SUPPORTING INFORMATION

Ionic liquid-high performance extractive approach to recover carotenoids from *Bactris gasipaes* fruits

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Tables

Table S1. 2^{5-1} fractional experimental design with three central mixture points for $[C_4mim]Cl$ and $[C_4mim][BF_4]$ using as independent variables the $R_{(S/L)}$, number of extractions, time and $R_{(IL/E)}$.

Assay	IL	$R_{(S/L)}$	Number of extractions	Time (min)	$R_{(IL/E)}$	Total carotenoid content ($\mu g.g^{-1}$)	Total all-*trans*-β-carotene ($\mu g.g^{-1}$)	Total all-*trans*-lycopene ($\mu g.g^{-1}$)	Total all-*trans*-γ-carotene ($\mu g.g^{-1}$)
	X1	*X2*	*X3*	*X4*	*X5*	*Y1 actual*	*Y2 actual*	*Y3 actual*	*Y4 actual*
1	**-1** (1 $[C_4mim]Cl$:0 $[C_4mim][BF_4]$	**-1** (1:2)	**-1** (2)	**-1** (2.5)	**1** (1:3)	38.13	17.94	4.62	5.08
2	**1** (0 $[C_4mim]Cl$:1 $[C_4mim][BF_4]$	**-1** (1:2)	**-1** (2)	**-1** (2.5)	**-1** (1:1)	115.09	38.21	11.34	16.19
3	**-1** (1 $[C_4mim]Cl$:0 $[C_4mim][BF_4]$	**1** (1:4)	**-1** (2)	**-1** (2.5)	**-1** (1:1)	92.06	33.57	8.39	13.33
4	**1** (0 $[C_4mim]Cl$:1 $[C_4mim][BF_4]$	**1** (1:4)	**-1** (2)	**-1** (2.5)	**1** (1:3)	118.41	39.61	10.27	17.45
5	**-1** (1 $[C_4mim]Cl$:0 $[C_4mim][BF_4]$	**-1** (1:2)	**1** (4)	**-1** (2.5)	**-1** (1:1)	108.65	35.14	11.76	14.65
6	**1** (0 $[C_4mim]Cl$:1 $[C_4mim][BF_4]$	**-1** (1:2)	**1** (4)	**-1** (2.5)	**1** (1:3)	127.95	42.00	11.60	18.52
7	**-1** (1 $[C_4mim]Cl$:0 $[C_4mim][BF_4]$	**1** (1:4)	**1** (4)	**-1** (2.5)	**1** (1:3)	122.38	40.97	12.26	17.27
8	**1** (0 $[C_4mim]Cl$:1 $[C_4mim][BF_4]$	**1** (1:4)	**1** (4)	**-1** (2.5)	**-1** (1:1)	132.71	43.09	10.83	19.79
9	**-1** (1 $[C_4mim]Cl$:0 $[C_4mim][BF_4]$	**-1** (1:2)	**-1** (2)	**1** (7.5)	**-1** (1:1)	96.72	30.69	11.26	13.96
10	**1** (0 $[C_4mim]Cl$:1 $[C_4mim][BF_4]$	**-1** (1:2)	**-1** (2)	**1** (7.5)	**1** (1:3)	128.16	43.26	12.13	18.42
11	**-1** (1 $[C_4mim]Cl$:0 $[C_4mim][BF_4]$	**1** (1:4)	**-1** (2)	**1** (7.5)	**1** (1:3)	114.71	36.89	12.98	16.09
12	**1** (0 $[C_4mim]Cl$:1 $[C_4mim][BF_4]$	**1** (1:4)	**-1** (2)	**1** (7.5)	**-1** (1:1)	117.69	39.7	10.56	17.00
13	**-1** (1 $[C_4mim]Cl$:0 $[C_4mim][BF_4]$	**-1** (1:2)	**1** (4)	**1** (7.5)	**1** (1:3)	112.26	35.09	14.10	16.44
14	**1** (0 $[C_4mim]Cl$:1 $[C_4mim][BF_4]$	**-1** (1:2)	**1** (4)	**1** (7.5)	**-1** (1:1)	127.47	41.42	13.48	18.79
15	**-1** (1 $[C_4mim]Cl$:0 $[C_4mim][BF_4]$	**1** (1:4)	**1** (4)	**1** (7.5)	**-1** (1:1)	103.77	33.85	13.21	14.70
16	**1** (0 $[C_4mim]Cl$:1 $[C_4mim][BF_4]$	**1** (1:4)	**1** (4)	**1** (7.5)	**1** (1:3)	119.10	39.12	10.59	39.13
17	**0** (1 $[C_4mim]Cl$:1 $[C_4mim][BF_4]$	**0** (1:3)	**0** (3)	**0** (5)	**0** (1:2)	107.68	35.16	11.78	15.14
18	**0** (1 $[C_4mim]Cl$:1 $[C_4mim][BF_4]$	**0** (1:3)	**0** (3)	**0** (5)	**0** (1:2)	108.55	35.53	11.81	15.37
19	**0** (1 $[C_4mim]Cl$:1 $[C_4mim][BF_4]$	**0** (1:3)	**0** (3)	**0** (5)	**0** (1:2)	100.84	42.73	10.65	12.65

