Industrial Crops and Products 43 (2013) 65–72

Contents lists available at SciVerse ScienceDirect

Industrial Crops and Products

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

Healthy blends of high linoleic sunflower oil with selected cold pressed oils: Functionality, stability and antioxidative characteristics

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ARTICLE INFO

Article history:
Received 13 March 2012
Received in revised form 7 July 2012
Accepted 9 July 2012

Keywords:
Healthy oils
Nigella sativa
Cuminum cyminum
Coriandrum sativum
Syzygium aromaticum

ABSTRACT

The consumption of health-promoting products such as cold pressed oils may improve human health and prevent certain diseases. Blends (10% and 20%, w/w) of cold pressed oils including black cumin oil (BC), cumin oil (Cum), coriander oil (Cor) and clove oil (Clo) with high linoleic sunflower oil (SF) were formulated. Oxidative stability (OS) and radical scavenging activity (RSA) of SF and blends stored under oxidative conditions (60 °C) for 8 days were studied. By increasing the proportion of cold pressed oils in SF, linoleic acid level decreased, while tocols level increased. Progression of oxidation was followed by measuring peroxide value (PV), *p*-anisidine value (Av), conjugated dienes (CD) and conjugated trienes (CT). Inverse relationships were noted between PV as well as Av and OS at termination of storage. Levels of CD and CT in SF and blends increased with increase in time. Cold pressed oil blends gave about 70% inhibition of DPPH• radicals. Oxidative stabilities of oil blends were better than SF, most likely as a consequence of changes in fatty acids and tocols' profile, and minor bioactive lipids found in cold pressed oils.

1. Introduction

Lipid oxidation is an important problem for food and cosmetic industry. This is relevant when the lipidic substrates are composed of unsaturated or polyunsaturated fatty acids (PUFA) that are sensitive to oxidation. Antioxidants' effectiveness depends on their chemical reactivity (as radical scavengers or metal chelators), interaction with food components, environmental conditions (*e.g.*, pH and concentration) and physical location of the antioxidant in food systems (Lucas et al., 2010). Oxidation imparts undesirable flavors and aromas, compromises the nutritional quality of oils, and leads to the induction of toxic compounds. Lipids involved in the oxidation process contain unsaturated fatty acids and long chain PUFA; however, other unsaturated lipids such as sterols do become oxidized. The oxidation of edible fats and oils can be controlled by application of antioxidants and using processing techniques that minimize loss of tocopherols and other antioxidants (Miraliakbaru and Shahidi, 2008).

Sunflower oil (SF) with high levels of PUFA is one of the main oils used for cooking and frying. These oils, however, is not quite suitable for frying due to oxidation at elevated temperatures (Anwar et al., 2007). Therefore, the use of more stable frying oils of comparatively low price would be desirable. To overcome the problem of poor oxidative stability (OS) of traditional oils, ways of reducing the unstable PUFA content and increasing natural antioxidants were sought. One way to improve the OS of these oils is by blending with oils of high-oleic acid contents and/or high antioxidants' levels (Mariod et al., 2005; Anwar et al., 2007; Ramadan et al., 2008).

The need for widely usable and easily available bioactive lipids and natural antioxidants continues to grow. Over the last few years, increased interest in cold pressed oils has been observed as these oils have high nutritive properties. The cold pressing procedure is becoming an interesting substitute for conventional practices because of consumers' desire for natural and safe food products (Parry et al., 2006; Lutterodt et al., 2010). Cold pressing is a technology for seed oil production, which involves no heat treatment or chemical treatments. Cold pressing also involves no refining process and may contain a higher level of lipophilic phytochemicals including natural antioxidants. Black cumin (BC), cumin (Cum), coriander (Cor) and clove (Clo) are traditional food spices and are commonly used in the food industry because of their special aroma as well as their health-promoting properties. Bioactivities of these spices are most attributed to a number of phenolic compounds and fat-soluble bioactives (tocols, sterols and polar lipids). Few reports have been published on cold pressed BC oil, but it is hard to find any data on cold pressed Cum, Cor and Clo oils.

