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ScienceDirect
Food Chemistry 110 (2008) 522–530
FOOD CHEMISTRY
www.elsevier.com/locate/foodchem

Analytical Methods

HPLC-DAD-MS^n characterisation of carotenoids from apricots and pumpkins for the evaluation of fruit product authenticity

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Received 9 October 2007; received in revised form 30 January 2008; accepted 10 February 2008

Dedicated to Prof. Dr. Rainer Wild, Heidelberg, on the occasion of his 65th birthday

Abstract

Carotenoids including carotenoid esters from six apricot (*Prunus armeniaca* L.) cultivars and from eight cultivars from three pumpkin species (*Cucurbita maxima* Duch., *Cucurbita pepo* L., and *Cucurbita moschata* Duch.) were extracted without saponification, separated on a C-30 reversed-phase column and characterised by high-performance liquid chromatography/atmospheric pressure chemical ionisation–mass spectrometry (LC–MS). The predominant free carotenoids were quantified by HPLC with diode array detection. In contrast to previously published data, α-carotene could not be detected in apricots. Although the pumpkins showed significant differences in their free carotenoid profiles, major unesterified compounds different from those found in apricots could be determined. However, due to the natural heterogeneity, authentication of the apricot products cannot be accomplished exclusively using the profile of free carotenoids. Therefore, the investigations were extended to carotenoid esters. The xanthophyll ester profiles in pumpkins significantly differed from those in apricots in that the latter also contained both saturated and unsaturated fatty acids, whereas in pumpkins exclusively saturated fatty acids were detected. Admixtures of lower cost pumpkins could be detected in quantities of $\geqslant 5\%$ by increased contents of lutein and zeaxanthin, and by the appearance of antheraxanthin and α-carotene, respectively, depending on the added pumpkin cultivar, as well as the presence of characteristic lutein and antheraxanthin esters. However, pronounced differences in the carotenoid profiles of the investigated pumpkins and the partly minor amount of characteristic compounds lead to limitations of the detection of 5% level of admixture of pumpkin to apricot and of the method in general.

Keywords: Apricot; Authenticity; Carotenoids; LC–MS; Pumpkins

1. Introduction

Fruits are the quality-determining and most costly ingredients of jams, spreads, fruit preparations and related products. As the fruit market is highly competitive with relatively narrow profit margins, unscrupulous producers may be tempted to maximise revenues by the fraudulent admixture of low cost to higher priced specified fruits. Therefore, to avoid unfair competition and to protect consumers from deception, product authentication is essential. In the past, several strategies have been described for plant species determination and for the detection of adulterations, for example profiling of phenolic compounds (Bengoechea, Sancho, Estrella Bartolomé, Gómez-Cordovés, & Hernández, 1997; Zimmermann & Galensa, 2007). However, more recent studies have shown that some polyphenols that have so far been assumed to be characteristic of certain plant species can also be found in other species (Hilt et al., 2003). While PCR methods have successfully been applied to species identification of e.g. meat and fish, degradation of DNA under heat and acidic conditions makes these methods inapplicable to jams and spreads

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doi:10.1016/j.foodchem.2008.02.022

Table 1
Specification of fruit samples

Fruit species	Taxonomic name	Cultivar	Geographical origin	Harvest year	Sample code
Apricot	*P. armeniaca*	Bergeron (I)	France	2006	A-B I
		Bergeron (II)	France	2006	A-B II
		Harogen	France	2006	A-H
		Moniqui	Spain	2006	A-MO
		Orangered	France	2006	A-OR
		Redsun	France	2006	A-R
Pumpkin	*Cucurbita maxima*	Bischofsmütze	Germany	2006	PK-BM
		Golden Nuggets	Germany	2005	PK-GN
		Halloween	Germany	2006	PK-HA
		Hokkaido I	Germany	2005	PK-HO I
		Hokkaido II	Germany	2006	PK-HO II
	C. pepo	Sweet Lightning	Germany	2006	PK-SL
	C. moschata	Muscade de Provence	Germany	2005	PK-MU
		Butternuts	Germany	2006	PK-BN

(Bauer, Weller, Hammes, & Hertel, 2003; Jonas et al., 2001; Moreano, Busch, & Engel, 2005). We have recently demonstrated that the neutral sugar profile of cell wall polysaccharides can also be used for authentication of fruit-derived products (Kurz, Carle, & Schieber, 2008).