Table S2. Real and coded values and experimental values for total carotenoids content and major compounds extracted by $[C_4mim][BF_4]$ in the CCRD (2^3) assays.

Assay	$R_{(S/L)}$	Number of extractions	Time (min)	Total carotenoid content ($\mu g_{carotenoids} \cdot g_{dried\ biomass}^{-1}$)	Total all-*trans*-β-carotene ($\mu g_{carotenoids} \cdot g_{dried\ biomass}^{-1}$)	Total all-*trans*-lycopene ($\mu g_{carotenoids} \cdot g_{dried\ biomass}^{-1}$)	Total all-*trans*-γ-carotene ($\mu g_{carotenoids} \cdot g_{dried\ biomass}^{-1}$)
	X1	*X2*	*X3*	*Y1*	*Y2*	*Y3*	*Y4*
1	**-1** (1:2)	**-1** (2)	**-1** (5)	130.64	41.69	12.03	19.13
2	**1** (1:6)	**-1** (2)	**-1** (5)	130.11	40.9	12.73	19.48
3	**-1** (1:2)	**1** (6)	**-1** (5)	121.64	38.36	13.6	18.15
4	**1** (1:6)	**1** (6)	**-1** (5)	113.78	35.5	11.7	17.11
5	**-1** (1:2)	**-1** (2)	**1** (10)	134.96	42.03	12.7	20.43
6	**1** (1:6)	**-1** (2)	**1** (10)	117.17	35.53	12.44	18.06
7	**-1** (1:2)	**1** (6)	**1** (10)	157.03	44.5	15.28	20.8
8	**1** (1:6)	**1** (6)	**1** (10)	144.57	47.7	13.8	24.17
9	**-1.68** (1:1)	**0** (4)	**0** (7.5)	145.8	41.69	12.72	19.04
10	**1.68** (1:7)	**0** (4)	**0** (7.5)	114.07	37.1	10.31	17.26
11	**0** (1:4)	**-1.68** (1)	**0** (7.5)	98.66	32.7	9.39	14.7
12	**0** (1:4)	**1.68** (7)	**0** (7.5)	125.64	40.13	12.07	19.05
13	**0** (1:4)	**0** (4)	**-1.68** (3)	109.10	37.08	9.42	16.16
14	**0** (1:4)	**0** (4)	**1.68** (12)	157.65	48.03	16.17	22.86
15	**0** (1:4)	**0** (4)	**0** (7.5)	126.06	41.95	12.06	17.62
16	**0** (1:4)	**0** (4)	**0** (7.5)	143.98	44.21	13.13	21.8
17	**0** (1:4)	**0** (4)	**0** (7.5)	146.47	45.01	13.17	22.15

Table S3. Predicted results found through the mathematical model developed and the respective relative deviation from the independent variables $R_{(S/L)}$, number of extractions and time to define the 2^3 CCRD for $[C_4mim][BF_4]$. V1, V2, and V3 represent the validation assays.

Assays	$R_{(S/L)}$	Number of extractions	Time (min)	Experimental values	Predicted values	Relative deviation (%)
Total carotenoids content ($\mu g_{carotenoids} \cdot g_{dried\ biomass}^{-1}$)						
V1	-1.68	0	+1.68	192.09	164.86	14.17
V2				163.65		-0.74
V3				159.56		-3.32
Assays	**$R_{(S/L)}$**	**Number of extractions**	**Time (min)**	**Experimental values**	**Predicted values**	**Relative deviation (%)**
Total all-*trans*-β-carotene ($\mu g_{carotenoids} \cdot g_{dried\ biomass}^{-1}$)						
V1	-1.68	0	+1.68	55.5	46.30	16.57
V2				49.14		5.77
V3				48.2		3.94

Table S4. Kinetic parameters obtained by fitting HPLC data for degradation of carotenoids during the extracts' thermal treatment obtained with acetone and $[C_4mim][BF_4]$ in both the organic and aqueous media.

