

Table 1 - Compounds detected in aqueous extract of propolis samples from Barra do corda collected during the twelve months

	R T M in	UV- vis λ_{max} - nm	HPLC/(-) ESI- MS/MS m/z (%) base peak) [M - H] ⁻ m/z	HPLC/(+) ESI- MS/MS m/z (%) base peak) [M + H] ⁺ m/z	Proposed structure	references
(1) months 2,6,8,10	2. 6	235, 290, 320 sh	--	[M + H] ⁺ - 557 MS/MS - 381 (C ₁₇ H ₁₇ O ₁₀) ⁺	maclurin-3- <i>C</i> - 6''- <i>O</i> - hydrocinnamy l glucoside	Beelders et al., (2014), Abdel-Mageed et al., (2014), Marinov et al., (2023), Zhang et al. (2019), Berardini et al., (2004) Sferrazzo et al., (2022) Kumar et al., (2021), Du et al., (2024)
(2) months 1,4,5, 6,7,9, 10,11,12	2. 7	235, 290, 318 sh	[M - H] ⁻ - 357 MS/MS - 339, 321		6-hydroxy benzophenone -2- <i>O</i> -(2''),3- <i>C</i> -(1'')-1''- desoxy- fructofuranosi de	Zhang et al. (2019), Berardini et al., (2004) Pan et al., (2016, 2018) Quintana et al., (2021)
(3) months 4,5,9	2. 7	320	[M - H] ⁻ - 341 MS/MS - 179		caffeoyl-4- <i>O</i> - glucoside**	Negri et al., 2022 Leng et al., (2022)
(4) months 2,6,8,10	2. 9			[M + H] ⁺ - 490 MS/MS - 472	7-(2,2,3- trihydroxy-3- methyl butyryl)-9- (3'- acetylechimid inyl) retronecine	El-Shazly and Wink (2014), Cantero et al., (2022), Mädge et al., (2020), Kowalczyk et al., (2018)
(5) months 2,6,8,10 ,11	2. 7	235, 290, 320 sh		[M + H] ⁺ - 571 MS/MS - 381 (C ₁₇ H ₁₇ O ₁₀) ⁺	maclurin-3- <i>C</i> - 6''- <i>O</i> - <i>p</i> - coumaroyl glucoside	Beelders et al., (2014), Abdel-Mageed et al., (2014), Marinov et al., (2023), Zhang et al. (2019), Berardini et al., (2004) Sferrazzo et al., (2022)

						Kumar et al. (2021), Du et al. (2024)
(6) months 1,2,6,7, 8,11	2. 9	235, 290, 320 sh	[M - H] ⁻ – 427 MS/MS – 409, 391		3'-acetyl-4'- ethoxy- benzophenone -2-O-(2''),3- C-(1'')-1''- desoxy- fructofuranosi de	Sferrazzo et al., (2022) Kumar et al. (2021), Zhang et al. (2019), Berardini et al., (2004), Pan et al., (2016, 2018) Quintana et al., (2021)
(7) months 1,7,8,11	3. 1		[M - H] ⁻ – 191 MS/MS – 173		quinic acid	Gouveia and Castilho, (2010)
(8) months 1,2,6,7, 8,11	3. 3	235, 290, 320 sh	[M - H] ⁻ – 435 MS/MS – 417, 331		2,4,5,6- tetrahydroxy- 4'-ethyl- benzophenone -3-C- glucoside	Beelders et al. (2014), Zhang et al. (2019), Sferrazzo et al., (2022), Kumar et al. (2021), Pan et al., (2016)
(9) months 2,3,4,5, 6,8, 9,10,11, 12	5. 6		[M - H] ⁻ – 428 MS/MS – 398, 354	[M + H] ⁺ - 430 MS/MS – 412 (100), 385 (70), 315 (50)	7-(2-methyl- 2- methoxybutyr yl)-9- echimidinyl retronecine**	Coelho et al., (2015), Negri et al., (2022), Cantero et al., (2022), Mädge et al., (2020), El-Shazly and Wink (2014),
(10) months 2,6, 8, 10,11	6. 0			[M + H] ⁺ - 444 MS/MS – 426	viridinate	Cantero et al., (2022), Mädge et al., (2020), El-Shazly and Wink (2014),
(11) months 1,2,3,4, 5,6,7, 8,9,10,1 1,12	6. 2	294	[M - H] ⁻ – 539 MS/MS – 495, 451	[M + H] ⁺ - 541 MS/MS – 523, 479	iriflophenone- 3-C-6''-O- hydrocinnamy l glucoside	Beelders et al., (2014), Abdel-Mageed et al., (2014), Marinov et al., (2023), Zhang et al. (2019), Berardini et al., (2004) Sferrazzo et al., (2022) Kumar et al. (2021), Du et al. (2024)
(12) months 2,10,11	7. 5		[2M - H] ⁻ –363 [M - H] ⁻ – 181		homovanillic acid	Buzgaia et al., (2021)

