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Supplementary material

Two aspects of honeydew honey authenticity: application of advance analytical methods and chemometrics

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Content

Table S1. Number of samples of certain botanical origin collected per year

Botanical origin (BO)	Year of production						Total per BO
	2011	2012	2013	2014	2015	2016	
Silver fir	/	/	6	2	3	11	22
Hungarian oak	/	/	/	/	2	2	4
Evergreen oak	3	5	1	2	2	2	15
Montpellier maple	/	2	/	2	2	/	6
Conifers	/	1	1	3	4	8	17
Total per year	3	8	8	9	13	23	64

Table S2. Experimental conditions for determination on ICP-OES

Nebulizer	Concentric
Spray chamber	Cyclonic
Rf power (W)	1150
Principal argon flow rate (L/min)	12
Auxiliary argon flow rate (L/min)	0.5
Nebulizer argon flow rate (L/min)	0.5
Sample flow rate (mL/min)	1.0
Detector	CID86
Selected wavelengths (nm)	Al (308.2); Ca (422.6); Fe (238.2); K (769.8); Mg (280.2);

Table S3. Instrument operating conditions for determination on ICP-MS

Rf power (W)	1548
Gas flows (L/min)	13.9; 1.09; 0.8
Acquisition time	3 x 50s
Points per peak	3
Dwell time (ns)	10
Detector mode	Pulse
Measured isotopes	^{75}As, ^{137}Ba, ^{111}Cd, ^{59}Co, ^{53}Cr, ^{65}Cu ^{202}Hg, ^{55}Mn, ^{60}Ni, ^{207}Pb, ^{88}Se, ^{88}Sr, ^{66}Zn

Table S4. Parameters of linear models for determination of carbohydrate content in honeydew honey samples

	Slope	***r***	**SD**	**RSD (%)**	**LOD (mg/L)**	**LOQ (mg/L)**
Sorbitol	3.201	0.9983	0.131	3.79	0.028	0.093
Trehalose	2.232	0.9981	0.527	3.94	0.052	0.171
Arabinose	5.006	0.9974	0.640	4.61	0.026	0.087
Glucose	4.602	0.9982	7.220	4.07	0.040	0.132
Fructose	2.611	0.9970	5.,641	4.92	0.069	0.229
Melibiose	3.691	0.9981	0.446	4.25	0.030	0.097
Isomaltose	2.702	0.9987	2.748	3.36	0.031	0.101
Sucrose	1.370	0.9975	1.949	4.62	0.042	0.139
Melezitose	0.540	0.9997	0.122	1.72	0.052	0.171
Turanose	1.015	0.9976	0.207	4.47	0.041	0.134
Raffinose	1.863	0.9967	1.834	4.99	0.149	0.448
Maltose	2.175	0.9979	2.789	4.14	0.038	0.124
Panose	2.336	0.9981	1.862	3.91	0.117	0.387
Maltotriose	0.866	0.9971	1.567	4.82	0.145	0.478

Table S5. Parameters of descriptive statistics for $\delta^{13}C$ values

Botanical origin	Parameter	$\delta^{13}C$ honey	$\delta^{13}C$ protein
Abies alba Mill. (n = 22)	Mean	-25.39	-26.12
	Median	-25.44	-26.25
	St dev	0.60	0.52
	Min	-26.60	-26.86
	Max	-24.29	-25.04
Conifers (n = 17)	Mean	-25.46	-26.32
	Median	-25.31	-26.41
	St dev	0.78	0.60
	Min	-26.66	-27.21
	Max	-23.81	-25.40
Quercus frainetto Ten. (n = 4)	Mean	-25.50	-24.36
	Median	-25.18	-24.26
	St dev	0.56	0.28
	Min	-26.15	-24.68
	Max	-25.18	-24.15
Quercus ilex L. (n = 15)	Mean	-25.39	-25.64
	Median	-25.47	-25.84
	St dev	0.71	0.59
	Min	-26.48	-26.78
	Max	-24.00	-24.29
Acer monspessulanum L. (n = 6)	Mean	-24.83	-25.86
	Median	-25.12	-25.77
	St dev	1.23	0.54
	Min	-26.54	-26.82
	Max	-23.10	-25.22

Table S6. Parameters of descriptive statistics of sugars content in the honeydew honey (g/100g)

