

Off-line SPE LC-LRMS Polyphenolic Fingerprinting and Chemometrics to Classify and Authenticate Spanish Honey

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Table S1. Multiclass predictions by cross-validation for the set of blossom-honey samples using 3 LVs. BL: Orange/lemon blossom; RO: Rosemary; EU: Eucalyptus; TH: Thyme, and HE: Heather.

Sample class variety	Sensitivity (%)	Specificity (%)	Classification Error (%)
BL	100	100	0
EU	95.4	90.1	10.5
HE	92.2	86.4	11.6
RO	91.3	85.4	10.2
TH	90.4	93.1	12.4

Table S2. Multiclass predictions by cross-validation for the set of honeydew-honey samples using 3 LVs. HO: Holm oak; MO: Mountain; and FO: Forest.

Sample class variety	Sensitivity (%)	Specificity (%)	Classification Error (%)
HO	100	100	0
MO	100	100	0
FO	100	100	0

Table S3. Number of analyzed honey samples considering botanical varieties and geographical origins

Honey	Botanical variety	Number of samples	Geographical origin	Number of samples	Climatic geographical origin
Blossom-honeys	Orange/Lemon Blossom (BL)	12	Aragon	1	LIR
			Balearic Islands	2	MSR
			Cantabria	1	CSR
			Castile and Leon	2	LIR
			Catalonia	3	MSR
			Extremadura	1	LIR
			Spain ^a	2	-
	Eucalyptus (EU)	13	Andalusia	1	MSR
			Asturias	2	CSR
			Cantabria	1	CSR
			Castile and Leon	2	LIR
			Catalonia	1	MSR
			Extremadura	4	LIR
			Navarre	1	CSR
			Spain and others ^a	1	-
	Rosemary (RO)	26	Andalusia	1	MSR
			Aragon	4	LIR
			Asturias	1	CSR
			Balearic Islands	4	MSR
			Castile and Leon	1	LIR
			Cantabria	2	CSR
			Catalonia	6	MSR
			Extremadura	4	LIR
			Navarre	1	CSR
			Spain ^a	2	-
	Thyme (TH)	7	Castile and Leon	1	LIR
			Castile La Mancha	2	LIR
			Catalonia	1	MSR
			Extremadura	2	LIR
			Spain ^a	1	-
	Heather (HE)	18	Asturias	2	CSR
			Basque Country	1	CSR
			Cantabria	3	CSR
			Castile and Leon	5	LIR
			Catalonia	2	MSR
			Extremadura	5	LIR
Honeydew-honeys	Mountain (MO)	6	Asturias	2	CSR
			Castile and Leon	1	LIR
			Castile La Mancha	1	LIR
			Catalonia	2	MSR
	Forest (FO)	10	Balearic Islands	2	MSR
			Cantabria	2	CSR
			Castile and Leon	1	LIR
			Catalonia	1	MSR
			Spain ^a	4	-
	Holm Oak (HO)	10	Aragon	2	LIR
			Castile and Leon	2	LIR
			Extremadura	6	LIR
Other honeys	Multifloral (MF)	34	Asturias	1	CSR
			Balearic Islands	4	MSR
			Cantabria	1	CSR
			Castile and Leon	7	LIR
			Castile La Mancha	2	LIR
			Catalonia	8	MSR
			Extremadura	4	LIR
			Navarre	4	CSR
			Spain ^a	1	-
			Spain and others ^a	2	-

^a Spain: Honeys produced in Spain but geographical region not specified; Spain and others: Honeys that include mixtures of honey produced in Spain and other countries such as Uruguay, Cuba, Mexico, Romania or Ukraine

Table S4. Monitored polyphenolic compounds and MRM acquisition conditions.

Polyphenolic compound	Retention time (min)	Precursor ion (m/z)	Product ion (m/z)	Declustering potential (DP, V)	Collision energy (CE, V)	Cell exit potential (CXP, V)
Gallic acid	3.1	169	125	-40	-22	-19
Caffeic acid	7.3	179	135	-45	-20	-1
Quercetin	12.6	301	151	-80	-32	-1
Hesperidin	11.8	609	301	-115	-36	-19
Resveratrol	13.0	227	143	-70	-34	-1
Ferulic acid	11.3	193	134	-30	-22	-1
Vanillic acid	7.0	167	152	-65	-20	-1
Ethyl gallate	9.5	197	124	-60	-34	-3
Catechin	6.3	289	109	-110	-42	-19
Epicatechin	7.5	289	125	-85	-33	-7
<i>p</i> -Coumaric acid	6.7	163	119	-60	-18	-1
Rutin	11.3	609	300	-95	-48	-23
Myricetin	12.9	317	151	-95	-40	-9
Syringic acid	7.2	197	121	-40	-26	-9
Astilbin	11.6	449	285	-100	-32	-1
<i>trans</i> -Coutaric acid	6.7	295	163	-30	-20	-11
Caftaric acid	5.4	311	179	-50	-22	-11
Diosmin	11.8	607	299	-105	-34	-23
Hesperetin	11.8	301	286	-105	-36	-5
Naringin	11.8	579	271	-140	-36	-5
Naringenin	14.2	271	151	-90	-32	-25
Catechol	5.8	109	91	-25	-26	-5
4-Hydroxybenzoic acid	6.3	137	93	-55	-18	-7
Ellagic acid	14.2	301	284	-95	-98	-1
Vanillin	9.0	151	136	-50	-14	-31
Epigallocatechin	5.6	305	125	-80	-26	-25
Chlorogenic acid	6.1	353	191	-60	-20	-17
3-Methylcatechol	11.0	123	108	-50	-22	-13
4-Ethylcatechol	12.7	137	122	-80	-22	-5
2,5-Dihydroxybenzoic acid	6.6	153	108	-50	-18	-15
4-Methylcatechol	11.0	123	108	-75	-22	-7
3,4-Dihydroxybenzoic acid	4.7	153	109	-70	-20	-3
Procyanidin B2	7.0	577	407	-5	-26	-11
Procyanidin A2	11.7	575	285	-135	-38	-1
Procyanidin C1	10.9	865	125	-180	-86	-7
3-Hydroxytyrosol	7.2	153	123	-50	-18	-5
Kaempferol	11.6	285	151	-85	-26	-7
Apigenin	11.7	269	117	-95	-48	-7
Luteolin	13.3	285	133	-95	-50	-7
Oleuropein	11.6	539	59	-60	-78	-11
4-Vinylguaiacol	12.6	149	121	-125	-16	-9
<i>trans</i> -Cinnamic acid	12.8	147	103	-50	-16	-17
Guaiacol	9.4	123	95	-160	-20	-15
Pyrogallol	1.4	125	79	-10	-6	-1
Quinic acid	6.1	191	85	-80	-30	-5
Polydatin	13.5	389	227	-85	-20	-19
3,4-di-O-Caffeoylquinic acid	10.7	515	353	-75	-28	-25
4,5-di-O-Caffeoylquinic acid	11.8	515	173	-105	-36	-1
Pinocembrin	15.7	255	151	-65	-38	-1
Tricetin	12.6	301	149	-75	-52	-25
Galangin	15.8	269	41	-80	-100	-3

Chrysin	15.6	253	63	-90	-46	-3
Pinobanksin	14.2	271	253	-75	-32	-11