Food Chemistry 134 (2012) 1156–1164

Contents lists available at SciVerse ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Analytical Methods

Liquid chromatography/mass spectrometry based fingerprinting analysis and mass profiling of *Euterpe oleracea* (açaí) dietary supplement raw materials

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ARTICLE INFO

Article history:
Received 24 June 2011
Received in revised form 13 January 2012
Accepted 19 February 2012
Available online 27 February 2012

Keywords:
Açaí
Euterpe oleracea
Fingerprinting
Mass profiling
Polyphenols

ABSTRACT

Chemical fingerprinting and mass profiling methods to identify biologically active compounds in botanical dietary supplements is gaining much attention in recent years. *Euterpe oleracea* (açaí) has been reported to be rich in health-beneficial chemical constituents. We have developed LC/MS based fingerprinting and mass profiling methods to identify fatty acids, anthocyanins and non-anthocyanin polyphenols in three processed raw materials; non-organic açaí powder (ADSR-1), raw-organic açaí powder (ADSR-2) and freeze-dried açaí powder (ADSR-3) that are used in the preparation of botanical dietary supplements. For LC/MS analysis of fatty acids and non-anthocyanin polyphenols, the açaí samples were extracted sequentially with dichloromethane followed by methanol. To study fingerprinting analysis of anthocyanins, açaí samples were extracted with acidic methanol–water. The LC separation of fatty acids, non-anthocyanin polyphenols and anthocyanins in açaí raw materials was achieved using a C18 column with a gradient mobile phase consisting of solvents A (0.1% formic acid in water), and B (0.1% formic acid in methanol). MS experiments were carried out with negative and positive mode electrospray ionization. LC/MS analysis of dichloromethane extracts of (ADSR-1), (ADSR-2) and (ADSR-3) açaí powders have shown to contain fatty acids, γ-linolenic acid, linoleic acid, palmitic acid, and oleic acid. Whereas, the fingerprinting analysis of methanol extracts of ADSR-1, ADSR-2 and ADSR-3 led to the identification of phenolic acids, anthocyanin and non-anthocyanin polyphenols. The results from our study may be useful for the authentication and quality assessment of açaí dietary supplement raw materials.

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1. Introduction

Dietary supplements are the most rapidly growing products in the complementary and alternative medicine (CAM) and food industries. According to the Nutritional Business Journal Global Supplement and Nutrition Industry Report 2010, the sales of dietary supplements and natural organic food and beverages increased by 8% to $270 billion in 2008 (Anon. NBJ's Global Supplement, 2010). Based on the national surveys, more than 40% of adults in the United States take some form of dietary supplements to promote their health and wellness or to prevent and treat diseases. Dietary supplements containing açaí (*Euterpe oleracea* Mart.) extracts are available on the market in dosage forms such as tablets, capsules, soft gels, juice, smoothies, and instant drink powders (Taylor, 2010). The marketing potential of açaí products is gaining more importance due to their potential health benefits such as antioxidant (Kang et al., 2010; Lichtenthaler et al., 2005; Schauss et al., 2006a,b), anti-inflammatory (Jensen et al., 2008; Matheus, de Olivera Fernandes, Silveira, & de Sousa Menezes, 2006) and tumor cell proliferation inhibitory properties (Hogan et al., 2010; Pacheo-Palencia, Mertens-Talcott, & Talcott, 2010). Quality of these products is one of the greatest uncertainties that consumers, clinicians, regulators, and researchers face, especially in the case of botanicals, which contain a large number of phytochemicals. In order to insure the consumer's proper health protection, the critical step is to ascertain the identity, consistency and authenticity by developing suitable fingerprinting and mass profiling methods to assess the quality of botanical dietary supplements (Fu et al., 2009).

Due to the complexity of botanical dietary supplements, a comprehensive analysis of chemical constituents of these materials is difficult and time consuming. Recently, the chromatographic fingerprinting technique has been used in systematic characterization and identification of these chemical constituents and, consequently, considered to be useful analytical tools in the quality assessment of botanical dietary supplements (Fu et al., 2009). This approach was accepted in 1991 by the World Health Organization (WHO) as a strategy for identification and quality assurance of herbal medicine (WHO, 1991). Fingerprinting analysis using chromatographic methods such as thin layer chromatography (TLC) (Cui, Fu,

Abbreviations: ADSR-1, non-organic açaí powder; ADSR-2, raw-organic açaí powder; ADSR-3, freeze-dried açaí powder.

