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Chemical Composition, Antioxidant Properties, and Thermal Stability of a Phytochemical Enriched Oil from Açai (*Euterpe oleracea* Mart.)

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Phenolic compounds present in crude oil extracts from açai fruit (*Euterpe oleracea*) were identified for the first time. The stability of açai oil that contained three concentrations of phenolics was evaluated under short- and long-term storage for lipid oxidation and phenolic retention impacting antioxidant capacity. Similar to açai fruit itself, açai oil isolates contained phenolic acids such as vanillic acid (1,616 ± 94 mg/kg), syringic acid (1,073 ± 62 mg/kg), *p*-hydroxybenzoic acid (892 ± 52 mg/kg), protocatechuic acid (630 ± 36 mg/kg), and ferulic acid (101 ± 5.9 mg/kg) at highly enriched concentrations in relation to açai pulp as well as (+)-catechin (66.7 ± 4.8 mg/kg) and numerous procyanidin oligomers (3,102 ± 130 mg/kg). Phenolic acids experienced up to 16% loss after 10 weeks of storage at 20 or 30 °C and up to 33% loss at 40 °C. Procyanidin oligomers degraded more extensively (23% at 20 °C, 39% at 30 °C, and 74% at 40 °C), in both high- and low-phenolic açai oils. The hydrophilic antioxidant capacity of açai oil isolates with the highest phenolic concentration was 21.5 ± 1.7 μmol Trolox equivalents/g, and the total soluble phenolic content was 1252 ± 11 mg gallic acid equivalents/kg, and each decreased by up to 30 and 40%, respectively, during long-term storage. The short-term heating stability at 150 and 170 °C for up to 20 min exhibited only minor losses (<10%) in phenolics and antioxidant capacity. Because of its high phenolic content, the phytochemical-enriched açai oil from açai fruit offers a promising alternative to traditional tropical oils for food, supplements, and cosmetic applications.

KEYWORDS: Açai; oil; *Euterpe oleracea*; phenolic; stability

INTRODUCTION

Açai (*Euterpe oleracea* Mart.) is currently among the most economically significant palm species in the Brazilian Amazon (*1*) and has become one of the main export products of the Amazon estuary to other regions in the world. International growth of the açai trade has been attributed to the açai beverage industry and related products (*2*), where much attention has been given to its antioxidant capacity and associated potential health benefits (*2–7*). As such, research efforts have focused on the study of açai pulps and juices (*3, 5*) and factors affecting their stability and functional properties (*6, 7*). A distinguishing feature of açai fruit pulp is the presence of lipids that may account for up to 9% of the total fresh weight of the edible pulp (*8, 9*) and potentially represent a valuable byproduct given its unique sensory characteristics, dark green color, and potential health benefits related to its traditional therapeutic uses by inhabitants (*10*). A previous study on açai oil composition (*9*) reported 60% oleic acid, 22% palmitic acid, 12% linoleic acid, and 6% each of palmitoleic and stearic acids along with other fatty acids in trace amounts. At least five sterols were also identified including β-sitosterol (78%), stigmasterol (6.5%), δ5-avenasterol (6.5%), campesterol (6.0%), and cholesterol (2.0%) (*9*). However, no reports on the phenolic and antioxidant composition of açai oil are available, and its stability during processing and storage has not been previously assessed. Therefore, the present study was conducted to characterize the main phenolic compounds in açai oil extracts from açai fruit and to evaluate short- and long-term stability of these compounds in terms of lipid oxidation and their impact on antioxidant capacity and total soluble phenolic contents. On the basis of these trials, the potential uses of açai oil extracts for food, supplement, and cosmetic applications were determined.

MATERIALS AND METHODS

Materials and Processing. The food-grade açai oil used in these trials was isolated using hydroalcoholic solvents from a water-insoluble filter cake commercially used to clarify açai pulp in the manufacture of açai juice using a patent-pending process (*11*) to recover both triacylglycerides and polar phenolic compounds. The filter cake was obtained from the Bossa Nova Beverage Group (Los Angeles, CA) and was held frozen (−20 °C) until the açai oil isolation procedure on a pilot scale. Solvent removal was accomplished using a falling film

