Food Chemistry 271 (2019) 224–231

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Surfactant TWEEN20 provides stabilisation effect on anthocyanins extracted from red grape pomace

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ARTICLE INFO

Keywords:
Grape pomace
Anthocyanins stability
Colloidal gas aphrons
Surfactant
Storage

ABSTRACT

Red grape pomace, a wine-making by-product is rich in anthocyanins and has many applications in food and pharmaceutical industry. However, anthocyanins are unstable during processing and storage. This study aimed to investigate the stability of anthocyanins obtained by hydroalcoholic extraction (with and without sorbic acid) and colloidal gas aphrons (CGA) separation; a surfactant (TWEEN20) based separation. Anthocyanins in CGA samples showed higher stability (half-life = 55 d) than in the crude extract (half-life = 43 d) and their stability increased with the concentration of TWEEN20 in the CGA fraction (6.07–8.58 mM). The anthocyanins loss in the CGA sample (with the maximum content of surfactant, 8.58 mM) was 34.90%, comparable to that in the crude ethanolic extract with sorbic acid (EE-SA) (31.53%) and lower than in the crude extract (44%). Colour stabilisation was also observed which correlated well with the stability of individual anthocyanins in the EE and CGA samples. Malvidin-3-o-glucoside was the most stable anthocyanin over time.

1. Introduction

Grapes are one of the most important fruit crop cultivated across the world, whereby 80% of the grape productions are used in wine-making industry (Fontana, Antoniolli, & Bottini, 2013). Wine production is considered one of the most important agricultural activities, generating large amount of residues including grape skins, stems and seeds (Yu & Ahmedna, 2013). At the end of the fermentation process, large amounts of residues are being discharged containing high amount of phenolic compounds including anthocyanins, catechins, flavonol glycosides, phenolic acids and stilbenes (Kammerer, Kammerer, Valet, & Carle, 2014). This is seen by the environmental management authorities as a serious threat because they are low in pH and high in organic matter thus potentially causing a phytotoxic effect if applied to crops or wetlands (Kammerer, Claus, Carle, & Schieber, 2004; Lavelli, Harsha, Laureati, & Pagliarini, 2017). Therefore, converting and utilising this by-product to another useful product would be a solution to this problem. For instance, the anthocyanins from this pomace can be used as natural food colourant (Thakur & Arya, 1989). Anthocyanins are sensitive to thermal degradation making the recovery rather difficult and complex, but they are on demand due to their wide applications in food (already being used as food colourants, E163, approved by EC) as well as in pharmaceuticals and cosmetics. Thus, various extraction techniques have been studied and used, including acidified alcohol, sub- and supercritical fluid and high pressure processing (Barba et al., 2016; Drosou, Kyriakopoulou, Bimpilas, Tsimogiannis, & Krokida, 2015; Lozovskaya, Brenner Weiss, Franzreb, & Nusser, 2012).

Food processing generally involves thermal processing prior to consumption and this process has a great influence on the anthocyanins content in the final product. Thermal processing involves high temperatures ranging from 50 °C to 150 °C, depending on the pH and the desired shelf life of the product. Anthocyanins are expected to degrade over time. However, the storage temperature has been found to be an important factor that is affecting anthocyanins' shelf life. Degradation of anthocyanins is greatly affected by the type of anthocyanin, the origin of the samples and the storage temperature (Hellström, Mattila, & Karjalainen, 2013). The thermal degradation of anthocyanins in extracts and model systems are reported to follow first-order reaction kinetics (Presilski, Presilska, & Tomovska, 2016).

