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Antioxidative effect of extracts from red grape seed and peel on lipid oxidation in oils of sunflower

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Abstract

The antioxidative effect of red grape seed (RGS) and red grape peel (RGP) ethanolic extracts on primary and secondary lipid oxidation in sunflower and conjugated sunflower (SF/CSF) oils was evaluated. Lipid oxidation was analysed at 60 °C using three methods; conjugated diene (CD) measurements for primary oxidation product development, static headspace gas chromatography (SHGC), and proton transfer reaction-mass spectrometry (PTR-MS) to follow the formation of secondary lipid oxidation products (propanal, 1-penten-3-one, hexanal and octanal).

The phenolic content (200 mg/kg) in extracts did not have any effect on the conjugated diene hydroperoxides. After 6 days, high antioxidative effect was found for the secondary oxidation products in CSF for peel extract followed by seed extract. The antioxidative activity for the peel extract was up to 41.2% for propanal measured by PTR as compared with 17.1% for seed extract. On the other hand, at 6 days the peel and seed extracts were shown to expect prooxidative effect on SF for the secondary oxidation products. It has been noticed that SF has high stability for lipid oxidation among all the mixtures tested using the three determination methods. Obviously, PTR-MS succeeded, as an accurate method, to measure the concentration as low as 10 μg/kg, and also to solve the solvent interference.

Keywords: Sunflower oil; Seed grape; Peel grape; Static headspace gas chromatography; Proton transfer reaction

1. Introduction

Lipid oxidation has been reported to be responsible for off-flavors, toxic compounds formation, and the cause of many diseases. The possible of synthetic antioxidants mutagenicity led the consumers to natural antioxidants. In the last few years, an increased attention has been focused on the industrial wastes, especially those containing residual phenols from the plant raw material used. Grape (*Vitis vinifera*) is one of the world's largest fruit crops, with an annual production of approx. 58 million metric tons (FAO, 1997). Polyphenolic grape procyanidin and flavonol showed low aquatic toxicity and weak influence on proliferation of human melanoma cells (Torres et al., 2002). Calabrese (2003) concluded that grapes are antimutagenic, antineoplastic, reduce human low-density lipoprotein (LDL) oxidation and reduce allergic inflammation.

Negro, Tommasi, and Miceli (2003) found a rich source in polyphenolic compounds with a clear antioxidant activity for the ethanolic extract from red grape marc and its components, peels and seeds. The antioxidant activity has manifested itself in the protection of β-carotene in emulsion with linoleic acid against oxidation. A large part of the phenolics may act selectively at very low concentrations to inhibit ex vivo LDL oxidation in vitro (Frankel, Kanner, German, Parks, & Kinsella, 1993). On the other hand, Teissedre, Frankel, Waterhouse, Peleg, and German (1996) reported that phenolics in grapes and red wines inhibit human LDL oxidation in vitro.

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These natural antioxidants have many favourable effects on human health, such as inhibition low-density protein oxidation, decreasing the heart disease risks, and possessing anticarcinogenic properties (Williams & Elliot, 1997; Miyake et al., 1999). They also have been proven (Wang et al., 1999) to be food lipid antioxidants for their safety considerations as compared to synthetic antioxidants such as butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT).

Jayaprakasha, Singh, and Sakariah (2001) mentioned high antioxidative activity (AOA) for ethyl acetate and water grape seed extracts at different concentrations, higher than other extracts. They used the carotene protection besides the thiocyanate method. On the other hand, the phenols of the red grape marc extract showed a lower AOA than the synthetic food antioxidants (BHT) (Bonilla, Mayen, Merida, & Medina, 1999). They determined the antioxidant lipid activity of the phenols in the extract using the Rancimat method to measure the antioxidative lipid activity on refined olive oil. Monoacylated anthocyanins from the pericarps of grapes can be used as powerful antioxidants, as well as colorants (Tamura & Yamagami, 1994). They measured the antioxidants using the thiobarbituric acid (TBA) method. Guendez, Kallithraka, Makris, and Kefalas (2005) mentioned that utilizing 1 kg of grape seeds may afford, on average, almost 3.8 g of polyphenols, consisting mainly of flavanol monomers and dimers, which have appreciable antiradical activity.