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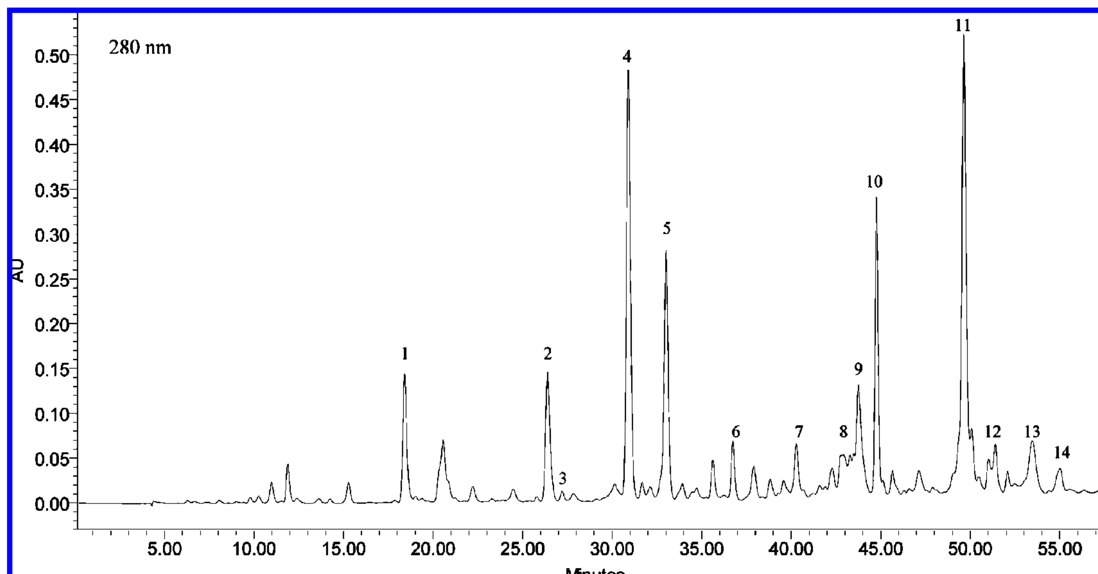

Figure 1. HPLC chromatogram of phenolics present in a typical *E. oleracea* oil extract. Peak assignments: 1, protocatechuic acid; 2, *p*-hydroxybenzoic acid; 3, (+)-catechin; 4, vanillic acid; 5, syringic acid; 6 and 7, procyanidin dimers; 8, ferulic acid; 9 and 10, procyanidin dimers; and 11−14, procyanidin trimers.

evaporator, and the resultant açai oil was essentially free of water and solvent. This initial açai oil was designated as "high phenolics" açai oil, since the oil was naturally enriched in phenolics trapped in the filter cake. A modified version of this açai oil was prepared by repeatedly (five times) extracting the high phenolics açai oil with water (1:5 ratio) to remove water-soluble phenolic compounds and then extracted with 100% hexane to facilitate isolation of predominantly the triacylglycerols. Hexane was removed from the açai oil under reduced pressure at <40 °C, resulting in an açai oil that contained phenolics at a concentration <5% of the original and was designated as a "low phenolics" açai oil. A third modification of the original açai oil was prepared as a 50:50 (v/v) blend of the first two açai oils and designated as "intermediate phenolics" açai oil.

Equal amounts of each açai oil (5 mL) were loaded into screw-cap glass test tubes in triplicate, and the headspace was flushed with nitrogen, and the samples were stored at 20, 30, and 40 °C in the dark for 10 weeks. Individual tubes were removed from storage periodically and held at −20 °C until analysis. Additionally, a short-term evaluation of the thermal stability of phenolics in the high phenolic açai oil was evaluated by loading 2 mL into a screw-cap glass test tube and heating to an internal temperature of 150 and 170 °C for 0, 5, 10, and 20 min using peanut oil as the heating medium. Samples were immediately cooled by immersion in cold water. Following each stability trail, açai oil samples (100 mg) were extracted with 4 mL of a 1:1 (v/v) hexane: methanol mixture until the oil was fully dissolved. After dissolution, a known volume of 0.1 M aqueous citric acid buffer at pH 3.0 was added to form a bilayer from which the lower, hydrophilic phase was retained for subsequent chemical analyses.

Phytochemical analyses of the enriched açai oil were also compared to a nonanthocyanin phenolic extract obtained from açai fruit. A fruit pulp was obtained from the frozen skins of açai fruit by cold maceration with water and was subsequently clarified by removing lipids and insoluble solids with centrifugation and filtration. To obtain chemically similar phenolic extracts as was obtained from the açai oil, the açai fruit extract was extensively liquid/liquid extracted with ethyl acetate (1:1) to isolate nonanthocyanin phenolics. The solvent was passed through a 5 cm bed of sodium sulfate to remove residual water and evaporated under reduced pressure at <40 °C, and the isolate was redissolved in a known volume of 0.1 M citric acid buffer (pH 3.5) for subsequent analyses.

