



SUPPLEMENTARY MATERIAL TO

**Phytochemical study of the genus *Amphoricarpos***

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TABLE S-I. Volatile components profiles given as contribution of peak area of compounds relative to the total area of GC/FID signal from plants of genus *Amphoricarpos*

Component	R <sub>f</sub> <sup>a</sup>	t <sub>R</sub> min	Contributions of peak are (relative to the total area), %						
			*OR04	**KD05	**KT05	***VIS05	***VK05	***POP05	***SINJ05
Hex-2 <i>E</i> -enal	845	3.745	–	–	1.65	2.41	–	–	–
<i>n</i> -Nonane	900	4.102	–	1.17	–	0.79	–	–	–
1-Octen-3-ol	968	4.648	–	–	0.89	0.74	–	–	0.58
Dehydro-1,8-cineole	991	4.884	0.83	0.72	1.46	0.80	–	1.51	1.39
(2 <i>E</i> ,4 <i>E</i> )-Hepta-2,4-dienal	1010	5.039	–	0.88	1.76	–	2.30	–	1.25
Benzeneacetaldehyde	1042	6.101	4.76	3.70	2.84	0.99	2.09	3.27	4.44
5-Methyl-4-hexen-3-one		6.411	–	–	–	–	0.93	–	–
3,5-Octadiene-2-one		6.767	–	4.07	0.84	–	1.55	–	0.73
<i>n</i> -Nonan-1-al	1090	7.745	1.82	3.02	5.26	–	7.08	5.02	5.00
Phenethyl alcohol	1110	7.956	–	–	0.87	–	–	–	0.83
Camphor	1143	8.833	–	–	–	–	–	3.58	–
Nonan-1-ol	1171	9.741	–	0.43	0.84	–	1.58	0.87	0.73
Decanal	1198	10.722	5.28	12.83	13.58	4.20	11.98	8.52	9.96
2-Decenal	1261	12.908	–	–	–	–	0.73	–	–

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Component	RI <sup>a</sup>	t <sub>R</sub> min	Contributions of peak are (relative to the total area), %						
			*OR04	**KD05	**KT05	***VIS05	***VK05	***POP05	***SINJ05
Pelargonic acid	1275	13.070	–	–	1.23	–	1.46	0.90	–
Indole	1288	13.390	–	0.43	0.57	0.70	1.47	1.48	2.83
( <i>E,E</i> )-2,4-Decadienal	1312	14.069	–	0.64	0.97	–	2.67	–	0.84
Capric acid		15.971	–	–	–	–	0.72	–	–
Sativen		16.238	1.13	2.88	3.48	0.49	–	2.13	2.17
$\beta$ -Caryophyllene	1414	17.028	6.80	1.55	0.90	3.38	–	1.57	0.84
Geranyl acetone	1451	18.025	1.34	0.49	0.48	0.83	0.87	–	–
$\beta$ -Ionone	1486	18.982	–	0.72	0.73	–	1.33	–	1.16
$\beta$ -Selinene	1490	19.084	1.07	1.55	1.43	0.61	1.93	1.29	1.32
$\gamma$ -Cadinene	1513	20.060	1.33	0.50	0.55	1.05	0.75	–	–
$\delta$ -Cadinene	1524	20.214	1.35	1.41	1.02	1.04	1.53	1.69	2.64
Caryophyllene oxide	1584	21.840	37.68	36.68	28.53	53.07	10.96	24.86	24.07
Longifolenaldehyde		22.309	–	0.51	–	–	–	–	–
Humulene epoxide II	1606	22.443	–	0.47	–	0.70	–	–	–
Diepicedrene-1-oxide		23.246	5.65	6.15	3.70	7.76	1.22	3.45	2.87
<i>cis</i> -6-Do-decen-4-olide		23.771	3.11	1.44	1.65	2.49	1.73	0.94	1.24
Myristic acid		26.781	2.11	–	1.11	–	1.95	1.73	1.26
Hexahydrophatensyl acetone	1849	28.709	2.72	1.96	1.79	1.42	2.83	3.49	4.17
Palmitic acid	2003	31.769	9.93	7.50	8.18	4.33	18.39	17.40	15.52
<i>n</i> -Heneicosane	2100	34.584	2.07	0.62	1.08	0.80	5.68	3.46	1.62
Linolenic acid	2170	35.391	1.56	–	0.73	–	1.07	–	1.32
Oleic acid	2175	35.527	–	–	1.08	–	3.14	4.89	1.62
<i>n</i> -Tricosane	2302	38.771	–	0.62	–	–	–	–	–
<i>n</i> -Heptacosane	2704	46.228	0.97	0.79	0.93	–	1.94	1.54	1.90
<i>n</i> -Nonacosane	2898	49.578	1.01	0.67	1.02	–	2.21	1.64	1.45
Total			92.52	94.71	91.15	90.90	92.09	95.23	94.37

