

Table S1. Characterisation of phenolic compounds from Portuguese propolis by UHPLC-DAD-ESI-MSn.

Nr	t _R (min)	UV max	[M – H] [–] m/z	UHPLC/ESI-MS m/z (% base peak)	Compound
1	2.36	297, 323	179	MS ² [179]: 135 (100)	Caffeic acid
2	3.50	309	163	MS ² [163]: 119 (100)	<i>p</i> -Coumaric acid
3	3.98	295, 320	193	MS ² [193]: 178 (56), 149 (100), 134 (25)	Isoferulic acid
4	4.35	299, 322	193	MS ² [193]: 178 (100), 149 (8), 134 (15)	Ferulic acid
5	8.13	295, 321	207	MS ² [207]: 163 (100), 133 (80), 131 (60), 103 (100)	3,4-Dimethyl-caffeic acid
6	10.06	255, 368	301	MS ² [301]: 179 (100), 151 (46)	Quercetin
7	10.91	287	285	MS ² [285]: 267 (100), 252 (8), 239 (40)	Pinobanksin-5-methyl- ether
8	11.38	257, 355	315	MS ² [315]: 300 (100); MS ³ [300]: 271 (100), 255 (56), 151 (<1)	Quercetin-3-methyl-ether
9	11.49	275	147	MS ² [147]: 103 (100)	Cinnamic acid
10	11.80	308	177, [M+46] [–] :223	MS ² [177]:	<i>p</i> -Coumaric acid methyl ester
11	13.01	267, 338	269	MS ² [269]: 225 (100), 201 (28), 151 (20), 149 (40)	Apigenin
12	13.23	291	271	MS ² [271]: 253 (100), 225 (28)	Pinobanksin
13	13.61	265, 367	285	MS ² [285]: 285 (100), 257 (43), 213 (40), 151 (47)	Kaempferol
14	14.11	255, 368	315	MS ² [315]: 300 (100); MS ³ [300]: 283 (34), 271 (100), 227 (39), 151 (90)	Isorhamnetin
15	14.62	286	269	MS ² [269]: 254 (100), 227 (100), 165 (44)	Pinocembrin-5-methyl-ether
16	15.15	266, 351	299	MS ² [299]: 284 (100)	Kaempferol-methyl ether
17	15.70	255, 355	329	MS ² [329]: 314 (100); MS ³ [314]: 299 (100), 285 (50), 271 (43), 243 (10)	Quercetin-dimethyl-ether
18	17.75	261, 300sh, 352	283	MS ² [283]: 268 (100), 240 (12), 239 (25)	Galangin-5-methyl ether
19	18.11	290	327	MS ² [327]: 285 (100), 267 (7), 239 (7)	Pinobanksin-5-methyl-ether-3- <i>O</i> -acetate
20	18.44	311	173	MS ² [173]: 129 (100), 102 (2)	Cinnamylidenacetic acid
21	18.68	256, 367	315	MS ² [315]: 300 (40), 287 (19), 193 (45), 165 (100)	Rhamnetin
22	20.70	255, 355	329	MS ² [329]: 314 (100); MS ³ [314]: 299 (100), 271 (10)	Quercetin-dimethyl ether
23	22.80	268, 315	253	MS ² [253]: 253 (86), 209 (100), 180 (15), 165 (10)	Chrysin
24	22.97	297, 324	247	MS ² [247]: 179 (100), 135 (14)	Caffeic acid isoprenyl ester
25	23.53	268, 331	283	MS ² [283]: 268 (100)	Acacetin
26	23.89	299, 325	247	MS ² [247]: 179 (100), 135 (14)	Caffeic acid isoprenyl ester (isomer)

Table S1 (continued). Characterisation of phenolic compounds from Portuguese propolis by UHPLC-DAD-ESI-MSn.