Chemical Analyses. Major phenolic compounds present in açai oil were analyzed by reversed-phase high-performance liquid chromatography (HPLC) with a Waters 2695 Alliance system (Waters Corp., Milford, MA) over 60 min, according to previously described chromatographic conditions (*6*). Phenolics were identified and quantified based on their spectral characteristics and retention times, as compared to authentic standards (Sigma Chemical Co., St. Louis, MO). Further structural information was obtained by mass spectrometric analyses, performed on a Thermo Finnigan LCQ Deca XP Max MS^n ion trap mass spectrometer equipped with an ESI ion source (ThermoFisher, San Jose, CA). Separations were conducted using the Phenomenex (Torrace, CA) Synergi 4 μm Hydro-RP 80A (2 mm × 150 mm; 4 μm; *S/N* = 106273−106275) with a C18 guard column. Mobile phases consisted of 0.5% formic acid in water (phase A) and 0.5% formic acid in 50:50 methanol:acetonitrile (phase B) run at 0.25 mL/min. Phenolics were separated with a gradient elution program in which phase B changed from 5 to 30% in 5 min, from 30 to 65% in 70 min, and from 65 to 95% in 30 min and was held isocratic for 20 min. Electrospray ionization was conducted in the negative ion mode under the following conditions: sheath gas (N_2), 60 units/min; auxiliary gas (N_2), 5 units/min; spray voltage, 3.3 kV; capillary temperature, 250 °C; capillary voltage, 1.5 V; and tube lens offset, 0 V. Total soluble phenolics, measuring the metal reduction capacity of açai oil extractions, was analyzed by the Folin−Ciocalteu assay (*12*) and quantified in gallic acid equivalents (GAE). The antioxidant capacity was determined using the oxygen radical absorbance capacity assay (*13*), using fluorescein as the fluorescent probe on a BMG Labtech FLUOstar fluorescent microplate reader (485 nm excitation and 538 nm emission). Results were quantified in μmol Trolox equivalents per milliliter of açai oil. The overall oxidative stability of the açai oils was determined by measuring free fatty acids and peroxide value according to AOAC official methods (*14*).

Statistical Analyses. Data from each chemical analysis were analyzed by one-way analysis of variance using SPSS version 15.0 (SPSS Inc., Chicago, IL). Mean separations were conducted using Tukey−Kramer HSD ($p < 0.05$) as a posthoc analysis. Linear and nonparametric correlations among chemical analyses were obtained, and linear regression analyses were conducted using a significance level of 0.05.

RESULTS AND DISCUSSION

The phenolic-enriched açai oil from the byproduct of açai fruit clarification was physically characterized by its dark green color, viscous nature, and a distinctive aroma reminiscent of açai fruit pulp. Further chemical tests were conducted by an independent contract laboratory (Medallion Laboratories, Minneapolis, MN), including specific gravity (0.9247 g/cm^3), refractive index (1.4685), iodine value (75.0 I_2/100 g oil),

Table 1. HPLC-ESI-(−)-MS^n Analyses of Phenolics in *E. oleracea* Oil Extracts

peak	RT (min)	λ_{max} (nm)	compound	$[M - H]^-$ (m/z)	MS^2 (m/z)[a]	MS^3 (m/z)
1	18.5	263, 292	protocatechuic acid	153.2	109.2	91.0
2	26.4	253.9	*p*-hydroxybenzoic acid	137.3	112.9	
3	27.2	277.5	(+)-catechin	289.2	**245.2**, 205.2, 179.2	203.2, 187.2, 161.3
4	30.9	263, 291.7	vanillic acid	167.3	140.9, **108.0**	95.2
5	33.0	271	syringic acid	196.9	182.2, 153.1, **138.1**	123.1, 121.0, 106.0
6	37.9	235, 282	procyanidin dimer	577.1	425.0, **407.2**	289.2, 287.1
7	40.3	235, 282	procyanidin dimer	577.1	425.0, **407.2**	289.2, 287.1
8	42.8	324.9	ferulic acid	193.2	149.1, **134.1**	117.0
9	43.7	235, 282	procyanidin dimer	577.1	425.0, **407.2**	289.2, 287.1
10	44.8	235, 282	procyanidin dimer	577.1	425.0, **407.2**	289.2, 287.1
11	49.7	235, 291.7	procyanidin trimer	865.1	**577.2**, 559.1	451.0, 425.0,407.3, 287.1
12	51.6	235, 291.7	procyanidin trimer	865.1	**577.2**, 559.1	451.0, 425.0,407.3, 287.1
13	52.9	235, 291.7	procyanidin trimer	865.1	**577.2**, 559.1	451.0, 425.0,407.3, 287.1
14	55.0	235, 291.7	procyanidin trimer	865.1	**577.2**, 559.1	451.0, 425.0,407.3, 287.1

[a] Ions in bold indicate the most intense product ion, on which further MS analyses were conducted.

