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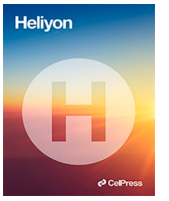

Decoding the enhanced antioxidant activities of the combined small berry pomaces by widely targeted metabolomics analysis

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A R T I C L E I N F O

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A B S T R A C T

Small berry pomaces (SBPs) are poorly utilized as an inexpensive source of bioactive compounds. This study investigated the impact of compounding treatment on nutritional and antioxidant characteristics of combined SBPs, in comparison with single SBP. The results showed that the amounts of protein, minerals, dietary fiber (DF) and anthocyanidins were significantly ($\mathbf{p < 0.05}$) higher in combined SBPs than in combined fruits. Moreover, the combined SBPs were characterized by an elevated abundance of minerals and anthocyanidins (6 kinds, and 5 kinds, respectively), substantiating the effectiveness of compounding treatment on SBP nutrition. A total of 776 secondary phytochemicals were detected in combined SBPs by a widely targeted metabolomics approach. Each SBP contained approximately 100 kinds of unique natural antioxidants. Furthermore, the combined SBPs group had the highest antioxidant activity compared with single SBP. Meanwhile, the antioxidant activities determined in combined SBPs were higher than arithmetic mean value of single SBP. The synergism and interaction of active components in different sources of SBPs play vital role in the high antioxidant capacity of combined SBPs. All the results provide reference for the comprehensive development and utilization of fruit residues. The SBPs should be highly prized for their substantial amount of nutritional and bioactive constituents, including protein, DF, essential minerals and secondary metabolites. These secondary metabolites are positively associated with antioxidant benefits. The present study summarizes the knowledge about bioactive compounds and antioxidant activities of combined SBPs group and discusses the relevant mechanisms. A conclusion can be educed that combined process is an effective way to improve properties of the pomaces.

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1. Introduction

Small berry plants generally refer to species that produced smallish and juicy fruit [1], including raspberry, blackberry, blueberry, etc. Small berry fruits are gaining an expanded market due to their abundant health-protective constituents [2] and excellent antioxidant activities [3]. It is believed that the compounds which are largely responsible for antioxidant effects are secondary metabolites [4]. Amongst the richest sources of natural polyphenolics and antioxidant compounds, small berries are referred to as natural functional foods [5]. When associated with a healthy diet, the frequent intake of small berries has been positively correlated to improvements in human health. Blackberry and blueberry are listed in the "Top 5 health foods" by the Food and Agriculture Organization of the United Nations.

Although small berries are best eaten freshly picked, they cannot be consumed fresh all year long due to high perishability resulting in short life. A large proportion of the harvested blueberries are processed into various longer shelf-life food products [6]. Considerable amounts of pomace are generated and discarded as a waste during processing of berry fruits, thus causing loss of natural antioxidants. Previous researches have reported methods to recover various healthy constituents from pomaces [7–9]. Numerous studies demonstrated that fruit byproduct-derived foods have received increasing attention owing to their valuable health-promoting properties as well as their technological potential as a food additive [10–13]. In recent decades, the focus of processing sub-product studies has shifted from extraction and characterization of pectin and its utilization research [14] to the composition and physicochemical properties analysis of pomace [15,16].

A growing body of literature confirms that healthfulness of fresh berries is influenced by their contents of secondary healthful constituents [17]. The secondary plant metabolism is closely related to the growth conditions and is activated under stress. In recent years, phytochemicals naturally synthesized by secondary metabolism have attracted great attention due to their potential therapeutic effects on health [18,19]. In addition to activating antioxidant enzymes, restraining oxidative stress and inflammation, the functional properties of secondary bioactive compounds are mainly attributed to their ability to sequester or inhibit reactive oxygen and nitrogen species, and transfer electrons to free radicals [20]. Evaluation results (i.e. dietary fibers and phenolics) of apple and three berry fruits pomace demonstrated their potential as fiber rich [21] and antioxidant functional ingredient that can be selectively utilized in food applications [22–24]. Interest in plant natural products is mainly due to their antioxidant properties. Many fruits recognized as small berries have higher antioxidant capacity than other fruits and vegetables [25].

Previous studies only focus on one kind of pomace, but there is a lack of comparative studies of different species, let alone the nutritional and bioactive properties of combined SBPs. Therefore, the objectives of this study were: 1) to investigate the nutritional properties, bioactive compounds, and in vitro antioxidant activities of five different types of SBPs, 2) to determine the influences of compounding treatment on the chemical and bioactive characteristics of SBPs. Mixtures consisting in five small berry (bilberry, blackberry, strawberry and raspberry) fruits pomace were developed and characterized. A widely targeted metabolome method [26] was employed to analyze the types and relative contents of secondary antioxidant functional ingredient. The antioxidant synergistic effect of combined SBPs was studied. This study would provide baseline data for the selection of suitable SBP as functional ingredients in various food applications for converting waste into commercial products.

2. Materials and methods

2.1. Sample collection

Ripe fruits from the selected species were collected during the summer and autumn seasons of 2020 at the farms and surrounding area in Jinan, Shandong province. The species names are as follows: red raspberry (RER) (*Rubus idaeus* L.)_'Harriettz'; mulberry (MUL) (*Morus nigra* L.)_'Dashi'; blackberry (BLA) (*Rubus fruticosus Pollich*)_'Hul'; blueberry (BLU) (*Vaccinium Spp*)_'Sweetheart'; black chokeberry (BLC) (*Aronia melanocarpa* (*Michx.*), *Elliott*)_'Fukangyuan No1'. Approximately 1–2 kg of cleaned berries per sample were first dipped in water heated to 95 °C for 10 s, being cooled to 30 °C and then pressed by a hydraulic juicer (BUGYZJ, Yiqianjia Winemaking Equipment Co., Ltd, China). Berries and pomaces were freeze-dried using a laboratory lyophilizer (Lab-1A-50E, Beijing Boyikang Laboratory Instrument Co., Ltd, China). The sample was ground and sieved (60 mesh) to produce particles less than 250 μm in size. The sample was then vacuum-packed and stored at −20 °C for analysis. The moisture content of fruit and berry pomace was determined by drying at 105 °C to constant mass.