The stability of anthocyanins can be improved, by self-association of the anthocyanins, removal of oxygen and inactivation of enzymes (Hellström et al., 2013). In the food industry, the sensitivity of bioactive

Abbreviations: ABTS, 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid); AOP, antioxidant power; CGA, colloidal has aphrons; EE, ethanolic extract; EE-SA, ethanolic extract with addition of sorbic acid; GAE, gallic acid equivalents; $t_{1/2}$, half-life; glc, 3-o-glucoside; ME, malvidin glucoside equivalent; V4, CGA fraction separated at volumetric ratio 4; V8, CGA fraction separated at volumetric ratio 8; V16, CGA fraction separated at volumetric ratio 16

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https://doi.org/10.1016/j.foodchem.2018.07.083
Received 1 March 2018; Received in revised form 9 July 2018; Accepted 12 July 2018

compounds is addressed by incorporating edible coatings as a structural matrix, used widely to create a barrier from oxygen, moisture and solute movement (Falguera, Quintero, Jiménez, Muñoz, & Ibarz, 2011). Encapsulating methods such as spray drying/spray chilling or liposomes have been used. The former requires liquid droplets or small particles being incorporated within a continuous edible coating, thus it requires an emulsifier. Liposomes are microscopic spherical particles consisting of one or more lipid bilayers that can encapsulate or bind a variety of molecules. Therefore, particularly in food applications, food grade surfactants such as TWEEN20 have been used as emulsifying agents to fit this purpose (Quirós-Sauceda, Ayala-Zavala, Olivas, & González-Aguilar, 2014). Moreover, TWEEN20 has been seen as having a profound protective effect on five different polyphenols, by slowing down the auto-oxidation process at pH 4.5 (Lin, Wang, Qin, & Bergenståhl, 2007).

A surfactant-based separation technique, colloidal gas aphrons (CGA) has been previously studied in our group to recover various valuable bioactive compounds from different feedstock such as astaxanthin (Dermiki, Bourquin, & Jauregi, 2010; Dermiki, Gordon, & Jauregi, 2009), proteins (Fuda & Jauregi, 2006; Fuda, Bhatia, Pyle, & Jauregi, 2005) and polyphenols (MohdMaidin, Michael, Oruna-Concha, & Jauregi, 2017; Spigno, Dermiki, Pastori, Casanova, & Jauregi, 2010; Spigno, Amendola, Dahmoune, & Jauregi, 2015). The type of surfactant (i.e cationic, anionic and non-ionic) determines the outer charge of the CGA, where molecules with the opposite charge will attract to the CGA resulting in their effective separation into the CGA phase.

In our previous work it was shown that 70% of the anthocyanins could be recovered from the ethanolic extract of grape pomace using CGA generated from TWEEN20. The CGA fraction will be rich in surfactant therefore, it will be interesting to test what will be the added value of extracting the anthocyanins in such a solution and whether this can offer any advantage to their formulation for subsequent applications. Thus the present study aimed at assessing the stability of anthocyanins in the CGA separated fraction over time in comparison with their stability in the crude ethanolic extract (EE) (before the CGA separation) as well as in the crude ethanolic extract with a commercial additive, sorbic acid (EE-SA). It is therefore hypothesised that the anthocyanins in the CGA sample will show higher stability than in the crude extract over time.

2. Materials and methods

2.1. Materials

Grape pomace (Barbera variety) was obtained from a winery in Northern Italy. All the solvents (purity of 95% and above) used in this project were obtained from Sigma-Aldrich Company Ltd., Dorset, UK. For the HPLC analysis, the solvents used were of HPLC grade (purity of 98–99.9%) also from Sigma Aldrich.

2.2. Extract preparation

The grape pomace (Barbera variety) was kindly provided by a winery located in Northern Italy. At the winery, the fermented pomace was recovered and oven dried at 60 °C until the residual moisture content is < 5%. The dried pomace powder was sieved with a 5 mm sieve to separate the skins from the seeds and milled into fine powders with particles size < 2 mm and stored in the freezer at −20 °C until further use.

