	1401	-	-	0.92 (17.7)	0.69 (25.8)	-
61	726	0.540	Longifolene	1395	1431	1.09 (18.3)	3.80 (4.3)	-	1.82 (17.4)	-
62	738	0.540	$\beta$ -Caryophyllene <sup>h</sup>	1417	1432	4.34 (6.3)	11.84 (6.4)	3.27 (28.7)	4.84 (17.9)	-
63	750	0.480	Aromadendrene	1447	1447	2.65 (20.7)	13.10 (12.0)	4.28 (8.5)	6.54 (19.8)	7.23 (7.9)
64	762	0.560	$\alpha$ -Humulene <sup>h</sup>	1450	1462	2.05 (23.9)	2.68 (17.3)	1.03 (14.9)	4.50 (17.7)	0.60 (17.5)
65	792	0.506	$\alpha$ -Muurolene	1490	1499	1.78 (18.0)	3.38 (10.8)	0.16 (13.9)	0.49 (23.9)	0.11 (7.0)
66	810	0.570	$\Delta$ -Cadinene	1525	1528	0.54 (18.7)	0.86 (15.0)	0.38 (2.2)	0.74 (11.3)	0.16 (16.0)
67	810	0.630	Calamenene	1525	1528	0.14 (6.3)	0.38 (26.5)	0.59 (24.2)	0.33 (12.5)	0.14 (20.2)
68	828	0.680	$\alpha$ -Calacorene	1554	1556	-	0.08 <sup>f</sup>	0.56 (3.0)	0.15 (19.8)	-
<b>Subtotal (GC Peak Area)</b>				<b>12.85</b>		<b>37.37</b>		<b>11.66</b>		<b>20.89</b>
<b>Subtotal (%)</b>				<b>4.1</b>		<b>12.7</b>		<b>7.5</b>		<b>10.2</b>
<b>Subtotal (Number of Compounds)</b>				<b>8</b>		<b>9</b>		<b>10</b>		<b>11</b>
<i>Oxygen containing</i>										
69	822	0.810	$\beta$ -Bourbonen-13-ol	-	1547	-	-	-	-	-
70	840	0.670	Epiglobulol	1588	1572	0.56 (9.0)	0.42 (28.0)	0.52 (14.0)	0.66 (13.2)	0.45 (12.0)
71	858	0.710	Caryophyllene oxide	1610	1601	1.53 (4.2)	0.77 (16.6)	0.11 (8.3)	1.45 (18.0)	0.42 (9.2)
72	870	0.730	Globulol	1592	1618	-	-	-	-	-
73	888	0.730	Cubenol	1643	1643	0.04 <sup>f</sup>	0.03 (1.5)	0.61 (17.2)	-	0.42 (28.1)
74	894	0.830	t-Cadinol	1650	1651	0.85 (10.6)	0.03 (2.3)	-	-	-
75	918	0.900	<i>m/z</i> 91, 119, 105		-	1685	0.25 (16.6)	0.46 (17.9)	0.27 (29.5)	0.22 (16.9)
76	1014	0.710	<i>m/z</i> 69, 41, 55		-	1841	0.61 (12.1)	0.06 <sup>f</sup>	0.28 (26.7)	0.25 (13.7)
<b>Subtotal (GC Peak Area)</b>				<b>3.82</b>		<b>1.53</b>		<b>1.79</b>		<b>2.32</b>
<b>Subtotal (%)</b>				<b>1.2</b>		<b>0.5</b>		<b>1.2</b>		<b>1.77</b>
<b>Subtotal (Number of Compounds)</b>				<b>6</b>		<b>6</b>		<b>5</b>		<b>5</b>
<b>Total</b>				<b>313.81</b>		<b>293.82</b>		<b>155.44</b>		<b>204.94</b>
<b>Number of Identified Compounds</b>				<b>60</b>		<b>52</b>		<b>49</b>		<b>57</b>
<b>95.06</b>										
<b>48</b>										

<sup>a</sup> Retention times for first ( $^1t_R$ ) and second ( $^2t_R$ ) dimensions in seconds.

<sup>b</sup> RI, Retention Index reported in the literature for Equity-5 GC column or equivalents.

<sup>c</sup> RI: Retention Index obtained through the modulated chromatogram.

<sup>d</sup> Mean of three independent assays (n=3). GC peak areas were expressed as arbitrary units.

<sup>e</sup> The compound was detected in two assays.

<sup>f</sup> The compound was detected in one assay.

<sup>g</sup> The relative amount (%) for the different identified chemical families represents their relative content compared to the total content.

