View metadata, citation and similar papers at core.ac.uk
brought to you by CORE
provided by JKI Open Journal Systems (Julius Kühn-Institut)

Journal of Applied Botany and Food Quality 89, 249 - 257 (2016), DOI:10.5073/JABFQ.2016.089.032

Fraunhofer Institute for Process Engineering and Packaging, Department of Process Engineering, Freising, Germany

In vitro-study of antioxidant extracts from *Garcinia mangostana* pericarp and Riesling grape pomace – a contribution to by-products valorization as cosmetic ingredients

Judith Wittenauer*, Ute Schweiggert-Weisz, Reinhold Carle

(Received May 13, 2016)

Summary

The objective of the present study was to compare extracts from two different plant sources regarding their suitability as antioxidant cosmetic ingredients. Both, *Garcinia mangostana* pericarp, in Europe being widely considered as the non-edible part of a 'superfruit', and Riesling grape pomace accruing from vinification, represent important by-products from food processing. Mixtures of ethanol and water in different ratios were used for the preparation of polyphenol containing extracts. Antioxidant properties of the extracts were determined using well-established *in vitro* assays (Folin-Ciocalteu, ORAC, DPPH, and ABTS), and skin penetration was investigated by Franz-type diffusion experiments with porcine skin.

Extraction of polyphenols was most effective using an equimolar ratio of ethanol and water for both raw materials. Absolute polyphenol contents of mangosteen pericarp extract (65360.71 ± 1168.51 mg/kg DM) were higher than for grape pomace extract (18085.70 ± 411.50 mg/kg DM). However, Folin-Ciocalteu reducing capacities as well as *in vitro* antiradical activities did not adequately correspond to quantitative polyphenol estimations, as grape pomace extract showed relatively high antiradical capacities. When applied to pig skin, polyphenols from grape pomace extract were detected in low concentrations in the dermis as well as in the transdermal receptor fluid. In contrast, mangosteen pericarp xanthones were almost completely recovered with highest amounts detected in the dermis. In conclusion, both raw materials revealed potential as antioxidant ingredients for cosmetic formulations.

Keywords

Grape pomace; *Garcinia mangostana* L.; antioxidants; polyphenols; Franz-type diffusion

Introduction

Constituting the outer barrier of the body, the skin is perfectly designed for confining and protecting the inner organs from the outer environment. Exposure to exogenous noxae such as UV radiation and toxins is a big challenge to this interface function. Therefore, harmful reactive oxygen species (ROS) and other free radicals are readily produced in the skin through diverse pathways (Rittie and Fisher, 2002; Scharffetter-Kochanek et al., 2000). Like any other organ, the skin disposes of an antioxidant network that helps to cope with ROS which are continuously formed intrinsically in the course of normal aerobic metabolism (Shindo et al., 1994; Thiele et al., 2002). However, overwhelming radical production by external prooxidant stimuli may disturb the sensitive balance between oxidants and antioxidants in the skin resulting in the harmful state of oxidative stress (Thiele et al., 2002; Thiele et al., 1998). Consequently, inflammatory processes may occur, resulting in premature skin aging, and the formation of skin disorders such as photosensitivity and even cutaneous malignancy (Bickers and Athar, 2006). Topically applied antioxidants are seen to be a potential measure to prevent such adverse effects at an early stage. Some of the most commonly employed antioxidants in the cosmetic sector are synthetic vitamins, e.g. ascorbic acid, niacin and tocopherol, and also lipoic acid, butylated hydroxytoluene, and butylated hydroxyanisole. In order to ensure stability and solubility of these substances in cosmetic emulsions, chemically modified derivatives thereof are applied (Austria et al., 1997; Kerscher and Buntrock, 2011; Thiele et al., 2005). Since consumer acceptance of synthetic and chemically modified ingredients decreases, natural alternatives from plants are urgently demanded. Due to their ubiquitous occurrence in nature, and because polyphenols act as potent hydrogen donators, they have been recognised as potent antioxidant bioactives (Leopoldini et al., 2011; Quideau et al., 2011; Rice-Evans et al., 1996). So far, only few plant extracts being rich in polyphenolics are applied in cosmetic products, and sound scientific data about their contribution to skin health are scarce (Briganti and Picardo, 2003; Ribeiro et al., 2015). Most studies have been performed with green tea, and, in particular, individual polyphenols thereof, e.g. epigallocatechin and epigallocatechin gallate, have been evaluated (dal Belo et al., 2009; Dvorakova et al., 1999; Gianeti et al., 2013; Wisuitiprot et al., 2011). Due to their appealing image and with emphasis on marketing in the cosmetic sector, fruits, herbs and flowers are the most popular plant sources for cosmetic bioactives. The so-called 'superfruits' are considered to be most interesting for cosmetic purposes, since they are rich sources of antioxidants with alleged health benefits (Gross, 2010). Among this fruit category, mangosteen (*Garcinia mangostana* L.), and, particularly, the purple coloured pericarp of the fruit has gained the attention of several research groups as they are rich sources of xanthones (Obolskiy et al., 2009; Pedraza-Chaverri et al., 2008; Wittenauer et al., 2012). The edible part of the fruit, constituting the aril, which is freshly eaten, dried, frozen or canned only amounts to about 30 % of its fresh weight, while the pericarp and seed are considered as waste (Okonogi et al., 2007). Thailand is the most important producer with an annual production of approximately 240,000 t. Hence, sustainable production through waste valorization is an urgent challenge (Diczbalis, 2009). Xanthones recently identified in mangosteen pericarp seem to be suitable antioxidants in cosmetics for various reasons (Wittenauer et al., 2012). Firstly, due to the hydroxyl groups, attached to the unsaturated heterocyclic xanthone core, xanthones exert high antioxidant activity (Martinez et al., 2011; Sze Lim et al., 2013). Secondly, mangosteen extracts have been suggested as biopreservatives in food industry (Sze Lim et al., 2013). Thirdly, the prenyl substituents might enhance skin penetration by increasing their lipophilicity, and, thus, the affinity to cell membranes (Botta et al., 2005). By analogy to tropical fruit processing, large amounts of grape pomace accrue from vinification (Balasundram et al., 2006), thus also representing polyphenol rich by-products which may be valorised for cosmetic purposes (Balasundram et al., 2006; Schieber et al., 2001). Grape pomace has been reported to contain a complex spectrum of low molecular weight polyphenols such as phenolic acids and flavonoids as well as higher molecular procyanidins, and tannins (Kammerer et al., 2004; Katalinić et al., 2010; Maier et al., 2009; Schieber et al.,

* Corresponding author

2001). Although many attempts have been made for the exploitation of grape pomace (Maier et al., 2009; Wittenauer et al., 2015), its valorisation has not been implemented in wine making industry up to now. As grape pomace extracts contain a variety of bioactive molecules, allowing intermolecular interactions of the individual compounds, such interdependencies may not only affect the overall antioxidant activity, but also their penetration behaviour to the targeted skin layer (Abou Samra et al., 2011; Choueiri et al., 2012; Seeram et al., 2004).

The objective of the present study was the comparison of mangosteen pericarp and grape pomace extracts regarding their antiradical properties and their potential as antioxidative cosmetic ingredients. To allow their direct comparison, both plant extracts were made based on identical extraction conditions and by using the same aqueous ethanolic solvent, which can readily be used for their incorporation in cosmetic products due to their toxicological innocuousness. Additionally, both plant materials were extracted with different concentrations of aqueous ethanol to obtain samples of different polyphenol pattern and polarities. The respective extracts were analysed by means of the commonly used *in vitro* assays ORAC, DPPH, ABTS, and Folin-Ciocalteu. Finally, Franz-type diffusion experiments were executed with the most promising extracts of both raw materials enabling insight into the penetration depth of the polyphenols and, therefore, the presumed antioxidant performance of the polyphenolic molecules after topical application.