Table 2. Concentration (mg/L) and Relative Abundance (%) of Nonanthocyanin Phenolics Present in *E. oleracea* Clarified Pulp and Oil Extracts

phenolic	*E. oleracea* pulp (mg/L)	relative abundance (%)[a]	*E. oleracea* oil (mg/L)	relative abundance (%)[a]
protocatechuic acid	1.8 ± 0.1	4.8 ± 0.3 a	630.8 ± 36	8.4 ± 0.5 b
p-hydroxybenzoic acid	1.9 ± 0.2	5.1 ± 0.6 a	892 ± 52	11.9 ± 0.7 b
(+)-catechin	5.3 ± 0.6	14.1 ± 1.6 a	66.7 ± 4.8	0.9 ± 0.1 b
vanillic acid	5.5 ± 0.2	14.6 ± 0.6 a	1616 ± 94	21.6 ± 1.3 b
syringic acid	3.7 ± 0.4	9.8 ± 1.3 a	1073 ± 62	14.3 ± 0.8 a
(−)-epicatechin	1.1 ± 0.1	2.9 ± 0.2		
ferulic acid	1.1 ± 0.1	2.9 ± 0.3 a	101 ± 5.9	1.4 ± 0.1 b
procyanidin dimers	6.1 ± 0.7	16.1 ± 1.3 a	1086 ± 121	14.5 ± 1.3 a
procyanidin trimers	11.2 ± 1.2	29.7 ± 3.1 a	2016 ± 53	27.0 ± 2.4 a

[a] Values with different superscript letters between columns represent a significant difference (paired samples *t* test, $p < 0.05$).

Table 3. Major Phenolics Present in *E. oleracea* Oil Extracts (mg/L) Adjusted to Three Different Phenolic Levels

phenolic	phenolics (mg/L) in açai oil		
	high phenolics	intermediate phenolics	low phenolics
protocatechuic acid	630 ± 36	319 ± 18	11.8 ± 1.6
p-hydroxybenzoic acid	892 ± 527	578 ± 33	18.9 ± 1.2
(+)-catechin	66.7 ± 4.8	35.1 ± 2.4	2.2 ± 0.3
vanillic acid	1616 ± 94	884 ± 51	31.4 ± 1.8
syringic acid	1073 ± 62	602 ± 35	21.1 ± 1.4
ferulic acid	101 ± 5.9	57.7 ± 3.3	2.0 ± 0.2
procyanidin dimers	2016 ± 53	633 ± 34	18.3 ± 1.1
procyanidin trimers	1086 ± 121	1175 ± 72	33.9 ± 2.3

peroxide value (5.71 meq/kg oil), and fatty acid composition (17.4% palmitic acid, 0.3% palmitoleic acid, 3.2% stearic acid, 69.2% oleic acid, 8.4% linoleic acid, and 1.1% linolenic acid).