Botanical origin	Parameter	Tre*	Glu	Fru	Melibi	Suc	Isomal	Mel	Tur	Maltos	Sor	Ara	Pan	Mal	Raf
Abies alba Mill. (n = 22)	Mean	1.20	24.0	31.0	0.50	4.0	0.30	0.400	1.0	0.30	0.10	0.090	0.090	0.100	0.30
	Median	0.90	24.0	32.0	0.09	5.0	0.20	0.300	0.9	0.30	0.10	0.050	0.050	0.050	0.30
	St dev	0.90	3.0	4.0	0.90	2.0	0.30	0.400	0.6	0.30	0.20	0.200	0.200	0.400	0.30
	Min	0.10	19.0	24.0	0.01	0.8	0.01	0.003	0.3	0.01	0.01	0.010	0.009	0.003	0.02
	Max	3.70	28.0	36.0	4.10	6.0	1.01	1.300	2.2	1.00	0.40	0.500	0.600	1.400	1.10
Conifers (n = 17)	Mean	1.10	24.0	30.0	0.20	4.0	0.40	0.500	1.1	0.50	0.30	0.070	0.060	0.100	0.50
	Median	0.90	24.0	31.0	0.20	4.0	0.20	0.400	1.0	0.30	0.20	0.060	0.060	0.090	0.30
	St dev	0.90	3.0	4.0	0.20	2.0	0.50	0.500	0.4	0.40	0.20	0.080	0.060	0.080	0.60
	Min	0.30	21.0	24.0	0.01	2.0	0.03	0.020	0.5	0.03	0.01	0.004	0.002	0.005	0.05
	Max	3.80	29.0	36.0	0.70	7.0	1.60	1.400	1.8	1.10	0.60	0.300	0.190	0.300	1.70
Quercus ilex L. (n = 15)	Mean	1.20	24.0	31.0	0.20	4.0	0.40	0.500	1.1	0.40	0.20	0.100	0.100	0.300	0.40
	Median	1.10	23.0	31.0	0.10	4.0	0.20	0.400	0.9	0.30	0.30	0.050	0.070	0.040	0.10
	St dev	0.90	4.0	4.0	0.20	2.0	0.50	0.500	0.7	0.40	0.20	0.300	0.200	0.800	0.50
	Min	0.30	19.0	25.0	0.01	0.8	0.01	0.010	0.2	0.03	0.01	0.010	0.002	0.010	0.03
	Max	3.70	29.0	38.0	0.70	6.0	1.50	1.300	2.5	1.50	0.40	0.900	0.700	3.000	1.50
Quercus frainetto Ten. (n = 4)	Mean	0.90	25.0	32.0	0.60	4.0	0.50	0.300	1.0	0.80	0.30	0.070	0.040	0.030	0.50
	Median	0.90	26.0	35.0	0.60	5.0	0.40	0.300	0.9	0.80	0.30	0.050	0.040	0.040	0.40
	St dev	0.50	6.0	8.0	0.30	2.0	0.30	0.300	0.4	0.30	0.30	0.050	0.030	0.040	0.30
	Min	0.30	18.0	21.0	0.30	2.0	0.20	0.040	0.6	0.60	0.05	0.040	0.007	0.003	0.20
	Max	1.50	30.0	37.0	0.90	6.0	0.90	0.600	1.4	1.20	0.60	0.200	0.070	0.070	0.90
Acer monspessulanum L. (n = 6)	Mean	1.40	24.0	33.0	0.30	4.1	0.50	0.800	1.4	0.50	0.50	0.200	0.050	0.050	0.50
	Median	1.00	25.0	33.0	0.10	4.2	0.20	0.800	1.4	0.40	0.50	0.100	0.050	0.040	0.50
	St dev	0.90	3.0	3.0	0.30	0.8	0.70	0.200	0.7	0.40	0.40	0.100	0.050	0.040	0.30
	Min	0.60	21.0	30.0	0.06	3.0	0.10	0.500	0.5	0.20	0.02	0.050	0.020	0.020	0.07
	Max	2.80	28.0	37.0	0.70	4.9	1.80	0.900	2.1	1.00	0.90	0.400	0.100	0.100	0.80

*Tre - trehalose; Glu - glucose; Fru - fructose; Melibi - melibiose; Suc - sucrose; Isomal - isomaltose; Mel - melezitose; Tur - turanose; Maltos - maltose; Sor - sorbitol; Ara - arabinose; Pan - panose; Mal - maltotriose; Raf - raffinose.

