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Analytical Methods

Quantification of main phenolic compounds in sweet and bitter orange peel using CE–MS/MS

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A B S T R A C T

The food and agricultural products processing industries generate substantial quantities of phenolics-rich subproducts, which could be valuable natural sources of polyphenols. In oranges, the peel represents roughly 30% of the fruit mass and the highest concentrations of flavonoids in citrus fruit occur in peel. In this work we have carried out the characterisation and quantification of citrus flavonoids in methanolic extracts of bitter and sweet orange peels using CE–ESI–IT–MS. Naringin (m/z 579.2) and neohesperidin (m/z 609.2) are the major polyphenols in bitter orange peels and narirutin (m/z 579.2) and hesperidin (m/z 609.2) in sweet orange peels. The proposed method allowed the unmistakable identification, using MS/MS experiments, and also the quantification of naringin (5.1 ± 0.4 mg/g), neohesperidin (7.9 ± 0.8 mg/g), narirutin (26.9 ± 2.1 mg/g) and hesperidin (35.2 ± 3.6 mg/g) in bitter and sweet orange peels. CE coupled to MS detection can provides structure-selective information about the analytes. In this work we have developed a CE–ESI–IT–MS method for the analysis and quantification of main phenolic compounds in orange peels.

1. Introduction

Polyphenols are amongst the most popular antioxidants and many natural sources are being suggested for their recovery (Tura, 2002). Crud extract of fruits, herbs, vegetables, cereals, nuts and other plant material rich in phenolics are increasingly of interest in the food industry (Sang et al., 2002). Citrus is a common term and genus of flowering plants in the family Rutaceae, originating in tropical and subtropical areas in southeast Asia. Citrus fruits are notable for their fragrance, partly due to flavonoids and limonoids (a kind of terpenes) contained in the peel, they are also good sources of vitamin C and flavonoids. Cultivated Citrus may be derived from as few as four ancestral species. Numerous natural and cultivated origin hybrids include commercially important fruit such as the orange, grapefruit, lemon, some limes, and some tangerines. Oranges are one of the most popular fruits in the world. Orange processing in the United States produces ~700.000 tons of peel as byproduct solids annually (Winter, 1995). Plant material wastes from these industries contain high levels of phenolic compounds. Importantly, most of this phytonutrient is found in the orange peel and inner white pulp, rather than in its liquid orange centre, so this beneficial compound is too often removed by the processing of oranges into juice. Polyphenols compounds have health-related properties, which are based on their antioxidant activity including anticancer, antiviral and antiinflammatory activities (Bouskela, Cyrino, & Lerond, 1997; Tanaka et al., 1997). The group of flavonoids is a widely distributed group of polyphenolic compounds according to the above fact. Flavonoids in orange peel are comprised primarily of flavanone glycosides (narirutin 4′-O-glucoside, eriocitrin, narirutin, hesperidin, isosakuranetin rutinoside), polymethoxylated flavone aglycons (sinensetin, hexa-O-methylquercetagetin, nobiletin, hexa-O-methylgossypetin, 3,5,6,7,8,3′,4′-heptamethoxyflavone, tetra-Omethylscutellarein, tangeritin and 5-hydroxy-3,7,8,3′,4′-pentamethoxyflavone) (Horowitz & Gentili, 1977), flavone glycosides (diosmin, isorhoifolin, rutin) (Kanes, Tisserat, Berhow, & Vandercook, 1993) and C-glycosylated flavones (6,8-di-C-glucosylapigenin) (Manthley & Grohmann, 2001). Naritutin, hesperidin, naringin and neohesperidin (Fig. 1) are the most abundant flavonoids in the edible part of many species of citrus fruits (Kawai, Tomono, Katase, Ogawa, & Yano, 1999). As is well documented naritutin and hesperidin have been determined in common sweet orange (Ooghe, Ooghe, Detavernier, & Huyghebaert, 1994), and it is worthwhile referring to the recovery of hesperidin and naringin from orange peel (El-Nawawi, 1995), which is considered to be the most popular source, recovery of naringin from bitter orange (Calvarano, 1996).

Even though the characterisation of phenolic compounds in orange has been successfully carried out using HPLC (Anagnostopoulou, Kefalas, Kokkalou, Assimopoulou1, & Papageorgiou1, 2005; Belajová & Suhaj, 2004; Justesen, Knuthsen, & Leth, 1998; Kanaze,

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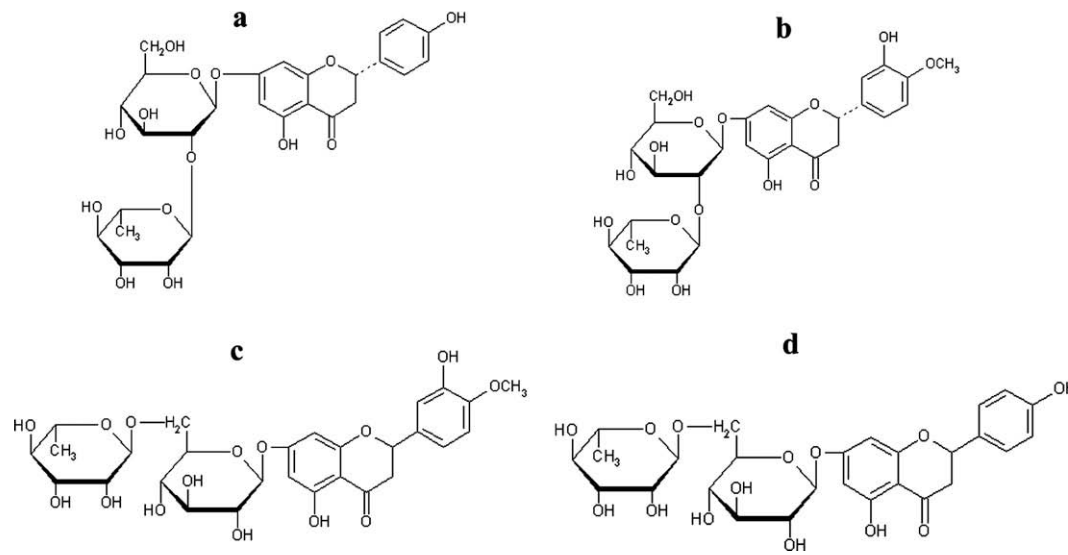

Fig. 1. Chemical structures of: (a) naringin, (b) neohesperidin, (c) hesperidin and (d) narirutin.