Nigella sativa (BC) seed components have also been used to prepare functional cosmetic and dietary supplemental products. Studies were conducted on pharmacological properties of BC essential oil (Ramadan, 2007; Lutterodt et al., 2010). BC seed oil is rich in essential fatty acids as well as bioactive phytosterols and

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0926-6690/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.indcrop.2012.07.013

tocopherols (Ramadan and Moersel, 2002; Ramadan, 2007). Cumin (*Cuminum cyminum* L.) is the second most popular spice in the world after black pepper. The proximate composition of the seeds indicates that they contain fixed oil (*ca*. 10%), protein, cellulose, sugar, mineral elements and volatile oil (Li and Jiang, 2004). Cumin seeds contain volatile oil (1–5%), which has been the subject of previous studies (Oroojalian et al., 2010). However, data on *C. cyminum* lipids are limited (Shahnaz et al., 2004; Rebey et al., 2012). Coriander (*Coriandrum sativum* L.) fruit-seeds contain high levels of petroselinic acid (Δ^6-*cis*-octadecenoic acid, 18:1$n-12$) as part of triacylglycerols. Coriander seed oil had recently been investigated and the results indicated that crude seed oil is highly promising edible oil with high levels of bioactive lipids (Ramadan et al., 2008). Clove (*Syzygium aromaticum*, Myrtaceae) is cultivated as a spice in many tropical countries. For oil production, clove buds are brought to European and American distilleries. Clove oil is frequently used in perfumery and medicine, but the largest part by far is used in flavorings (Zheng et al., 1992). The clove species have been demonstrated to produce a wide variety of potentially useful compounds that include sesquiterpenes, tannins, and triterpenoids. It is well-known that clove possesses a phenolic compound, 4-allyl-2-methoxyphenol, commonly called eugenol. Eugenol acts as an antioxidant on oleogenous foods, as an anticarminative, antispasmodic, antiseptic in pharmacy, and also as an antimicrobial agent (Farag et al., 1989; Miyazawa and Hisama, 2003).

Blending vegetable oils can increase the levels of bioactive lipids and natural antioxidants in the blends and improve nutritional value at affordable prices. Oil blends has been a common permitted practice in the many countries. Lately, it has permitted to manufacture and market blended oils containing commonly edible oil mixed with unconventional oil (Ramadan et al., 2008). Cold pressed oils are a good source of beneficial components, such as antioxidative phenolic compounds and other health-beneficial phytochemicals. As a continuation of efforts in developing healthy oils rich in health beneficial components, the present study was designed to investigate the effects of blending cold pressed BC, Cum, Cor and Clo with SF on the OS, functionality and radical scavenging activity of high linoleic SF. There is no such previous studies yet been conducted on the blending of cold pressed oils with SF. This report might serve as a milestone toward development of healthy blended oils with improved OS and nutritional value.

2. Materials and methods

2.1. Materials

Cold pressed black cumin (*N. sativa*), cumin (*C. cyminum*), coriander (*C. sativum*) and clove (*S. aromaticum*) oils were obtained from a local market (Zagazig, Egypt). Refined, bleached and deodorized SF was purchased from a local market (Zagazig, Egypt). Eight oil blends were formulated by blending SF with cold pressed BC, Cum, Cor and Clo oils in proportions of 9:1 and 8:2 (w/w). The oils were thoroughly mixed to form uniform blends at room temperature. Standards used for tocols (α-, β-, γ- and δ-tocopherol and tocotrienols) were purchased from Merck (Darmstadt, Germany). 1,1-Diphenyl-2-picrylhydrazyl (DPPH, approximately 90%) was purchased from Sigma (St. Louis, MO, USA). Galvinoxyl was from Aldrich (Milw., WI, USA). Toluene of HPLC grade was used throughout the antiradical test. All solvents and reagents from various suppliers were of the highest purity needed for each application and used without further purification.