Table S7. Parameters of descriptive statistics of elements content in the honeydew honey (mg/kg)

Botanical origin	Parameter	Ca	Fe	K	Mg	P	S	Al	Zn	Mn	Cu
Abies alba Mill. (n = 22)	Mean	14.0	1.60	2712	51.0	154	81.0	15.0	1.20	2.70	1.50
	Median	11.0	1.40	2775	51.0	151	83.0	15.0	1.20	2.60	1.50
	St dev	14.0	2.00	450	11.0	29	15.0	8.0	0.30	0.90	0.50
	Min	1.0	0.50	1861	25.0	114	52.0	5.0	0.90	1.40	0.50
	Max	56.0	5.70	3333	75.0	205	108.0	32.0	1.90	5.30	2.00
Conifers (n = 17)	Mean	19.0	2.00	2504	53.0	161	75.0	9.0	1.40	3.00	1.30
	Median	16.0	1.90	2493	53.0	157	75.0	10.0	1.20	2.60	1.10
	St dev	14.0	2.00	695	14.0	50	21.0	6.0	0.60	2.00	0.70
	Min	1.0	0.20	1110	33.0	104	43.0	0.9	0.70	0.60	0.50
	Max	50.0	4.90	4117	79.0	246	135.0	21.0	2.40	6.80	2.70
Quercus ilex L. (n = 15)	Mean	36.0	2.30	3090	56.0	245	86.0	0.40	1.70	1.10	1.00
	Median	31.0	1.40	3189	59.0	227	91.0	0.20	1.60	0.90	1.00
	St dev	22.0	4.00	516	18.0	82	19.0	0.60	2.00	1.00	0.40
	Min	8.0	0.01	1789	27.0	142	54.0	0.04	0.70	0.30	0.60
	Max	85.0	15.8	3687	99.0	372	119.0	1.40	5.70	3.70	1.80
Quercus frainetto Ten. (n = 4)	Mean	101.0	2.00	2937	154	238	111.0	0.10	1.00	26.0	1.20
	Median	94.0	3.00	3042	152	236	114.0	0.06	0.90	25.0	1.10
	St dev	23.0	2.00	261	21	45	10.0	0.20	0.60	3.0	0.30
	Min	83.0	1.00	2549	134	193	97.0	0.06	0.50	24.0	1.00
	Max	132.0	3.00	3112	177	288	118.0	0.40	1.70	31.0	1.50
Acer monspessulanum L. (n = 6)	Mean	24.0	0.90	2905	48.0	236	81.0	1.70	1.40	0.80	0.90
	Median	25.0	0.80	3134	51.0	233	80.0	0.30	1.20	0.60	0.80
	St dev	7.0	0.60	781	13.0	70	26.0	3.00	0.80	0.50	0.30
	Min	13.0	0.30	1817	31.0	153	54.0	0.09	0.80	0.40	0.60
	Max	30.0	1.90	3632	61.0	319	124.0	5.00	2.80	1.60	1.20