Materials and methods

Materials

Thai mangosteens (*Garcinia mangostana* L.) were obtained from a local retailer. Pericarp of the fruits was manually separated, minced in a bowl chopper, and immediately flash-frozen with liquid nitrogen prior to lyophilisation. The lyophilised mangosteen pericarp was kept at 5 °C until analysis. Grape pomace from white wine grapes (*Vitis vinifera* L. cv. 'Weisser Riesling') was used in this study. Pomace samples were kindly provided by the Baden-Badener Winzergenossenschaft (Baden-Baden-Neuweier, Germany) and directly collected after pressing the mash, lyophilised, and kept at 5 °C until further use.

Polyphenols used as standards for HPLC-analysis were α-mangostin (97 %), *trans*-resveratrol (98 %) (ABCR, Karlsruhe, Germany), gallic acid (≥97 %), epicatechin (≥99 %) (Sigma, St. Louis, MO, USA); caftaric acid (≥97 %), procyanidin B1 (≥90 %), procyanidin B2 (≥90 %), quercetin 3-*O*-glucoside (≥98 %), and quercetin 3-*O*-glucuronid (≥95 %) (Fluka, Buchs, Switzerland). ABTS (2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonicacid)), DPPH (2,2-diphenyl-1-picrylhydrazyl), trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid), sodium fluorescein, 2,2'-Azobis(2-amidinopropane) dihydrochloride (AAPH), Folin-Ciocalteu reagent, and gallic acid were used for the determination of the antiradical activity and the Folin-Ciocalteu assay, respectively, and purchased from Sigma (St. Louis, MO, USA).

Preparation of polyphenol rich extracts

Lyophilised mangosteen pericarp and grape pomace, respectively, were ground using a ZM 100 centrifugal mill with a 1 mm ring sieve (Retsch, Haan, Germany). Aliquots of 1 g of the powdered samples were extracted with 50 mL of different ethanol/water mixtures (30/70; 50/50; 70/30 (v/v)) at room temperature for 60 min under continuous stirring. The thus obtained plant extracts were filtered through a folded filter (Munktell, Bärenstein, Germany), and directly used for antiradical activity assays. For HPLC-analysis, the extracts were filtered through a 0.2 µm syringe filter (Sartorius, Göttingen, Germany).

HPLC analyses

Identification and quantitation of individual polyphenols contained in the plant extracts were performed using an Agilent HPLC series 1200 system (Agilent, Waldbronn, Germany) with ChemStation software, a model G1379 degasser, a model G1312B binary gradient pump, a model G1367D thermo autosampler, a model G1316B column oven and a model G1315C diode array detector.

For the separation of grape pomace polyphenols, a Kinetex F5 column (150 × 3.0 mm i.d.; 4 µm particle size) was used. Xanthones from mangosteen pericarp were separated on a Kinetex C18 column (150 × 3.0 mm i.d.; 4 µm particle size) (Phenomenex (Torrance, CA, USA)) operated at 25 °C. The mobile phases were composed of 0.5 % acetic acid (eluent A) and acetonitrile (eluent B). Analyses were performed in quadruplicate at 25 °C using gradient programs as follows: grape pomace extract - 0-20 % B (80 min), 20-100 % B (20 min), 100 % B isocratic (3 min), 100-0 % B (10 min) at a flow rate of 0.4 mL/min; mangosteen pericarp extract - 50-60 % B (20 min), 60-70 % B (35 min), 70-100 % B (5 min), 100 % B isocratic (3 min), 100-0 % B (2 min) at a flow rate of 0.6 mL/min.

Injection volumes varied between 8 and 40 µL. Identification and quantitation of individual polyphenols was performed as described previously (Wittenauer et al., 2012; Wittenauer et al., 2015).

Total phenolic content (Folin-Ciocalteu)

Total phenolics were determined by the Folin-Ciocalteu method, according to Singleton and Rossi (1965) with slight modifications. Aliquots of 20 µL diluted extract, 1 mL water and 0.1 mL Folin reagent were mixed. After 3 min, 0.2 mL sodium carbonate solution (7.5 %, w/v) and 0.68 mL water were added. Absorption was measured at 765 nm after 30 min using a Specord 210 plus spectrophotometer (Analytik Jena, Jena, Germany). Total polyphenols were quantitated by calibration using gallic acid (GA) as a reference. The reducing capacity was calculated as gallic acid equivalent (GAE). All determinations were performed in triplicate.

Antiradical activity

Antiradical activity by **$ABTS^{+\bullet}$** was carried out following the method of Re et al. (1999). $ABTS^{+\bullet}$ stock solution was prepared dissolving 38.4 mg ABTS diammonium salt and 6.62 mg potassium persulfate in 10 mL water, and stored at 8 °C until needed. Final radical solution was prepared by diluting the stock solution with water until an initial absorption value (734 nm) of 0.70 ± 0.02 was reached. For the determination of the antiradical activity, 10 µL of each extract was mixed with 9.99 mL ABTS radical solution, and the absorption was measured at 734 nm on a Specord 210 plus spectrophotometer (Analytik Jena, Jena, Germany) after incubation at 30 °C for 15 min. Ethanolic solutions of trolox in the range of 25-1500 µmol/L were used for calibration of the ABTS, DPPH and ORAC assays.

The **DPPH** assay was performed according to the method of Brand-Williams et al. (1995) with some modifications. DPPH stock solution was prepared dissolving 24 mg DPPH in 100 mL absolute ethanol (100 %), and stored at 8 °C until needed. The working solution was obtained by 10 fold dilution of the stock solution. Aliquots of 10 µL of the extracts were mixed with 9.99 mL of the working solution. Immediately after 15 min of incubation at 25 °C, the absorption was measured at 517 nm using a Specord 210 plus spectrophotometer.

The **ORAC** assay was carried out on an automated plate reader (Synergy H1, BioTek, Winooski, VT, USA) with 96-well plates. The procedure was based on a previous report by Huang et al. (2002). Analyses were conducted at 37 °C in 75 mM phosphate buffer (pH 7.4) with 25 µL of extract. Peroxyl radicals were generated using freshly prepared AAPH (2,2'-azobis(2-amidino-propane) dihydro-

chloride) solution for each run (153 mM). Fluorescein was used as the substrate (4 nM). Fluorescence conditions were as follows: excitation at 485 nm; emission at 520 nm, and fluorescence was recorded every minute after addition of AAPH. When the absorbance value measured exceeded the linear range of the standard curve, samples were further diluted. ORAC values were calculated as described by Cao and Prior (1999) using a regression equation between the trolox concentration and the net area under the fluorescence decay curve. The area under the curve was calculated as

$$AUC = 0.5 + \left(\frac{f1}{f0}\right) + \left(\frac{f2}{f0}\right) + \left(\frac{f3}{f0}\right) + \cdots + \left(\frac{fi}{f0}\right)$$

where f_0 is the initial fluorescence reading at 0 min and f_i the fluorescence reading at time i. The net AUC was obtained by subtracting the AUC of the blank from that of the sample.

All antiradical activity measurements were performed in triplicate, and results were expressed in µM TE/ kg dry mass (DM).

In vitro skin permeation studies

Preparation of pig ear skin

Pig ears were obtained from a local butcher immediately after slaughter. Hairs were carefully removed by shaving. Excision of skin segments from the underlying cartilage was carried out using a scalpel. The skin segments were carefully inspected to ensure the absence of perforations or other defects. Skin disks of 25 mm were punched out with a hollow punch, wrapped in aluminium foil, and stored in polyethylene bags at -20 °C until use.