2.2. Chemicals and reagents

Anthocyanidin standards, ABTS, DPPH and Trolox, were purchased from Sigma–Aldrich. (St.Louis, MO, USA). The T-AOC Assay Kit (Total antioxidant capacity assay kit with a rapid ABTS method) and FRAP assay kit were obtained from Beyotime Biochemistry Co., Ltd. (Shanghai, China). HPLC-grade methanol, ethanol, acetonitrile and formic acid were provided by Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). The water used in this research was produced from a Millipore Milli-Q™ water system (Millipore Corporation, Milford, MA, USA). All other reagents used were of analytical grade.

2.3. Determination of the crude protein content

Approximately 0.5 g of ground powder was used for crude protein concentration analysis. Crude protein content was determined by the Kjeldahl procedure. A factor of 5.3 was used for protein content conversion [16].

2.4. Determination of dietary fiber contents

Insoluble dietary fiber (IDF), soluble dietary fiber (SDF) and total dietary fiber (TDF) contents were quantified using an enzymatic gravimetric procedure according to the Association of Official Analytical Chemists (AOAC 991.43) method [27].

2.5. Determination of mineral element content

Mineral contents in fruit and pomace were analyzed using an inductively coupled plasma optical emission spectrometer (ICP–OES) (Optima 2100 DV; PerkinElmer, Waltham, USA) after wet acid digestion with 65 % HNO_3.

2.6. Mass spectrometric analysis

Berry pomaces were vacuum freeze-dried by a lyophilizer and then ground to powder by a combined crusher (MM 400, Retsch, Dusseldorf, Germany). The freeze–dried powder (100 mg) was dissolved in 1.2 mL of 70 % methanol extraction solution, vortexed, and placed in a refrigerator at 4 °C overnight. After centrifugation at 12,000 rpm for 10 min, the extract was filtered through a 0.22 μm microporous membrane before UPLC–MS/MS analysis. Fifteen pomace samples were divided into five groups according to species. A UPLC–ESI–MS/MS system (UPLC, Nexera X2, Shimadzu, Japan; MS, Applied Biosystems 4500 QTRAP, Thermo Scientific) was used to analyze the pomace extract. Metabolome analysis, including the identification and quantification of metabolites, was performed by Wuhan MetWare Biotechnology Co., Ltd. (Wuhan, China) by standard procedures [26]. The chromatographic column was an Agilent SB-C18 column (1.8 μm, 2.1 mm × 100 mm), phase A was ultrapure water with 0.1 % formic acid, and phase B was acetonitrile with formic acid. Analyst 1.6.1 software (AB SCIEX, city, ON, Canada) was used to analyze the metabolite data. Principal component analysis (PCA) and orthogonal projections to latent structures discriminant analysis (OPLS–DA) were performed on data from all samples. Metabolites whose variable importance in the projection (VIP) value was ≥ 1 with $p < 0.05$ for the model variables were defined as differentially accumulated metabolites.

2.7. Anthocyanidin quantitative analysis

Briefly, 2.0 g of each fruit/pomace sample was combined with 10 mL of methanol/water/formic acid (80:19.5:0.5, v/v/v) using an ultrasonic extractor (Type JY99-IIDN, Huxi Industrial Co., Ltd, Shanghai, China) for 1 min and centrifuged for 15 min at 12,000 rpm. The residue was collected, and the extraction was repeated two more times. All the extracts were pooled together and evaporated under vacuum in a rotary evaporation concentrator (HR-21A; Huxi Industrial Co., Ltd, Shanghai, China) at 50 °C. The residues were resuspended in 1 mL of water/formic acid (97:3, v/v). All extractions were conducted in triplicate. Extracts were stored at −20 °C for the following determination of anthocyanidin and antioxidant activity.

Chromatography was performed on a 1260 series HPLC system (Agilent Technologies Canada Incorporated, Mississauga, ON) according to the method described by Souza, Willems, & Low [28] with slight modification. Anthocyanidin separation was achieved using a C-18 reverse-phase column (250 mm × 4.6 mm id, 5 μm particle sizes, HICHROM, UK) at 30 °C. The gradient mobile phase system used for anthocyanidin separation consisted of solvent A (5 % formic acid) and solvent B (acetonitrile). The calibration curves for quantification were obtained by running reference standards and the regression for all anthocyanidins was found to be ≥ 0.999. The flow rate was kept constant at 1 mL min^{-1} using gradient programming. The gradient elution program was as follows: 5 % mobile phase B to 3 min; gradually increasing to 15, 20, 25, 40 and 80 % B at 8, 10, 18, 25 and 35 min, respectively; decreasing to 5 % at 40 min; and re-equilibration for 10 min at 5 % B. The eluent was continuously monitored by measuring absorbance at a wavelength of 530 nm. Anthocyanidins were identified by comparing retention times with those of their respective standards. The content of anthocyanidins was quantified using an external calibration curve.

2.8. DPPH radical scavenging assay

The DPPH radical scavenging assay was carried out based on Granato et al. [29]. Fresh DPPH solution was prepared in 70 % methanol/water (v/v). Aliquots (100 μL) of sample extracts were added to 1.5 mL DPPH solution. After 60 min of incubation at room temperature in the dark, the absorbance was measured at 517 nm using a spectrophotometer. The calibration curve was plotted using Trolox as a standard. A considerable amount of water was retained in the pomace after juice processing. To eliminate the influence of moisture, the results were expressed as mg Trolox equivalents (TE) per 100 g of dry weight of pomace. The percent DPPH radical scavenging activity consumed was calculated from the following equation:

$$\text{DPPH radical scavenging activity } (\%) = [(A0 - A1)/A0] \times 100 \quad (1)$$

where A0 is the initial absorbance (no extracts) and A1 is the absorbance in the presence of the extracts. The DPPH radical scavenging capacity of the MIX-M group was experimentally determined, while the theoretical antioxidant value of the MIX group was calculated by arithmetic averages of five SBPs.

2.9. ABTS radical scavenging assay

The measurements of ABTS radical scavenging activity were performed according to the instructions of the ABTS kits. The calibration curve was plotted using Trolox as a standard. ABTS radical scavenging activity is expressed as mg TE per 100 g of dry weight of pomace. The ABTS radical scavenging capacity of the MIX-M group was experimentally determined, while the theoretical antioxidant value of the MIX group was calculated by arithmetic averages of five SBPs.

