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Effect of water, metallic ions, fatty acid and temperature on oxidative stability of 1-octacosanol from sugarcane rind

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ABSTRACT

The chemical composition and selected physical parameters of crude 1-octacosanol (1-OC) extracted from sugarcane rind have been determined. GC–MS results exhibited that 1-OC sample was primarily composed of 1-OC (45.17%), 1-docosene (12.04%), 1-triacontanol (0.23%), 1-heneicosanol (0.33%), 1-tetracosanal (0.28%), campesterol (4.5%), stigmasterol (9.12%) and β-sitosterol (8.23%). The linoleic acid had important effects on physical and chemical properties of 1-OC sample, as it notably changed the melting point and the onset oxidation temperature T_o of 1-OC sample from 83.75 ± 0.35 °C to 63.25 ± 0.35 °C and 245.64 ± 2.04 °C to 160.03 ± 0.01 °C, respectively. It was also proved that the oxidation reactions were significantly different at different temperature levels. 1-OC was stable up to 245.64 ± 2.04 °C. However, when the temperature continued to rise, 1-OC and its oxidation products started to be oxidized. Therefore, attention should be paid to the quality of 1-OC during the preparation of food and to minimize the undesirable breakdown products.

1. Introduction

1-Octacosanol (1-OC) is a major component of policosanol, the primary aliphatic 24- to 34-carbon alcohols derived from the wax constituent of plants and seeds (Irmak & Dunford, 2005; Ou, Zhao, Wang, Tian, & Wang, 2012). 1-OC was often acted as a test substance and has been a focus of much research in recent years due to its potential beneficial effects, such as lowering cholesterol, antiaggregatory properties, cytoprotective use and ergogenic properties for human health (Taylor, Rapport, & Lockwood, 2003). Cholesterol-lowering properties of 1-OC have been widely studied, and many studies have shown that 1-OC is very effective in lowering LDL content and increasing HDL level (Gouni-Berthold & Berthold, 2002; Kato et al., 1995). An increased risk of death from coronary heart disease is associated with increases in serum cholesterol levels. Therefore, for the sake of our health, a number of dietary supplements containing 1-OC are commercially available and many studies have demonstrated that 1-OC is well tolerated and safe both in human and animals (Irmak, Dunford, & Milligan, 2006; Taylor et al., 2003). However, thermal decomposition of 1-OC will occur when 1-OC is heated to certain temperatures. It was reported that a 87.5% mass loss of 1-OC was detected as the temperature rose from 185 to 340 °C (Martinez, Uribarri, & Laguna, 1999).

Heating is an important processing procedure for many foods, such as fried or baked foods. When heated at elevated temperature the oil and phytochemicals in food undergo a series of physical and chemical reactions, including hydrolysis, oxidation and thermal decomposition (Dobarganes, Marquez-Ruiz, & Velasco, 2000; Soupas, Huikko, Lampi, & Piironen, 2007). As these reactions proceed, the functional and nutritional qualities of these foods will change, eventually some hazardous oxidation products will be produced. For example, phytosterol oxidation products, which may cause cytotoxic and pro-apoptotic effects, have been produced and identified during the processing and preparation of foodstuffs (O'callaghan, McCarthy, & O'Brien, 2014). A good understanding of phytochemicals, such as 1-OC and phytosterol oxidation, can improve our ability to minimize the appearance of undesirable breakdown products.

Differential scanning calorimetry (DSC) is a thermal technique that has been applied in the analysis of auto-oxidation process of oils and fats (Kowalska, Kostecka, Tarnowska, & Kowalski, 2014; Naik, Meda, & Lele, 2014; Tan, Man, Selamat, & Yusoff, 2002), chocolate technology, food emulsion stability and lipid performance during dairy product processing, and several other

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circumstances (Caponio et al., 2013). This method is advantageous as it is more precise and sensible, requires less sample and time, and avoids the use of toxic chemicals (Chiavaro et al., 2013; Garcia, Franco, Zuppa, Antoniosi, & Leles, 2007; Pardauil et al., 2011). Oxidation is an exothermic process and the reaction heat produced makes it possible to use DSC for this study (Cibulkova, Certik, & Dubaj, 2014). Non-isothermal (dynamic) and isothermal are two modes that can be performed in DSC studies when the oxidative stability of phytochemicals is studied. Non-isothermal DSC was reported to be more suitable to analysis the oxidative stability of phytochemical (Cibulkova et al., 2014; Litwinienko, 2001). However, until now, there are no reports on the use of non-isothermal DSC to study production and oxidative stability of 1-OC.

Sugarcane (*Saccharum officinarum* L.) is an important economic plant that is primarily cultivated for sugar production. Currently, sugarcane, bees and wheat wax are reported as three main sources of policosanol (Dunford, Irmak, & Jonnala, 2010). Policosanol from sugarcane is proven to be an ideal source of 1-OC. It was reported that filter mud from sugarcane juice clarification contains 6.85 g/100 g waxes, and a high content (29.65 g/100 g) of 1-OC in the waxes was observed (Ou et al., 2012). Molasses and vinasses were evaluated as new sources of sugarcane wax and 1-OC content was up to 81% in a fraction of the wax extraction (Nuissier, Bourgeois, Grignon-Dubois, Pardon, & Lescure, 2002). Sugarcane bagasse was reported to contain a higher content of policosanol than sugarcane leaves and other materials, and have a high and stable content of 1-OC (Irmak et al., 2006; Oliaro-Bosso et al., 2009). Sugarcane rinds, where most sugarcane waxes were attached to, are about 20% weight of sugarcane. To the best of our knowledge, elaborate studies about recovery of 1-OC from sugarcane rind are still rare. In addition to 1-OC, phytosterols that also possess cholesterol-lowering properties were also extracted from sugarcane rind as major phytochemicals. Stigmasterol (31%), campesterol (19%) and β-sitosterol (45.8%) were isolated from sugarcane wax extraction as the principal sterols (Georges, Sylvestre, Ruegger, & Bourgeois, 2006). Recently, phytosterols have received increased attention due to their capability to inhibit cholesterol intestinal absorption, resulting in lowering serum total plasma cholesterol and low-density lipoprotein levels (Klingberg et al., 2012; Plat & Mensink, 2001). Research of recovery 1-OC from sugarcane rind will provide valuable information and have potential commercial value to the health food industry.