Phenolic Characterization. The phenolic compounds (**Figure 1**) present in açai oil were coextracted from the water-insoluble residues of açai pulp processing and were identified based on their spectrophotometric characteristics and mass spectra and quantified against authentic standards when available. Phenolic acids such as vanillic acid (1616 ± 94 mg/L), syringic acid (1073 ± 62 mg/L), *p*-hydroxybenzoic acid (892 ± 52 mg/L), protocatechuic acid (629 ± 36 mg/L), and ferulic acid (101 ± 5.9 mg/L) were predominantly present in the açai oil, while (+)-catechin (66.7 ± 4.8 mg/L), four B type procyanidin dimers [1085.6 ± 121.3 mg (+)-catechin equiv/L], and four procyanidin trimers [2016.2 ± 53.2 mg (+)-catechin equiv/L] were also detected in high concentrations (**Tables 1** and **2**). In addition, five compounds exhibiting typical flavonoid spectral characteristics were detected at trace concentrations, from 0.58 to 4.21 mg rutin equiv/kg in açai oil. Previous studies on phenolics in açai pulp (*4–7*), seeds (*15*), and freeze-dried açai fruit (*16*) reported the presence of phenolic acids such as vanillic, syringic, *p*-hydroxybenzoic, protocatechuic, and ferulic acid, as well as (+)-catechin, (−)-epicatechin, and B type procyanidins, from dimers to high molecular weight polymers that were not characterized. In this study, structural information was obtained by means of mass spectrometric analyses that confirmed the identities of the phenolics previously identified by HPLC and provided additional information on the identity and degree of polymerization of procyanidin dimers and trimers (**Table 1**). Both the catechin-like UV spectroscopic properties and the characteristic signals at m/z 577.1 ($[M - H]^-$) indicated the presence of procyanidin dimers, while signals at m/z 865.1 ($[M - H]^-$) were attributed to procyanidin trimers. Previous LC-ESI-MS^n studies on proanthocyanidins agreed that the m/z 577.1 ion is indicative of B type procyanidin dimers (*17, 19*) while fragmentation to the m/z 425.0 ion was characteristic of the product obtained from retro-Diels−Alder reaction of ring C and subsequent elimination of ring B from the flavan-3-ol (*17, 18*). Finally, m/z 289.2 and 287.1 fragments, likely from cleavage of the interflavanoid bond (*17, 19*), suggested that these procyanidin dimers consisted of two (+)-catechin or (−)-epicatechin units, although no differentiation between isomers was possible. Similarly, procyanidin trimers (m/z 865.1) were characterized by a predominant product ion at m/z 577.2, likely corresponding to a dimeric fragment ion from cleavage of interflavanoid linkages, which has been recognized as the most important fragmentation mechanism in proanthocyanidin trimers (*17*). Further fragmentation of m/z 577.2 occurred in a similar manner as in the previously described procyanidin dimers.

Açai oil extracts used in these trials did not contain anthocyanins and were therefore compared with nonanthocyanin phenolics present in clarified açai pulp by chemically contrasting contents and concentrations under identical chromatographic conditions (**Table 2**). Similar phenolic profiles were observed

Table 4. Percent Phenolic Losses in *E. oleracea* Oil Extracts Adjusted to Different Phenolic Levels Following Storage (10 Weeks) at 20, 30, and 40 °C

	phenolic losses in açai oil					
	high phenolics			intermediate phenolics		
phenolic	20 °C[a]	30 °C	40 °C	20 °C	30 °C	40 °C
	% loss from initial					
protocatechuic acid	1.33 ± 0.4 a	1.51 ± 0.6 a	1.52 ± 0.3 a	1.57 ± 0.2 a	1.62 ± 0.4 a	1.63 ± 0.4 a
p-hydroxybenzoic acid	0.48 ± 0.2 a	0.46 ± 0.2 a	1.97 ± 0.2 b	0.43 ± 0.2 a	0.52 ± 0.8 a	2.02 ± 0.5 b
(+)-catechin	0.55 ± 0.1 a	1.12 ± 0.3 b	2.35 ± 0.6 c	0.52 ± 0.1 a	0.95 ± 0.2 b	2.44 ± 0.5 c
vanillic acid	0.33 ± 0.1 a	1.03 ± 0.2 b	2.55 ± 0.3 c	0.32 ± 0.3 a	1.17 ± 0.2 b	2.65 ± 0.4 c
syringic acid	0.86 ± 0.1 a	0.85 ± 0.2 a	8.36 ± 1.0 b	0.82 ± 0.2 a	0.81 ± 0.1 a	8.07 ± 1.0 b
ferulic acid	14.8 ± 1.4 a	16.3 ± 0.3 a	32.2 ± 1.4 b	13.6 ± 1.2 a	15.2 ± 1.4 a	33.1 ± 1.9 b
procyanidin dimers	9.27 ± 2.1 a	20.3 ± 2.7 b	33.2 ± 3.4 c	12.1 ± 2.0 a	20.9 ± 2.2 b	29.3 ± 3.0 c
procyanidin trimers	23.2 ± 1.8 a	39.1 ± 3.3 b	73.5 ± 4.4 c	23.8 ± 2.2 a	36.3 ± 4.0 b	69.2 ± 5.0 c

[a] Values with different letters within rows are significantly different (LSD test, $p < 0.05$).