<sup>h</sup> Identification confirmed by chemical standards

<sup>i</sup> The used standards are a mixture of isomers

**Table S2 Monoterpene, sesquiterpenic and norisoprenoid metabolites detected in ‘Sabugueiro’ elderberries (*S. nigra* L.) during ripening, from the harvesting season of 2013. The harvesting date in light gray corresponds to the ripe stage.**

Peak number	${}^1t_R$ <sup>a</sup> (s)	${}^2t_R$ <sup>a</sup> (s)	Compound	$RI_{lit}^b$	$RI_{calc}^c$	GC Peak Area (x10 <sup>6</sup> ) <sup>d</sup> and RSD (%)				
						Harvesting date				
						2 <sup>nd</sup> Aug	8 <sup>th</sup> Aug	21 <sup>st</sup> Aug	28 <sup>th</sup> Aug	5 <sup>th</sup> Sep
<i>Monoterpene compounds</i>										
<i>Hydrocarbon-type</i>										
1	312	0.430	$\alpha$ -Pinene	941	938	15.82 (28.5)	12.21 (8.0)	2.49 (2.5)	2.95 (27.7)	1.66 (24.1)
2	330	0.490	Verbenene	967	957	-	0.08 <sup>f</sup>	-	-	0.05 <sup>f</sup>
3	342	0.401	Camphene	960	961	0.12 (9.0)	0.24 (19.4)	-	0.74 (21.3)	0.15 (27.5)
4	348	0.470	$\beta$ -Pinene	987	975	16.57 (25.1)	9.08 (10.7)	2.42 (29.3)	20.99 (8.2)	2.41 (15.8)
5	360	0.500	Myrcene	1008	988	1.87 (24.3)	-	0.88 (27.7)	5.92 (15.9)	1.10 (28.2)
6	378	0.447	$\beta$ -Phellandrene	1035	1008	0.97 (20.5)	-	0.24 (23.8)	1.72 (22.7)	0.29 (21.0)
7	396	0.500	Limonene <sup>h</sup>	1035	1027	144.71 (13.8)	142.23 (18.3)	52.89 (21.0)	43.75 (8.2)	36.60 (26.7)
8	396	0.570	p-Cymene <sup>h</sup>	1039	1027	16.29 (18.0)	30.85 (15.4)	7.11 (9.7)	38.22 (8.7)	2.58 (1.0)
9	426	0.590	1,3,8-p-Menthatriene	1121	1060	18.75 (13.6)	20.25 (15.5)	3.18 (27.9)	28.60 (23.7)	1.86 (1.2)
10	456	0.530	Terpinolene	1097	1094	1.15 (15.4)	1.51 (15.8)	0.28 (23.1)	2.42 (25.8)	0.34 (22.0)
11	456	0.620	p-Cymenene	1090	1094	1.36 (13.4)	-	0.10 (2.3)	1.85 (16.3)	0.59 (22.3)
12	582	0.620	<i>m/z</i> 93, 43, 77	-	1237	-	0.38 (4.6)	-	-	0.28 (16.1)
Subtotal (GC Peak Area)						<b>217.62</b>	<b>216.78</b>	<b>69.59</b>	<b>147.15</b>	<b>47.88</b>
Subtotal (%) <sup>e</sup>						<b>71.3</b>	<b>60.4</b>	<b>49.4</b>	<b>71.0</b>	<b>45.8</b>
Subtotal (Number of Compounds)						<b>10</b>	<b>9</b>	<b>9</b>	<b>10</b>	<b>12</b>
<i>Oxygen containing</i>										
13	438	0.640	Linalool oxide isomer (furanoid) <sup>h, i</sup>	1078	1074	-	0.44 (20.2)	0.04 <sup>f</sup>	-	0.54 (25.3)
14	438	0.730	Dihydromyrcenol	1076	1074	-	-	-	0.34 (21.2)	-
15	456	0.720	Linalool oxide isomer (furanoid) <sup>h, i</sup>	1097	1094	0.08 <sup>f</sup>	-	0.20 (6.4)	-	0.12 (22.0)
16	462	0.820	Linalool <sup>h</sup>	1108	1101	2.51 (5.1)	11.55 (25.9)	7.46 (10.5)	2.31 (10.3)	7.48 (13.6)