Nr	t _R (min)	UV max	[M-H] ⁻ m/z	UHPLC/ESI-MS m/z (% base peak)	Compound
27	24.23	290	255	MS ² [255]: 213 (58), 211 (24), 151 (12)	Pinocembrin
28	24.83	266, 290sh,358	269	MS ² [269]: 269 (100), 241 (<1), 227 (<1), 213 (<1), 197 (<1)	Galangin
29	25.42	266, 363	299	MS ² [299]: 284 (100), 271 (30), 255 (10), 240 (10), 165 (47)	Kaempferide
30	26.35	293	313	MS ² [313]: 271 (18), 253 (100)	Pinobanksin-3-O-acetate
31	27.02	300, 325	283	MS ² [283]: 179 (100), 135 (20)	Caffeic acid phenylethyl ester
32	27.96	267, 345	313	MS ² [313]: 298 (100); MS ³ [298]: 283 (100), 269 (<1), 255 (5)	Chrysoeriol-methyl-ether
33	30.16	310	231	MS ² [231]: 163 (100), 119 (14)	<i>p</i> -Coumaric acid isoprenyl ester
34	30.28	295, 313	433	MS ² [433]: 415 (4), 401 (32), 309 (100), 323 (5), 294 (7), 269 (7)	Pinocembrin-5-O-3-hydroxyl-4-methoxyphenylpropionate
35	31.02	313	253	MS ² [253]: 209 (20), 163 (100), 145 (10), 118 (65)	<i>p</i> -Coumaric benzyl ester
36	31.42	313	231	MS ² [231]: 163 (100), 119 (12)	<i>p</i> -Coumaric acid isoprenyl ester (isomer)
37	32.08	294, 325	295	MS ² [295]: 251 (66), 211 (49), 178 (100), 134 (66)	Caffeic acid cinnamyl ester (isomer)
38	33.15	293	327	MS ² [327]: 271 (10), 253 (100)	Pinobanksin-3-O-propionate
39	33.56	313	231	MS ² [231]: 163 (100), 119 (12)	<i>p</i> -Coumaric acid isoprenyl ester (isomer)
40	33.86	339	269	MS ² [269]: 254 (100), 251 (75), 236 (40), 226 (15), 165 (35)	Unknown
41	34.68	280	369	MS ² [317]: 317 (100), 287 (37), 217 (6), 191 (25), 190 (56), 189 (34)	Pinobanksin-5-methyl-ether-3-O-pentanoate
42	36.37	268, 307	387	MS ² [387]: 387 (100), 293 (34), 281 (78), 267 (76), 255 (25)	<i>p</i> -Coumaric acid derivative
43	36.73	291	279	MS ² [279]: 235 (78), 195 (100), 162 (80), 118 (35)	<i>p</i> -Coumaric cinnamyl ester
44	37.05	294, 322	475	MS ² [475]: 433 (15), 415 (100), 400 (5), 365 (5), 253 (<1)	Pinobanksin-7-methyl-ether-5-O- <i>p</i> -hydroxyphenylpropionate
45	37.36	292	341	MS ² [341]: 253 (100)	Pinobanksin-3-O-butyrate or isobutyrate
46	37.78	292	353	MS ² [353]: 271 (1), 253 (100)	Pinobanksin-3-O-pentanoate
47	38.42	259, 299	381 or 377	MS ² [377]: 359 (47), 335 (28), 333 (2), 319 (6), 317 (100), 315 (15), 273 (3), 264 (2)	Unknown
48	38.60	294, 322	399	MS ² [399]: 355 (39), 179 (100), 135 (50)	Caffeic acid derivative
49	39.51	283, 347	565	MS ² [565]: 455 (8), 417 (18), 283 (100), 269 (32)	<i>p</i> -Coumaric acid-4-hydroxyphenylethyl ester dimer

Table S1 (continued). Characterisation of phenolic compounds from Portuguese propolis by UHPLC-DAD-ESI-MSn.

Nr	t _R (min)	UV max	[M-H] ⁻ m/z	UHPLC/ESI-MS m/z (% base peak)	Compound
50	40.25	292	355	MS ² [355]: 271 (100)	Pinobanksin-3- <i>O</i> -pentenoate or 2-methylbutyrate
51	40.41	293	367	MS ² [367]: 271 (100), 253 (48); MS ³ [271]: 253 (100), 225 (25), 151 (10)	Pinobanksin- <i>O</i> -hexenoate
52	40.58	322	319	MS ² [319]: 275 (100), 259 (34), 205 (15), 189 (<1)	Unknown
53	41.16	322	295	MS ² [295]: 251 (66), 211 (49), 178 (100), 134 (66)	Caffeic acid cinnamyl ester (isomer)
54	41.29	322	315	MS ² [315]: 179 (100), 135 (30)	Caffeic acid derivative
55	42.12	290	369	MS ² [369]: 271 (14), 253 (100)	Pinobanksin-3- <i>O</i> -hexanoate
56	42.64	283	293	MS ² [293]: 275 (25), 249 (12), 209 (7), 197 (42), 185 (100), 149(9), 125(9)	<i>p</i> -Methoxy-cinnamic acid cinnamyl ester
57	42.72	295, 322	323, [M+46] ⁻ :369	MS ² [323]:	Caffeic acid derivative
58	43.18	276	293	MS ² [293]: 275 (25), 249 (12), 209 (7), 197 (42), 185 (100), 149(9), 125(9)	<i>p</i> -Methoxy-cinnamic acid cinnamyl ester (isomer)
59	43.37	275	429 or 383		Unknown
60	45.66	289	315	MS ² [315]: 297 (30), 271 (20), 259 (3), 228 (5), 205 (100)	Unknown
61	45.67	311	473, [M+46] ⁻ :519	MS ² [473]:	<i>p</i> -Coumaric acid derivative
62	48.56	273, 283,307	365	MS ² [365]: 365 (100), 239 (15), 228 (96), 213 (21), 174 (24)	Unknown