in the açai oil extracts and nonanthocyanin phenolic extracts of açai pulp; yet, their concentrations differed markedly. Because of an enhanced extraction and concentration of compounds from water-insoluble residues from açai pulp clarification, the individual phenolics were significantly higher in açai oil than in açai pulp by 12.6−469.4 times. Dimeric and trimeric procyanidins were predominant in both açai oil extracts (3102 ± 127 mg/L) and açai pulp extracts (17.2 ± 2.2 mg/L) and accounted for over 40% of the total phenolics present. Similarly, phenolic acids such as vanillic, syringic, protocatechuic, *p*-hydroxybenzoic, and ferulic acids were predominant in both the açai oil extracts (101−1616 mg/L) and the açai pulp extracts (1.1−5.5 mg/L). However, their respective abundances differed significantly ($p < 0.05$) between products, and with the exception of ferulic acid, phenolic acids were appreciably enhanced in the açai oil (**Table 2**). Although both (+)-catechin and (−)-epicatechin were found in açai pulp (1.1 and 5.3 mg/kg, respectively), only (+)-catechin (66.7 ± 4.8 mg/kg) was present in açai oil extracts. The similarities between the phenolic profiles of açai pulp and açai oil extracts suggest that these phenolics have the ability to be extracted from açai byproduct sources (e.g., insoluble solids from açai pulp) as free or bound compounds and deposited to a nonpolar lipid phase, which serves to appreciably enhance phenolic concentrations in the açai oil when compared to the fruit pulp from which they were derived.

Phenolic Storage Stability. The influence of naturally occurring phenolics on the phytochemical stability of extracted açai oil during storage was evaluated by monitoring changes to individual phenolics, total soluble phenolic content, and antioxidant capacity of polar isolates in açai oil stored at 20, 30, or 40 °C for 10 weeks. Initial phenolic concentrations in the açai oil were adjusted to three concentration levels containing high, intermediate, and low phenolic concentrations by diluting original açai oil extracts with açai oil whose phenolics were removed by aqueous extraction. The açai oil containing the lowest phenolic concentration contained <5% of the original açai oil's concentration, whereas the intermediate oil was 50% of the original (**Table 3**). Individual phenolic concentrations were monitored periodically during storage, and no significant differences ($p < 0.05$) were found between high and intermediate phenolic oils (**Table 4**), suggesting that phenolic losses were independent of initial phenolic contents. Moreover, no significant changes in (+)-catechin, protocatechuic acid, *p*-hydroxybenzoic acid, vanillic acid, or syringic acid concentrations were detected after 10 weeks of storage at 20 or 30 °C, and only minor changes (<10%) were observed following storage at 40 °C, indicating excellent storage stability of these compounds even under adverse handling conditions. Storage effects were more pronounced for ferulic acid and procyanidin dimers and trimers, as concentrations decreased by 9.3 and 23.2%, respectively, when stored at 20 °C, by 20.3 and 39.1% when stored at 30 °C, and by 33.1 and 73.4% when stored at 40 °C. Because of the high stability of flavanol monomers during storage and earlier reports on the stable nature of procyanidins (*20*), it was hypothesized that decreased concentrations of procyanidin dimers and trimers during storage might be attributed to açai oil matrix effects on procyanidin extraction efficiency, such as the formation of complexes between procyanidins and proteins or other oil-soluble components over time. Evidence for complexation that decreased solubility of procyanidins was found upon further analyses of the açai oil following the initial phenolic extraction. Because phenolic acids and monomeric flavonoid concentrations remained constant during storage, total soluble phenolic contents were used as a potential indicator of the presence of residual procyanidins in the phenolic-extracted açai oil. Results indicated that total soluble phenolic contents in the phenolic-extracted açai oil were 64.7 ± 3.9 mg GAE/L and thus reflected the presence of oil-bound procyanidins in the oil that was enhanced during oil storage.

Açai oil extracts were additionally evaluated for soluble phenolic contents, as a measure of total reducing capacity, and for changes in antioxidant capacity throughout the storage period. A statistically significant ($p < 0.01$) correlation was found between total soluble phenolic content and antioxidant capacity by both linear ($r = 0.94$) and nonparametric ($\rho = 0.92$) methods during storage at 20, 30, and 40 °C. The high phenolic oil had an initial antioxidant capacity of 21.5 ± 1.7 μM TE, Trolox equivalents/mL, and a total soluble phenolic content of 1252 ± 42 mg GAE/L, whereas the intermediate phenolic oils were about half the SE levels at 14.3 ± 1.2 μM TE/mL and 695 ± 28 mg GAE/L and low phenolic oils at 4.8 ± 0.3 μM TE/mL and 192 ± 8.3 mg GAE/L, respectively. Total soluble phenolics expressed as GAE were found at appreciably lower concentrations than the sum of individual phenolic concentrations (**Table 3**) and were attributable to the high concentration of hydroxybenzoic acids in the açai oil that was previously shown to exhibit poor reducing capacity and radical scavenging activity (*21, 22*). The antioxidant activity of phenolic acids was shown to be dependent on the number of hydroxy substitutions on their aromatic ring (*21*); however, the electron-withdrawing properties of the carboxyl group in benzoic acids have a negative effect on hydrogen-donating abilities of hydroxybenzoic acids (*22*). During storage, the total soluble phenolic content of the high phenolic oil decreased by 36.1−40.3% when stored at 20, 30, or 40 °C (**Figure 2**), corresponding to a 18.6−26.8% decrease in antioxidant capacity (**Figure 3**). Both the intermediate and the low phenolic oils experienced significantly ($p <$