17	468	0.950	Hotrienol	1122	1108	0.87 (21.1)	2.59 (6.3)	1.98 (1.6)	0.19 (10.5)	0.94 (8.9)
18	474	0.510	Rose oxide	1117	1114	0.67 (19.2)	-	1.26 (22.9)	-	0.34 (9.5)
19	480	0.870	Fenchol	1118	1121	-	-	-	0.30 (26.5)	-
20	492	0.510	Rose oxide isomer	1130	1131	0.24 (7.8)	0.39 (26.6)	0.25 (25.9)	-	0.10 (10.6)
21	498	0.600	Artemisia alcohol	1083	1141	1.18 (28.1)	0.35 (9.9)	0.29 (19.6)	0.45 (3.6)	1.87 (21.8)
22	504	0.740	Camphor	1147	1148	0.74 (17.1)	0.14 (29.3)	-	0.65 (24.8)	-
23	510	0.650	Citronella <sup>h</sup>	1159	1154	-	0.56 (6.3)	0.35 (16.2)	-	0.42 (7.7)
24	516	0.990	Hotrienol isomer	1122	1162	2.86 (30.4)	2.04 (0.5)	2.00 (5.6)	-	1.67 (15.8)
25	522	0.690	Pinocarvone	1164	1167	1.11 (6.7)	1.58 (11.9)	-	1.34 (18.9)	-
26	528	0.850	Menthol <sup>h</sup>	1173	1174	0.14 (17.9)	0.14 (2.4)	0.21 (2.1)	-	0.14 <sup>e</sup> (25.1)
27	528	0.990	Borneol <sup>h</sup>	1172	1174	-	1.54 (22.7)	-	-	-
28	528	1.070	Epoxylinalool	1173	1175	2.43 (14.1)	2.86 (29.0)	1.83 (14.2)	0.47 (10.7)	3.06 (29.5)
29	534	0.787	Terpinen-4-ol	1181	1181	1.07 (17.8)	1.00 (13.7)	-	1.93 (28.9)	-
30	540	1.380	<i>p</i> -Cymen-8-ol	1203	1188	-	-	-	-	-
31	546	0.500	3(10)-Caren-2-ol	1211	1194	0.47 (11.3)	-	0.25 (6.6)	0.19 (9.4)	-
32	546	0.920	$\alpha$ -Terpineol <sup>h</sup>	1206	1194	1.67 (17.9)	1.53 (22.1)	0.77 (9.6)	1.57 (27.7)	0.73 (6.8)
33	576	0.950	$\beta$ -Citronellol <sup>h</sup>	1237	1230	-	-	-	-	0.89 (14.3)
34	576	1.050	<i>trans</i> -Geraniol <sup>h</sup>	1235	1230	-	-	-	-	-
35	588	0.750	<i>m/z</i> 59, 68, 43	-	1244	0.38 (16.2)	0.60 (22.6)	-	-	0.12 (24.6)
36	588	0.800	Citral isomer <sup>h, i</sup>	1241	1244	1.36 (1.7)	0.90 (25.1)	-	1.76 (13.6)	0.28 (29.9)
37	588	0.910	Carvone <sup>h</sup>	1245	1244	0.17 (21.3)	-	-	0.22 (6.4)	-
38	600	1.070	Nerol <sup>h</sup>	1242	1258	2.03 (13.7)	2.51 (14.2)	0.99 (22.1)	-	1.40 (8.2)
39	612	0.820	Citral isomer <sup>h, i</sup>	1287	1272	2.11 (27.2)	1.96 (16.7)	0.90 (4.1)	3.00 (13.9)	1.07 (3.3)
40	684	0.600	$\beta$ -Terpinyl acetate	-	1357	3.85 (16.6)	2.32 (8.9)	0.65 (15.2)	6.20 (9.6)	0.43 (16.0)
41	702	0.607	Geranyl acetate	1383	1385	6.53 (19.4)	0.93 (22.9)	-	3.63 (24.1)	0.42 (22.8)
42	714	0.680	10-(Acetyl methyl)-3-carene	1380	1401	1.95 (28.2)	9.71 (18.6)	5.73 (23.7)	0.04 <sup>f</sup>	4.18 (2.9)
Subtotal (GC Peak Area)						<b>34.34</b>	<b>45.64</b>	<b>25.12</b>	<b>24.57</b>	<b>26.03</b>
Subtotal (%)						<b>11.3</b>	<b>12.7</b>	<b>17.8</b>	<b>11.9</b>	<b>24.9</b>
Subtotal (Number of Compounds)						<b>22</b>	<b>21</b>	<b>17</b>	<b>17</b>	<b>20</b>