Media	Temperature ± 1 (°C)	Parameters	Carotenoids' extract	
			Acetone	$[C_4mim][BF_4]$
Oily	60	y_0	0.877	0.867
		y_∞	41340.5	-65848.8
		A_1	-0.17	-0.67
		γ_1	126.6	2.24
		A_2	-41340.3	65849.3
		γ_2	7.87×10^8	-2.41×10^7
Oily	90	y_0	0.877	0.867
		y_∞	0.58	45296.3
		A_1	-0.27	-0.68
		γ_1	26.1	1.74
		A_2	-0.23	-45295.6
		γ_2	614.3	1.05×10^7
Aqueous	60	y_0	0.807	0.819
		y_∞	-0.09	0.22
		A_1	-0.64	-0.11
		γ_1	2.51	1,41
		A_2	0.68	-0.10
		γ_2	-124.1	840.2
Aqueous	90	y_0	0.902	0.819
		y_∞	1.83	0.31
		A_1	-0.23	-0.10
		γ_1	1.04	0.58
		A_2	-1.63	-0.21
		γ_2	46.2	82.5

Table S5. Yield of extraction of carotenoids obtained by using the same $[C_4mim][BF_4]$ used for 10 cycles compared to the yield obtained when acetone is used.

Assays	Yield of extraction of carotenoids ($\mu g_{carotenoids} \cdot g_{dried\ biomass}^{-1}$)	all-*trans*-β-carotene ($\mu g_{carotenoids} \cdot g_{dried\ biomass}^{-1}$)	all-*trans*-lycopene ($\mu g_{carotenoids} \cdot g_{dried\ biomass}^{-1}$)	all-*trans*-γ-carotene ($\mu g_{carotenoids} \cdot g_{dried\ biomass}^{-1}$)	$[C_4mim][BF_4]$ recovery (%)
Acetone	88.37 ± 9.70[b]	30.99 ± 1.03[b]	8.09 ± 0.50[b]	16.05 ± 0.58[b]	-
IL recycled					
Cycle 0	142.97 ± 11.42[a]	45.34 ± 1.95[a]	15.23 ± 1.53[a]	19.38 ± 3.03[a]	92.30
Cycle 1	144.97 ± 17.08[a]	47.17 ± 4.20[a]	14.63 ± 2.13[a]	20.86 ± 2.86[a]	96.95
Cycle 2	141.86 ± 4.38[a]	46.49 ± 1.64[a]	13.17 ± 0.50[a]	20.08 ± 0.81[a]	91.24
Cycle 3	164.04 ± 12.37[a]	52.70 ± 3.58[a]	14.72 ± 1.10[a]	23.04 ± 1.31[a]	94.43
Cycle 4	141.03 ± 17.08[a]	45.18 ± 4.34[a]	12.13 ± 1.42[a]	22.07 ± 2.66[a]	90.16
Cycle 5	123.17 ± 12.15[a]	41.65 ± 3.56[a]	11.41 ± 0.82[a]	17.21 ± 1.60[b]	89.40
Cycle 6	115.01 ± 7.60[a]	36.64 ± 1.76[a]	10.91 ± 1.56[a]	15.60 ± 0.80[b]	92.60
Cycle 7	107.33 ± 6.52[a]	34.39 ± 1.95[a]	10.39 ± 0.32[a]	15.76 ± 0.89[b]	94.38
Cycle 8	111.26 ± 12.85[a]	36.09 ± 3.33[a]	10.28 ± 1.04[a]	16.36 ± 2.04[b]	95.64
Cycle 9	114.51 ± 7.97[a]	37.56 ± 0.92[a]	12.52. ± 1.17[a]	15.94 ± 0.76[b]	95.34
Cycle 10	104.98 ± 12.2[b]	33.47 ± 4.89[b]	10.83 ± 0.30[a]	14.61 ± 2.15[b]	95.63

* Same letters in the same column represent statistically equivalent results.

Table S6. Real and coded values used in the fractional experimental design with three central points (2^{5-1}) and CCRD (2^3).

Factorial design	Coded variable level	Ionic liquid proportion	$R_{(S/L)}$	Number of extractions	Time (min)	$R_{(IL/E)}$
Fractional (2^{5-1})	-1	1 IL_1:0 IL_2	1:2	2	2.5	1:3
	0	1 IL_1:1 IL_2	1:3	3	5.0	1:2
	+1	0 IL_2:1 IL_2	1:4	4	7.5	1:1
CCRD (2^3)	-1.68	-	1:1	1	3.0	-
	-1	-	1:2	2	5.0	-
	0	-	1:4	4	7.5	-
	+1	-	1:6	6	10.0	-
	+1.68	-	1:7	7	12.0	-

Table S7. Chromatographic, UV-Vis and mass spectroscopy characteristics of carotenoids from *Bactris gasipaes* pulp fruits, obtained by HPLC-PDA-MS/MS.