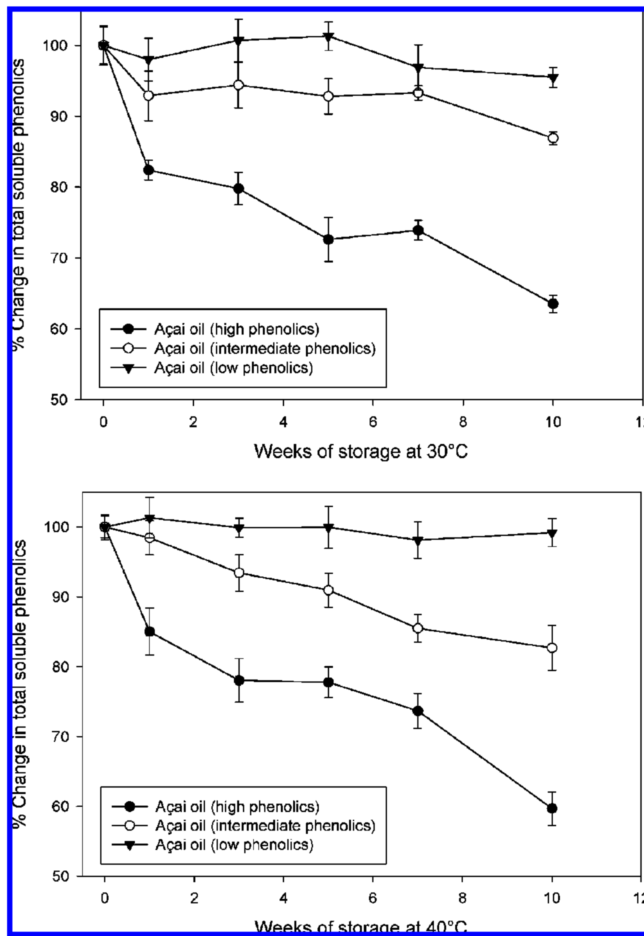

Figure 2. Percent changes in total soluble phenolic contents during storage (30 and 40 °C) of *E. oleracea* oil extracts adjusted to three different initial phenolic contents (high, intermediate, and low). Error bars represent the standard error of the mean ($n = 3$).

0.05) smaller losses for these attributes during storage ranging from minor losses (<10%) in the low phenolic oil at all storage temperatures and as high as 21.8% in the intermediate phenolic oil at 40 °C. Linear regression analyses of antioxidant capacity and total soluble phenolic contents during storage further confirmed a significant ($p < 0.01$) influence of açai oil phenolic concentration on retention of both total soluble phenolics and antioxidant capacity during storage, but no significant effect was attributed to storage temperature. Such differences might be attributed, at least partially, to previously observed differences in procyanidin concentrations (**Table 3**), which were more pronounced in high and intermediate phenolic oils.

Oil Storage Stability. The oxidative stability of açai oil extracts adjusted to three different phenolic concentrations was further assessed by monitoring changes in free fatty acid (% oleic acid) and peroxide values (mequiv/kg) following storage. Free fatty acid (<0.1%) and peroxide values (<10 mequiv/kg) were unchanged prior to and after storage of the açai oils at each temperature, indicating that lipids did not experience significant oxidative changes (data not shown) after 10 weeks of storage at 20, 30, or 40 °C.