RT: 0.00 – 55.00

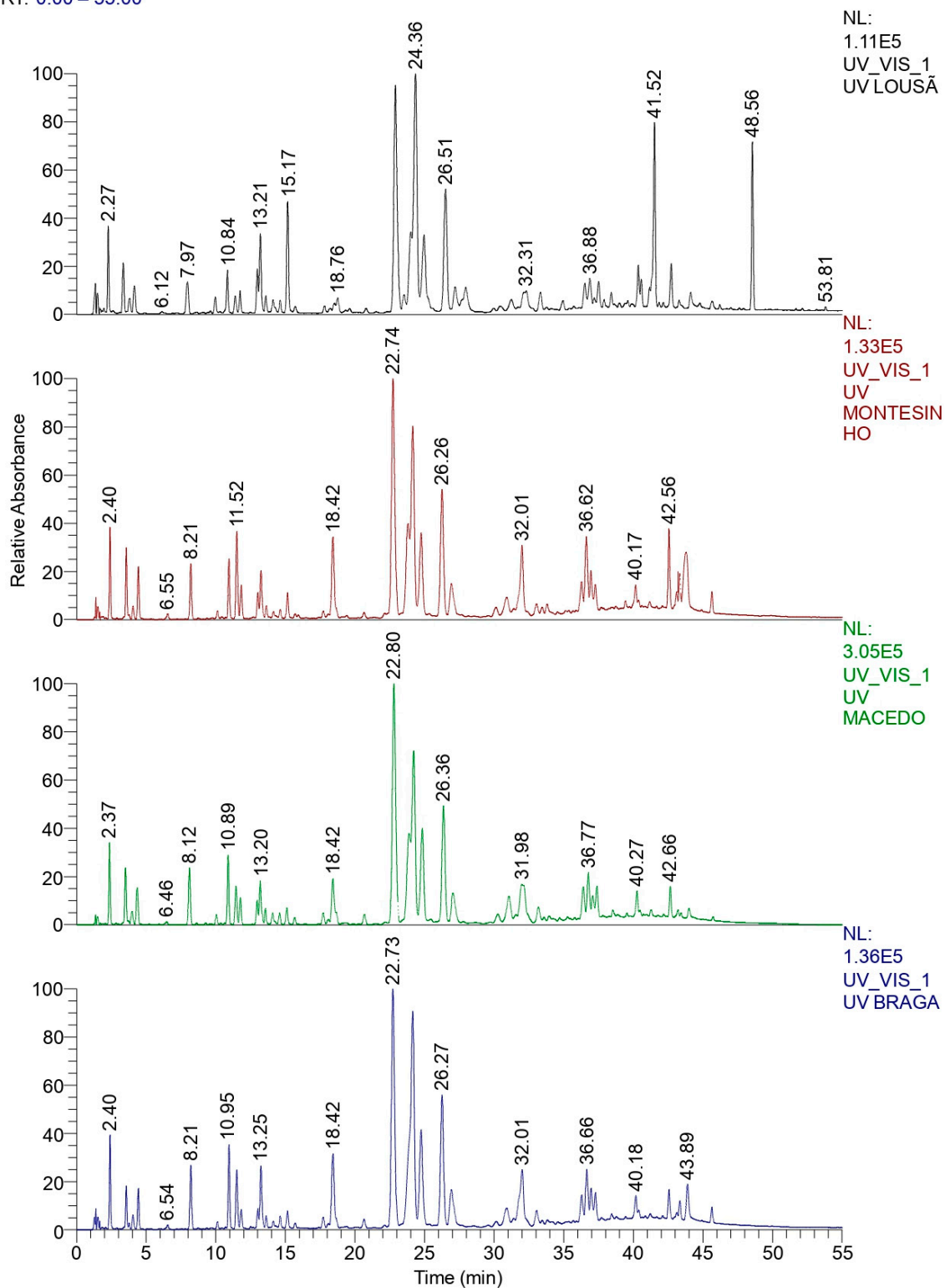


Figure S1. Chromatograms with UV detector (280 nm) of the four propolis samples.