<b>Nosioprenoids</b>								
43	402	0.620	2,2,6-Trimethyl-cyclohexanone	1051	1034	1.59 (29.9)	1.62 (7.4)	0.78 (5.7)
44	504	1.080	Ketoisophorone	1171	1148	0.19 (11.3)	0.74 (14.9)	0.11 (21.1)
45	552	0.830	Safranal	1241	1201	-	-	-
46	570	0.670	$\beta$ -Cyclocitral	1261	1222	1.18 (21.4)	0.89 (7.3)	0.46 (117.)
47	636	0.570	Dihydroedulan	1289	1300	20.67 (30.7)	49.97 (8.9)	18.57 (23.0)
48	654	0.500	Theaspirane	1308	1322	-	0.27 (17.0)	0.11 (19.4)
49	708	0.760	Damascenone	1379	1393	-	0.23 (28.4)	0.18 (28.6)
50	738	0.740	$\alpha$ -Ionone	1422	1432	0.10 (7.2)	-	-
51	744	0.950	Megastigma-3,5-dien-9-ol	1430	1440	0.14 (6.2)	0.33 (7.9)	0.28 (18.6)
52	750	0.850	$\beta$ -Ionon-5,6-epoxide	1428	1447	0.69 (24.8)	0.09 (18.3)	0.17 (29.1)
53	756	0.700	Geranyl acetone <sup>h</sup>	1454	1455	4.91 (19.2)	5.47 (27.1)	3.27 (22.4)
54	780	0.680	$\alpha$ -Methyl ionone	1486	1486	0.19 (18.5)	0.11 (26.4)	0.10 (6.0)
55	780	0.780	$\beta$ -Ionone <sup>h</sup>	1481	1487	-	0.13 (11.9)	0.23 (4.0)
56	900	0.970	Methyl dihydrojasmonate	1650	1660	0.09 <sup>e</sup> (9.7)	-	0.07 (12.1)
Subtotal (GC Peak Area)								
					29.62	59.84	24.29	8.65
Subtotal (%)								
					9.7	16.7	17.2	4.2
Subtotal (Number of Compounds)								
					10	11	12	6
<b>Sesquiterpenic compounds</b>								
<i>Hydrocarbon-type</i>								
57	678	0.490	$\beta$ -Cubebene	1387	1354	0.03 <sup>f</sup>	0.73 (8.4)	2.33 (12.4)
58	702	0.500	$\alpha$ -Copaene <sup>h</sup>	1375	1385	0.89 (27.9)	-	0.19 (14.6)
59	708	0.510	$\beta$ -Bourbonene	1379	1393	-	2.70 (8.4)	-
60	714	0.540	$\beta$ -Elemene	1380	1401	-	-	1.17 (19.5)
61	726	0.540	Longifolene	1395	1431	-	0.72 (24.4)	1.06 (23.5)
62	738	0.540	$\beta$ -Caryophyllene <sup>h</sup>	1417	1432	-	2.24 (16.0)	2.71 (14.0)
63	750	0.480	Aromadendrene	1447	1447	10.82 (10.1)	13.96 (11.3)	1.16 (7.9)
64	762	0.560	$\alpha$ -Humulene <sup>h</sup>	1450	1462	0.13 (20.5)	5.19 (20.5)	16.81 (13.1)
65	792	0.506	$\alpha$ -Murolene	1490	1499	3.89 (13.7)	-	2.22 (25.7)
66	810	0.570	$\Delta$ -Cadinene	1525	1528	0.94 (11.7)	1.29 (17.1)	4.30 (9.2)
67	810	0.630	Calamenene	1525	1528	0.30 (15.6)	0.23 (13.4)	0.22 (16.4)
68	828	0.680	$\alpha$ -Calacorene	1554	1556	0.03 (21.6)	0.06 (8.4)	0.25 (28.3)
Subtotal (GC Peak Area)								
					16.79	32.55	17.13	24.04
Subtotal (%)								
					5.5	9.1	12.2	11.6
Subtotal (Number of Compounds)								
					8	9	10	9
<i>Oxygen containing</i>								
69	822	0.810	$\beta$ -Bourbonen-13-ol	-	1547	0.48 (25.6)	0.51 (21.2)	0.38 (21.7)
70	840	0.670	Epiglobulol	1588	1572	2.60 (14.3)	1.18 (28.1)	0.50 (9.0)
71	858	0.710	Caryophyllene oxide	1610	1601	0.52 (26.6)	0.67 (1.8)	1.54 (29.5)
72	870	0.730	Globulol	1592	1618	-	-	1.45 (20.5)
73	888	0.730	Cubenol	1643	1643	1.15 (16.8)	0.48 (18.4)	1.59 (10.1)
74	894	0.830	t-Cadinol	1650	1651	-	-	0.41 (8.6)
75	918	0.900	m/z 91, 119, 105	-	1685	0.48 (6.3)	0.27 (7.1)	0.31 (14.9)
76	1014	0.710	m/z 69, 41, 55	-	1841	1.44 (22.0)	0.84 (19.5)	0.40 (17.3)
Subtotal (GC Peak Area)								
					6.68	4.33	4.72	2.82
Subtotal (%)								
					2.2	1.2	3.4	1.4
Subtotal (Number of Compounds)								
					6	6	6	4
Total								
					305.04	359.14	140.86	207.23
Number of identified compounds								
					56	56	54	46
								54