\**A. neumayeri* Vis., \*\**A. autariatus* ssp. *autariatus* and \*\*\**A. autariatus* ssp. *Bertisceus* (according to Blečić and Mayer<sup>2</sup>); <sup>a</sup>Retention indices (RI) are calculated based on the retention times of the *n*-alkanes analyzed under the same conditions

TABLE S-II. Parameters for statistical analysis obtained by quantitative <sup>1</sup>H-NMR, gravimetric, LC-DAD and LC-ESI-MS analyses of extracts of plants of the genus *Amphoricarpus*

Population	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	
Code	OR04	OR05	OR07	KT04	KT05	KT11	KD05	SINJ04	SINJ05	PR01	ZEL02	ZEL09	VIS04	VIS05	VIS07	VK05	PLK05	POP05	KOT06	KOT011	GR07	
Entry Component	Content of sesquiterpene lactones in crude extracts of aerial parts (BEM) or on leaf-surface (SL) of various species of the genus <i>Amphoricarpus</i> , %.																					
1	$W_{\text{BEM}}$	1.76	1.60	2.26	0.52	0.57	–	0.52	0.86	0.97	0.61	0.75	–	0.93	1.04	1.06	0.83	0.72	1.12	0.36	–	0.52
2	$W_{\text{SL}}$	1.76	2.23	3.36	1.29	1.42	–	1.28	1.60	1.51	1.04	1.64	–	1.48	1.60	1.66	1.04	1.93	1.58	1.20	–	1.02
Content of the most abundant lactones in SL extracts based on the areas of LC/DAD peaks, % of all peaks detected at 210 nm.																						
3	<b>1</b>	0.00	0.00	0.00	0.00	0.00	–	0.00	2.25	0.00	4.67	6.85	–	17.28	0.90	15.17	0.90	15.46	0.90	16.10	–	0.90
4	<b>2</b>	6.92	12.03	4.41	0.00	0.00	–	0.00	1.79	2.35	4.28	3.98	–	1.54	6.16	4.19	14.95	2.05	3.18	4.86	–	1.87
5	<b>3</b>	23.19	33.85	19.99	0.00	0.00	–	0.00	4.59	5.58	3.48	10.57	–	0.90	14.11	10.65	24.42	10.16	11.85	7.87	–	8.29
6	<b>4</b>	18.24	7.08	20.30	0.00	0.00	–	0.00	0.00	0.00	0.00	0.00	–	0.00	0.00	0.00	0.00	0.00	0.00	0.00	–	0.00
7	<b>7</b>	6.57	2.01	8.85	0.00	0.00	–	0.00	0.00	0.00	0.00	0.00	–	0.00	0.00	0.00	0.00	0.00	0.00	0.00	–	0.00
8	<b>8</b>	13.94	11.41	12.36	0.00	0.00	–	0.00	3.45	3.13	0.00	1.12	–	2.75	4.41	3.33	4.26	1.92	8.49	8.85	–	5.43
9	<b>9</b>	0.00	0.00	0.00	0.90	21.57	–	21.65	0.00	0.00	0.00	0.00	–	0.00	0.00	0.00	0.00	0.00	0.00	0.00	–	0.00
10	<b>11</b>	0.00	0.00	0.00	38.59	7.80	–	39.52	22.80	25.10	6.03	5.07	–	7.20	10.94	4.65	9.47	7.23	18.21	2.68	–	20.43
11	<b>13</b>	5.16	2.00	4.70	25.55	21.39	–	26.90	27.39	31.55	9.70	18.65	–	5.24	24.56	10.53	17.54	11.54	17.55	14.98	–	19.76
12	<b>14</b>	0.00	0.00	0.00	16.23	7.80	–	2.12	10.67	7.38	2.48	1.27	–	0.90	3.25	1.31	6.13	1.18	4.86	2.51	–	8.43
13	<b>16</b>	0.00	0.00	0.00	0.00	0.00	–	0.00	0.90	0.00	0.90	0.90	–	6.57	0.90	2.85	0.00	8.07	0.00	0.90	–	0.00
14	<b>19</b>	0.00	0.00	0.00	0.00	0.00	–	0.00	0.00	0.00	8.76	3.46	–	7.82	0.90	0.90	0.90	2.64	0.00	4.53	–	0.00
15	<b>20</b>	0.00	0.00	0.00	0.00	0.00	–	0.00	0.00	0.00	5.14	0.90	–	6.99	0.00	0.90	0.90	0.90	0.90	0.90	–	0.00
16	<b>22</b>	0.00	0.00	0.00	0.00	0.00	–	0.00	0.00	0.90	3.48	10.57	–	0.00	0.90	0.00	0.90	10.16	0.00	7.87	–	0.00
Content of the lactones in BEM extracts based on the areas of LC/ESI ToF MS (positive mode) peaks, % of all peaks detected.																						
17	<b>2</b>	6.34	5.58	2.43	0.36	0.24	0.29	0.06	1.84	1.44	1.54	3.70	4.42	1.76	3.04	0.05	9.41	1.71	3.63	–	2.65	0.96
18	<b>3</b>	24.43	30.65	14.31	0.91	1.46	0.44	0.03	4.94	5.58	6.75	11.66	2.52	6.57	11.31	1.57	17.75	2.47	8.06	–	1.76	7.79
19	<b>4</b>	11.40	19.88	39.28	0.95	1.19	0.28	1.32	4.73	4.54	2.90	6.74	0.91	10.49	9.66	5.55	4.45	2.21	13.69	–	1.93	6.61
20	<b>5</b>	0.19	0.10	1.45	0.40	0.56	0.85	0.55	3.07	2.06	0.11	1.79	0.85	0.22	0.36	0.04	0.19	0.17	2.26	–	1.04	0.92