2.2. Methods

2.2.1. Fatty acids composition of SF, cold pressed oils and oil blends

Fatty acids and tocopherols of SF and oil blends were analyzed using GLC and HPLC according to Ramadan et al. (2006b, 2010). Fatty acids were transesterified into FAME using N-trimethylsulfoniumhydroxide (Macherey–Nagel, Düren, Germany). In brief, 10 mg of oil sample was dissolved in 500 μL of *tert*-butyl methyl ether then 250 μL of TMSH was added and the mixture was vortexed for 30 s before injection. FAME was identified on a Shimadzu GC-14A equipped with flame ionization detector (FID) and C-R4AX chromatopac integrator (Kyoto, Japan). The flow rate of the carrier gas helium was 0.6 mL/min and the split value with a ratio of 1:40. A sample of 1 μL was injected in a Supelco SP™-2380 (Bellefonte, PA, USA) capillary column (30 m × 0.25 mm × 0.2 μm film thickness). The injector and FID temperature was set at 250 °C. The initial column temperature was 100 °C programmed by 5 °C/min until 175 °C and kept for 10 min at 175 °C, then 8 °C/min until 220 °C and kept for 10 min at 220 °C. A comparison between the retention times of the samples with those of reference compounds mixture, run on the same column under the same conditions, was made to facilitate identification.

2.2.2. Tocols profile of SF and oil blends

For tocols analysis, a solution of 250 mg of oil in 25 mL *n*-heptane was directly used for the HPLC. The HPLC analysis was conducted using a Merck Hitachi low-pressure gradient system, fitted with an L-6000 pump, a Merck-Hitachi F-1000 Fluorescence Spectrophotometer (the detector wavelength was set at 295 nm for excitation, and at 330 nm for emission) and a D-2500 integration system. Twenty microliters of the samples were injected by a Merck 655-A40 Autosampler onto a Diol phase HPLC column 25 cm, 94.6 mm ID (Merck, Darmstadt, Germany) using a flow rate of 1.3 mL/min. The mobile phase used was *n*-heptane/tert-butyl methyl ether (99:1, v/v).

2.2.3. Extraction and purification of the phenolic compounds from cold pressed oils

Aliquots of oil (2 g) were dissolved in *n*-hexane (5 mL) and mixed with 10 mL methanol–water (80:20, v/v) in a glass tube for 2 min in a vortex. After centrifugation at 3000 rpm for 10 min, the hydroalcoholic extracts were separated from the lipid phase by using Pasteur pipette then combined and concentrated *in vacuo* at 30 °C until a syrup consistency was reached. The lipidic residue was redissolved in 10 mL methanol–water (80:20, v/v) and the extraction was repeated twice. Hydroalcoholic extracts were redissolved in acetonitrile (15 mL) and the mixture was washed three times with *n*-hexane (15 mL each). Purified phenols in acetonitrile were concentrated *in vacuo* at 30 °C then dissolved in methanol for further analysis.

2.2.4. Characterization of phenolic compounds in cold pressed oils

Aliquots of phenolic extracts were evaporated to dryness under nitrogen. According to Ramadan et al. (2003) the residue was redissolved in 0.2 mL water and diluted (1:30) Folin–Ciocalteu's phenol reagent (1 mL) was added. After 3 min, 7.5% sodium carbonate (0.8 mL) was added. After a further 30 min, the absorbance was measured at 765 nm using UV-260 visible recording spectrophotometer (Shimadzu, Kyoto, Japan). Gallic acid was used for the calibration and the results of triplicate analyses are expressed as parts per million of gallic acid. UV spectrum (200–400 nm) of 1% oil in 2,2,4-trimethylpentane was recorded using a Shimadzu UV-260 spectrophotometer (Kyoto, Japan).