2.10. Determination of ferric ion reducing antioxidant power (FRAP)

The FRAP values of the sample extracts were measured according to the instructions of the FRAP kits. The calibration curve was plotted using Trolox as a standard. The results are expressed as mg TE per 100 g of dry weight of pomace. The FRAP value of the MIX-M group were experimentally determined, while the theoretical antioxidant value of the MIX group was calculated by arithmetic averages of five SBPs.

2.11. Determination of metal ion chelating capacity (MCC)

The Fe^{2+}-chelating ability was determined according to the method of Decker, & Welch [30]. The Fe^{2+} content was monitored by measuring the formation of the ferrous iron ferrozine complex. The sample fluid extract was combined with 2 mM $FeCl_2$ and 5 mM ferrozine at a ratio of 10:1:2. The mixture was shaken and left at room temperature for 10 min. The absorbance of the resulting solution was measured at 562 nm. A lower absorbance of the reaction mixture indicated a higher Fe^{2+}-chelating ability. The capability to chelate the ferrous iron was calculated by the following equation:

$$\text{MCC}\ (\%) = [\text{1-absorbance of control at 562 nm/absorbance of sample at 562 nm}] \times 100 \quad (2)$$

The MCC value of the MIX-M group was experimentally determined, while the theoretical antioxidant value of the MIX group was calculated by arithmetic averages of five SBPs.

2.12. Statistical analysis

Each treatment in the experiment was repeated three times, and the data are expressed on the mean ± standard deviation. The results were analyzed by one-way analysis of variance (ANOVA) using SAS version 9.4 (SAS Inc., Chicago, IL, USA). Significant differences were considered at $p < 0.05$. Multiple comparisons of the means were conducted using Duncan's method to establish any differences among samples. The HCA (hierarchical cluster analysis) results of samples and metabolites are presented as heatmaps with

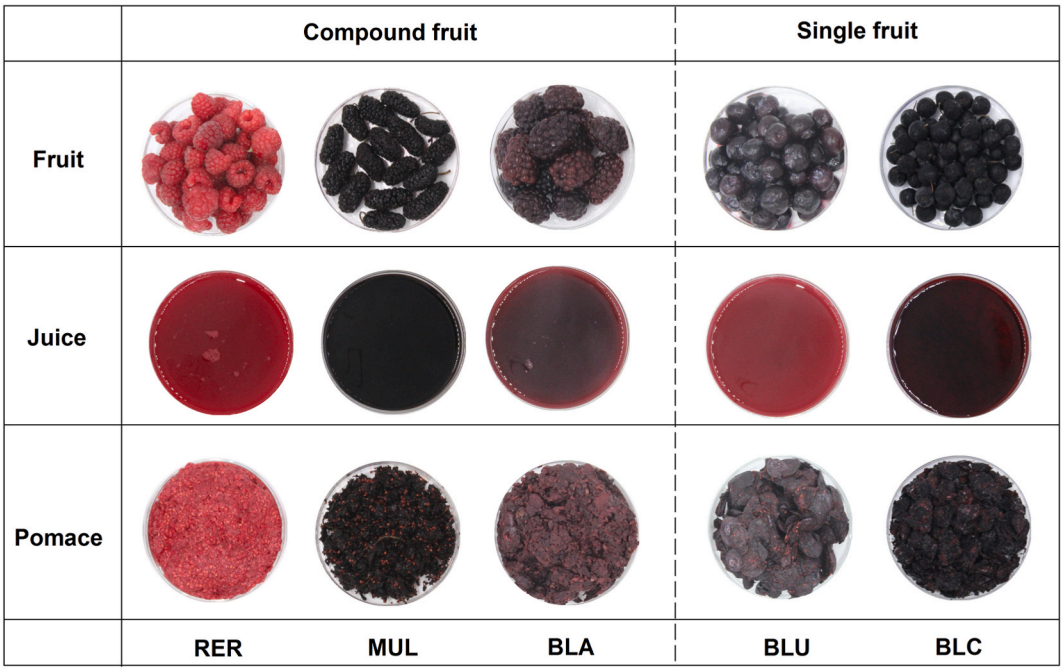

Fig. 1. Appearance of small berry fruits and corresponding pomaces. RER, red raspberry; MUL, mulberry BLA, blackberry; BLU, blueberry; BLC, black chokeberry.

dendrograms. HCA was carried out by the R package pheatmap. For HCA, normalized signal intensities of metabolites (unit variance scaling) are visualized as a color spectrum. The Venn diagram was plotted using the R package VennDiagram.

3. Results and discussion

3.1. Phenotypic characteristics of small berries before and after juicing

Small berries are favored by consumers because of their good taste, bright color, and high nutritional value [5]. Fruit skin color is affected by the synthesis of phenolic compounds, particularly anthocyanins and their underlying genetic factors [31]. We studied the fruits of five small berries composed of three aggregate fruits and two simple fruits (Fig. 1). Oxidation processes can strongly influence the properties of fresh fruits. Oxygen, heat and light etc. can intensify the oxidation process which will cause fruit color fading [32]. Although the juicing process was performed in exposed air at room temperature, the pomace color was bright as the corresponding fresh fruit.

3.2. Comparison of protein and DF contents in small berries before and after juicing

The protein and DF contents in small berry are presented in Fig. 2. The protein content in pomaces of RER, BLU and BLC were increased compared with that of fruits, while pomaces of MUL and BLA contained less protein than fruits (Fig. 2 (A)). The maximum protein value (18.28 g/100 g DW) appeared in BLU pomace. The protein content in the other four SBPs was 17–54 % that of the BLU pomace. The protein content in the combined group increased significantly to 9.54 g/100 g DW.

Dietary fiber is highly concentrated in different fruits and berries, most of which is IDF [33]. A similar trend was found in the work. IDF was the main form of DF in the fruit and pomace. In fruit and pomace, the IDF content was 1.64–8.67-fold and 1.76–12.48-fold SDF, respectively (Fig. 2 (B, C)). Except for BLC, the SDF contents in pomace were higher than those in fruit, especially in MUL pomace, which was 2.29-fold that in fruit. The IDF contents in the pomace of RER, BLA and BLU were 3.85-fold, 2.28-fold and 5.13-fold those in fruit, respectively. In contrast, the IDF content in the pomace of MUL and BLC decreased to 0.65-fold and 0.44-fold that in fruit, respectively. The variation of TDF in pomace and fruit was similar to that of IDF (Fig. 2 (D)).