Peak	Carotenoid	t_R (min)[a]	$\lambda_{(max)}$[b]	% III/II	% A_B/II	$[M+H]^+$ (*m/z*)	Fragment ions (*m/z*)
1	*cis*-β-carotene	15.1	339, 420, 443, 467	12	47	537	444 [M-92]
2	all-*trans*-α-carotene	16.1	418, 445, 472	0	50	537	481 [M-H-56], 444 [M-92]
3	all-*trans*-β-carotene	18.5	421, 451, 477	25	0	537	444 [M-92]
4	*cis*-δ-carotene (1)	19.8	348, 432, 453	0	49	537	444 [M-92]
5	*cis*-δ-carotene (2)	22.4	348, 430, 453, 481	16	46	537	444 [M-92]
6	*cis*-δ-carotene (3)	24.1	349, 430, 453, 482	41	42	537	444 [M-92]
7	all-*trans*-δ-carotene	24.9	430, 455, 485	46	0	537	481 [M+H-56], 444 [M-92]
8	*cis*-γ-carotene (1)	25.6	300, 360, 434, 458, 488	45	18	537	467 [M-69], 444 [M-92]
9	*cis*-γ-carotene (2)	30.0	(-), 430, 459, 490	66	0	537	467 [M-69], 444 [M-92]
10	all-*trans*-γ-carotene	31.0	430, 460, 491	50	36	537	467 [M-69], 444 [M-92]
11	*cis*-lycopene	39.7	300, 360, 440, 465, 496	70	18	537	467 [M-69], 444 [M-92]
12	all-*trans*-lycopene	58.4	445, 471, 502	70	0	537	467 [M-69], 444 [M-92]

[a] Retention time on C_{30} column; [b] Linear gradient of methanol/MTBE; λ_{max}: maximum absorption wavelength (nm); % III/II: spectral fine structure; % AB/II: intensity of *cis* peak.

Figures

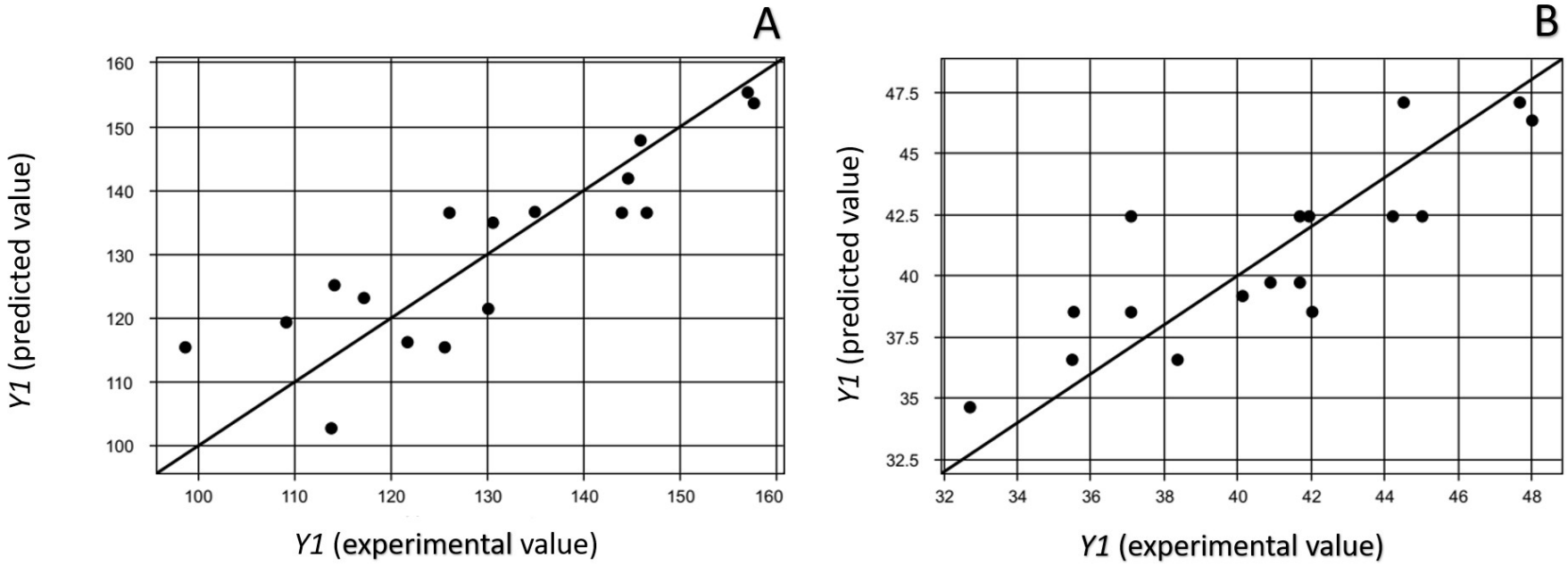

Figure S1. Graphical representation of the predicted *vs* experimental values by the model when $[C_4mim][BF_4]$ was used as solvent in the extraction of carotenoids from peach palm fruit. **(A)** total carotenoids content, **(B)** total all-*trans*-β-carotene.

