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Anthocyanin pigments in strawberry

Fátima Lopes da Silva[1], María Teresa Escribano-Bailón, José Joaquín Pérez Alonso, Julián C. Rivas-Gonzalo, Celestino Santos-Buelga*

Facultad de Farmacia, Laboratorio de Nutrición y Bromatología, Universidad de Salamanca, Campus Miguel de Unamuno s/n, E-37007 Salamanca, Spain

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Abstract

The anthocyanin composition was analysed in strawberry fruits from five different cultivars (cv. *Eris, Oso Grande, Carisma, Tudnew* and *Camarosa*). Twenty-five defined anthocyanin pigments were detected, most of them containing Pelargonidin (Pg) as aglycone; some cyanidin (Cy) derivatives were also found. Glucose and rutinose were the usual substituting sugars, although arabinose and rhamnose were also tentatively identified; some minor anthocyanins showed acylation with aliphatic acids. A relevant aspect was the detection of anthocyanin-derived pigments, namely 5-carboxypyranopelargonidin-3-glucoside and four condensed pigments containing C–C linked anthocyanin (Pg) and flavanol (catechin and afzelechin) residues. Total anthocyanin content ranged between 200 and 600 mg kg^{-1}, with Pg 3-gluc constituting 77–90% of the anthocyanins in the strawberry extracts followed by Pg 3-rut (6–11%) and Cy 3-gluc (3–10%). A notable variability was found among the anthocyanin concentrations in samples of a same variety and harvest, indicating a strongly influence of the degree of maturity, edaphic-climatic factors and post-harvest storage.

Keywords: Anthocyanins; Strawberry; Pelargonidin; Cyanidin; Anthocyanin-derived pigments

1. Introduction

Strawberry fruits (*Fragaria* × *ananassa* Duch.) have been shown to possess high in vitro antioxidant activity that has been positively correlated with the content of polyphenolic compounds and, specifically, anthocyanins, the type of polyphenols quantitatively most important in strawberry (Heinonen, Meyer, & Frankel, 1998; Wang & Jiao, 2000; Wang & Lin, 2000). The anthocyanin composition in strawberry has been the object of various studies, but is still not fully characterized regarding minor pigments. Strawberry anthocyanins derive from pelargonidin (Pg) and cyanidin (Cy) aglycones (Fig. 1a) (Mazza & Miniati, 1993). The major anthocyanin in the fruits is Pg 3-glucoside (Pg 3-gluc), as firstly identified by Robinson and Robinson (1931). In smaller proportions the presence of Cy 3-glucoside (Cy 3-gluc) seems also constant in all varieties (Bridle & Garcia-Viguera, 1997; Hong & Wrolstad, 1990a; Lukton, Chichester, & MacKiney, 1955) and Pg 3-rutinoside (Pg 3-rut) is also commonly found (Bakker, Bridle, & Bellworthy, 1994; Co & Markakis, 1968; Hong & Wrolstad, 1990b). Furthermore, Pg 3-arabinoside (Fiorini, 1995; Goiffon, Mouly, & Gaydou, 1999) and Cy 3-rutinoside (Bridle & Garcia-Viguera, 1997) have been cited in some strawberry cultivars, as well as various acylated anthocyanins. In particular, Pg 3-(6-malonylglucoside) was unequivocally identified by Tamura, Takada and Yoshida (1995) and indicated as one of the main pigments in several Japanese cultivars, comprising 5–30% of total anthocyanin content (Tamura et al., 1995; Yoshida, Koyama, & Tamura, 2002). Other acylated anthocyanins also reported in strawberry are Pg 3-acetylglucoside (Hong & Wrolstad, 1990b) and Pg succinylglucoside (Bakker et al., 1994).

In a previous study by our group (Lopes-da-Silva, de Pascual-Teresa, Rivas-Gonzalo, & Santos-Buelga, 2002), the anthocyanin composition in strawberries of cv. *Camarosa* was analysed using electrospray ionization mass spectrometry ESI-MS coupled to HPLC. In addition to the major anthocyanins (i.e. Pg 3-gluc, Pg 3-rut and Cy 3-gluc)

*Corresponding author. Fax: +34 923 294 515.
E-mail address: csb@usal.es (C. Santos-Buelga).
[1]Current address: Escola Superior Agrária de Bragança, Campus de Santa Apolónia, P-5301-855 Bragança, Portugal.