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http://dx.doi.org/10.1016/j.foodchem.2012.02.123

Lee, & Wang, 2005; Liu, Du, Li, Guan, & Liu, 2008; Rumalla et al. 2008), gas chromatography (GC) (Lin et al., 2010; Milchard et al., 1997), and high speed counter current chromatography (HSCCC) (Gu, Zhang, Su, & Ouyang, 2004), liquid chromatography (LC) (Chen, Fan, Zhang, Wu, & Wu, 2007; Chou et al., 2009; Ding et al., 2008; Kumar, Bhandari, & Brunonii, 2009; Lai, Ni, & Kokot, 2010; Sannomiya et al., 2007; Xia et al., 2009; Xiaohui, Yi, & Yiyu, 2006), and the spectroscopic methods such as fourier transform infrared (FTIR) (Kong, Liu, Zhao, & Zhang, 2010), nuclear magnetic resonance (NMR) (Caligiani, Palla, Maietti, Cirlini, & Brandolini, 2010; Nicoletti & Pettitto, 2010; Rezzi et al., 2005), and mass spectroscopy (MS) (Abreu, Mazzafera, Eberlin, Zullo, & Sawaya, 2007; Gomez-Ariza, Garcia-Barrera, & Lorenzo, 2006; Sannomiya et al., 2007; Sawaya et al., 2004; Xiaohui et al., 2006) have been employed so far.

Consequently, ongoing development in LC/MS interface technologies combined with powerful features for qualitative and quantitative analysis has resulted in a wider scope of application (He, Yang, & Yue, 2007). As a result LC/MS based methodologies are currently essential analytical methods in fingerprinting analysis of a multi-chemical class of compounds in plant extracts and botanical dietary and nutritional supplements (Ding et al., 2008; Tao, Li, Liang, & Van Breemen, 2009). The application of LC/MS based fingerprinting has also been revolutionized due to its improved performance in terms of selectivity, sensitivity, chromatographic resolution and ionization capability (Sawaya et al., 2004). In addition, it has been demonstrated that the LC/MS based mass profiling approach has the ability to quickly identify statistically meaningful differences between features (discrete molecular chemical entities defined by retention time and mass) in the same group or two different groups. In the current study, we describe LC/MS based fingerprinting and mass profiling methods developed for the first time to identify the major fatty acids, anthocyanin and non-anthocyanin polyphenols in three different processed açaí raw materials which are used in the preparation of botanical dietary supplements.

Table 1
Major compounds identified in non-organic (ADSR-1), organic (ADSR-2) and freeze-dried (ADSR-3) açaí powders.

