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Erratum

Corrigendum to "Analysis and biological activities of anthocyanins" [Phytochemistry 64 (2003) 923–933]

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The authors regret that significant excerpts of an original article (da Costa et al., 2000) were quoted verbatim in their review, without due credit to the original article. (The first author is to take full responsibility for the breach of ethics.) For this reason, the section from p. 925 (column 1, line 20) to p. 926 (column 1, line 33) should be replaced by the following.

Being soluble in polar solvents, anthocyanins are usually extracted from plant materials using acidified methanol, with a small quantity of formic or hydrochloric acid, to prevent degradation of the non-acylated anthocyanin pigments. However, even small quantities of acid may cause degradation of pigment during sample concentration, or cause hydrolysis of the acyl portions of the acylated anthocyanins present in some plants. For example, Revilla et al. (1998) studied various techniques for the extraction of anthocyanins from red grapes and found that solvents with up to 0.12 mol/L hydrochloric acid can cause partial hydrolysis of acylated anthocyanins (da Costa et al., 2000).

It was reported that acetone has also been used for extraction of anthocyanins from some plant samples (Giusti et al., 1998; Garcia-Viguera et al., 1998). As compared to acidified methanol, the extraction using acetone is more efficient and reproducible, prevents problems associated with pectins, and allows sample concentration at a lower temperature (Garcia-Viguera et al., 1998). For the prior purification of crude anthocyanin extracts, solid-phase extraction (SPE) on Sephadex or C_{18} (SPE) is commonly employed. This is because anthocyanins are strongly bound to these adsorbents via their unsubstituted hydroxyl groups and can be separated from unrelated compounds by a series of solvents with increasing polarity (da Costa et al., 2000).

For the characterization of anthocyanins, standard samples are necessary. In the absence of standards, however, alternative methods must be adopted. There have already been several techniques described for the characterization of anthocyanins in a mixture. These techniques include conventional high performance liquid chromatography (HPLC) and HPLC coupled with different detectors. HPLC combined with a mass spectrometry detector (HPLC–MS) is a powerful tool, as it gives the molar weights of eluted anthocyanins, which are of great importance for precise identification. Other options include the use of photodiode-array detector, electrospray ionization-mass spectrometry detector, continuous-flow fast atom bombardment (CF-FAB)-mass spectrometry detector (Tamura et al., 1994; Saito et al., 1983), atmospheric pressure chemical ionization (APCI)-mass spectrometry detector (Baldi et al., 1995), tandem mass spectrometry (Giusti et al., 1999), and matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry techniques (Wang and Sporns, 1999), which offer high selectivity and sensitivity. Anthocyanin structures and even conformations can eventually be elucidated using ^{1}H and ^{13}C nuclear magnetic resonance (NMR).

Several excellent reviews focusing on the characterization of anthocyanins are available. da Costa et al. (2000) and Ryan et al. (1999) give good summaries of the identification and characterization of plant anthocyanins. Some examples are given briefly here:

As early as 1983, Saito et al. (1983) employed FAB-MS in the structural analysis of the acylated anthocyanins violanin and platyconin. Since then, many new acylated anthocyanins have been found with the help of this technique. Glassgen et al. (1992) investigated anthocyanins from *Daucus carota L.* by using HPLC assisted by electrospray (ES) mass spectrometry. Anthocyanin compositions of different sources were also compared using on-line HPLC/ES mass spectrometry and tandem mass spectrometry. Baldi et al. (1995) identified two novel 3-caffeoylglucoside derivatives from *Vitis vinifera* L. by using LC–MS technique coupled with an atmospheric pressure-ionization (API) ion-spray interface. Piovan et al. (1998) reported the use of direct infusion electrospray (ESI) mass spectrometry and ion trap multiple mass spectrometry (MS/MS) to identify anthocyanins from *Catharanthus roseus* (L.) G. Don. Similarly, three 3-O-(6-O-*p*-coumaroyl)glucosides were identified for the first time in this species.

In 1997, Herderich et al. described the technical trend of utilizing atmospheric pressure-ionization (API) and electrospray ionization (ESI) mass spectrometry, coupled with liquid chromatography. This trend should have a bright future as both ESI and API can generate ions from polar and labile biomaterials with remarkable ease and efficiency. In particular, it opens up the possibility of using HPLC with tandem mass spectrometry (MS^n) in the field of natural products, and provides a new tool for the structure determination and elucidation of anthocyanins in a mixture.

da Costa et al. (1998) reported analyses of anthocyanins from blackcurrant fruit (*Ribes nigrum*). The technique used was an LC–MS system coupled with an APCI interface. The molecular ion peak and fragment peak appeared to prove a successive loss of sugar groups.

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Revilla et al. (1999) used LC–MS as a tool to detect and identify anthocyanins in grape skin extracts and red wines, and proved that it is a powerful method for the identification of anthocyanins.

Wang and Sporns (1999) and Wang et al. (2000) used, respectively, a matrix-assisted laser desorption/ionization–mass spectrometry (MALDI–MS) to perform both qualitative and quantitative analyses of anthocyanins in wine and fruit juice, and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF–MS) to analyze the content of anthocyanins in various foods (da Costa et al., 2000).

In a recent review, Kostiainen et al. (2003) gave a comprehensive account of LC–API–MS development and listed some of the most recent advances in hyphenated LC systems, HPLC–NMR and HPLC–NMR–MS, but their applications in anthocyanin identification and characterization are unclear due to the authors' limited access to journals.

Another technique recently used for anthocyanin analysis is capillary electrophoresis (CE). Its separation principle is based on the analyte's charge and mass, as well as frictional forces with capillary wall. This method is rapid, highly efficient, has an ultra high detection sensitivity and is cost effective in terms of chemicals and samples. There are broadly two kinds of CE methods: capillary zone electrophoresis (CZE) and micellar electrokinetic chromatography (MEKC). Some examples for anthocyanin separation using CE methods are given below.

Bridle et al. (1996) and da Costa et al. (1998) separately reported anthocyanin separations by CZE. The former used CZE for separation of strawberry and elderberry anthocyanins and the latter for separation of blackcurrant anthocyanins. The study of da Costa et al. employed a capillary column of fused-silica with acidic phosphate buffers containing 30% (v/v) acetonitrile at pH 1.5. They also investigated the interaction of the anthocyanins with the capillary wall, by comparison of anthocyanins on the above mentioned fused-silica capillary column and on a linear polyacrylamide (PLA) coated capillary column. Experimental results showed that there was little interaction between anthocyanins and the capillary wall silanols at pH 1.8. They also found that the time range for separating four anthocyanins in blackcurrant juice (cyanidin 3-glucosides, cyanidin 3-rutinosides, delphinidin 3-glucosides and delphinidin 3-rutinosides) was comparable to that using LC method, but requiring very small amounts of sample and solvent (da Costa et al., 2000).

For MEKC, Watanabe et al. (1998) exploited this method to analyze elderberry pigments (*Sanbucus nigra* L.) in candy, juice, and jelly, all from commercially available food samples. The separation times were all less than 10 min for those anthocyanins, all of which were cyanidin derivatives.

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