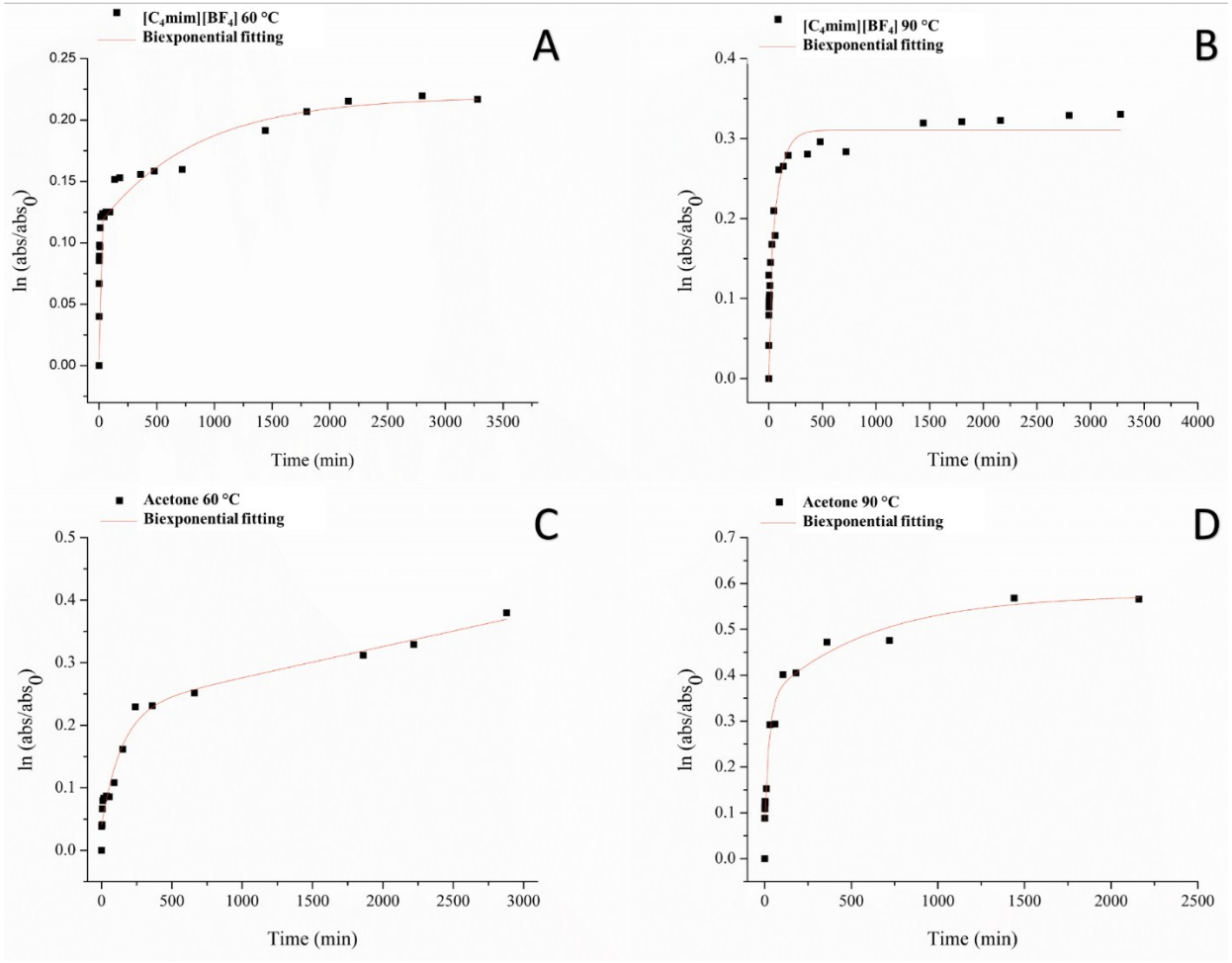

Figure S2. Kinetic of degradation of the carotenoids extracted with $[C_4mim][BF_4]$ at 60 °C (A) and 90 °C (B); acetone at 60 °C (C) and 90 °C (D) in aqueous medium. The coefficient of correlation of all curves are $R2 \geq 0.97$.