<sup>a</sup> Retention times for first ( $^1t_R$ ) and second ( $^2t_R$ ) dimensions in seconds.

<sup>b</sup> RI, Retention Index reported in the literature for Equity-5 GC column or equivalents.

<sup>c</sup> RI: Retention Index obtained through the modulated chromatogram.

<sup>d</sup> Mean of three independent assays (n=3). GC peak areas were expressed as arbitrary units.

<sup>e</sup> The compound was detected in two assays.

<sup>f</sup> The compound was detected in one assay.

<sup>g</sup> The relative amount (%) for the different identified chemical families represents their relative content compared to the total content.

<sup>h</sup> Identification confirmed by chemical standards

<sup>i</sup> The used standards are a mixture of isomers

**Table S3 Monoterpene, sesquiterpenic and norisoprenoid metabolites detected in ‘Bastardeira’ elderberries (*S. nigra* L.) during ripening, from the harvesting season of 2013. The harvesting date in light gray corresponds the ripe stage.**

Peak number	${}^1t_R$ <sup>a</sup> (s)	${}^2t_R$ <sup>a</sup> (s)	Compound	RI <sub>lit</sub> <sup>b</sup>	RI <sub>calc</sub> <sup>c</sup>	GC Peak Area (x10 <sup>6</sup> ) <sup>d</sup> and RSD (%)									
						2 <sup>nd</sup> Aug	8 <sup>th</sup> Aug	21 <sup>st</sup> Aug	28 <sup>th</sup> Aug	5 <sup>th</sup> Sep					
<b>Monoterpeneic compounds</b>															
<i>Hydrocarbon-type</i>															
1	312	0.430	$\alpha$ -Pinene	941	938	14.61 (18.5)	7.94 (11.9)	7.31 (0.3)	10.45 (2.8)	2.21 (8.0)					
2	330	0.490	Verbenene	967	957	0.09 (12.0)	-	-	-	-					
3	342	0.401	Camphepane	960	961	0.17 (19.0)	0.12 (1.2)	0.16 (10.4)	0.25 (14.5)	-					
4	348	0.470	$\beta$ -Pinene	987	975	6.34 (6.8)	7.45 (14.5)	7.15 (10.2)	17.51 (14.3)	1.75 (15.8)					
5	360	0.500	Myrcene	1008	988	2.83 (27.5)	2.47 (29.7)	3.39 (20.6)	5.41 (8.7)	0.55 (23.4)					
6	378	0.447	$\beta$ -Phellandrene	1035	1008	1.47 (32.4)	0.36 (9.0)	0.59 (25.3)	0.76 (9.9)	0.27 (24.8)					
7	396	0.500	Limonene <sup>h</sup>	1035	1027	130.17 (32.3)	112.77 (21.7)	13.26 (14.3)	53.03 (4.6)	47.80 (19.9)					
8	396	0.570	p-Cymene <sup>h</sup>	1039	1027	17.38 (28.2)	18.96 (11.6)	16.63 (14.8)	11.57 (11.7)	4.82 (17.7)					
9	426	0.590	1,3,8-p-Menthatriene	1121	1060	14.43 (19.3)	13.57 (24.6)	21.17 (20.0)	25.31 (12.0)	4.45 (24.0)					
10	456	0.530	Terpinolene	1097	1094	1.41 (23.9)	0.87 (21.6)	1.17 (22.1)	2.18 (12.3)	0.19 (8.3)					
11	456	0.620	p-Cymenene	1090	1094	1.69 (5.3)	1.35 (20.2)	1.53 (21.3)	2.25 (5.0)	0.13 (25.9)					
12	582	0.620	<i>m/z</i> 93, 43, 77	-	1237	0.18 (8.7)	0.29 (7.8)	-	-	-					
Subtotal (GC Peak Area)						190.15	166.07	72.36	128.74	62.14					
Subtotal (Number of Compounds)						12	11	10	10	9					
<i>Oxygen containing</i>															
13	438	0.640	Linalool oxide isomer (furanoid) <sup>h,i</sup>	1078	1074	-	-	0.05 <sup>f</sup>	-	-					
14	438	0.730	Dihydromyrcenol	1076	1074	-	-	0.88 (10.2)	1.21 (16.1)						