Franz-type skin permeation experiment

In vitro skin permeation studies were performed according to Zillich et al. (2013a) using static Franz-type diffusion cells (PermeGear, Hellertown, PA, USA) with effective diffusion area of 4.91 cm^2 and inner diameters of 25 mm. Permeation cells were heated by a thermostatic circulating water bath at 32 °C throughout the experiment. During the experiments, the receptor fluid (phosphate buffered saline, pH = 7.4) was continuously stirred by a magnetic stirrer. Porcine skin disks were positioned between donor and receptor compartments, assuring their direct contact with the receptor fluid and the absence of air bubbles. After an equilibration time of 15 min, 500 µL of the plant extracts were pipetted on each skin sample. Control cells were treated with 500 µL of ethanol/water (v/v). Diffusion cells were covered with parafilm (Brand, Wertheim, Germany), and protected from light by covering with aluminium foil. Experiments were carried out 8 fold for a time period of 24 h.

At the end of the permeation experiments, skin samples were dabbed carefully with a cellulose tissue to recover the remaining plant extract that did not penetrate the skin. Subsequently, *stratum corneum* samples were obtained by 10 fold stripping of the permeation area each with adhesive Tesa® tape (Beiersdorf, Hamburg, Germany). The remaining skin was cut into small pieces using a fine scissor, and ground under cryogen conditions at -196 °C (Cryomill, Retsch, Haan, Germany), and lyophilized to obtain a powder. Cellulose tissue, adhesive tape as well as the skin powder were extracted with 50 mL of methanol/water (90/10, v/v), evaporated to dryness at 40 °C in *vacuo*, dissolved in 1 mL of methanol and filtered through a 0.22 µm membrane filter (Whatman, Dassel, Germany) for HPLC analysis. The acceptor medium was concentrated from 21 to 1 mL by evaporation under nitrogen, membrane-filtered (0.22 µm), and used for HPLC analysis.

Statistical analysis

Results are presented as mean values with their standard errors. Statistical analysis was carried out using single-factor one-way ANOVA. Tukey's *post hoc* test was performed to determine the significant difference between the groups. Results were considered significantly different when $p<0.05$ was obtained. The relationship among HPLC-, Folin-Ciocalteu and antiradical assay results was described by the Pearson product-moment correlation coefficient (Katalinić et al., 2010).

Results and discussion

The polarity and type of solvent used for extraction of plant material had marked effects on the polyphenol composition of the antioxidant rich extracts. As ethanol is a usual solvent for the preparation of cosmetic ingredients, aqueous solutions of 30 %, 50 % and 70 % ethanol were applied for the extraction of grape pomace and mangosteen pericarp polyphenols. Subsequently, polyphenol patterns, antioxidative capacities as well as the skin permeation behaviour of extract obtained from both plant sources were studied.

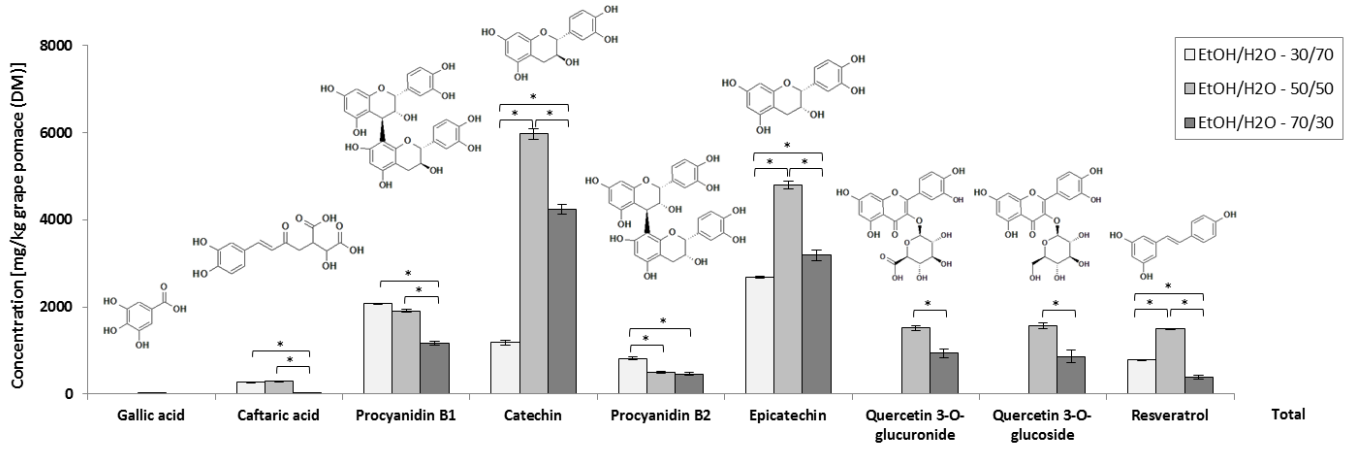
Identification and quantitation of polyphenolic constituents

Nine major polyphenols could be identified and quantitated in all grape pomace extracts by means of HPLC analysis (Fig. 1). In accordance with literature data (Kammerer et al., 2004; Wittenauer et al., 2015), the occurrence of gallic acid and caftaric acid, catechin and epicatechin, the procyanidins B1 and B2 as well as two quercetin-glycosides and resveratrol was confirmed. Variation of ethanol contents of the extraction medium had impact on the total amounts as well as the proportion of the individual polyphenols in the grape pomace extracts. Total amount of polyphenols, calculated as the sum of the nine individually quantified compounds, was highest using 50 % ethanol as solvent, resulting in 18,085.70 ± 411.50 mg/kg grape pomace (DM). In this case, highest extraction yields were obtained for catechin and epicatechin, but also flavanol-glycosides such as quercetin-3-*O*-glucuronide and quercetin-3-*O*-glucoside and resveratrol were extracted most efficiently. In contrast, yields of higher molecular procyanidins B1 and B2 reached a maximum, when applying 30 % of ethanol, probably due to their better water solubility (Zanchi et al., 2009). Application of 70 % ethanol as extraction solvent significantly lowered polyphenol contents of most compounds detected.

In all three mangosteen pericarp extracts α-mangosteen was the major constituent followed by γ-mangosteen, as reported in our previous study (Wittenauer et al., 2012) (Fig. 2). Variation of ethanol contents did not change the xanthones pattern. This might probably be due to their high structural similarity and polarities, in contrast to the complex composition of grape pomace extract comprising different phenol subclasses. Efficient extraction of xanthones from mangosteen pericarp was obtained by ethanol concentrations of the extraction solvent exceeding 50 % (65,360.71 ± 1168.51 mg/kg DM), while applying 70 % of ethanol did only slightly raise the yield reaching 66,769.37 ± 1239.27 mg/kg DM. Altogether, total amounts of individually quantified xanthones markedly exceeded that of grape pomace polyphenols when applying ethanol concentration of 50 % and 70 %.

Total polyphenol content (Folin-Ciocalteu)

The Folin-Ciocalteu assay being a non-specific standardized method solely allows a first indication of the total reducing potential of all reductive compounds contained in a sample. As polyphenols are the main components present in the extracts under investigation, results of the Folin-Ciocalteu assay may represent the total phenolic content. However, additive contributions of ascorbic acid, thiols, aromatic amines, and reducing sugars must be considered (Sanchez-Rangel et al., 2013).