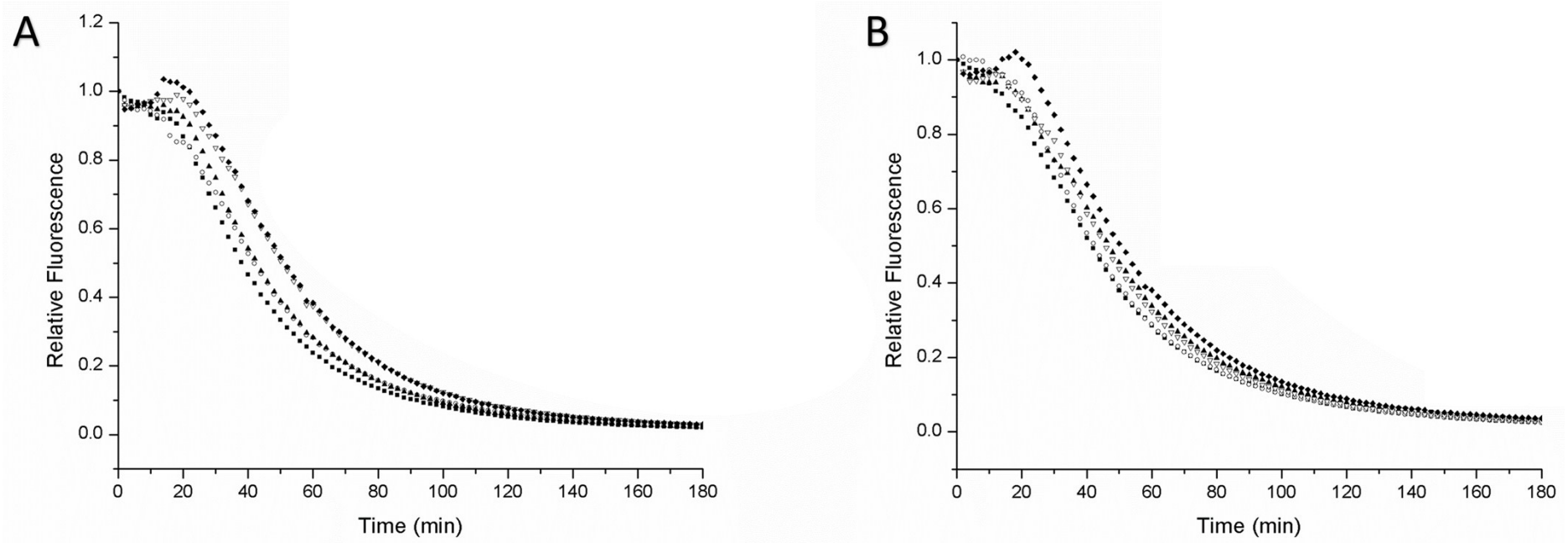

Figure S3. Fluorescence decay of C_{11}-BODIPY$^{581/591}$ induced by the peroxyl radicals generated from thermal decomposition using different concentrations of AIBN at 42°C, applying (**A**) [C_4mim][BF_4], and (**B**) acetone. The NET AUC *versus* concentration for the antioxidant activity response from the extracts was $r^2 > 0.9$.