15	456	0.720	Linalool oxide isomer (furanoid) <sup>h,i</sup>	1097	1094	0.25 (25.5)	-	-	-						
16	462	0.820	Linalool <sup>h</sup>	1108	1101	6.37 (8.3)	5.56 (7.1)	3.06 (24.9)	2.03 (9.9)	1.87 (14.4)					
17	468	0.950	Hotrienol	1122	1108	4.52 (24.0)	0.50 (8.2)	-	-	0.20 <sup>e</sup> (6.7)					
18	474	0.510	Rose oxide	1117	1114	0.87 (17.9)	2.03 (27.3)	0.55 (19.7)	0.15 (25.4)	0.79 (22.7)					
19	480	0.870	Fenchol	1118	1121	-	-	-	0.37 (26.1)	-					
20	492	0.510	Rose oxide isomer	1130	1131	0.25 (2.7)	0.44 (27.0)	0.17 (2.5)	-	0.37 (8.4)					
21	498	0.600	Artemisia alcohol	1083	1141	0.33 (27.6)	0.14 (25.9)	1.18 (9.9)	-	0.45 (4.6)					
22	504	0.740	Camphor	1147	1148	0.36 (14.1)	-	-	-	-					
23	510	0.650	Citronellal <sup>h</sup>	1159	1154	0.49 (17.3)	0.09 (5.4)	-	-	0.26 (10.8)					
24	516	0.990	Hotrienol isomer	1122	1162	1.37 (21.5)	0.62 (9.8)	0.77 (11.9)	0.50 (14.0)	0.40 (23.7)					
25	522	0.690	Pinocarvone	1164	1167	1.71 (26.9)	0.50 (32.5)	0.98 (12.2)	1.41 (15.5)	-					
26	528	0.850	Menthol <sup>h</sup>	1173	1174	-	-	0.15 (24.5)	0.13 (28.8)	-					
27	528	0.990	Borneol <sup>h</sup>	1172	1174	0.72 (4.9)	1.14 (20.8)	0.20 <sup>e</sup> (20.1)	-	-					
28	528	1.070	Epoxylinalool	1173	1175	21.32 (23.6)	2.22 (22.1)	2.77 (31.9)	1.84 (16.1)	2.87 (7.7)					
29	534	0.787	Terpinen-4-ol	1181	1181	0.63 (11.6)	0.70 (31.1)	0.57 (28.7)	1.14 (11.3)	-					
30	540	1.380	p-Cymen-8-ol	1203	1188	0.23 (12.3)	0.06 <sup>f</sup>	0.06 <sup>e</sup> (5.4)	0.01 <sup>f</sup>	-					
31	546	0.500	3(10)-Caren-2-ol	1211	1194	0.24 (24.1)	0.39 (12.8)	0.30 (23.6)	1.11 (7.2)	0.14 (7.7)					
32	546	0.920	$\alpha$ -Terpineol <sup>h</sup>	1206	1194	1.19 (29.0)	0.90 (21.4)	0.80 (26.7)	2.35 (18.2)	0.18 (10.2)					
33	576	0.950	$\beta$ -Citronellol <sup>h</sup>	1237	1230	0.72 (0.4)	-	-	-	0.46 (10.3)					
34	576	1.050	<i>trans</i> -Geraniol <sup>h</sup>	1235	1230	0.70 (4.9)	1.13 (31.6)	-	-	-					
35	588	0.750	<i>m/z</i> 59, 68, 43	-	1244	-	0.09 <sup>f</sup>	0.03 <sup>f</sup>	-	0.83 (27.5)					
36	588	0.800	Citral isomer <sup>h,i</sup>	1241	1244	-	0.48 (29.8)	0.85 (4.8)	1.09 (1.4)	0.36 (21.8)					
37	588	0.910	Carvone <sup>h</sup>	1245	1244	0.16 (19.1)	0.16 (30.2)	0.22 (29.2)	-	-					
38	600	1.070	Nerol <sup>h</sup>	1242	1258	2.09 (25.2)	2.11 (17.9)	1.71 (3.8)	0.40 (15.4)	0.76 (8.5)					
39	612	0.820	Citral isomer <sup>h,i</sup>	1287	1272	1.44 (22.4)	1.81 (13.2)	1.54 (22.8)	3.27 (18.6)	1.40 (15.1)					
40	684	0.600	$\beta$ -Terpinyl acetate	-	1357	1.64 (6.6)	0.46 (13.7)	2.31 (15.9)	3.63 (5.2)	0.18 (20.7)					
41	702	0.607	Geranyl acetate	1383	1385	0.70 (11.6)	2.83 (16.5)	0.44 (13.2)	0.89 (20.3)	0.17 (25.2)					
42	714	0.680	10-(Acetyl methyl)-3-carene	1380	1401	0.71 (15.0)	6.53 (16.9)	1.34 (24.0)	0.55 (26.2)	1.31 (1.7)					
Subtotal (GC Peak Area)						48.28	29.8	18.85	21.6	13.62					
Subtotal (Number of Compounds)						15.7	10.1	15.0	13.0	13.5					
Subtotal (GC Peak Area)						24	23	22	18	19					