(13) months 1,4, 5,6,8, 9,10,11, 12	7. 7		[2M - H] ⁻ – 487 [M - H] ⁻ – 243		1- <i>O</i> - galloylglycero l	Orabi et al. (2023)4 https://pubchem.ncbi.nlm.nih.gov Human Metabolome Database (HMDB)
(14) months 2,6, 8, 10,11	7. 9			[M + H] ⁺ - 456 MS/MS – 324, 306	7-(2-methyl- butyryl)-9- (2'-acetyl lasiocarpyl) retronecine	El-Shazly and Wink (2014), Mädge et al., (2020)
(15) months 1,4, 5,6,8, 9,10,11, 12	9. 4		[2M - H] ⁻ – 451 [M - H] ⁻ – 225		4,5,6- trihydroxy-3- methoxycinna mic acid (5,6- dihydroxy ferulic acid)	Pyrzynska (2024), Sharise et al., (2020), Mao et al., (2023) https://pubchem.ncbi.nlm.nih.gov Human Metabolome Database (HMDB)
(16) months 1, 11, 12	13 .3		[2M - H] ⁻ – 419 [M - H] ⁻ – 209		5-hydroxy ferulic acid	Misawa et al. (2018) Sharise et al., (2020), Mao et al., (2023), Berton et al., (2020)
(17) months 1,2,3,4, 5, 6,7,8,9, 10,11,12	13 .8	270 - 335	[M - H] ⁻ - 593 MS/MS – 575 (20), 503 (40), 473 (100), 383 (40), 353 (60)	[M + Na] ⁺ - 617 MS/MS – 599, 581, 509 [M + H] ⁺ - 595 MS/MS – 577 (100), 511 (50), 457 (90)	vicenin-2 - (apigenin 6,8- di-C- glucoside)**	Negri et al., (2022), Cantero et al., (2022), Wang et al., (2019), Karar and Kuhnert (2015)
(18) months 2,3,5,6, 7,8,9, 10,11,12	13 .9	260, 320, 360	[M - H] ⁻ - 421 MS/MS – 403 (30), 331 (80), 301(100)		mangiferin**	Negri et al., (2022), Navarro et al., (2019), Mei et al., (2023)

(19) months 1,2, 3,4,5	15 .2	270 - 335	[M - H] ⁻ - 623 MS/MS – 503, 383	[M + H] ⁺ - 625 MS/MS – 607, 589	diosmetin 6,8- di-C- glucoside	Wang et al., (2019), Karar and Kuhnert (2015)
(20) months 8,9,10,1 1,12	15 .7	260 - 355		[M + H] ⁺ - 465 MS/MS – 303	quercetin-3- <i>O</i> -glucoside	Tokuyama-Nakai et al., (2019), Karar and Kuhnert (2015)
(21) months 3,7,8, 9,10,11	16 .0		[M + HCOO] ⁻ 487 [M - H] ⁻ - 441 MS/MS – 279		4'- pentadienylox y benzophenone -3- <i>O</i> - glucoside	Marinov et al., (2023), Zhang et al. (2019), Olugbenga et al., (2015)
(22) months 1,2,3,5, 6, 8,11,12	16 .3	270 - 335	[M - H] ⁻ - 563 MS/MS – 473 (100), 503 (60), 545 (60), 383 (50), 443 (40), 353 (40)	[M + H] ⁺ - 565 MS/MS – 547 (100), 529, 499 (60), 457 (30), 427	isoschaftoside - (apigenin 6- C- arabinoside-8- C- glucoside)**	Negri et al., (2022), Cantero et al., (2022), Wang et al., (2019), Karar and Kuhnert (2015)
(23) months 1,2,3,4, 5,6, 11,12	18 .0	231, 280	[M - H] ⁻ - 361 MS/MS – 343, 325	[M + Na] ⁺ - 385 MS/MS – 339, 293 [M + H] ⁺ - 363 MS/MS – 317, 271	2- <i>O</i> -galloyl galactaric acid	Zhou et al., (2022) Wang et al. (2021)
(24) months 2,5,6,7, 8,9,10,1 1	19 .5	260 - 355	[M+HC OO] ⁻ - 509 [M - H] ⁻ - 463		myricetin-3- <i>O</i> -methyl ether 7- <i>O</i> - arabinoside	Tokuyama-Nakai et al., (2019), Karar and Kuhnert (2015)