In the MIX group, the protein/SDF/IDF/TDF content was significantly higher than that in combined fruit. In particular, the IDF/TDF content in combined pomace was significantly higher than that in individual fruit. The protein and DF contents before and after

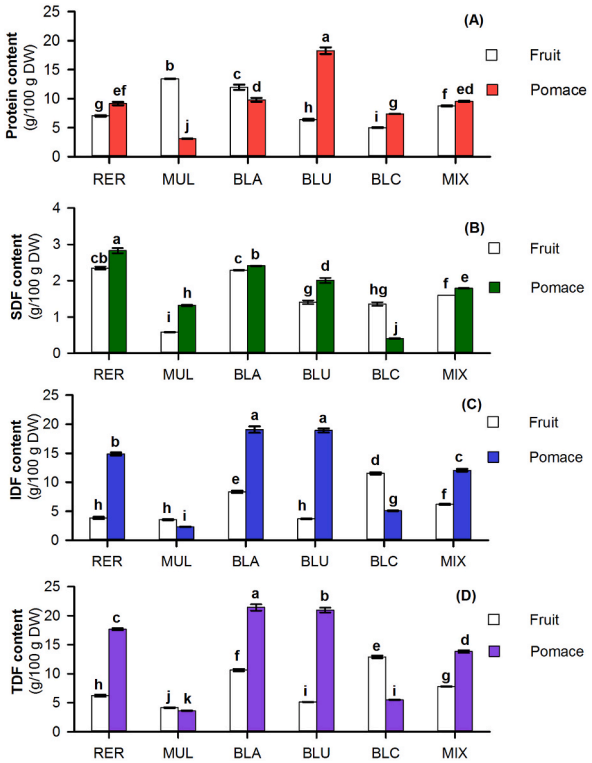

Fig. 2. Comparison of (A) protein, (B) insoluble dietary fiber (IDF), (C) soluble dietary fiber (SDF) and (D) total dietary fiber (TDF) contents in small berries before and after juicing. RER, red raspberry; MUL, mulberry; BLA, blackberry; BLU, blueberry; BLC, black chokeberry; MIX, compounding five kinds of fruit/pomace in equal weight. The results represent the means ± SD. Values without a common letter are significantly different ($p < 0.05$).

juicing (Fig. 2 (A, D)) show that the nutritional quality of pomace has no significant relationship with fruit color and fruit type. In conclusion, the combined pomace contains more kinds and higher content of DF than the fruit, greatly improving the nutritional quality.

3.3. Comparison of minerals between small berry fruit and pomace

Berry is the important source of essential elements. Of the six kinds of mineral elements in this study, K, Ca and Mg are abundant (Table 1). The K contents in the five kinds of pomaces were lower than those in the corresponding fruits, ranging from 17 % to 63 % of fruit. The K content was highest in MUL fruit, while the lowest content in its pomace. Except for MUL (the Ca content in pomace was 0.02-fold that in fruit), the Ca contents in the other four kinds of pomace were all higher than those in the corresponding fruit. The Mg content in pomace showed no significant change in RER and BLC, decreased in MUL and BLA, and increased in BLU compared with the corresponding fruit.

Fe, Se and Co are trace elements. Compared with that in fruit, the Fe content in pomace showed no significant change in RER, decreased in MUL and BLA, and increased in BLU and BLC. The Se content cannot be determined in MUL pomace but increased in RER, BLA and BLC compared with that in fruit. Interestingly, Se was not detected in BLC fruit, but its content was as high as 6.44 mg/100 g DW in pomace. The Co content in pomace showed no significant change in RER, BLU and BLC, but decreased in MUL and BLA compared with that in fruits.

The comprehensive evaluation of nutritional and healthful components lays the foundation of SBP effective utilization. The above results show that mineral elements in pomace varied with berry species. Furthermore, the changes in mineral elements had no relationship with fruit color and fruit type, according to the mineral content in five kinds of berries before and after juicing. The minerals in pomace generally combine with phytic acid, protein and cellulose [34]. The combined SBPs could be a natural mineral source for food development because of the rich mineral.

3.4. Secondary metabolites in SBPs

SBPs have a large amount of bioactive compounds. A total of 776 secondary metabolites were detected based on the UPLC−MS/MS detection platform and a self-built database. The compounds were differed on structure and could be divided into seven categories. Intensity values were adjusted by log transformation and then normalized. Principal component analysis (Fig. 3 (A)) was performed to preliminarily understand the total metabolic differences among groups. PC1 and PC2 represent the first and second principal component, respectively. The percentage represents the interpretation rate of this principal component to the dataset. PC1 and PC2 accounted for 32.24 % and 25.04 % of the variation, respectively. The distance between combined SBP and BLU SBP was the closest, indicating the most similar secondary metabolome composition. According to relative abundance, 776 metabolites were divided into 5 categories by cluster analysis, and each category contained approximately 100 metabolites (Fig. 3 (B)). Interestingly, each SBP contained one unique category, and there was no overlap among the groups. The BLC pomace group had the highest metabolite abundance, which was about 2-fold that of BLA.

According to biological annotation, 666 bioactive compounds were selected for further analysis. Most of compounds exist as natural antioxidants in small berries. Large amounts of polyphenolic compounds were found in SBPs and can be divided into flavonoids, lignans, phenolic acids and stilbenes primarily [3]. SBPs were rich in flavonoids, followed by phenolic acid compounds (Fig. 3 (C)). The compound numbers in other five categories were less than 100. Venn diagram clearly shows the distribution of bioactive compounds in pomace. Some bioactive compounds were present in SBPs simultaneously (Fig. 3 (D-J)). Except for alkaloids (64 %), the coexistence rates of other bioactive compounds in SBPs were all less than 50 %, and the lowest coexistence rate of tannins was 17 %. In seven categories (Fig. 3D–J), the number of flavonoids was higher than the figures in other groups. In five SBPs, the number of specific flavonoids (21) in BLU was the highest, which was higher than that in the other four SBPs. In the category of stilbenes and others, there

Table 1
Comparison of minerals between small berry fruit and pomace.