Table S7. Continuation

Botanical origin	Parameter	As	Ba	Cd	Co	Cr	Hg	Ni	Pb	Se	Sr
Abies alba Mill. (n=22)	Mean	0.0030	0.070	0.010	0.020	0.060	0.030	0.400	0.0010	0.0020	0.0300
	Median	0.0030	0.020	0.010	0.020	0.060	0.020	0.400	0.0004	0.0003	0.0200
	St dev	0.0030	0.200	0.004	0.006	0.030	0.030	0.200	0.0030	0.0040	0.0400
	Min	0.0010	0.001	0.007	0.010	0.030	0.004	0.040	0.0004	0.0001	0.0007
	Max	0.0110	0.400	0.020	0.040	0.100	0.100	0.700	0.0200	0.0100	0.2000
Conifers (n=17)	Mean	0.0030	0.090	0.010	0.020	0.060	0.030	0.300	0.0004	0.0020	0.0300
	Median	0.0030	0.030	0.010	0.020	0.060	0.020	0.300	0.0004	0.0001	0.0200
	St dev	0.0020	0.200	0.004	0.020	0.006	0.020	0.200	0.0001	0.0070	0.0300
	Min	0.0009	0.001	0.008	0.009	0.050	0.004	0.060	0.0004	0.0001	0.0030
	Max	0.0090	0.300	0.020	0.050	0.060	0.070	0.600	0.0004	0.0300	0.0800
Quercus ilex L. (n=15)	Mean	0.0020	0.090	0.009	0.010	0.060	0.020	0.100	0.0004	0.0040	0.0600
	Median	0.0020	0.080	0.007	0.009	0.060	0.020	0.070	0.0004	0.0040	0.0500
	St dev	0.0020	0.090	0.005	0.007	0.030	0.020	0.200	0.0005	0.0030	0.0400
	Min	0.0005	0.001	0.005	0.005	0.040	0.003	0.040	0.0004	0.0001	0.0200
	Max	0.0060	0.300	0.020	0.030	0.100	0.070	0.500	0.0006	0.0090	0.1000
Quercus frainetto Ten. (n=4)	Mean	0.0010	1.300	0.007	0.009	0.060	0.090	0.200	0.6000	0.0001	0.2000
	Median	0.0010	1.300	0.008	0.008	0.060	0.040	0.100	0.1000	0.0001	0.2000
	St dev	0.0020	0.300	0.002	0.003	0.006	0.200	0.070	2.0000	0.0001	0.0200
	Min	0.0005	1.100	0.004	0.006	0.050	0.009	0.100	0.0004	0.0001	0.1000
	Max	0.0030	1.600	0.009	0.010	0.060	0.300	0.200	2.200	0.0001	0.2000
Acer monspessulanum L. (n=6)	Mean	0.0060	0.060	0.008	0.010	0.060	0.020	0.080	0.0004	0.0060	0.0300
	Median	0.0020	0.040	0.008	0.009	0.060	0.020	0.060	0.0004	0.0040	0.0300
	St dev	0.0200	0.070	0.002	0.004	0.030	0.030	0.060	0.0001	0.0090	0.0200
	Min	0.0006	0.001	0.006	0.007	0.040	0.007	0.030	0.0004	0.0001	0.0200
	Max	0.0300	0.200	0.010	0.020	0.100	0.060	0.200	0.0004	0.0200	0.0500

Table S8. Statistical parameters for PLS-DA models

	Evergreen oak	**Hungarian oak**	**Silver fir**
R^2_{cal}	0.8972	0.9641	0.9191
R^2_{CV}	0.7658	0.9275	0.8521
RMSEC	0.1544	0.0561	0.1418
RMSECV	0.2335	0.0801	0.1919