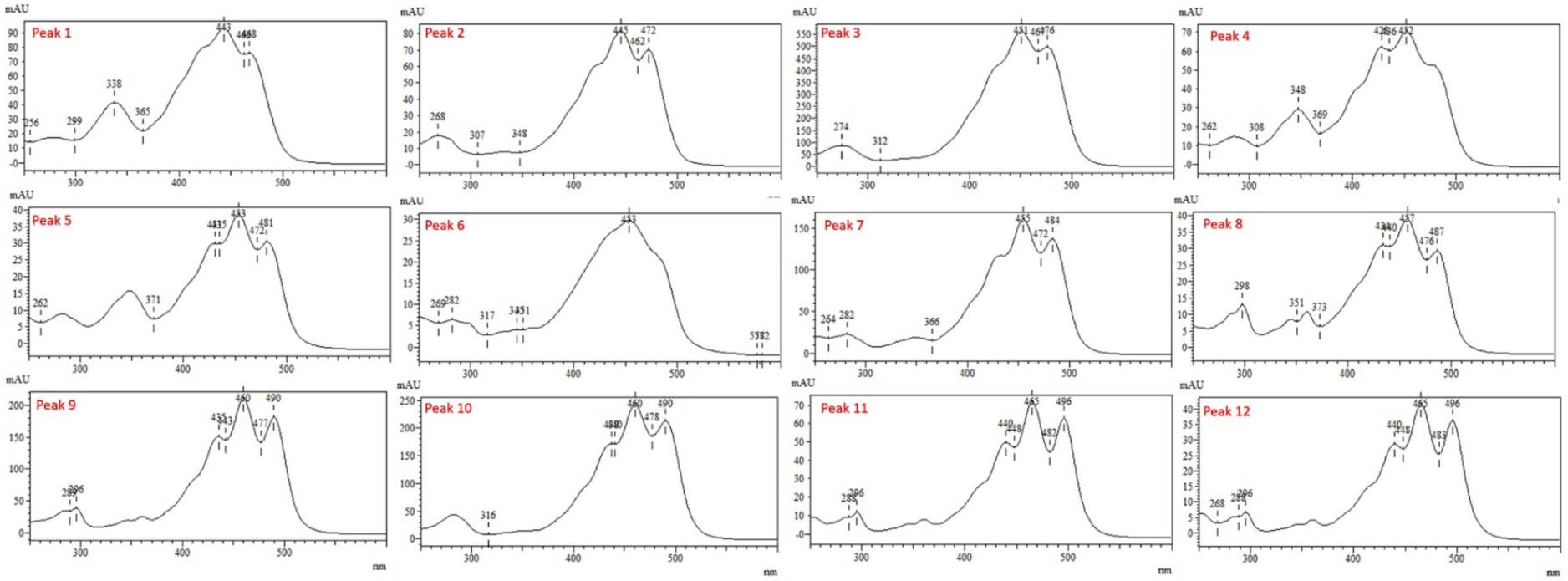

Figure S4. UV-vis spectra at 453 nm of each peak representing each carotenoid present in the biomass (*B. gasipaes* fruits).

PEAK	Carotenoid
1	*cis*-β-carotene
2	all-*trans*-α-carotene
3	all-*trans*-β-carotene
4	*cis*-δ-carotene (1)
5	*cis*-δ-carotene (2)
6	*cis*-δ-carotene (3)
7	all-*trans*-δ-carotene
8	*cis*-γ-carotene (1)
9	*cis*-γ-carotene (2)
10	all-*trans*-γ-carotene
11	*cis*-lycopene
12	all-*trans*-lycopene

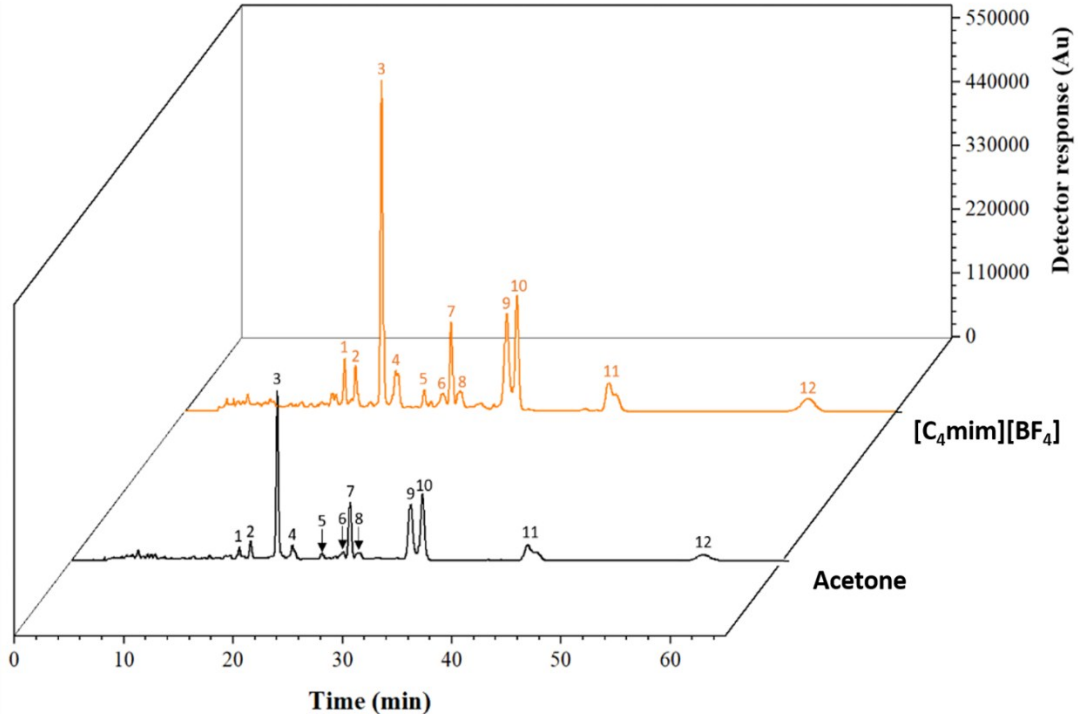

Figure S5. Chromatogram obtained by HPLC-PDA on the analysis of the carotenoids extracted from peach palm fruit. The orange profile represents the chromatogram obtained when $[C_4mim][BF_4]$ was used; the black profile corresponds to the chromatogram obtained for acetone as solvent.