□	nd	269.53 ± 10.79	2069.07 ± 9.55	1178.57 ± 49.43	817.65 ± 27.10	2680.21 ± 23.31	nd	nd	778.97 ± 16.45	7794.00 ± 136.63
▒	35.27 ± 0.92	284.53 ± 14.78	1911.36 ± 42.42	5970.92 ± 116.47	504.69 ± 20.18	4802.00 ± 87.52	1514.11 ± 51.23	1573.27 ± 70.55	1489.66 ± 7.43	18085.70 ± 411.50
■	nd	33.01 ± 0.10	1157.05 ± 41.53	4238.26 ± 106.04	459.89 ± 25.77	3185.25 ± 117.32	931.08 ± 96.33	862.48 ± 147.85	389.69 ± 49.59	11256.72 ± 584.43

Fig. 1: Polyphenolic composition of cv. 'Riesling' grape pomace extracts obtained by extraction with different ethanol/water ratios (v/v) as determined by HPLC-DAD.
* p-value < 0.05

□	154.41 ± 47.63	1095.76 ± 58.27	214.19 ± 62.09	156.30 ± 64.94	nd	1372.21 ± 77.52	182.97 ± 20.50	3175.84 ± 330.95
▒	767.61 ± 30.38	10438.28 ± 51.38	1285.90 ± 10.85	309.79 ± 11.74	1847.96 ± 106.96	47442.06 ± 855.35	2969.12 ± 101.85	65360.71 ± 1168.51
■	755.20 ± 23.70	10636.55 ± 205.23	1316.21 ± 26.24	623.38 ± 18.81	2088.99 ± 56.08	48234.06 ± 827.78	3114.97 ± 81.43	66769.37 ± 1239.27

Fig. 2: Xanthone composition of mangosteen pericarp extracts obtained by extraction with different ethanol/water ratios (v/v) as determined by HPLC-DAD.
*p-value < 0.05

Concerning the three grape pomace extracts, maximum total polyphenol content was determined for the 70 % ethanol extract amounting to 50.94 g GAE/kg DM (Fig. 3). Folin-Ciocalteu values rose significantly with increasing ethanol content of the extraction medium from 30 % ethanol to 50 % ethanol. However, differences between Folin-Ciocalteu values of extracts prepared with 50 % ethanol and with 70 % ethanol were insignificant. Results of the Folin-Ciocalteu assay for the grape pomace extracts are in contrast to the HPLC results, where total polyphenol amounts were considerably lower for extracts produced with 70 % ethanol. Poor correlation of Folin-Ciocalteu and HPLC-DAD values reflected this incongruity, which was supported by the moderate correlation coefficient of 0.717. It appears, that by extracting with 70 % ethanol further reducing compounds were dissolved, which were not determined by HPLC; however, reacting with the Folin-Ciocalteu reagent. Additionally, higher ethanol concentrations in the extract might increase the reducing capacities of the grape pomace polyphenols by a solvent induced enhancement of hydrogen-atom transfer, which has previously been reported for polar compounds such as the grape pomace polyphenols (NENADIS and TSIMIDOU, 2002).

Reducing capacities of mangosteen pericarp extracts ranged from 45.61 to 85.44 g GAE/kg DM applying 30 % and 50 % ethanol, respectively. In contrast to the grape pomace extracts, Folin-Ciocalteu values of mangosteen pericarp extracts well correlated with the results of the HPLC analysis (R = 0.997). Despite their superior individual polyphenol contents as determined by HPLC-analysis, reducing capacities of mangosteen pericarp extracts were only about 1.7 fold higher than those of grape pomace extracts. This may be due to the generally lower reducing power of individual xanthones, because, with the exception of γ-mangostin and garcinon E, potent

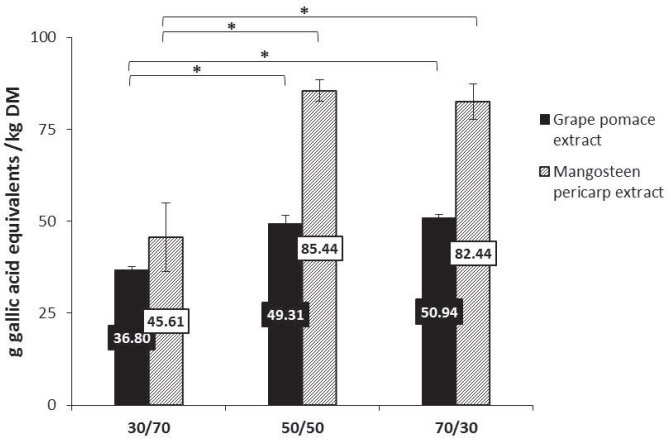


Fig. 3: Reducing capacity of cv. 'Riesling' grape pomace and mangosteen pericarp extracts as determined by Folin-Ciocalteu-assay.
* p-value < 0.05

reductive *ortho*-diphenolic components such as gallic and caftaric acids, catechin and epicatechin, procyanidin B1 and B2 as well as quercetin-glycosides are typical of grape.

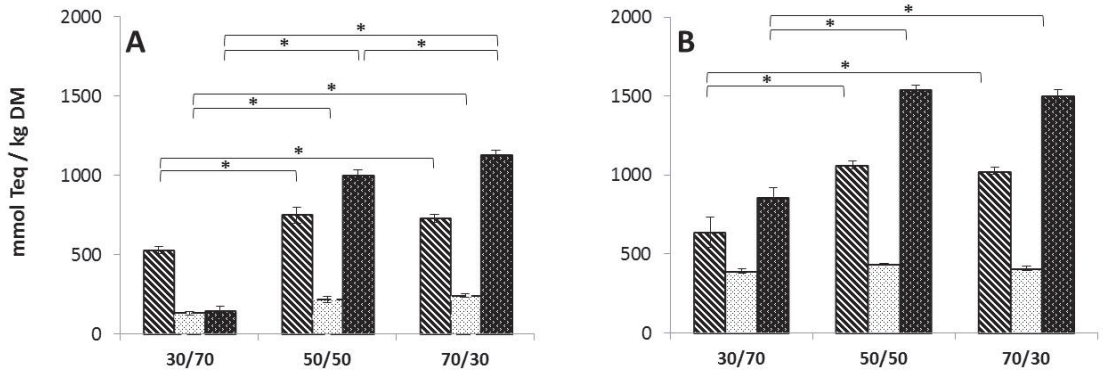
In vitro antioxidant activity

Various i*n vitro* assays mimicking the radical scavenging activity of isolated compounds and complex preparations are commonly carried out, each of them only partially reflecting their potential antioxidant power (Lopez-Alarcon and Denicola, 2013; Prior et al., 2005). To overcome specific limitations and reflect sample complexity as close as possible, analyses of the plant extracts were carried out based on multiple assays, namely the ABTS, DPPH, and ORAC systems. The non-physiological radical molecules $ABTS^{\bullet+}$ and $DPPH^{\bullet}$ are useful to get first indications of the radial-scavenging ability of polyphenols by single electron transfer (SET) reactions in general (Jiménez et al., 2004). Complementary to $ABTS^{\bullet+}$ and $DPPH^{\bullet}$, inhibition of peroxyl radical induced oxidations, and, thus, to some extent, the classical radical chain-breaking antioxidant activity (Prior et al., 2005) may be estimated by the ORAC assay.

Analyses of *in vitro* antioxidant capacities by the ABTS, DPPH and ORAC assays resulted in higher values for the mangosteen pericarp extracts than for the grape pomace extracts (Fig. 4). However, in accordance with the results of the Folin-Ciocalteu assay, the clearly higher contents of individual polyphenols contained in mangosteen pericarp extracts were not adequately reflected by the respective antioxidant activity values. All three grape pomace extracts showed similar antioxidant behaviour when applying the ABTS and DPPH assays. With increasing ethanol contents of the extraction solvent, the antioxidant activity of the grape pomace extracts also increased. DPPH values were generally lower than ABTS values, probably indicating less reactivity of grape pomace polyphenols towards this radical in contrast to ABTS radical. Regarding the ORAC assay, increasing ethanol content of the extraction medium was paralleled by a significant rise of the antioxidant activity resulting in maximum values of 1131.12 mmol Teq/kg (DM) for the highest ethanol concentration (70 %).

Investigation of the mangosteen pericarp extracts resulted in comparable trends for both the ABTS and ORAC assays. Maximum ABTS (1063.69 mmol Teq/kg (DM)) and ORAC (1543.09 mmol Teq/kg (DM)) values were found when using 50 % ethanol as extraction solvent. Concordant with the results of grape pomace extracts, DPPH values were generally lower. In addition, differences between the extracts resulting from three different ethanol concentrations were insignificant.