Gabrieli, Kokkalou, Georgarakis, & Niopas, 2003; Theodoridis et al., 2006). Capillary electrophoresis (CE) has become an alternative or complement to chromatographic separations because it needs no derivatization step, requires only small amounts of sample and buffer and has proved to be a high-resolution technique (Arráez-Román, Gómez-Caravaca, Gómez-Romero, Segura-Carretero, & Fernández-Gutiérrez, 2006). The hyphenation of CE as analytical separation technique coupled to mass spectrometry (MS) as detection system can provide important advantages in food analysis because of the combination of the high separation capabilities of CE and the power of MS as identification and confirmation method (Arráez-Román et al., 2007; Gómez-Romero et al., 2007; Simó, Barbas, & Cifuentes, 2005). In general, if a separation technique is coupled with MS the interpretation of the analytical results can be more straightforward (Brocke, Nicholson, & Bayer, 2001; Macià, Borrull, Calull, & Aguilar, 2004; Schmitt-Kopplin & Frommberger,

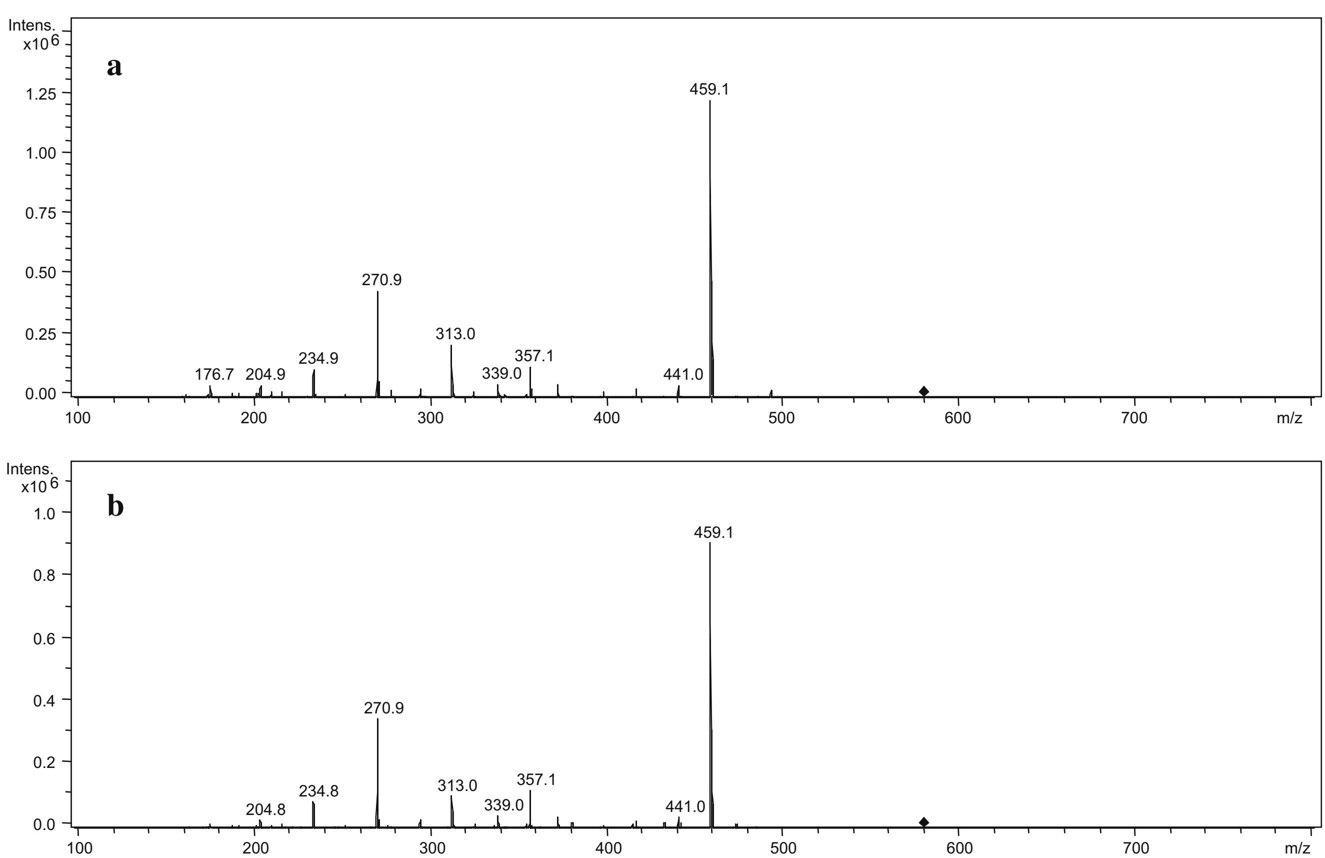

Fig. 2A. (a) MS/MS naringin (m/z 579.2) standard, (b) MS/MS naringin (m/z 579.2) in bitter orange peel sample.