The aim of this work was to evaluate the oxidative stability of 1-OC sample from sugarcane rind by non-isothermal DSC. The chemical composition of the 1-OC sample was first identified by GC–MS. To understand the environmental effects on the oxidation of 1-OC sample, water, metallic ions and fatty acid were mixed with 1-OC sample and the onset oxidation temperatures were then investigated. The 1-OC sample was also heated to different specified temperatures and the oxidation products were finally identified by GC-FID.

2. Materials and methods

2.1. Plant materials and chemicals

Sugarcanes (*Saccharum officinarum Linn. cv. badila*) used as a starting material were collected at commercial maturity from Zhejiang, PR China. Rind samples were obtained by hand peeling and outer layer rinds were carefully separated from soft white inner fibers with sharp knives. Then the rind samples were air dried at 30 °C for about 18 h, smashed into powder with a pulverizer (Huangchen HC-280T, Zhejiang, China), passed through a 60-mesh sieve and stored in the dark at −18 °C until analyzed. All the other chemicals used were of analytical grade or HPLC grade.

2.2. 1-OC from sugarcane rind

Dry powder of sugarcane rind was soaked in anhydrous ethanol with liquid–solid ratio 8:1 ml/g and extracted for 4 h at 80 °C. After filtration through filter paper, ethanol was collected. Crude sugarcanes waxes were obtained after the solvent was removed under reduced pressure at 40 °C with a rotary evaporator (IKA-Werke-RV10, Stanfer, Germany). About 46.308 g of crude sugarcanes waxes were saponified with 18 ml ethanolic KOH (2 M) for 2 h at 80 °C. After added 360 ml water, the unsaponifiable matter was extracted twice with 450 ml diethyl ether. The diethyl ether extracts washed with 360 ml water twice and dried with anhydrous sodium sulfate and then evaporated to dryness using rotatory evaporation at 60 °C. About 3.132 g of 1-OC samples were collected.

2.3. GC–MS analysis of 1-OC sample

1-OC sample was analyzed by GC–MS according to the method of Tayade et al. (2013) with minor modifications, using an Agilent (Wilmington, DE) 6890 series N_2 gas chromatograph and an Agilent 5975B mass selective detector using electron impact ionization, under the following conditions: HP-5MS column (5% diphenyl and 95% dimethylpolysiloxane; 30 m, 0.25 mm i.d., 0.25 μm film); 1.0 μl injection volume; helium carrier gas at 1.00 ml/min; split ratio, splitless; injector temperature, 250 °C; oven temperature, 120 °C, hold for 0 min, then raised at 20 °C/min to 240 °C, hold for 10 min; then raised at 10 °C/min to 300 °C; hold for 15 min; transfer line temperature, 300 °C; electron energy, 70 eV; and scan range, 35–550 amu. 1-OC and other phytochemicals were identified by comparison of the mass spectra fragmentation pattern with the MS data of corresponding compounds obtained from the National Institute of Standards and Technology (NIST) MS Library, Version 2005, or by mass spectra with those in the literature.

2.4. Non-isothermal DSC analysis

2.4.1. Oxidative stability tests by on-isothermal DSC

Oxidative stability of sugarcane phytosterol was determined with a non-isothermal DSC (Mettler DSC 30) method. Calibration was performed using indium as a reference, and the baseline was obtained with an open empty aluminium pan sample. Approximately 3.0 ± 0.3 mg of each sample was enclosed in 100 μl aluminium sample pans with perforated lids. The samples were scanned between 50 and 400 °C at a heating rate of 10 °C/min, and purified oxygen (99.8%) passed through the sample enclosure at 40 ml/min.

2.4.2. Effect of water, metallic ions and fatty acid on oxidation of 1-OC sample

To observe the effect of metallic ions and fatty acids on oxidation of 1-OC sample, 10 μl of pure water, linoleic acid, solution (0.10 mg/ml) of sodium chloride, calcium chloride and magnesium chloride was mixed with 3.00 ± 0.30 mg 1-OC sample, respectively. All samples were scanned by non-isothermal DSC according to the method described in Section 2.4.1.

2.4.3. Effect of temperature on oxidation of 1-OC sample

In a set of test pans, 3.0 ± 0.3 mg 1-OC samples were tested directly under four different heating program: 50 °C raised at 10 °C/min to 100 °C, hold for 30 min; 50 °C raised at 10 °C/min to 200 °C, hold for 20 min; 50 °C raised at 10 °C/min to 300 °C, hold for 10 min; 50 °C raised at 10 °C/min to 400 °C. After cooling to room temperature, 5 ml acetone was add to test tube to dissolve remaining 1-OC as well as their oxidation product in test pans. 200 μg 5α-cholestane was added to each test tube, which was used