To correlate the results obtained based on the *in vitro* antioxidant capacity assays with polyphenol concentrations in the extracts obtained by Folin-Ciocalteu and HPLC measurements, Pearson coefficients were calculated (Tab. 1). Results from the ABTS and DPPH assays of grape pomace extracts fairly correlated with the amounts quantified by HPLC yielding Pearson coefficients of 0.81 and 0.62, respectively. By contrast, there was no correlation between the values attained by ORAC assay and the corresponding HPLC data, while ABTS and DPPH values correlate very well with the Folin-Ciocalteu values (R = 0.99). This may be due to similar reaction mechanisms of the latter assays, since the ABTS, DPPH and Folin-Ciocalteu assay are all based on electron transfer reactions (Huang et al., 2005). The considerably poorer correlation of the Folin-Ciocalteu values with the results of the ORAC assay (R = 0.74) confirmed this assumption, probably due to the underlying hydrogen atom transfer mechanism of the ORAC assay. The results indicate that the primary step of the antioxidant behaviour of the grape pomace polyphenols might be an electron transfer, as the detected compounds displayed stronger interaction with the ABTS and DPPH radicals. In the case of man-



	A 30/70	A 50/50	A 70/30	B 30/70	B 50/50	B 70/30
ABTS	528.71 ± 22.98	751.44 ± 51.60	731.04 ± 26.59	638.13 ± 95.68	1063.69 ± 27.66	1025.13 ± 22.36
DPPH	132.68 ± 9.62	220.41 ± 18.77	242.21 ± 10.57	391.33 ± 13.29	436.24 ± 6.11	407.55 ± 14.82
ORAC	144.07 ± 33.20	1000.57 ± 33.43	1131.13 ± 26.77	857.63 ± 59.61	1543.09 ± 26.15	1504.49 ± 38.32

Fig. 4: Antioxidant activities of cv. 'Riesling' grape pomace (A) and mangosteen pericarp (B) extracts as determined by the ABTS, DPPH, and ORAC assays.
* p-value < 0.05

Tab. 1: Pearson correlation coefficients between the results of diverse antioxidant assays and total polyphenol contents as determined by HPLC and Folin-Ciocalteu assay, respectively.

Antioxidant assay	Grape pomace		Mangosteen pericarp	
	HPLC	Folin-Ciocalteu	HPLC	Folin-Ciocalteu
ABTS	0.81	0.99	0.99	1.00
DPPH	0.62	0.99	0.76	0.81
ORAC	0.07	0.74	0.98	1.00

gosteen pericarp extracts, the ABTS and ORAC values showed remarkable correlation with the data of HPLC and the Folin-Ciocalteu assay. It may be assumed that the primary antioxidative action of xanthones is based on both, an electron transfer and a hydrogen atom abstraction mechanism.

In vitro skin permeation studies

It was expected that the pattern and quantity of the polyphenols probably may change on their passage across porcine skin. Therefore, information about the penetration of the applied polyphenols may be helpful to approximate to the resulting antioxidant activities in the different skin layers. According to literature, lipophilicity and molecular weight of the bioactives are key parameters influencing percutaneous absorption, apart from their release from the vehicle and the kind of vehicle used (Abla and Banga, 2013; Alonso et al., 2014; Dvorakova et al., 1999; Suppasrivasuseth et al., 2006; Zillich et al., 2013b). Percutaneous absorption of polyphenols contained in the plant extracts was investigated by Franz-type diffusion experiments. For this purpose, extracts from grape pomace and mangosteen pericarp prepared with 50 % ethanol were topically applied, as they showed maximum polyphenol contents and correspondingly high antioxidant activities. To minimalize interfering effects of the vehicle system regarding the penetration of bioactives, hydroalcoholic extracts were used for skin penetration experiments without further formulation.

After their application on porcine ear skin, polyphenols from grape pomace extract were detected at low concentrations in the skin and in the transdermal receptor fluid after 24 h of expose (Tab. 2). Among the individual compounds recovered from the skin and receptor fluid, low molecular weight polyphenols such as gallic acid, and, in particular, caftaric acid were found to readily pass the *stratum corneum* and penetrate the skin, as only low amounts were contained in the extracts applied, and yet were detected in the skin and the receptor fluid. The octanol-water partition coefficients (log p) of gallic acid and caftaric acid were determined to be -0.5 and -0.6, respectively (Lu et al., 2006; Potts and Guy, 1992). Accordingly, penetration efficacy of these phenolic acids was expected to be rather low. Presumably, low molecular weight of both substances may have had strong impact on their penetration. These findings are concordant with Zillich et al. (2013b), who suggested superior penetration of low molecular weight polyphenols based on the release and penetration of some individual polyphenols. However, unexpectedly, significant amount of high molecular procyanidins B1 and B2 were also detected in the skin and the receptor fluid. This may be due to penetration enhancing effects of hydroalcoholic solvent systems directly applied to the skin. Overall amounts of polyphenols recovered were low, in particular, for the catechins and glycosidically bound quercetin, possibly due to the high reactivity of these phenolic species. Beside epimerization, oxidation and polymerization may occur upon exposure to light and temperature. Additionally, polyphenol-protein-interactions might also be responsible for their poor recoveries from porcine tissues. This phenomenon has also been reported by other researchers (Charlton et al., 2002; Dall'Acqua et al., 2012; Zillich et al., 2013a).

Contrary to the grape pomace polyphenols, xanthones from mangosteen pericarp extract were almost completely recovered, indicating that these molecules are more stable without interacting with the skin proteins (Tab. 3). Consequently, highest xanthone concentrations were detected in the skin, while the polyphenol pattern of the pericarp extract remained completely identical. Therefore, similar penetration behavior of the individual xanthones may be assumed, which is probably due to their similar structures, molecular weights, and polarities. In literature, octanol-water partition coefficient of α-mangostin is reported to be 6.4, confirming its strong hydrophobic nature, thus favoring skin penetration (Koh et al., 2013). The higher concentrations of xanthones in the extracts may also contribute to improved penetration owing to their more pronounced concentration gradient. However, in our experiment, diffusion of lipophilic xanthones compounds may be restricted to the skin, as their poor water solubility prevents further penetration into the buffered aqueous receptor fluid. This might explain why xanthones were not detected in the receptor fluid.

Tab. 2: Deposition of polyphenols in various tissues of porcine ear skin 24h after *in vitro* topical application of grape pomace extract as determined by HPLC-DAD.

	Polyphenol	Applied amount [µg] (Crude extract)	Recovered amount [µg]			
			Surface	*Stratum corneum*	Skin	Receiving chamber
1	**Gallic acid**	1.74 ± 0.17	0.04 ± 0.01	0.01 ± 0.00	0.05 ± 0.01	0.66 ± 0.05
2	**Caftaric acid**	5.99 ± 0.25	0.54 ± 0.01	n.d.	0.65 ± 0.04	4.58 ± 0.53
3	**Procyanidin B1**	31.76 ± 0.82	2.64 ±0.83	n.d.	0.62 ± 0.21	14.41 ± 0.34
4	**Catechin**	92.28 ± 11.09	1.09 ± 0.04	0.48 ± 0.06	1.98 ± 0.42	4.50 ± 0.64
5	**Procyanidin B2**	51.24 ± 5.62	3.21 ±0.81	0.14 ± 0.11	4.41 ± 1.91	2.84 ± 1.52
6	**Epicatechin**	115.02 ± 14.24	2.32 ± 0.47	0.89 ± 0.27	0.82 ± 0.04	3.10 ± 1.10
7	**Quercetin-3-glucuronide**	26.87 ± 1.45	0.46 ± 0.01	n.d.	0.80 ± 0.00	0.82 ± 0.00
8	**Quercetin-3-glusoside**	18.61 ± 0.48	0.56 ± 0.11	n.d.	0.93 ± 0.00	0.85 ± 0.00
9	**Resveratrol**	5.41 ± 0.10	1.48 ± 0.01	n.d.	0.38 ± 0.12	0.62 ± 0.20
	Total	348.92 ± 34.22	12.34 ± 2.30	1.52 ± 0.44	10.64 ± 2.33	32.38 ± 4.38

Tab. 3: Deposition of xanthones in various tissues of porcine ear skin 24h after *in vitro* topical application of mangosteen pericarp extract as determined by HPLC-DAD.