Population	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	
Code	OR04	OR05	OR07	KT04	KT05	KT11	KD05	SINJ04	SINJ05	PR01	ZEL02	ZEL09	VIS04	VIS05	VIS07	VK05	PLK05	POP05	KOT06	KOT011	GR07	
21	6	4.46	3.57	7.95	0.23	0.22	0.03	0.14	0.06	4.01	0.19	0.88	0.51	0.64	1.68	0.33	0.64	0.53	0.30	–	0.98	5.24
22	7	12.55	3.99	9.87	0.42	0.38	0.06	0.40	1.48	6.49	0.24	0.23	0.12	2.45	2.46	0.17	0.06	0.29	6.12	–	1.39	2.01
23	8	14.33	12.67	5.82	0.40	0.29	0.21	0.01	2.01	1.72	1.98	1.54	0.12	1.38	3.12	0.50	2.96	1.61	7.05	–	0.11	3.03
24	11	7.26	5.02	3.04	32.26	44.03	32.78	36.05	24.87	10.56	4.70	11.44	5.12	13.97	11.00	2.37	13.52	3.84	23.47	–	1.18	19.90
25	13	7.34	11.81	10.70	46.31	23.22	45.72	59.47	31.95	39.38	23.14	14.68	9.67	10.52	31.45	13.58	30.33	7.30	14.11	–	9.16	31.83
26	14	0.28	0.25	0.05	10.05	14.48	10.58	0.89	8.36	7.91	0.74	1.83	2.15	2.03	3.35	0.16	5.78	2.54	5.10	–	1.38	3.92
27	15	0.19	0.14	0.08	1.12	0.88	0.54	0.42	4.37	1.92	0.97	4.65	5.98	0.62	0.97	0.07	1.75	0.55	0.42	–	5.29	0.24
28	17	0.07	0.05	0.04	0.03	0.02	0.03	0.02	0.06	0.02	0.40	0.39	1.67	0.21	0.08	0.31	0.15	0.89	0.10	–	2.35	0.01
Content of the lactones in SL extracts based on the areas of LC/ESI ToF/MS (positive mode) peaks, expressed as a percentage of all peaks detected.																						
29	2	6.18	7.67	3.39	2.39	0.27	0.29	0.08	3.02	3.62	0.05	3.90	3.93	1.59	5.47	2.05	11.64	5.10	4.00	–	4.47	1.73
30	3	21.14	30.84	15.59	0.91	0.54	0.15	0.10	6.01	6.67	0.59	10.63	4.70	0.77	6.06	10.40	15.92	5.70	9.97	–	7.45	9.42
31	4	22.73	20.21	33.05	0.52	1.50	0.43	1.54	3.09	5.01	1.17	4.30	2.15	6.71	5.22	6.36	2.38	2.95	10.23	–	1.50	3.77
32	5	0.16	0.63	0.05	5.27	0.24	0.84	0.79	0.13	5.79	0.06	0.30	1.06	0.92	0.28	0.26	0.24	3.79	4.37	–	2.04	1.32
33	6	2.64	3.22	9.42	0.70	0.32	0.02	0.33	0.20	3.60	0.04	0.86	0.16	1.46	4.53	1.42	0.10	3.10	0.09	–	3.62	4.95
34	7	3.48	4.95	10.37	1.43	0.16	0.11	0.58	2.03	3.79	0.12	0.18	0.16	2.62	1.78	0.21	0.04	4.36	4.02	–	4.27	1.48
35	8	10.75	9.71	7.35	2.46	0.16	0.37	0.07	1.95	2.22	0.23	1.08	0.23	2.56	4.21	1.86	3.97	2.97	8.27	–	0.24	4.20
36	11	2.19	4.68	4.10	6.95	30.00	36.74	25.48	19.04	5.59	4.67	12.05	0.30	4.53	4.67	6.38	6.05	1.27	19.48	–	0.60	20.74
37	13	14.29	9.01	12.42	43.07	45.76	48.73	66.43	32.36	35.67	0.11	35.86	1.17	13.90	29.95	12.16	31.97	0.75	19.02	–	2.16	28.62
38	14	0.22	0.15	0.11	5.67	13.27	4.83	3.20	8.54	8.10	0.26	2.14	2.64	1.77	4.45	1.26	8.67	5.74	6.74	–	3.93	6.95
39	17	0.19	0.23	0.06	0.32	0.03	0.02	0.03	0.33	0.06	0.47	0.22	2.07	0.69	0.82	0.35	0.12	3.51	0.08	–	2.91	0.06