<b>Nosioprenoids</b>											
43	402	0.620	2,2,6-Trimethyl-cyclohexanone	1051	1034	5.96 (20.7)	4.43 (16.1)	1.18 (17.1)	-	0.75 (3.4)	
44	504	1.080	Ketoisophorone	1171	1148	0.79 (7.5)	0.23 (15.5)	0.08 (28.8)	0.06 <sup>f</sup>	0.05 (18.9)	
45	552	0.830	Safranal	1241	1201	0.53 (3.4)	0.03 <sup>f</sup>	-	-	-	
46	570	0.670	$\beta$ -Cyclocitral	1261	1222	4.77 (29.8)	3.70 (29.4)	0.65 (15.0)	0.15 (9.1)	0.27 (15.2)	
47	636	0.570	Dihydroedulan	1289	1300	21.98 (24.5)	53.47 (5.8)	9.93 (22.4)	4.63 (16.2)	14.74 (15.9)	
48	654	0.500	Theaspirane	1308	1322	0.08 <sup>f</sup>	0.37 (8.8)	-	-	-	
49	708	0.760	Damascenone	1379	1393	1.59 (3.9)	-	-	-	-	
50	738	0.740	$\alpha$ -Ionone	1422	1432	0.10 (18.7)	0.37 <sup>e</sup> (9.0)	0.14 (20.2)	-	0.08 (2.4)	
51	744	0.950	Megastigma-3,5-dien-9-ol	1430	1440	0.16 (18.5)	0.21 (16.8)	-	-	-	
52	750	0.850	$\beta$ -Ionon-5,6-epoxide <sup>h</sup>	1428	1447	-	0.41 (13.7)	0.25 (4.5)	0.10 (14.8)	0.11 (9.6)	
53	756	0.700	Geranyl acetone <sup>h</sup>	1454	1455	3.52 (16.0)	4.42 (14.7)	3.22 (26.6)	1.49 (29.1)	1.77 (9.8)	
54	780	0.680	$\alpha$ -Methyl ionone	1486	1486	0.14 (13.8)	0.20 (18.7)	0.07 (7.0)	-	-	
55	780	0.780	$\beta$ -Ionone <sup>h</sup>	1481	1487	0.30 <sup>e</sup> (10.1)	0.85 (30.4)	0.22 (15.9)	-	0.07 (26.4)	
56	900	0.970	Methyl dihydrojasmonate	1650	1660	-	-	0.10 (5.7)	-	0.02 <sup>f</sup>	
				<b>Subtotal (GC Peak Area)</b>		<b>39.31</b>	<b>68.4</b>	<b>15.67</b>	<b>6.4</b>	<b>17.54</b>	
				<b>Subtotal (%)</b>		<b>12.7</b>	<b>23.2</b>	<b>12.5</b>	<b>3.8</b>	<b>17.4</b>	
				<b>Subtotal (Number of Compounds)</b>		<b>12</b>	<b>12</b>	<b>10</b>	<b>5</b>	<b>9</b>	
<b>Sesquiterpenic compounds</b>											
<i>Hydrocarbon-type</i>											
57	678	0.490	$\beta$ -Cubebene	1387	1354	0.08 (2.4)	0.18 (26.0)	1.26 (4.7)	0.06 (26.1)	0.08 <sup>f</sup>	
58	702	0.500	$\alpha$ -Copaene <sup>h</sup>	1375	1385	0.52 (30.3)	0.82 (19.1)	0.60 (6.8)	0.58 (20.7)	0.27 (4.6)	
59	708	0.510	$\beta$ -Bourbonene	1379	1393	-	0.83 (15.4)	-	-	-	
60	714	0.540	$\beta$ -Elemene	1380	1401	-	-	-	-	-	
61	726	0.540	Longifolene	1395	1431	1.40 (14.8)	3.16 (10.3)	-	-	0.72 (24.5)	
62	738	0.540	$\beta$ -Caryophyllene <sup>h</sup>	1417	1432	1.42 (10.7)	17.16 (14.8)	0.40 (22.5)	1.88 (6.3)	0.31 (24.2)	
63	750	0.480	Aromadendrene	1447	1447	17.05 (5.5)	3.58 (10.1)	6.35 (25.0)	2.50 (11.8)	5.03 (23.8)	
64	762	0.560	$\alpha$ -Humulene <sup>h</sup>	1450	1462	1.58 (7.3)	2.41 (21.0)	0.66 (5.0)	-	-	
65	792	0.506	$\alpha$ -Muurolene	1490	1499	1.30 (21.5)	0.26 (18.3)	2.34 (19.7)	1.12 (10.3)	-	
66	810	0.570	$\Delta$ -Cadinene	1525	1528	0.32 (29.2)	0.15 (23.3)	1.04 (25.8)	-	0.28 (26.1)	
67	810	0.630	Calamenene	1525	1528	0.21 (28.1)	0.11 (25.8)	1.17 (23.9)	0.04 (29.3)	0.10 (19.6)	
68	828	0.680	$\alpha$ -Calacorene	1554	1556	0.08 <sup>f</sup>	0.11e (3.4)	-	-	-	
				<b>Subtotal (GC Peak Area)</b>		<b>23.69</b>	<b>28.7</b>	<b>13.11</b>	<b>6.2</b>	<b>6.74</b>	
				<b>Subtotal (%)</b>		<b>7.7</b>	<b>9.7</b>	<b>10.5</b>	<b>3.7</b>	<b>6.7</b>	
				<b>Subtotal (Number of Compounds)</b>		<b>10</b>	<b>11</b>	<b>8</b>	<b>6</b>	<b>7</b>	
<i>Oxygen containing</i>											
69	822	0.810	$\beta$ -Bourbonen-13-ol	-	1547	-	-	-	-	-	
70	840	0.670	Epiglobulol	1588	1572	0.68 (28.2)	0.49 (21.8)	0.68 (16.4)	1.04 (27.1)	-	
71	858	0.710	Caryophyllene oxide	1610	1601	2.34 (25.1)	0.72 (13.7)	2.14 (1.0)	2.25 (29.7)	0.33 (16.0)	
72	870	0.730	Globulol	1592	1618	2.79 (4.3)	0.13 (3.1)	-	-	-	
73	888	0.730	Cubenol	1643	1643	-	-	-	0.30 (16.7)	-	
74	894	0.830	<i>t</i> -Cadinol	1650	1651	0.21 (2.0)	0.19 (6.0)	1.45 (22.1)	-	-	
75	918	0.900	<i>m/z</i> 91, 119, 105	-	1685	0.34 (13.3)	0.30 (19.1)	0.45 (6.4)	0.33 (5.6)	0.21 (2.4)	
76	1014	0.710	<i>m/z</i> 69, 41, 55	-	1841	0.60 (26.7)	0.64 (23.8)	0.57 (15.4)	-	0.11 (13.4)	
				<b>Subtotal (GC Peak Area)</b>		<b>7.05</b>	<b>2.2</b>	<b>5.27</b>	<b>3.9</b>	<b>0.66</b>	
				<b>Subtotal (%)</b>		<b>2.3</b>	<b>0.7</b>	<b>4.2</b>	<b>2.4</b>	<b>0.7</b>	
				<b>Subtotal (Number of Compounds)</b>		<b>6</b>	<b>6</b>	<b>5</b>	<b>4</b>	<b>3</b>	
				<b>Total</b>		<b>308.47</b>	<b>295.2</b>	<b>125.27</b>	<b>166.8</b>	<b>100.70</b>	
				<b>Number of identified compounds</b>		<b>64</b>	<b>63</b>	<b>55</b>	<b>43</b>	<b>47</b>	