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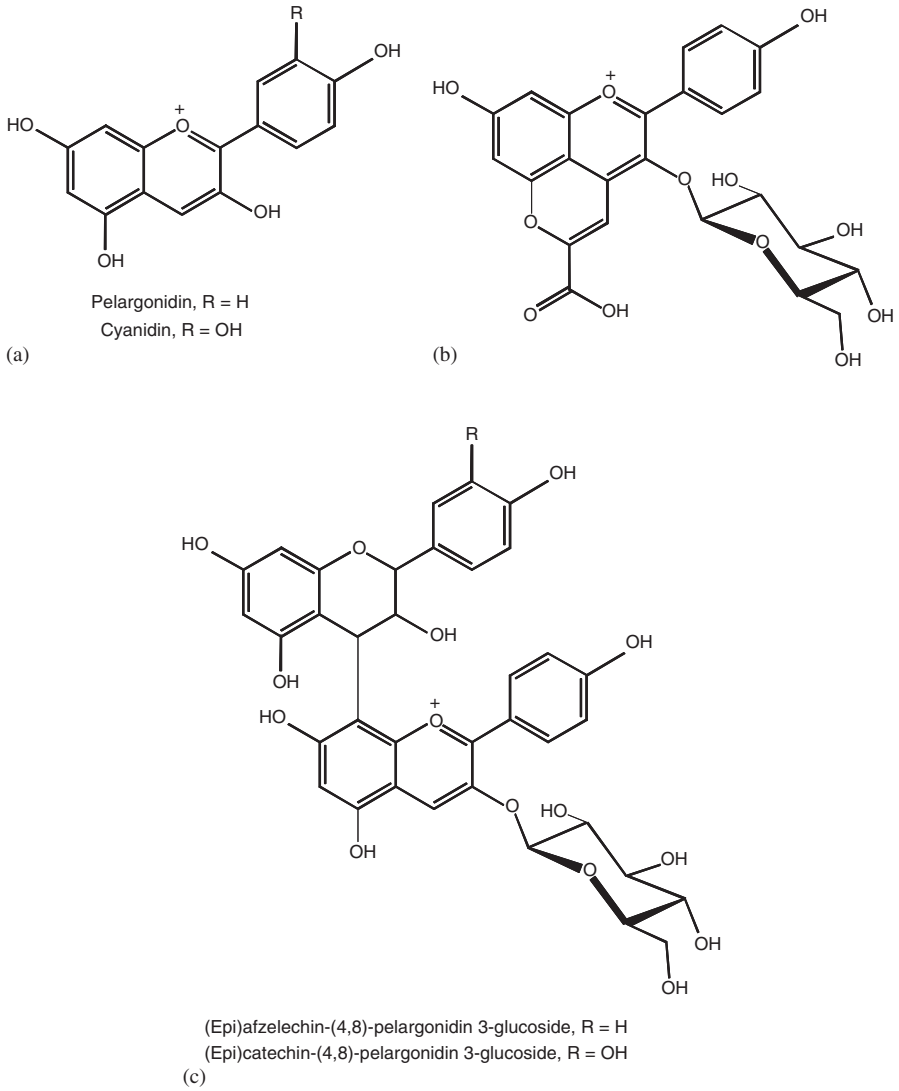

Fig. 1. Structures of pigments found in strawberry. (a) Anthocyanin aglycones; (b) 5-carboxypyranopelargonidin 3-glucoside (Andersen et al., 2004); and (c) anthocyanin-flavanol condensed pigments (Fossen et al., 2004).

12 minor anthocyanins were detected although identity could be only assigned to five of them as Pg 3-acetylglucoside, Cy 3-rutinoside, Pg 3-malylglucoside, Pg diglucoside, and Cy 3-malonylglucosyl-5-glucoside, the three latter not being described previously in strawberry.

Quite recently, small amounts of some anthocyanin-related pigments have also been detected and identified in strawberries, including 5-carboxypyranopelargonidin 3-glucoside (Fig. 1b) (Andersen, Fossen, Torskangerpoll, Fossen, & Hauge, 2004) and four purple anthocyanin–flavanol complexes consisting of pelargonidin 3-glucoside C–C linked to (epi)catechin and (epi)afzelechin moieties (Fig. 1c) (Fossen, Rayyan, & Andersen, 2004). That was the first evidence of the occurrence in a natural plant source of this type of condensed pigments, whose formation was associated to reactions taking place during maturation and ageing of red wines (Jurd, 1969; Salas et al., 2004; Somers, 1971; Vivar-Quintana, Santos-Buelga, Francia-Aricha, & Rivas-Gonzalo, 1999). Further evidence about the presence of anthocyanin–flavanol condensed pigments in strawberry fruits and other plants has also been recently contributed by our group (González-Paramás et al., 2005).

The aim of the present work is to update the knowledge about strawberry anthocyanins, for which the anthocyanin composition, qualitative and quantitative, has been analysed in strawberry fruits from five different cultivars, using HPLC coupled to diode array and MS detection.

2. Materials and methods

2.1. Samples

Strawberries (*Fragaria* × *ananassa* Duch.) from five selected cultivars (cv. *Camarosa*, *Carisma*, *Eris*, *Oso Grande* and *Tudnew*) grown at an experimental station at Instituto de la Grasa-CSIC in Seville (Spain) and picked at commercial maturity were collected in years 2001 and