	Xanthone	Applied amount [µg] (Crude extract)	Recovered amount [µg]		
			Surface	*Stratum corneum*	Skin
1	**1,7-Dihydroxy-3-methoxy-2-(3-methylbut-2-enyl)xanthone**	7.87 ± 0.73	3.56 ± 0.09	1.82 ± 0.12	3.78 ± 0.68
2	**γ-Mangostin**	103.51 ± 1.87	7.97 ± 0.18	3.02 ± 0.66	59.27 ± 2.15
3	**8-Desoxygartanin**	12.75 ± 0.21	5.68 ± 0.06	2.28 ± 0.31	8.34 ± 1.97
4	**1,3,7-Trihydroxy-2,8-di-(3-methylbut-2-enyl)xanthone**	6.18 ± 0.20	2.27 ± 0.03	2.02 ± 0.06	3.03 ± 0.47
5	**Gartanin**	18.62 ± 0.51	2.94 ± 0.47	2.26 ± 0.02	2.44 ± 0.54
6	**α-Mangostin**	480.28 ± 7.78	148.49 ± 1.12	26.07 ± 4.61	397.95 ± 60.37
7	**Garcinon E**	30.55 ± 0.39	4.59 ± 0.17	2.24 ± 0.00	10.22 ± 0.40
	Total	659.76 ± 11.69	175.50 ± 2.12	39.71 ± 5.78	485.03 ± 66.58

Conclusions

The results obtained in the present study demonstrate the antioxidant potential of 'Riesling' grape pomace and mangosteen pericarp extracts in ABTS and ORAC systems, and hence, their potential as antioxidant ingredients in cosmetic formulations. Deviating from the findings for mangosteen extracts, grape pomace extracts were demonstrated to contain further components in their matrix which seem to enhance their overall reducing capability. To evaluate the influence of such accompanying substances, further studies including fractionation and purification steps are required. Their low reactivity towards the DPPH radical was a common feature of phenolic extracts from both raw materials, thus confirming the necessity to apply multiple radical assays.

When investigating the penetration behaviour of individual phenolic compounds, complete qualitative and quantitative recovery of xanthones from pig skin was achieved. In contrast, grape pomace polyphenols were only partially recovered after their topical application, indicating higher reactivity of these molecules and interactions with skin proteins. Therefore, e.g. vehicle system may play a decisive role affecting skin permeability.

Finally, the results of this study confirmed a great potential of grape pomace as well as mangosteen pericarp extracts for their application as an antioxidant cosmetic ingredient. The high antioxidant activity of grape pomace constituents allows efficient topical application at low extract dosages in cosmetic products. In addition to its impressive antioxidant potential, our previous study demonstrated that grape pomace extract may also inhibit collagenase and elastase. The latter enzymes are responsible for the degradation of structural proteins of the dermis, thus confirming their suitability for anti-aging cosmetic preparations (Wittenauer et al., 2015). Many attempts have been made to exploit grape pomace (Balasundram et al., 2006; Kammerer et al., 2014; Maier et al., 2009; Schieber et al., 2001); its value-added valorisation has not been implemented in industrial practice up to now. Grape pomace utilisation was mainly considered for human nutrition but is limited due to its strong bitter and astringent taste (Drewnowski and Gomez-Carneros, 2000). Extracts from mangosteen pericarp also revealed their suitability for cosmetic purpose due to their rich content of antioxidant xanthones, which are readily able to penetrate the skin. The problems arising from mangosteen fresh waste disposals in the countries of production are recognized as a significant environmental concern, and only first steps are made for its exploitation (Pathak et al., 2015; Sze Lim et al., 2013; Takolpuckdee, 2014; Wittenauer et al., 2012). The use of grape pomace and mangosteen pericarp extracts in cosmetics may be a more promising field of application for these underestimated by-products.

Acknowledgments

This study was financially supported by the Fraunhofer Gesellschaft zur Förderung der angewandten Forschung (FhG). The authors are grateful to Baden-Badener Winzergenossenschaft, Baden-Baden-Neuweier, Germany, for providing the grape pomace.

References

Abla, M.J., Banga, A.K., 2013: Quantification of skin penetration of antioxidants of varying lipophilicity. Int. J. Cosmet. Sci. 35, 19-26. doi: 10.1111/j.1468-2494.2012.00728.x.

Abou Samra, M., Chedea, V.S., Economou, A., Calokerinos, A., Kefalas, P., 2011: Antioxidant/prooxidant properties of model phenolic compounds: Part I. Studies on equimolar mixtures by chemiluminescence and cyclic voltammetry. Food Chem. 125, 622-629. doi: http://dx.doi.org/10.1016/j.foodchem.2010.08.076.

Alonso, C., Rubio, L., Tourino, S., Marti, M., Barba, C., Fernandez-Campos, F., Coderch, L., Parra, J.L., 2014: Antioxidative effects and percutaneous absorption of five polyphenols. Free Rad. Biol. Med. 75, 149-155. doi: 10.1016/j.freeradbiomed.2014.07.014.

Austria, R., Semenzato, A., Bettero, A., 1997: Stability of vitamin C derivatives in solution and topical formulations. Pharmaceut. Biomed. 15, 795-801. doi: http://dx.doi.org/10.1016/S0731-7085(96)01904-8.

Balasundram, N., Sundram, K., Samman, S., 2006: Phenolic compounds in plants and agri-industrial by-products: Antioxidant activity, occurrence, and potential uses. Food Chem. 99, 191-203. doi: http://dx.doi.org/10.1016/j.foodchem.2005.07.042.

Bickers, D.R., Athar, M., 2006: Oxidative stress in the pathogenesis of skin disease. J. Invest. Dermatol. 126, 2565-2575. doi: 10.1038/sj.jid.5700340.

Botta, B., Vitali, A., Menendez, P., Misiti, D., Delle Monache, G., 2005: Prenylated flavonoids: Pharmacology and biotechnology. Curr. Med. Chem. 12, 717-739.

Brand-Williams, W., Cuvelier, M.E., Berset, C., 1995: Use of a free radical method to evaluate antioxidant activity. LWT – Food Sci. Technol. 28, 25-30. doi: http://dx.doi.org/10.1016/S0023-6438(95)80008-5.

Briganti, S., Picardo, M., 2003: Antioxidant activity, lipid peroxidation and skin diseases. What's new. J. Eur. Acad. Dermatol. 17, 663-669. doi: DOI 10.1046/j.1468-3083.2003.00751.x.

Cao, G., Prior, R.L., 1999: Measurement of oxygen radical absorbance capacity in biological samples. In: Lester, P. (ed.), Methods Enzymol. Academic Press.

Charlton, A.J., Baxter, N.J., Khan, M.L., Moir, A.J.G., Haslam, E., Davies, A.P., Williamson, M.P., 2002: Polyphenol/peptide binding and precipitation. J. Agric. Food Chem. 50, 1593-1601. doi: 10.1021/jf010897z.

Choueiri, L., Chedea, V.S., Calokerinos, A., Kefalas, P., 2012: Antio-

xidant/pro-oxidant properties of model phenolic compounds. Part II: Studies on mixtures of polyphenols at different molar ratios by chemiluminescence and lc-ms. Food Chem. 133, 1039-1044. doi: http://dx.doi.org/10.1016/j.foodchem.2012.01.057.