mg/100 g DW		K	Ca	Mg	Fe	Se	Co
RER	*Fruit*	1235.89 ± 6.65^{b}	134.88 ± 7.65^{g}	125.40 ± 4.76^{c}	4.71 ± 0.49^{g}	14.81 ± 0.29^{d}	5.13 ± 0.45^{d}
	Pomace	689.91 ± 3.74^{f}	179.39 ± 10.54^{f}	119.43 ± 6.23^{c}	4.72 ± 0.05^{g}	17.25 ± 0.49^{c}	5.20 ± 0.40^{d}
MUL	*Fruit*	1610.31 ± 42.17^{a}	873.95 ± 28.42^{a}	213.92 ± 4.78^{a}	12.40 ± 0.45^{a}	11.19 ± 0.47^{e}	7.82 ± 0.4^{b}
	Pomace	274.38 ± 8.75^{j}	16.75 ± 0.15^{i}	13.55 ± 0.31^{h}	1.98 ± 0.03^{i}	ND	ND
BLA	*Fruit*	1089.47 ± 9.17^{d}	186.80 ± 3.39^{f}	157.42 ± 12.61^{b}	6.21 ± 0.58^{dc}	24.69 ± 2.48^{b}	3.72 ± 0.07^{f}
	Pomace	673.94 ± 12.53^{f}	230.97 ± 19.98^{e}	125.10 ± 6.03^{c}	5.27 ± 0.24^{f}	32.03 ± 2.01^{a}	2.65 ± 0.18^{g}
BLU	*Fruit*	583.75 ± 4.36^{g}	30.51 ± 0.89^{i}	33.09 ± 0.28^{g}	2.78 ± 0.13^{h}	ND	5.02 ± 0.15^{d}
	Pomace	319.38 ± 9.17^{i}	67.77 ± 1.42^{h}	58.55 ± 0.62^{f}	5.83 ± 0.06^{de}	ND	5.02 ± 0.14^{d}
BLC	*Fruit*	1160.42 ± 37.84^{c}	279.11 ± 8.84^{d}	98.79 ± 0.72^{d}	6.46 ± 0.10^{c}	ND	8.47 ± 0.14^{a}
	Pomace	728.59 ± 0.63^{e}	376.54 ± 0.77^{b}	103.23 ± 0.14^{d}	9.74 ± 0.03^{b}	6.44 ± 0.64^{f}	8.72 ± 0.08^{a}
MIX	*Fruit*	1135.97 ± 16.48^{c}	301.05 ± 8.07^{c}	125.72 ± 2.59^{c}	6.51 ± 0.12^{c}	10.14 ± 0.47^{e}	6.03 ± 0.16^{c}
	Pomace	537.24 ± 6.50^{h}	174.28 ± 6.46^{f}	83.97 ± 0.14^{e}	5.51 ± 0.06^{fe}	11.15 ± 0.37^{e}	4.32 ± 0.15^{e}

RER, red raspberry; MUL, mulberry; BLA, blackberry; BLU, blueberry; BLC, black chokeberry; MIX, compounding five kinds of fruit/pomace in equal weight. ND, not detected. The results represent the means ± SD of 3 experiments. Values without a common letter in one column are significantly different ($p < 0.05$).