<sup>a</sup> Retention times for first ( $t_R$ ) and second ( $t_{R2}$ ) dimensions in seconds.

<sup>b</sup> RI, Retention Index reported in the literature for Equity-5 GC column or equivalents.

<sup>c</sup> RI: Retention Index obtained through the modulated chromatogram.

<sup>d</sup> Mean of three independent assays (n=3). GC peak areas were expressed as arbitrary units.

<sup>e</sup> The relative amount (%) for the different identified chemical families represents their relative content compared to the total content.

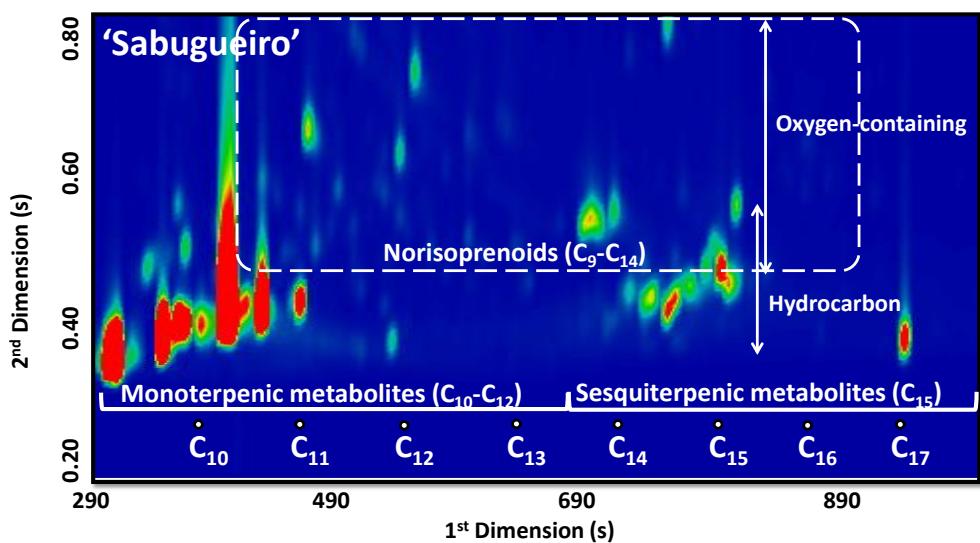
<sup>f</sup> The compound was detected in two assays.

<sup>g</sup> The compound was detected in one assay.

<sup>h</sup> The relative amount (%) for the different identified chemical families represents their relative content compared to the total content.

<sup>i</sup> Identification confirmed by chemical standards

<sup>j</sup> The used standards are a mixture of isomers



**Fig. S1** Blow up of total ion GC $\times$ GC–ToFMS chromatogram contour plot from ‘Sabugueiro’ ripe elderberries selected to illustrate structured chromatogram principle: clusters formed by structurally related compounds are highlighted. The white spots indicate the position of the series of alkanes (C<sub>10</sub>–C<sub>17</sub>).