DAL BELO, S.E., GASPAR, L.R., CAMPOS, P.M.B.G.M., MARTY, J.P., 2009: Skin penetration of epigallocatechin-3-gallate and quercetin from green tea and ginkgo biloba extracts vehiculated in cosmetic formulations. Skin Pharmacol. Phys. 22, 299-304.

DALL'ACQUA, S., MIOLO, G., INNOCENTI, G., CAFFIERI, S., 2012: The photodegradation of quercetin: Relation to oxidation. Molecules 17, 8898-8907. doi: 10.3390/molecules17088898.

DICZBALIS, Y., 2009: Farm and forestry production and marketing profile for mangosteen (garcinia mangostana). In: Elevitch, C.R. (ed.), Specialty Crops for Pacific Island Agroforestry. Permanent Agriculture Resources (PAR), Holualoa, Hawai'i. http://agroforestry.net/scps.

DREWNOWSKI, A., GOMEZ-CARNEROS, C., 2000: Bitter taste, phytonutrients, and the consumer: A review. Am. Clin. Nutr. 72, 1424-1435.

DVORAKOVA, K., DORR, R.T., VALCIC, S., TIMMERMANN, B., ALBERTS, D.S., 1999: Pharmacokinetics of the green tea derivative, egcg, by the topical route of administration in mouse and human skin. Cancer Chemoth. Pharm. 43, 331-335. doi: DOI 10.1007/s002800050903.

GIANETI, M.D., MERCURIO, D.G., MAIA CAMPOS, P.M.B.G., 2013: The use of green tea extract in cosmetic formulations: Not only an antioxidant active ingredient. Dermatol. Ther. 26, 267-271. doi: 10.1111/j.1529-8019.2013.01552.x.

GROSS, P.M., 2010: Superfruits. McGraw-Hill, New York.

HUANG, D., OU, B., HAMPSCH-WOODILL, M., FLANAGAN, J.A., PRIOR, R.L., 2002: High-throughput assay of oxygen radical absorbance capacity (orac) using a multichannel liquid handling system coupled with a microplate fluorescence reader in 96-well format. J. Agric. Food Chem. 50, 4437-4444. doi: 10.1021/jf0201529.

HUANG, D., OU, B., PRIOR, R.L., 2005: The chemistry behind antioxidant capacity assays. J. Agric. Food. Chem. 53, 1841-1856. doi: 10.1021/jf030723c.

JIMÉNEZ, A., SELGA, A., TORRES, J.L., JULIÀ, L., 2004: Reducing activity of polyphenols with stable radicals of the ttm series. Electron transfer versus h-abstraction reactions in flavan-3-ols. Orga. Lett. 6, 4583-4586. doi: 10.1021/ol048015f.

KAMMERER, D., CLAUS, A., CARLE, R., SCHIEBER, A., 2004: Polyphenol screening of pomace from red and white grape varieties (*Vitis vinifera* L.) by hplc-dad-ms/ms. J. Agric. Food Chem. 52, 4360-4367. doi: 10.1021/jf049613b.

KAMMERER, D.R., KAMMERER, J., VALET, R., CARLE, R., 2014: Recovery of polyphenols from the by-products of plant food processing and application as valuable food ingredients. Food Res. Int. 65, Part A, 2-12. doi: http://dx.doi.org/10.1016/j.foodres.2014.06.012.

KATALINIĆ, V., MOŽINA, S.S., SKROZA, D., GENERALIĆ, I., ABRAMOVIČ, H., MILOŠ, M., LJUBENKOV, I., PISKERNIK, S., PEZO, I., TERPINC, P., BOBAN, M., 2010: Polyphenolic profile, antioxidant properties and antimicrobial activity of grape skin extracts of 14 vitis vinifera varieties grown in dalmatia (croatia). Food Chem. 119, 715-723. doi: http://dx.doi.org/10.1016/j.foodchem.2009.07.019.

KERSCHER, M., BUNTROCK, H., 2011: Update on cosmeceuticals. Dtsch. Dermatol. Ges. 9, 314-328. doi: 10.1111/j.1610-0387.2010.07600.x.

KOH, J.-J., QIU, S., ZOU, H., LAKSHMINARAYANAN, R., LI, J., ZHOU, X., TANG, C., SARASWATHI, P., VERMA, C., TAN, D.T.H., TAN, A.L., LIU, S., BEUERMAN, R.W., 2013: Rapid bactericidal action of alpha-mangostin against mrsa as an outcome of membrane targeting. Biochim. Biophys. Acta – Biomembranes 1828, 834-844. doi: http://dx.doi.org/10.1016/j.bbamem.2012.09.004.

LEOPOLDINI, M., RUSSO, N., TOSCANO, M., 2011: The molecular basis of working mechanism of natural polyphenolic antioxidants. Food Chem. 125, 288-306. doi: 10.1016/j.foodchem.2010.08.012.

LOPEZ-ALARCON, C., DENICOLA, A., 2013: Evaluating the antioxidant capacity of natural products: A review on chemical and cellular-based assays. Anal. Chim. Acta 763, 1-10. doi: 10.1016/j.aca.2012.11.051.

LU, Z., NIE, G., BELTON, P.S., TANG, H., ZHAO, B., 2006: Structure-activity relationship analysis of antioxidant ability and neuroprotective effect of gallic acid derivatives. Neurochem. Int. 48, 263-274. doi: http://dx.doi.org/10.1016/j.neuint.2005.10.010.

MAIER, T., SCHIEBER, A., KAMMERER, D.R., CARLE, R., 2009: Residues of grape (*Vitis vinifera* L.) seed oil production as a valuable source of phenolic antioxidants. Food Chem. 112, 551-559. doi: 10.1016/j.foodchem.2008.06.005.

MARTINEZ, A., GALANO, A., VARGAS, R., 2011: Free radical scavenger properties of alpha-mangostin: Thermodynamics and kinetics of hat and raf mechanisms. J. Phys. Chem. B 115, 12591-12598. doi: 10.1021/jp205496u.

NENADIS, N., TSIMIDOU, M., 2002: Observations on the estimation of scavenging activity of phenolic compounds using rapid 1,1-diphenyl-2-picrylhydrazyl (dpph•) tests. J. Amer. Oil. Chem. Soc. 79, 1191-1195. doi: 10.1007/s11746-002-0626-z.

OBOLSKIY, D., PISCHEL, I., SIRIWATANAMETANON, N., HEINRICH, M., 2009: *Garcinia mangostana* L.: A phytochemical and pharmacological review. Phytothe. Res. 23, 1047-1065. doi: 10.1002/ptr.2730.

OKONOGI, S., DUANGRAT, C., ANUCHPREEDA, S., TACHAKITTIRUNGROD, S., CHOWWANAPOONPOHN, S., 2007: Comparison of antioxidant capacities and cytotoxicities of certain fruit peels. Food Chem. 103, 839-846. doi: 10.1016/j.foodchem.2006.09.034.

PATHAK, P.D., MANDAVGANE, S.A., KULKARNI, B.D., 2015: Fruit peel waste as a novel low-cost bio adsorbent. Rev. Chem. Eng. 31, 361-381. doi: 10.1515/revce-2014-0041.

PEDRAZA-CHAVERRI, J., CÁRDENAS-RODRÍGUEZ, N., OROZCO-IBARRA, M., PÉREZ-ROJAS, J.M., 2008: Medicinal properties of mangosteen (*garcinia mangostana*). Food Chem. Toxicol. 46, 3227-3239. doi: http://dx.doi.org/10.1016/j.fct.2008.07.024.

POTTS, R.O., GUY, R.H., 1992: Predicting skin permeability. Pharm. Res. 9, 663-669. doi: 10.1023/a:1015810312465.

PRIOR, R.L., WU, X., SCHAICH, K., 2005: Standardized methods for the determination of antioxidant capacity and phenolics in foods and dietary supplements. J. Agric. Food Chem. 53, 4290-4302. doi: 10.1021/jf0502698.