RT (min)	Calculated mass [M]	Experimental mass m/z $[M-H]^-$	Formula $[M-H]^-$	Error (ppm)	DBE	MS/MS (m/z)	Identification[a]
Non-anthocyanin polyphenols in methanol extracts of freeze-dried açaí powder (ADSR-3)							
3.52	594.1593	593.152	$C_{27}H_{29}O_{15}$	1.36	13	285.0403	Kaempherol rutinoside[b]
6.17	168.0426	167.0353	$C_8H_7O_4$	1.88	5	152.0107, 109.026	Vanillic acid
6.88	448.1006	447.0939	$C_{21}H_{19}O_{11}$	1.38	12	357.0582, 349.0322, 327.0496	Orientin
6.99	304.0583	303.0503	$C_{15}H_{11}O_7$	2.40	10	-	Taxifolin
7.17	448.1006	447.0942	$C_{21}H_{19}O_{11}$	2.00	12	357.0562, 349.0322, 327.0496	Isoorientin
7.88	432.1056	431.0994	$C_{21}H_{19}O_{10}$	2.48	12	341.0683, 311.0558, 283.0606	Vitexin
8.73	432.1056	431.0993	$C_{21}H_{19}O_{10}$	2.12	12	341.0662, 311.0569, 283.0583	Isovitexin
8.98	462.1162	461.1097	$C_{22}H_{21}O_{11}$	1.61	12	371.0775, 341.0663	Scoparin[b]
9.53	464.0955	463.0885	$C_{21}H_{19}O_{12}$	0.66	12	301.0354	Quercetin 3-glucoside
9.56	610.1534	609.1463	$C_{27}H_{29}O_{16}$	0.36	13	301.0334	Quercetin rutinoside
12.97	302.0429	301.0356	$C_{15}H_9O_7$	0.72	11	151.0032	Quercetin
15.41	300.0635	299.0562	$C_{16}H_{11}O_6$	0.38	11	284.0316	Chrysoeriol
Non-anthocyanin polyphenols in methanol extracts of organic açaí powder (ADSR-2)							
2.48	154.0266	153.0194	$C_7H_5O_4$	0.70	5	109.0928	Protocatechuic acid
6.17	168.0424	167.0351	$C_8H_7O_4$	0.78	5	-	Vanillic acid
7.19	434.1213	433.1142	$C_{21}H_{21}O_{10}$	0.49	11	-	Flavanoid glycoside[b]
9.38	464.0956	463.0884	$C_{21}H_{19}O_{12}$	0.33	12	301.0260	Quercetin 3-glucoside
9.50	610.1531	609.1458	$C_{27}H_{29}O_{16}$	0.54	13	301.0354, 323.0201	Quercetin rutinoside
10.70	434.0849	433.0783	$C_{20}H_{17}O_{11}$	1.47	12	301.0359	Quercetin arabinopyranoside
10.9	448.1006	447.0939	$C_{21}H_{19}O_{11}$	1.32	12	301.028	Quercetin rhamnoside[b]
12.43	432.1056	431.098	$C_{21}H_{19}O_{10}$	0.68	12	285.0407	Kaempherol rhamnoside[b]
12.58	592.1428	591.1369	$C_{27}H_{27}O_{15}$	0.94	14	301.0333, 447.0918, 489.1045, 529.1338	Quercetin hydroxylmethylglutaryl-rhamnoside[b]
12.95	302.0431	301.0358	$C_{15}H_9O_7$	1.52	11	151.0035	Quercetin
Non-anthocyanin polyphenols in methanol extracts of non-organic açaí powder (ADSR-1)							
2.43	154.0266	153.0193	$C_7H_5O_4$	0.04	5	109.0303	Protocatechuic acid
6.94	448.0936	447.0864	$C_{21}H_{19}O_{11}$	2.32	12	327.0428, 357.0536	Orientin
7.14	448.0996	447.0923	$C_{21}H_{19}O_{11}$	2.18	12	327.0507, 357.0616	Isoorientin
8.99	462.1167	461.1093	$C_{22}H_{21}O_{11}$	0.97	12	341.0664, 371.0773	Scoparin[b]
9.53	610.1534	609.1468	$C_{27}H_{29}O_{16}$	0.92	13	301.0386	Quercetin rutinoside
7.85	432.1082	431.099	$C_{21}H_{19}O_{10}$	1.39	12	283.0623, 311.0559, 341.0680	Vitexin
8.73	432.1071	431.0999	$C_{21}H_{19}O_{10}$	3.44	12	283.0538, 311.0561, 341.0667	Isovitexin
12.93	302.0429	301.0352	$C_{15}H_9O_7$	0.46	11	131.0032	Quercetin
15.36	300.0636	299.0583	$C_{16}H_{11}O_6$	0.78	11	284.0329	Chrysoeriol
Fatty acids in dichloromethane extracts of ADSR-1, ADSR-2 and ADSR-3							
22.72	294.2202	293.2128	$C_{18}H_{29}O_3$	2.34	4	–	Fatty acid[b]
25.73	278.2248	277.2176	$C_{18}H_{29}O_2$	0.95	4	–	γ-Linolenic acid
26.20	280.2410	279.2337	$C_{18}H_{31}O_2$	2.80	3	–	Linoleic acid
26.79	256.2411	255.2338	$C_{16}H_{31}O_2$	3.25	1	–	Palmitic acid
27.97	282.2570	281.2497	$C_{18}H_{33}O_2$	3.87	2	–	Oleic acid
Anthocyanins in acidic methanol extracts of ADSR-1, ADSR-2 and ADSR-3							
9.63	448.1008	449.1154	$C_{21}H_{20}O_{11}$	2.50	12	287.0555	Cyanidin 3-glucoside
9.41	580.1424	581.1591	$C_{26}H_{29}O_{15}$	1.41	13	287.0540	Cyanidin 3-sambubioside[c]
9.80	594.1593	595.1745	$C_{27}H_{31}O_{15}$	2.08	13	287.0543, 449.1102	Cyanidin 3-rutinoside
10.52	608.1742	609.1838	$C_{28}H_{33}O_{15}$	2.16	13	301.0734, 463.1238	Peonidin 3-rutinoside[c]

[a] Compounds were fully identified by MS and MS/MS spectral data and by comparison with commercially available standards.
[b] Compounds were tentatively identified by comparison of molecular formula and double bond equivalent and MS/MS spectral data with those reported in the literature.
[c] Anthocyanins were not found in ADSR-2.

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