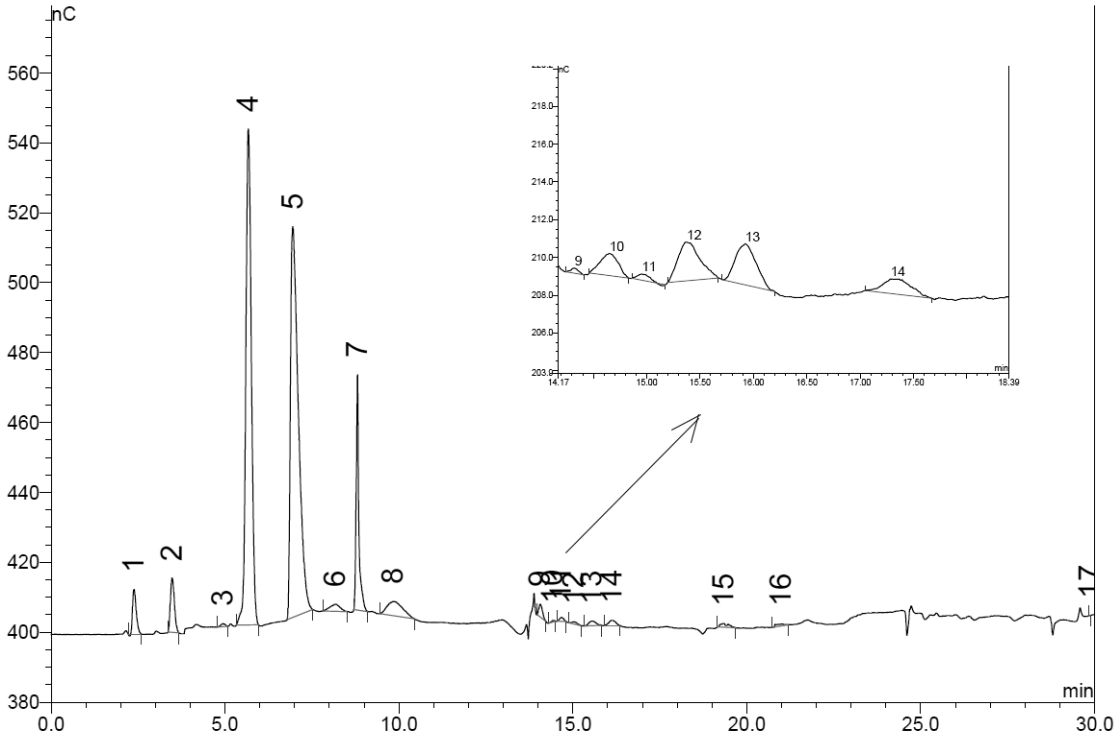

Figure S1. Chromatogram of sugar compounds identified in one Evergreen oak honeydew honey sample: 1 – sorbitol, 2 – trehalose, 3 – arabinose, 4 – glucose, 5 – fructose, 6 – melibiose, 7 – sucrose, 8 – isomaltose, 10 – melezitose, 12 – turanose, 13 – raffinose, 14 – maltose, 15 – panose, 16 – maltotriose.

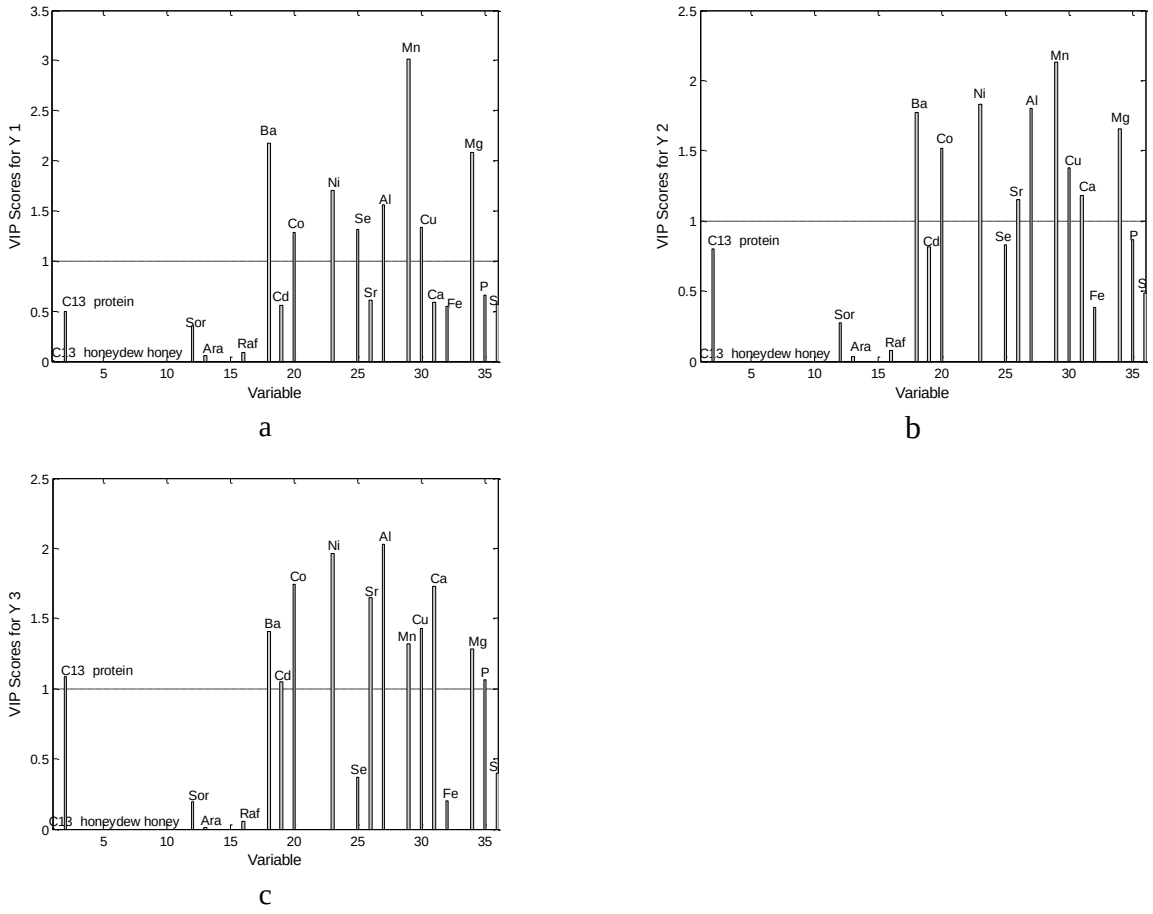

Figure S2. VIP scores for PLS-DA models, a) evergreen oak, b) Hungarian oak, c) silver fir.