QUIDEAU, S., DEFFIEUX, D., DOUAT-CASASSUS, C., POUYSÉGU, L., 2011: Plant polyphenols: Chemical properties, biological activities, and synthesis. Angew. Chemie Int. Ed. 50, 586-621. doi: 10.1002/anie.201000044.

RE, R., PELLEGRINI, N., PROTEGGENTE, A., PANNALA, A., YANG, M., RICE-EVANS, C., 1999: Antioxidant activity applying an improved abts radical cation decolorization assay. Free Rad. Biol. Med. 26, 1231-1237. doi: http://dx.doi.org/10.1016/S0891-5849(98)00315-3.

RIBEIRO, A., ESTANQUEIRO, M., OLIVEIRA, M., SOUSA LOBO, J., 2015: Main benefits and applicability of plant extracts in skin care products. Cosmetics 2, 48.

RICE-EVANS, C.A., MILLER, N.J., PAGANGA, G., 1996: Structure-antioxidant activity relationships of flavonoids and phenolic acids. Free Rad. Biol. Med. 20, 933-956. doi: http://dx.doi.org/10.1016/0891-5849(95)02227-9.

RITTIE, L., FISHER, G.J., 2002: Uv-light-induced signal cascades and skin aging. Ageing Res. Rev. 1, 705-720. doi: Pii S1568-1637(02)00024-7 Doi 10.1016/S1568-1637(02)00024-7.

SANCHEZ-RANGEL, J.C., BENAVIDES, J., HEREDIA, J.B., CISNEROS-ZEVALLOS, L., JACOBO-VELAZQUEZ, D.A., 2013: The folin-ciocalteu assay revisited: Improvement of its specificity for total phenolic content determination. Anal. Methods-Uk 5, 5990-5999. doi: 10.1039/c3ay41125g.

SCHARFFETTER-KOCHANEK, K., BRENNEISEN, P., WENK, J., HERRMANN, G., MA, W.J., KUHR, L., MEEWES, C., WLASCHEK, M., 2000: Photoaging of the skin from phenotype to mechanisms. Exp. Gerontol. 35, 307-316. doi: Doi 10.1016/S0531-5565(00)00098-X.

SCHIEBER, A., STINTZING, F.C., CARLE, R., 2001: By-products of plant food processing as a source of functional compounds – recent developments. Trends Food Sci. Tech. 12, 401-413. doi: http://dx.doi.org/10.1016/S0924-2244(02)00012-2.

SEERAM, N.P., ADAMS, L.S., HARDY, M.L., HEBER, D., 2004: Total cranber-

ry extract versus its phytochemical constituents: Antiproliferative and synergistic effects against human tumor cell lines. J. Agric. Food Chem. 52, 2512-2517. doi: 10.1021/jf0352778.

Shindo, Y., Witt, E., Han, D., Epstein, W., Packer, L., 1994: Enzymic and non-enzymic antioxidants in epidermis and dermis of human skin. J. Invest. Dermatol. 102, 122-124.

Singleton, V.L., Rossi, J.A., 1965: Colorimetry of total phenolics with phosphomolybdic-phosphotungstic acid reagents. Am. J. Enol. Vitic. 16, 144-158.

Suppasrivasuseth, J., Bellantone, R.A., Plakogiannis, F.M., Stagni, G., 2006: Permeability and retention studies of (-)epicatechin gel formulations in human cadaver skin. Drug Dev. Ind. Pharm. 32, 1007-1017. doi: 10.1080/03639040600599889.

Sze Lim, Y., Sze Hui Lee, S., Chin Tan, B., 2013: Antioxidant capacity and antibacterial activity of different parts of mangosteen (*Garcinia mangostana* linn.) extracts. Fruits 68, 483-489. doi: doi:10.1051/fruits/2013088.

Takolpuckdee, P., 2014: Transformation of agricultural market waste disposal to biochar soil amendments. Procedia Environ. Sci. 20, 64-70. doi: http://dx.doi.org/10.1016/j.proenv.2014.03.010.

Thiele, J.J., Dreher, F., Packer, L., 2002: Antioxidant defense systems in skin. J. Toxicol. Cutaneous Ocul. Toxicol. 21, 119-160. doi: 10.1081/CUS-120004330.

Thiele, J.J., Hsieh, S.N., Ekanayake-Mudiyanselage, S., 2005: Vitamin E: Critical review of its current use in cosmetic and clinical dermatology. Dermatol. Surg. 31, 805-813. doi: 10.1111/j.1524-4725.2005.31724.

Thiele, J.J., Traber, M.G., Packer, L., 1998: Depletion of human stratum corneum vitamin E: An early and sensitive in vivo marker of UV induced photo-oxidation. J. Invest. Dermatol. 110, 756-761. doi: http://dx.doi.org/10.1046/j.1523-1747.1998.00169.x.

Wisuitiprot, W., Somsiri, A., Ingkaninan, K., Waranuch, N., 2011: In vitro human skin permeation and cutaneous metabolism of catechins from green tea extract and green tea extract-loaded chitosan microparticles. Int. J. Cosmetic Sci. 33, 572-579. doi: 10.1111/j.1468-2494.2011.00673.x.

Wittenauer, J., Falk, S., Schweiggert-Weisz, U., Carle, R., 2012: Characterisation and quantification of xanthones from the aril and pericarp of mangosteens (*Garcinia mangostana* L.) and a mangosteen containing functional beverage by hplc-dad-msn. Food Chem. 134, 445-452. doi: 10.1016/j.foodchem.2012.02.094.

Wittenauer, J., Mackle, S., Sussmann, D., Schweiggert-Weisz, U., Carle, R., 2015: Inhibitory effects of polyphenols from grape pomace extract on collagenase and elastase activity. Fitoterapia 101, 179-187. doi: 10.1016/j.fitote.2015.01.005.

Zanchi, D., Konarev, P.V., Tribet, C., Baron, A., Svergun, D.I., Guyot, S., 2009: Rigidity, conformation, and solvation of native and oxidized tannin macromolecules in water-ethanol solution. J. Chem. Phys. 130, 245103. doi: doi:http://dx.doi.org/10.1063/1.3156020.

Zillich, O.V., Schweiggert-Weisz, U., Hasenkopf, K., Eisner, P., Kerscher, M., 2013a: Antioxidant activity, lipophilicity and extractability of polyphenols from pig skin – development of analytical methods for skin permeation studies. Biomed. Chromatogr. 27, 1444-1451. doi: 10.1002/bmc.2941.

Zillich, O.V., Schweiggert-Weisz, U., Hasenkopf, K., Eisner, P., Kerscher, M., 2013b: Release and in vitro skin permeation of polyphenols from cosmetic emulsions. Int. J. Cosmetic Sci. 35, 491-501. doi: 10.1111/ics.12072.

Address of the authors:
Judith Wittenauer, Fraunhofer Institute for Process Engineering and Packaging, Department of Process Engineering, Giggenhauser Straße 35, D-85354 Freising, Germany
Hohenheim University, Institute of Food Science and Biotechnology, Chair Plant Foodstuff Technology, Garbenstraße 25, D-70599 Stuttgart, Germany
E-mail address: judith.wittenauer@fraunhofer.ivv.de
Ute Schweiggert-Weisz, Fraunhofer Institute for Process Engineering and Packaging, Department of Process Engineering, Giggenhauser Straße 35, D-85354 Freising, Germany
Reinhold Carle, Hohenheim University, Institute of Food Science and Biotechnology, Chair Plant Foodstuff Technology, Garbenstraße 25, D-70599 Stuttgart, Germany
King Abdulaziz University, Biological Science Department, Faculty of Science, P.O. Box 80257, Jeddah 21589, Saudi Arabia

© The Author(s) 2016.

This is an Open Access article distributed under the terms of the Creative Commons Attribution Share-Alike License (http://creativecommons.org/licenses/by-sa/4.0/).