Carotenoids have extensively been studied in a large number of food commodities because of their health-promoting properties. However, only little attention has been paid to their suitability as markers for the detection of food adulteration. Most work has been dedicated to the detection of fraudulently added pigments such as synthetic β-carotene or extracts from citrus peels and marigold flowers to intensify the natural colour of foods (Philip, Chen, & Nelson, 1989). Oke and Shrikhande (1977) described a method for the detection of adulteration of tomato ketchup with red pumpkin which was based on the different carotenoid profiles. While today pumpkin extracts would hardly be expected to be used in ketchup, their fraudulent addition to apricot jams and spreads would result in a more intense colour giving the impression of higher fruit contents. Dragovic-Uzelac, Delonga, Levaj, Djakovic, and Pospisil (2005) reported that admixture of pumpkin purée to apricot products can be detected by the presence of syringic acid, which could be found in pumpkins but not in apricots. However, their assessment was based on a comparatively small selection of pumpkin varieties and peak assignment was not verified by mass spectrometry. Furthermore, one analytical technique is usually insufficient to detect all kinds of adulteration commonly practised. Therefore, in most cases only combined analyses allows reliable authenticity assessment of a product. Hence, the objective of the present study was to evaluate the potential of the carotenoid profile for authenticity studies of apricot purées and jams. For this purpose, a simple extraction protocol suitable for routine analysis and a method for the simultaneous separation of carotenoids and carotenoid esters were developed.

2. Experimental

2.1. Materials

All reagents and solvents used were purchased from VWR (Darmstadt, Germany) and were of analytical or HPLC grade. Antheraxanthin (5,6-epoxy-5,6-dihydro-β,β-carotene-3,3′-diol), α-carotene (β,ε-carotene), γ-carotene (β,ψ-carotene), β-cryptoxanthin (β,β-carotene-3-ol), lutein (β,ε-carotene-3,3′diol), and zeaxanthin (β,β-carotene-3,3′diol) were from CaroteNature (Lupsingen, Switzerland); β-carotene (β,β-carotene) and β-apo-8′-carotenal were from Fluka (Sigma–Aldrich, St. Louis, MO, USA). Lycopene (ψ,ψ-carotene) was purchased from AppliChem (Darmstadt, Germany). (*Z*)-Isomers of β-carotene were obtained by iodine-catalysed photoisomerisation of (*all-E*)-β-carotene (Zechmeister, 1962).

Fresh, fully ripe apricots (*Prunus armeniaca* L.) and yellow or orange fleshy pumpkins (*Cucurbita* sp.) were obtained from the local market (Stuttgart, Germany) (Table 1). Fruits were harvested in 2006, pumpkins in 2005 and 2006. Fresh apricots were manually cored at 4 °C. Pumpkins were lye peeled, manually cored at 4 °C, blanched at 85 °C for 10 min, and subsequently mashed through a sieve (mesh size: 1.5 mm). Blended products were prepared from apricot purées (cv. Bergeron I), which were produced from cored fruits treated as described above and mixed with pumpkin purée in proportions of 95:5, 90:10 and 80:20, respectively. Apricot purée for jam production was blended in proportions of 95:5, 90:10 and 85:15 with pumpkin cv. Muscade de Provence. Apricot jams were prepared by heating a defined amount of fruit purée with sucrose and highly esterified pectin (Classic AF 401, Herbstreith & Fox, Neuenbürg, Germany) under reduced pressure at 75 °C until a dry matter of 63% was obtained. Final fruit content of the jams was 45% (w/w). Samples were lyophilised in a Steris Lyovac® GT 4 Lyophiliser