OR – Orjen, KT – Tara Canyon, KD – Draga Canyon, SINJ – Sinjajevina, PR – Prokletije, ZEL – Zeletin, VIS – Visitor, VKOM – Vasojević's Kom, PLK – Planinica Kom, POP – Popadja, KOT – Kotlovi, GR – Greben; 01, 02, 04, 05, 06, 07, 09, 11 – year (2001, 2002, 2004, 2005, 2006, 2007, 2009, and 2011, respectively); BEM – crude extract of grounded dried aerial parts of plants in the petrol ether–diethylether–methanol (1:1:1) mixture; SL – polar (methanol soluble) fraction of dichloromethane extract of intact air-dried leaves; LC/DAD – liquid chromatography with diode-array detector; LC/ESI ToF MS – liquid chromatography with (electrospray ionization) time-of-flight mass spectrometer as detector

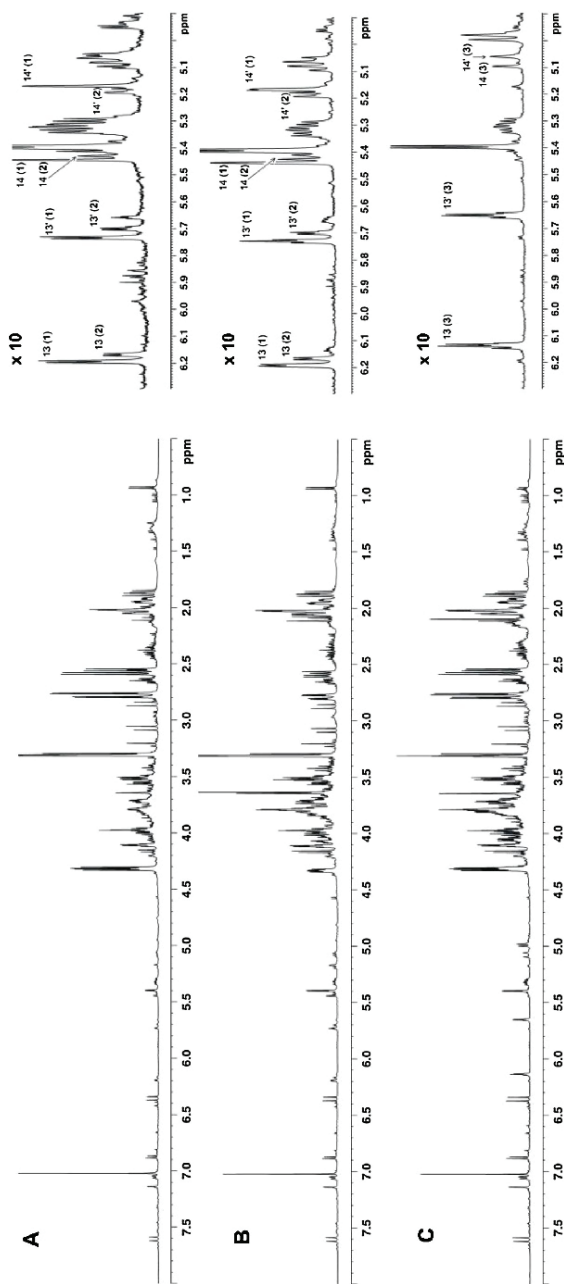


Fig. S-1. Examples of  $^1\text{H-NMR}$  spectra of the extracts of all three examined taxa; (A) – *A. autariatus* ssp. *autariatus*, (B) – *A. autariatus* ssp. *autariatus*; (C) – *A. neumayeri*; characteristic signals of amphitropolides in the spectral range 4.9–6.3 ppm are magnified 10 times (right part of the picture).