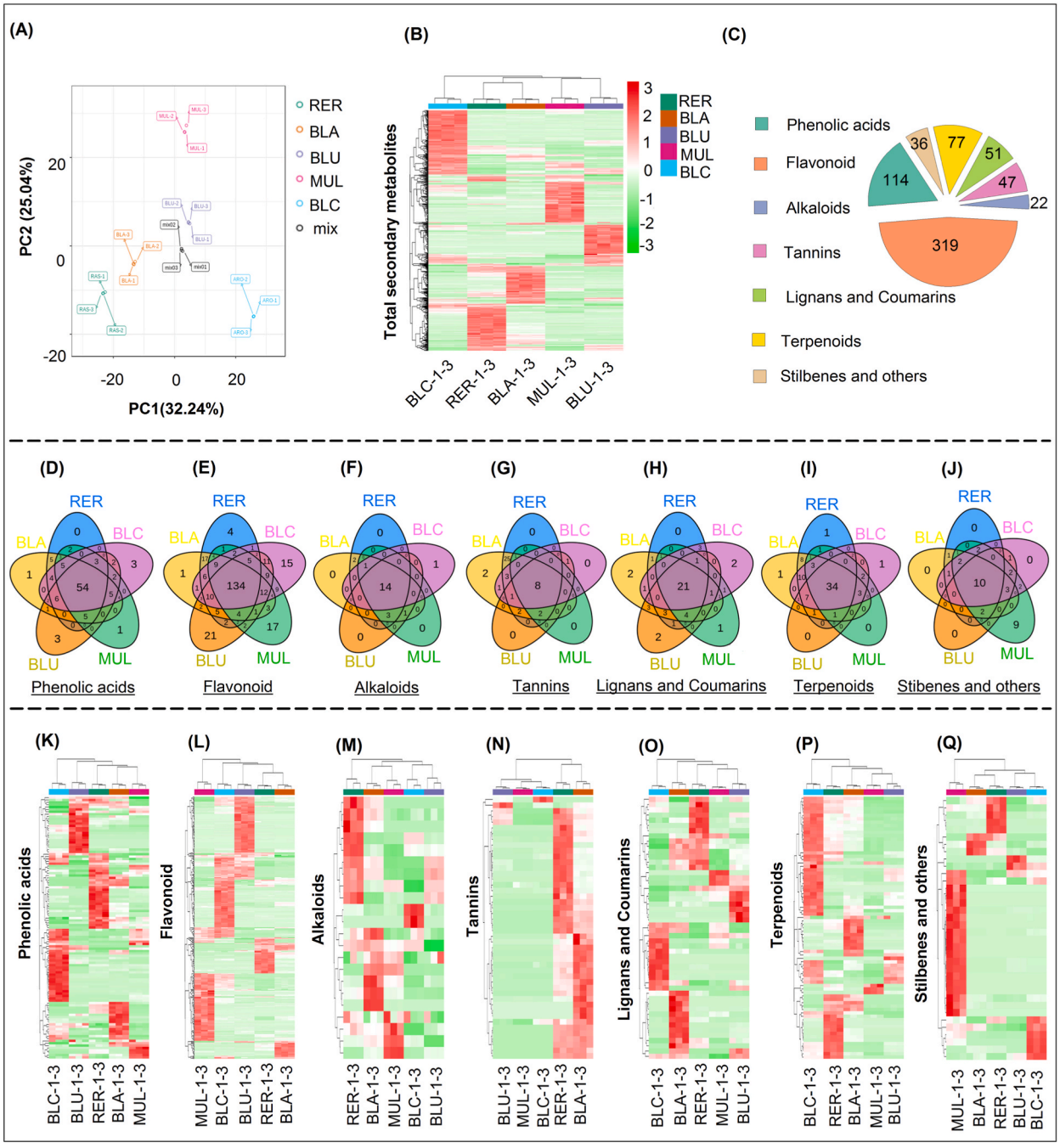

Fig. 3. Secondary metabolites in small berry pomaces. (A) PCA score plot, (B) clustering heatmap of all secondary metabolites, (C) pie chart of antioxidant related secondary metabolites, (D–J) Venn diagram and (K–Q) clustering heatmap of differential antioxidant related secondary metabolites in small berry pomances. RER, red raspberry pomace; MUL, mulberry pomace; BLA, blackberry pomace; BLU, blueberry pomace; BLC, black chokeberry pomace; mix, compounding five kinds of pomace in equal weight. 1–3 indicates three experiments. The abundance of each metabolite is represented by a bar with a specific color. Different colors are the values obtained after the standardization of relative content. Up-regulated and down-regulated metabolites are indicated by different shade colors of red and green, respectively.

were nine bioactive compounds in MUL (Fig. 3 (J)). In the remaining five categories, the number of unique bioactive compounds in SBPs was mostly in the range of 0–3.

Heatmap cluster figures are used to represent the relative content of bioactive metabolites. Except for that of tannins (Fig. 3 (N)), the metabolite abundance showed good complementary characteristics, and each species of SBP contained a unique class of highly abundant metabolites, with no overlap among classes (Fig. 3 (K, L, M, O, P, Q)). The detailed information of longitudinal metabolites in

Fig. 3 (K-Q) was exhibited in Supplementary Figure S (1–7). There was a certain correspondence between the Venn diagram and heatmap. Generally, the SBP with more unique active substances in the Venn diagram had highly bioactive substances enriched in the heatmap. The secondary metabolites content of SBPs is determined by many factors, such as the species, variety, region, ripeness, storage and manufacturing conditions [35], which results in each SBP having its own unique antioxidant characteristics.

3.5. Anthocyanin-related metabolites in SBPs

Small berries are a rich source of non-nutritive natural pigments [36]. In this paper, anthocyanins, proanthocyadins and

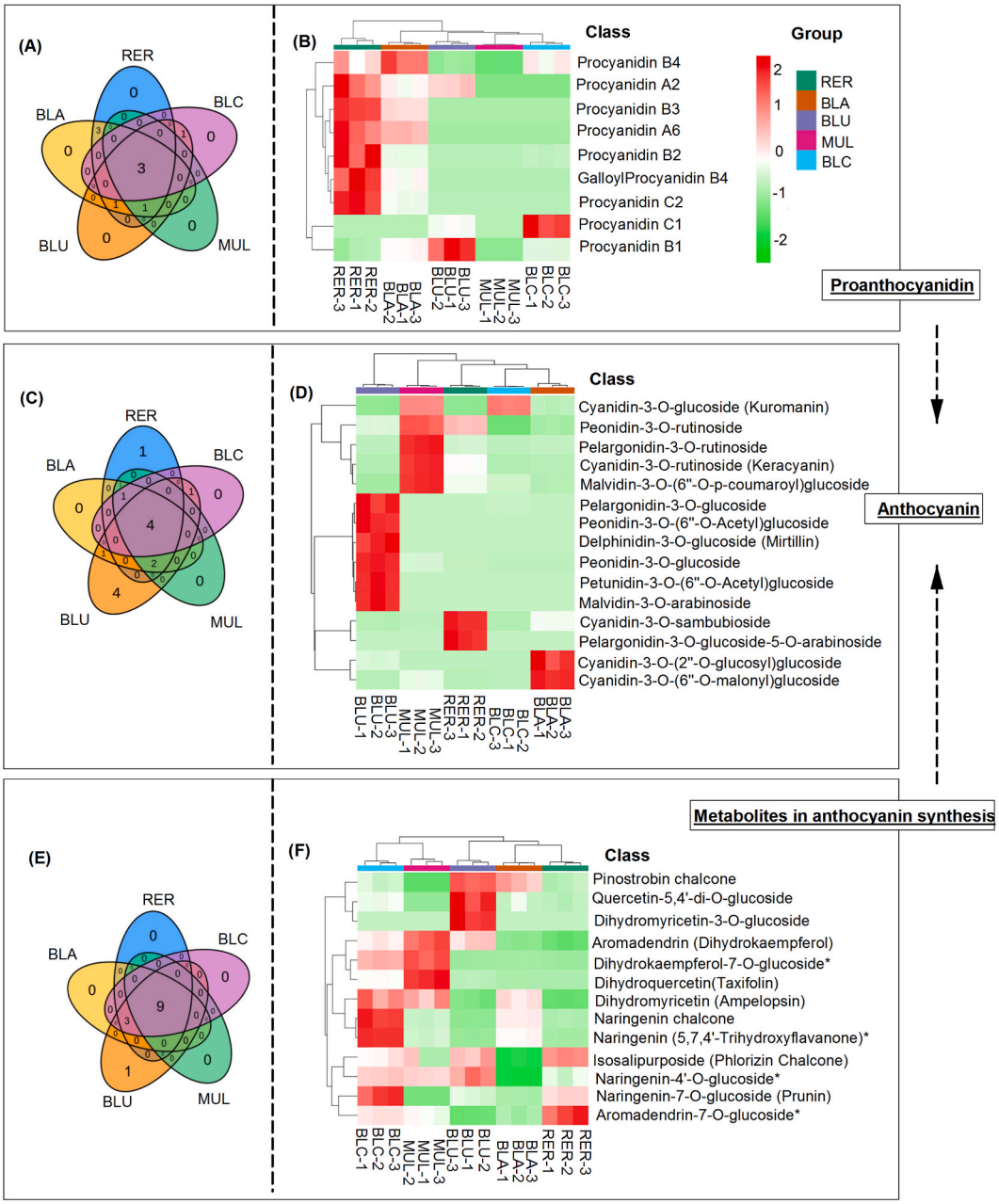

Fig. 4. Anthocyanin-related metabolites in small berry pomaces. (A, C, E) Venn diagram of the numbers of the differential metabolites (proanthocyanidins, anthocyanins, metabolites related to anthocyanin synthesis) among berry pomaces. (B, D, F) Clustering heatmap of the differential metabolites (proanthocyanidins, anthocyanins, metabolites related to anthocyanin synthesis) among berry pomaces. Group is the grouping, Class is the material classification, and different colors are the values obtained after the standardization of relative content. The legends in Fig. 4 are the same as those in Fig. 2 and 3.