The extraction procedure was done in accordance to our previous study using ethanol-aqueous solvent (MohdMaidin et al., 2017). The extract was filtered and two different samples were produced: (1) approximately, 400 mL of the ethanol extract labeled as EE and (2) another 400 mL ethanol extract with sorbic acid (> 99%) (Sigma, UK) and labelled as EE-SA. Sorbic acid was chosen in this study for its wide application as food additive, thus making it closer to the formulation of most low pH food products and neutral taste (Troller & Olsen, 1967). Both EE and EE-SA were considered control samples. The remaining filtrate of 800 mL was kept aside for CGA separation.

2.3. CGA separation using 10 mM TWEEN20

The separation of polyphenols from the crude ethanolic extract was carried out at different volume ratios of CGA to feed (V_{CGA}/V_{feed}). The ratios selected were 4, 8 and 16. The separations were individually carried out in a flotation glass column according to the method described in our previous work (MohdMaidin et al., 2017); each separation was carried out in triplicate. It should be noted that as the volumetric ratio increased, so did the concentration of TWEEN20 in the solution of the separated CGA fraction. The concentration of TWEEN20 in each of these fractions was estimated from a knowledge of the separated volume of CGA and corresponding liquid fraction which was determined from a measurement of gas hold-up (gas volumetric ratio defined as the volume of air incorporated in a given volume of CGA dispersion) of the CGA generated with this solution of TWEEN20 (61.3%). The estimated concentrations were: in V4, 6.07 mM, in V8, 7.56 mM and in V16, 8.58 mM. The summary of the extraction and separation process is briefly described in Fig. 1.

2.4. Determination of degradation of chemical and physical properties over time

Briefly, the EE, EE-SA and CGA fractions were divided in equal volumes and kept in sterilised containers in the darkness. These were then stored at room temperature 20 °C (SD 1 °C) which was regularly monitored using a thermometer for 32 days. The total phenolic content, total anthocyanin and antioxidant activity were determined as described in Sections 2.5–2.7. The total anthocyanins, individual anthocyanins, antioxidant capacity and the colour degradation over time (32 days; every day for the first 7 days and subsequently 5 days

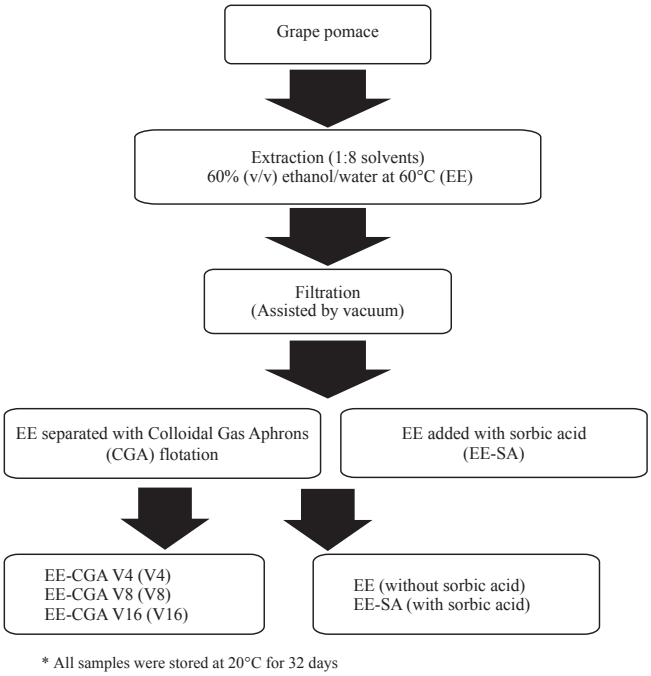

Fig. 1. Flow diagram of hydroalcoholic extraction and CGA separation processes applied to grape pomace, n = 3; EE is the ethanolic extract; EE-SA is the ethanolic extract with addition of sorbic acid; EE-CGA V4 is the ethanolic extract further processed with CGA at CGA to feed volumetric ratio of 4; V8 and V16 correspond to the extracts further processed with CGA at CGA to feed volumetric ratios 8 and 16 respectively.