In our study, we investigated the AOA of peel and seed of a French red grape on the lipid oxidation of sunflower and conjugated sunflower (CSF) oils. The oxidation was followed for storage time up to 7 days in the dark at 60 °C. The CD method was used for the primary oxidation products. The secondary oxidation products (propanal, 1-penten-3-one, hexanal and octanal) were followed using the SHGC and PTR-MS methods.

2. Materials and methods

Sunflower oils were produced and supplied by Archer Daniels Midland Co. (Red Wing, MN, USA), and stored in a nitrogen gas atmosphere in the dark at 4 °C until analysed. The fatty acid methyl ester composition determined by GC for SF and CSF was as follows; 5.2, 8.1% 16:0, 2.9, 4.9% 18:0, 27.2, 48.6% 18:1, 62.7, 18.7% 18:2 and 0.28, 17.8% 20:0. For the oxidation experiments for the different oil samples with and without the antioxidative extracts, the samples were stored in glass jars (22 ml) in the dark at 60 °C. Three replicate oil oxidations were carried out for each treatment and at each time an analysis was conducted.

2.1. Analysis of primary lipid oxidation products

2.1.1. Conjugated diene hydroperoxides (CD)

Oil samples of 0.01 g were dissolved in 5 ml cyclohexane (Sigma-Aldrich, Steinheim, Germany), forming a solution of 500:1 dilution and the absorbance of the solution was measured at 234 nm (Varian Cary 1E spectrophotometer; JVA Analytical Ltd., Dublin, Ireland). Absorbances were calculated as hydroperoxides in mmols/l oil, using a molar absorptivity of 26,000 for the hydroperoxides (AOCS Official Method Ce, 8–89, 1992).

2.2. Analysis of secondary lipid oxidation products

2.2.1. Static headspace gas chromatography (SHGC)

Two millilires of oil were transferred into 10 ml vials and incubated at 60 °C for 6 min in the automated headspace unit (Combipal-CTC Analytics system; JVA Analytical Ltd., Dublin, Ireland) of the gas chromatograph (Varian CP-3800; JVA Analytical Ltd, Dublin Ireland). The GC was equipped with a BPX5 capillary column (60 m length, 0.32 mm i.d. and 1 μm film thickness) and a flame ionization detector (FID) at 275 °C. An initial oven temperature of −30 °C was used for 1 min, followed by a rate of 100 °C/min to 60 °C. The oven temperature was kept at 60 °C for 5 min and was subsequently programmed to 110 °C at 3 °C/min, and further to 170 °C at 4 °C/min. Retention times of compounds were compared with previous GC/Mass Spectrometry analyses (GC/MS) (Van Ruth, Shaker, & Morrissey, 2001).

2.2.2. Proton transfer reaction-mass spectrometry (PTR-MS)

One millilters of oil in a 50 ml glass vial was kept for 2 h at room temperature to allow equilibration before the analysis was started. Samples were analysed according to the method described by Buhr, Van Ruth, and Delahunty (2002). Background and transmission corrected spectra were averaged over five cycles. The ions measured were related to compounds measured by GC/MS previously for identification. The concentrations of the oxidized compounds were calculated as ppb (V/V).

The PTR-MS technique, developed by Lindinger, Hansel, and Jordan (1998), is based on a novel chemical ionization cell allowing online measurements of trace gas components with concentrations as low as a few parts per trillion by volume. Absolute concentrations can be calculated without calibration or use of standards, and the volatile compound samples do not have to be prepared before the measurement. Moreover, the procedure allowed quantification of the effect of different stabilization treatments, and detection of low odor threshold compounds, which are not detected by