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Carotenoid and antioxidant content of ground paprika from indoor-cultivated traditional varieties and new hybrids of spice red peppers

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ABSTRACT

The content of carotenoids and the main antioxidant vitamins in traditional varieties and new hybrids of spice red pepper (*Ccapsicum annuum* L.) cultivated under plastic houseindoor conditions was studied. The varieties and hybrids were evaluated on the basis of results obtained from liquid chromatographic determination of carotenoid and antioxidant vitamins, and compared for their response to different drying conditions. Ground paprika from all varieties and hybrids cultivated under plastic houseindoor conditions were remarkably rich in colorants (average: 8629 μg/g d) and vitamin E (average: 1189 μg/g), but vitamin C level was found to be higher (average: 8.3 mg/g DWdm) in paprika from arable-landoutdoor cultivated peppers dried naturally. The paprika from the Spanish hybrids 'Jeromin', 'Jaranda', 1970/05 and the varieties Hungarian 'Remény' and 'SZ-80' varieties as well as the hybrid '1970/05' contained the highest level of carotenoids and antioxidants ($P < 0.05$). The different varieties and hybrids differed in their response, in terms of stability, to drying conditions. Natural drying was favourable for the highest carotenoid retention, but not for the retention of vitamin C. It was surprising that drying at 50 °C for 24 h resulted in a paprika with vitamin C content 1.5–3 times higher than that found in paprikas produced with other drying methods.

1. Introduction

Ripe fruits of either vegetable or spice red-bell pepper are a good source of nutritionally important phytochemicals including carotenoids, tocopherols, vitamin C and poly-phenols (Daood, 2009; Daood, Vinkler, Markush, Hebshi, & Biacs, 1996; Delgado-Vargas & Paredo-Lopez, 2003; Lee, Crosby, Pike, Yoo, & leskovar, 2005; Lee, Howard, & Villalion, 1995; Materska & Perucka, 2005; Materska et al., 2003). Adequate daily intake of carotenoids and other antioxidants especially from fruits and vegetables has been recommended to sustain optimal health; moreover, data from epidemiological studies consistently showed correlation between the intake of fruits and vegetables and the incidence of several diseases such as cardiovascular, ophthalmological, gastrointestinal or neurodegenerative disorder and some type of cancer (Christen, 1994; Hennekens, Gaziano, Manson, & Buring, 1995; Russel, 2006; Stahl & Sies, 2005; VAN Duyn & Pivonka, 2000).

Consumption of products of red pepper has been reported to have interesting biological effects. Cancer chemopreventive activity of carotenoids in the fruits of red paprika *Capsicum annuum* has been confirmed by Maoka et al. (2001). Hot pepper (*C. annuum* and *C. chinese*) has been found to prevent Fe^{+2}-induced lipid peroxidation in brain (Oboh, Puntel, & Rocha, 2007). Safety assessment of dietary administrated paprika colour in combined toxicity and carcinogenicity using F344 rats has been studied by Inoue et al. (2008). The authors concluded that paprika colour is not carcinogenic to male and female rats under the conditions of their experiment and concerning toxicity, in terms of histopathological change, a concentration in diet of 2826 mg/kg body weight/day is required to approach no observed adverse- effect level (NOAEL) of 5% for female rats.

The attractive red colour of red-bell peppers is due to a diverse composition of several yellow-and red-coloured carotenoids, which occur esterified with fatty acids in a form of mono- and di-esters (Biacs, Daood, Huszka, & Biacs, 1993; Biacs & Daood, 1994; Hornero-méndez & Mínguez-Mosquera, 2000; Mínguez-Mosquera & Hornero-Méndez, 1994a). Esterification, with fatty acids, of xanthophylls of red-bell pepper doesn't hinder their biological activity since lipolytic enzyme in the presence of bile salts in the intestinal track can hydrolyse fatty acid esters before absorption (Pérez-Gálvez & Mínguez-Mosquera, 2005; Zorn, Breithaupt, Takenburg, Schwack, & Berger, 2003). From the technological point of view the content and composition of

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carotenoids as well as the presence of another antioxidant compounds in red peppers can affect, to a high extent, the colour intensity and stability of the product (Biacs, Czinkotai, & Hoschke, 1992; Daood, Kapitany, Biacs, & Albrecht, 2006).

Many chromatographic methods have been developed for the separation and determination of carotenoids from red-bell peppers. In some of those methods the extract of fruits is simplified by alkaline hydrolysis of fatty acid esters and separated on reversed-phase adsorbents with gradient elution systems [Almela, López-Ropca, Candella, & Alcáraz, 1991]. In the other methods un-hydrolysed extracts were fractionated to their individual carotenoids on reversed-phase columns having analytical dimensions and gradient elution (Mínguez-Mosquera & Hornero-Méndez, 1993).

In most of European pepper producing countries, particularly Hungary, there was a marked decrease in the arable land production of spice red pepper, during the last 10 years, due to high cost of production, low level of financial support and climate change. To overcome such problems cultivation under plastic houses (idoor) has become an alternative solution. Among many advantages of such technology yield, period of cultivation and crop quality are accentuated (Somogyi, 2010). Availability of suitable varieties, mainly hybrids, is necessary for the indoor cultivation of spice red peppers. The hybrids are capable to grow vertically and reach a high between 2 and 3 m and, thereby, making the yield to reach a level several times higher than that achieved with traditional varieties, which have limited capability for ascending growth.

The objective of this work was to analyse, by recent chromatographic methods, the carotenoid-type pigments and antioxidant components in paprika (spice produced from ground dry fruit of bell pepper and/or chilli pepper) prepared from traditional varieties and new hybrids of spice red peppers cultivated under indoor conditions and to investigate their response to different drying conditions.