metabolites relating to anthocyanin synthesis were further studied simultaneously using data from metabolomics analysis. Proanthocyanidin, a more powerful antioxidant than anthocyanidins, displays an ability to convert into anthocyanidin by heating in acidic medium [37]. As powerful metal chelating agents, proanthocyanidins can chelate metal ions and form inert compounds in vivo [38]. Nine proanthocyanidins were detected, of which three proanthocyanidins existed in all pomaces (Fig. 4 (A)). Six proanthocyanidins accumulated in RER pomace abundantly (Fig. 4 (B)). Each of the MUL, BLU and BLC pomaces contained one proanthocyanidin with the highest content. In contrast, the least proanthocyanidin level was determined in BLA pomace.

As the most important and widely found pigments in fruits, anthocyanins are formed by the glycosidic bond between anthocyanidins and sugars. Both anthocyanins and proanthocyanidins are typical flavonoids. The types and quantities of anthocyanins are major factors affecting fruit quality. As many as 15 kinds of anthocyanin were detected in the form of glycoside, of which four components existed in five kinds of pomace simultaneously (Fig. 4 (C, D)). It should be noted that four anthocyanins (delphinidin-3-*O*-glucoside, petunidin-3-*O*-(6″-*O*-acetyl) glucoside, peonidin-3-*O*-(6″-*O*-acetyl) glucoside and malvidin-3-*O*-arabinoside) were detected only in BLU pomace (Fig. 4 (C)). As shown in the enrichment heatmap, six components were mainly enriched in BLU pomace. In contrast, fewer components were highly enriched in pomace (Fig. 4 (D)).

The synthetic pathway is mainly the source of anthocyanin. A total of 13 metabolites related to anthocyanin synthesis were detected, of which nine were distributed in five kinds of pomace simultaneously (Fig. 4 (E)). The enrichment heatmap showed that 4, 3, 3, 1 and 2 metabolites related to anthocyanin biosynthesis were enriched in BLC, MUL, BLU, BLA and RER, respectively (Fig. 4 (F)). It is worth noting that dihydromyricetin-3-*O*-glucoside is found in BLU pomace at the highest concentration. Similar to proanthocyanidins and anthocyanin, intermediate metabolites related to anthocyanin synthesis was the least enriched in BLA pomace..

3.6. Anthocyanidin content in berry fruits and pomaces

Free-form anthocyanidins are directly related to small berry color. Anthocyanins are glycosides of aglycones anthocyanidins and belong to the phenolic group as flavonoids. Six major anthocyanidins included in this study were wide spread in fruits and vegetables (Table 2).

Six major anthocyanidins were identified, none of which could be detected in fruit or pomace simultaneously. A high concentration of anthocyanidins was detected in BLU, which contained 5/6 pigments, and only pelargonidin was not detected. Except for BLU, only one or two kinds of anthocyanidins were detected in the other four small berries. This result was mostly consistent with the anthocyanin content in Fig. 4 (B), which once again verified the uniqueness of anthocyanidins in blueberries. Higher anthocyanidin content was found in BLU fruit which was consistent with the result of a previous report [39]. It is worth noting that the contents of delphinidin, cyanidin, petunidin and malvidin in BLU pomace increased 6.73-, 4.46-, 4.69- and 5.01-fold, respectively, compared to that in BLU fruit, and the pomace peonidin content also increased from undetectable levels to 3.06 mg/100 g DW. It can be said that anthocyanidins are greatly concentrated in blueberry pomace. Similar to blueberries, MUL and BLC pomaces contained higher levels of anthocyanidins than their fruits. Phenolic compounds concentrations are usually higher in the epidermis and in the tissue directly beneath than in the central part of the fruit [17]. Changes in phenolic compounds during juice processing showed that water soluble antioxidant components located in the cell vacuole were released into the juice whereas compounds with low solubility that are associated with the cell wall remained in SBP [16]. Therefore, it is speculated that the differential distribution of phenolics together with lower moisture content results in some anthocyanidins content being higher in pomace than in fruit.

Of six kinds of anthocyanidins, cyanidin was the only one that could be detected in fruits and pomaces of all five small berries. After juicing, the cyanidin content in pomace did not show a consistent trend compared with fruit, increasing in MUL, BLU and BLC (1.17-, 4.46- and 1.38-fold that in the fruit, respectively) and decreasing in RER and BLA (0.39- and 0.69-fold that in the original fruit, respectively). It has been reported that anthocyanidin concentrations differ depending on species factors [40]. In berry fruits, a certain pigment may exist in different parts of the fruit. After juicing, some of the pigments in the fruit will enter the juice, and the others will remain in the pomace, which will lead to the difference in the anthocyanin content in SBP.