Phenolic Thermal Stability. The short-term, high-temperature storage stability of phenolics in açai oil extracts was evaluated by monitoring changes in total soluble phenolic contents, antioxidant capacity, and individual phenolic concentrations following heating of the high phenolic oil to a temperature of 150 or 170 °C and holding for 5, 10, and 20 min. This short-term trial was to simulate cooking effects on

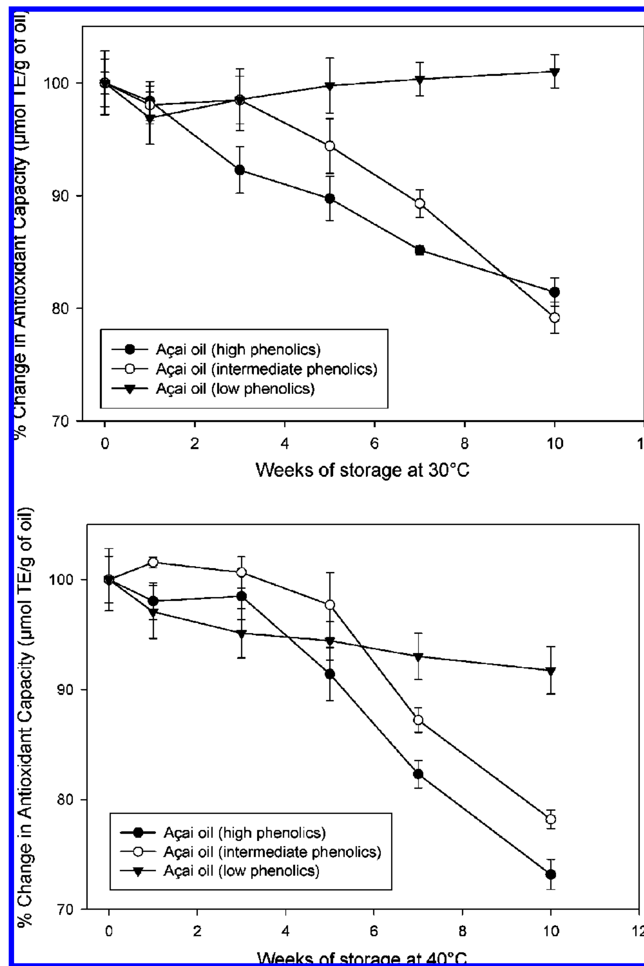

Figure 3. Percent changes in antioxidant capacity during storage (30 and 40 °C) of *E. oleracea* oil extracts adjusted to three different initial phenolic contents (high, intermediate, and low). Error bars represent the standard error of the mean ($n = 3$).

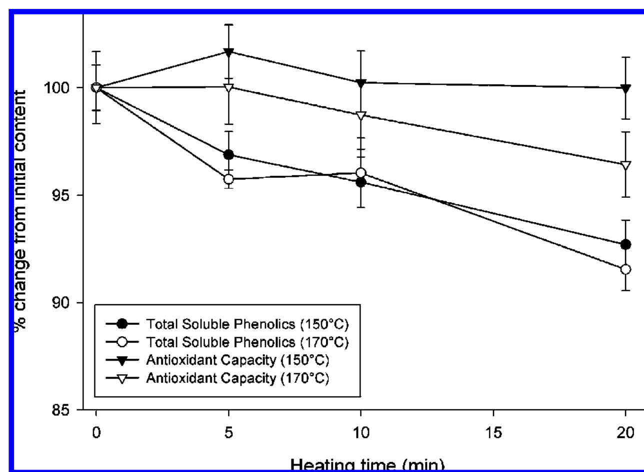

Figure 4. Percent changes in total soluble phenolics and antioxidant capacity in 100% *E. oleracea* oil extracts following heating (150 or 170 °C). Error bars represent the standard error of the mean ($n = 3$).

the açai oil and to determine if the phytochemical composition and stability would degrade under moderate to high temperatures. However, even under the most extreme time and temperature combination, no changes in the physical nature of the açai oil (color alterations and viscosity changes) were observed, and no significant ($p < 0.05$) changes to individual phenolic concentrations were detected during this evaluation. Minor

variations in overall antioxidant capacity (<5%) and soluble phenolic contents (<10%) were observed under these same conditions (**Figure 4**), with slightly greater losses observed at 170 °C as compared to 150 °C. Therefore, the extracted açai oil demonstrated excellent thermal stability for the phenolics present and indicated its potential for culinary applications involving moderate exposure times to high temperatures.

Conclusion. The phytochemical composition of açai oil extracts from water-insoluble residues of açai pulp processing was characterized and found to be appreciably enhanced in nonanthocyanin phenolics such as phenolic acids and procyanidins. Individual phenolic contents were not significantly altered by long-term storage at temperatures up to 40 °C for 10 weeks nor by short-term heating at temperatures up to 170 °C for 20 min, indicating good stability of these compounds and their antioxidant properties. Because of its high phenolic content, storage stability, and unique sensory characteristics, açai oil is a promising new alternative to traditional oils for food, supplements, and cosmetic applications.

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