2. Materials and methods

2.1. Materials and chemicals

The new hybrids were produced by cross breeding of different Hungarian('SZ-80', 'SZ-178' and 'Remény') and Spanish ('Jaranda', 'Jeromin' and 'Jariza') varieties cultivated in the plastic houses (indoor) of the Spice Paprika Research Developing Non-profit Ltd, Szegedi Department in the season of 2010. The seeds obtained were used in the cultivation of the new hybrids in 2011 under agronomical conditions described by Somogyi (2010) with traditional spice red pepper cultivation technology. The seeds were sown in glass house at the end of February and the seedlings were transplanted to the UV light-protected polytunnels at the mid of April with a density of 4–5 plants/m^2 using etched herd and complete trellising throughout barricades. The pods of the different varieties and hybrids were harvested (3 replicates) at biological ripeness stage (deep red colour) at the end of August and left to over-ripen (to reach dry matter content around 23%) for 2 weeks at ambient conditions. The peppers were then dried in a drying cabin with air circulation at different temperatures (shown in tables) till a dry matter content of 11% was approached. The dry pods were left to cool to ambient temperature and grinded by a coffee mill. The ground paprika samples were packaged in nylon bags, vacuumed and stored at −20 °C when not immediately analysed.

Traditional Hungarian varieties were outdoor cultivated in the experimental farms of the Spice Paprika Research Developing Non-profit Ltd, Kalocsa Department. Seeds were sown on the 13th of April in greenhouse and transplanted to field on the 8th of May in 2011. The pepper seedlings were planted out in twin rows, with 0.3 m spacing inside the row and 1.2 m between adjacent twin rows. The space between the plants in the row was 25 cm. The experimental design was randomised complete block (RCBD) with three replications. The experimental field was a brown forest soil, with mechanical composition of sand, sandy-clay. Basic nutrition supply was given out when plants were transplanted with Agroblen 18-8-16 + 2 MgO. The biologically ripe (red-coloured) fruits from each variety were harvested at the mid of September and dried naturally by the same way used for the indoor-cultivated ones.

Standard β-carotene and zeaxanthin were purchased from Sigma-Aldrich (Budapest, Hungary). Authentic material for capsanthin was prepared after alkaline hydrolysis, extraction with ethyl acetate and thin-layer chromatography on silica gel. The major red band was scraped of the plate and re-dissolved in acetone. Capsanthin was identified according to its spectral characteristics, whereas its concentration was determined by spectrophotometric method using an extinction coefficient of 2600 (Vinkler & Kiszel-Richter, 1972).

All analytical and HPLC grade solvents were from VWR (Debrecen, Hungary). Other chemicals used were from Merck (Darmstat, Germany).

2.2. Extractions

Carotenoids from ground spice paprika were extracted by procedures described previously (Biacs & Daood, 1994). One gram of well homogenised sample from each variety and hybrid was extracted by adding 50 ml of a solvent mixture consisting of 2:1:1 1,2-dichloroethane–acetone–methanol followed by ultrasonication for 5 min in a water-bath ultrasonic device, mechanical shaking for 15 min, filtration through MN 615 type filter paper and evaporation of solvent under vacuum at maximum 40 °C by a rotary evaporator. The residues were re-dissolved in 5 ml of solvent mixture consisting of 55:35:10 isopropanol–acetonitrile–methanol followed by addition of 5 ml methanol. The extract was further cleaned by passing through a 22 μm PTEF syringe filter before injection onto the HPLC column.

Tocopherols, the components of vitamin E, were extracted by a procedure including alkaline hydrolysis (saponification) of 0.5 g of ground paprika by adding 5 ml 30%methanolic KOH, 0.5 g ascorbic acid and 20 ml methanol followed by refluxing the mixture for 35 min at the boiling point of methanol (Speek, Schrijver, & Shreure, 1985). After cooling with cold trap water, the tocopherol fraction was extracted twice by shaking with 40 ml n-hexane in a separating funnel. The hexane fractions were pooled and washed 3 times with distilled water to remove the alkali. The hexane phase was then dried over anhydrous $Na_2SO_4$and the solvent was evaporated with vacuum at 30 °C by a rotary evaporator. The residue were re-dissolved in 10 ml of HPLC grade n-hexane and further cleaned by passing a 22 μm PTEF syringe filter before injection onto the HPLC column.

To extract vitamin C, 05–1 g sample of ground paprika was mixed with 20–30 ml of 3% meta-phosphoric acid solution and subjected, in a conical flask, to ultrasonication using a water-bath ultrasonic device. The mixture was then shaken mechanically for 30 min at ambient temperature and filtered. The filtrate was further cleaned up by passing through a 0.45 μm nylon syringe filter before injection.

2.3. HPLC instrument and conditions

A Waters Alliance liquid chromatographic instrument consisting of a Model 2696 Separation Module, a Model 2695 photodiode-array detector and a Model 2674 fluorescent detector was used for the HPLC analysis of carotenoids and vitamin C and tocopherols. Operation and data processing were performed by Empower software.

The un-hydrolysed carotenoid extract was separated on Purospher C-18, 3 um, 250 × 4.6 mm column using gradient elution starting with 7% water in methanol, changes to 100% methanol in 3 min, to 100% methanol–isopropanol–acetonitrile (10:55:35) in 32 min and returns to 7% water in methanol in 5 min according to Daood & Biacs (2005). Diode-array detection was adjusted between190 and 600 nm to detect carotenoids and characterise their spectra.

Peak identification was based on comparison of retention and spectral characteristics of each sample peak with those of available