Section S1. ILs' synthesis

1-butyl-3-methylimidazolium chloride ([C_4mim]Cl) was synthesized in a round-bottom flask by mixing 0.5 mol of 1-butyl-3-methylimidazole and 0.5 mol of 1-chloro-butane. The content was stirred at 150 rpm with a magnetic stirrer at 80 °C for 72 h. A viscous yellow-reddish liquid was obtained and crystallized at -40 °C. To prepare 1-butyl-3-methylimidazolium hexafluorophosphate ([C_4mim][PF_6]), an ion exchange reaction was performed. Briefly, a mixture containing 0.05 mol of [C_4mim]Cl and 0.05 mol of potassium hexafluorophosphate in distilled water was shaken vigorously for 45 min. The upper aqueous phase formed after shaking was separated and discarded. Then, 40 mL of distilled water was added and stirred for 15 min. Afterwards, 40 mL of chloroform was added, and the organic phase was separated and dried under vacuum, in which a slightly yellowish viscous liquid [C_4mim][PF_6] was obtained, with a purity level of ~97%.

Section S2. Environmental assessment

The carbon footprint is the sum of the greenhouse gas (GHG) emissions of the system, expressed as carbon dioxide equivalent (CO_{2eq}), and calculated according to Equation S1.

$$CF = \frac{\sum (A_i \times GHG_i)}{C} \quad \text{Eq. S1}$$

where CF is the carbon footprint of each scenario ($g_{CO2eq.}\mu g_{carotenoids}^{-1}$), A_i is the amount of each input i presented in Table 2, except fruit, for each scenario (units in Table 2: g, mL or Wh), GHG_i is the GHG emission factor of each input *i* presented in Table 3 (units in Table 3: kg_{CO2eq} kg^{-1} or kgC_{O2eq} kWh^{-1}), and C is the amount of carotenoids extracted in each scenario presented in Table 2 (in $\mu g_{carotenoids}$).

The carbon footprint of fruit production was excluded from this study because fruits are considered as a residue and thus, all GHG emissions from *Bactris gasipaes* cultivation are allocated to the main product (palm heart).

The A_i values considered for chemicals and water were obtained during the experiments based on the real amounts consumed. The A_i values for electricity were estimated based on the time of operation and nominal power of each equipment. Thus, they can be overestimated as the real power can be lower than the nominal power.

The GHG_i values were taken from the Ecoinvent database. For $[C_4mim][BF_4]$ and Celite 545, GHG_i values were not available in the database and GHG_i values from similar chemicals were used instead, as explained in Table 3. However, this approximation has low effect in the total carbon footprint of the system as the contribution of these chemicals is very small. Table S8 presents the contribution of each input to the total carbon footprint for each scenario.

Table S8. Breakdown of the carbon footprint for the three scenarios assessed in this work.

	Scenario 1		**Scenario 2**		**Scenario 3**	
	g_{CO2eq} $\mu g_{carotenoids}^{-1}$	%	g_{CO2eq} $\mu g_{carotenoids}^{-1}$	%	g_{CO2eq} $\mu g_{carotenoids}^{-1}$	%
Electricity	1.32	39.0	1.47	87.5	1.08	25.2
Fruit freezing	*1.96×10^{-6}*		*2.17×10^{-6}*		*3.15×10^{-6}*	
Fruit lyophilization	*1.23×10^{-4}*		*1.37×10^{-4}*		*1.99×10^{-4}*	
Ultrasonic homogenization	*0.460*		*0.513*		-	
Filtration	*0.0243*		*0.0271*		*0.0687*	
IL freezing	*7.63×10^{-4}*		*8.50×10^{-4}*		-	
Rotary evaporation	*0.830*		*0.926*		*1.01*	
Water	2.10×10^{-6}	~0	2.34×10^{-6}	~0	0.0340	0.8
$[C_4mim][BF_4]$	0.0529	1.6	5.36×10^{-3}	0.3	-	-
Ethanol	2.01	59.4	0.203	12.1	-	-
Acetone	-	-	-	-	1.43	33.5
Celite 545	-	-	-	-	0.0391	0.9
Ethyl ether	-	-	-	-	1.54	36.0
Petroleum ether	-	-	-	-	0.156	3.6