			MS/MS – 331			
(25) months 1,2,3,5, 6, 8,11,12	20 .5	270 - 335	[M - H] ⁻ - 563 MS/MS – 443 (100), 473 (80), 545 (20), 383 (40), 353 (60)	[M + Na] ⁺ - 587 MS/MS – 569, 551 [M + H] ⁺ - 565 MS/MS – 547 (100), 499 (60), 457 (30)	schaftoside - (apigenin 8- C- glucoside 6-C- arabinoside)* *	Negri et al., (2022), Cantero et al., (2022), Wang et al., (2019), Karar and Kuhnert (2015)
(26) months 8,9,10,1 1	20 .6	255 - 355	[M - H] ⁻ - 317		myricetin	Tokuyama-Nakai et al., (2019), Karar and Kuhnert (2015)
(27) months 2,6,8, 9,10,11	24 .4			[M + H] ⁺ - 487 MS/MS – 355, 335	5- caffeoylquinic acid-1- <i>O</i> - arabinoside	Coelho et al., (2015) Nguyen et al., 2024 Leng et al., (2022) Liu et al., (2020)
(28) months 1,5,6,7, 8,9, 10,11,12	27 .1	235, 290, 318 sh	[M - H] ⁻ - 417 MS/MS – 295	[M + Na] ⁺ - 441 MS/MS – 423, 301	6-methoxy-4'- ethoxy- benzophenone -3-C- glucoside	Beelders et al., (2014), Abdel-Mageed et al., (2014), Marinov et al., (2023), Zhang et al. (2019), Berardini et al., (2004) Sferrazzo et al., (2022) Kumar et al., (2021), Du et al., (2024)
(29) months 1,5,6,7, 8,9, 10,11,12	32 .6	235, 290, 318 sh	[M - H] ⁻ - 417 MS/MS – 295	[M + Na] ⁺ - 441 MS/MS – 423, 301	4-methoxy-4'- ethoxy- benzophenone -3-C- glucoside	Beelders et al., (2014), Abdel-Mageed et al., (2014), Marinov et al., (2023), Zhang et al. (2019), Berardini et al., (2004) Sferrazzo et al., (2022) Kumar et al., (2021), Du et al., (2024)
(30) months	33 .0	235, 290,		[M + H] ⁺ - 401	4-methyl-4'- ethoxybenzop	Sferrazzo et al., (2022)

2,6,8,10,11		318 sh		MS/MS – 279	henone-2- <i>O</i> -(2''),3- <i>C</i> -(1'')-1''-desoxy-fructofuranoside	Kumar et al. (2021), Zhang et al. (2019), Berardini et al., (2004), Pan et al., (2016, 2018) Quintana et al., (2021)
(31) months 2,6,8,10,11	36.4	235, 290, 318 sh		[M + H] ⁺ - 415 MS/MS – 293	4-ethyl-4'-ethoxybenzop henone-2- <i>O</i> -(2''),3- <i>C</i> -(1'')-1''-desoxy-fructofuranoside	Sferrazzo et al., (2022) Kumar et al. (2021), Zhang et al. (2019), Berardini et al., (2004), Pan et al., (2016, 2018) Quintana et al., (2021)
(32) months 1,2,3,5,6,7,8,9,10,11,12	37.0	235, 290, 318 sh	[M - H] ⁻ - 453 MS/MS – 409, 331, 287		2, 3',4,5,6-pentahydroxy-4'-methoxy-benzophenone -3- <i>C</i> -glucoside	Beelders et al., (2014), Abdel-Mageed et al., (2014), Marinov et al., (2023), Zhang et al. (2019), Berardini et al., (2004) Sferrazzo et al., (2022) Kumar et al., (2021), Du et al., (2024)
(33) months 6,8,11,12	54.0	260, 355		[M + H] ⁺ - 579 MS/MS – 301	kaempferol-3- <i>O</i> -methyl ether 7- <i>O</i> -coumaroyl arabinoside	Tokuyama-Nakai et al., (2019), Karar and Kuhnert (2015)
(34) months 1,2,6,8,10,12	56.4	235, 290, 318 sh	[M - H] ⁻ - 327 MS/MS – 309		Benzophenone 3- <i>C</i> -rhamnoside	Xia et al. (2022), Marinov et al., (2023)
(35) months 1,2,6,11,12	58.8	235, 290, 318 sh	[M - H] ⁻ - 369 MS/MS – 351, 307		Benzophenone 3- <i>C</i> -(3''- <i>O</i> -acetyl) rhamnoside	Xia et al. (2022), Marinov et al., (2023)
(36) months 6,8,11,12	59.2		[M - H] ⁻ – 471 MS/MS – 453 (100), 407 (60)		pomolic acid**	Negri et al. (2022) Sut et al., (2019)

(37) 6,8, 11,12	60 .2		[M - H] ⁻ – 469 MS/MS – 451 (70), 407 (100)		11-keto-β- boswellic acid**	Negri et al. (2022) Schmiech et al., (2021)
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** Compounds **3,9, 17, 18, 22, 25, 36** and **37** was also identified in hydroethanolic extract of propolis from Barra do Corda