As shown in Table 2, the anthocyanidin content had no relationship with fruit color and fruit type. However, the distribution of the six anthocyanidins in the five species of fruits/pomaces showed an interesting complementarity. In combined fruits/pomaces,

Table 2
Composition analysis of anthocyanidins in fruit and pomace of small berries.
The legends in Table 2 are the same as those in Table 1.

mg/100 g DW		Delphinidin	Cyanidin	Petunidin	Pelargonidin	Peonidin	Malvidin
RER	*Fruit*	ND	317.32 ± 2.23	ND	11.46 ± 0.24	ND	ND
	Pomace	ND	123.01 ± 6.61	ND	3.17 ± 0.15	ND	ND
MUL	*Fruit*	ND	1239.86 ± 26.63	ND	ND	8.04 ± 0.21	ND
	Pomace	ND	1447.76 ± 75.93	ND	ND	9.04 ± 0.70	ND
BLA	*Fruit*	ND	154.76 ± 0.94	ND	ND	ND	ND
	Pomace	ND	106.83 ± 5.56	ND	ND	ND	ND
BLU	*Fruit*	135.36 ± 0.45	44.96 ± 10.78	87.96 ± 0.72	ND	ND	185.82 ± 5.91
	Pomace	911.25 ± 37.87	200.46 ± 5.77	412.69 ± 17.35	ND	3.06 ± 0.53	931.86 ± 16.71
BLC	*Fruit*	4.34 ± 0.09	940.25 ± 113.80	ND	ND	ND	ND
	Pomace	4.55 ± 0.76	1295.17 ± 46.96	ND	ND	ND	ND
MIX	*Fruit*	27.94 ± 0.07	539.43 ± 30.88	17.59 ± 0.14	2.29 ± 0.05	1.61 ± 0.04	37.16 ± 1.18
	Pomace	183.16 ± 7.72	634.65 ± 28.17	82.54 ± 3.47	0.63 ± 0.03	2.42 ± 0.24	186.37 ± 3.34

although the content of a particular anthocyanidin may not be the highest, the anthocyanidin class is the most complete. This result helps to exert the synergistic effect among different anthocyanins, which may result in higher antioxidant activity.

3.7. Comparison of antioxidant properties in SBPs before and after compounding

Natural antioxidants have many biological functions. It is now widely held that the antioxidants contained in small berries can provide protection against certain human degenerative conditions [41]. Although the antioxidant activities of many berry species have been evaluated, research related to the synergistic antioxidant activity of various species is not well studied. Antioxidant capacity of SBPs was appreciably influenced by cultivar. BLU pomace showed higher value of four antioxidant items than others (Fig. 5). The lowest value of ABTS/DPPH radical scavenging capacity was found in the group of BLA pomace. FRAP had the lowest value in MUL pomace. In all of the items, non-experimental statistical average values of combined pomace were lower than measured value of BLU pomace. In the comparison of theoretical and experimental group, the measured value was higher than the theoretical value. ABTS radical scavenging capacity was higher in combined SBPs than in BLU pomace (Fig. 5 A). For DPPH radical scavenging capacity, FRAP and MCC, there was no statistically significant difference between the two groups (Fig. 5 B ~ D). This result shows a combination of SBPs inhibits the intensity of redox reactions more strongly than a single pomace.

The antioxidant activity of combined SBPs was determined by their ability to scavenge free radicals, FRAP, MCC, etc. It is well known that flavonoids (especially anthocyanins) contribute to the antioxidant properties of blueberries [39,42]. Antioxidant capacity of the phenolic compounds depends on their chemical structures [43] and interactions between them [44]. A strong ability to scavenge both DPPH• and ABTS•+ free radical ability due to changes in the phenolic compounds composition [45]. Phenolic compounds from fruits are characterized by higher antioxidant activity compared with that of single component. In human systems, the synergistic antioxidant effects were found in the combinations of vitamins plus polyphenols and polysaccharides plus flavonoids [46]. Pomace species richness promotes antioxidant capacity in combined SBP through strong complementarity between species (Fig. 3). This paper was aimed to study nutritional quality and potential health benefits of the mixed SBPs. Overall, SBPs belong to good dietary sources of bioactive compounds, which exert a synergistic and cumulative effect on antioxidant capacity.

By optimizing the compounding ratio of SBPs, the antioxidant activities of combined pomaces could be further improved. A future aim will be the identification of many other biological functions from secondary metabolites that were not assessed in this work. The results from this study may be further expanded towards other berry co-products, which would increase the total production value by utilizing press-residue from juice production. This study will serve as a potential reference for applications in functional food.

4. Conclusion

An object of the present study is to provide a method for SBP treatment, by which berry pomace can be quickly performed with good efficiency. It is suggested that SBPs are first well blended and then processed together. Combined SBPs showed better and comparable nutritional quality to fresh fruit, and its ABTS, FRAP, MCC antioxidant capacity were higher than single SBP. Furthermore, the antioxidant capacity of combined SBPs, estimated by various radical scavenging, reducing antioxidant power assays correlated strongly with high contents of natural antioxidants survived in pomaces. For significant protein/DF/phenolic acid/anthocyanidins content, the combined SBPs will be identified as a source of nutritional compounds for food product formulations and as a natural

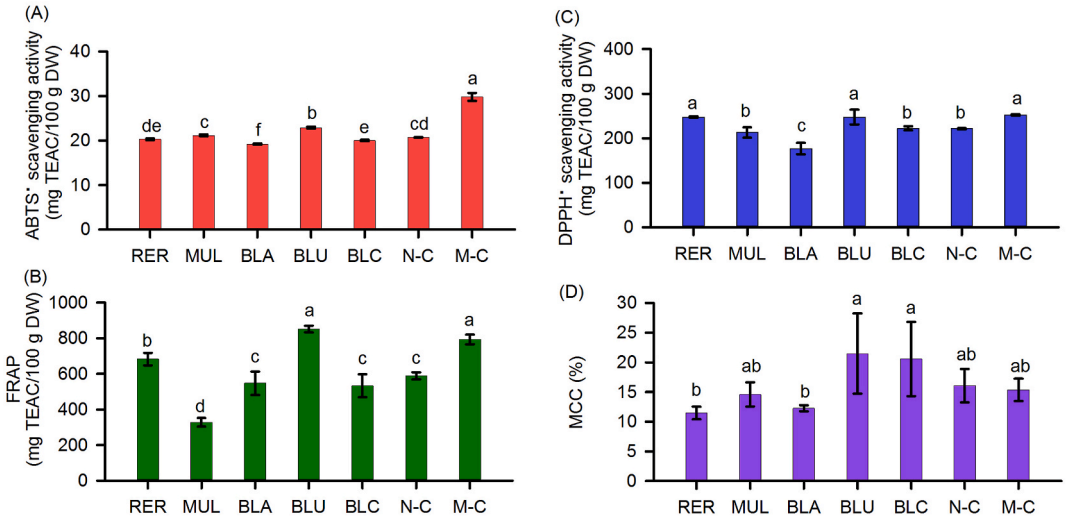

Fig. 5. Comparison of antioxidant activity of SBPs before and after compounding. (A) ABTS· scavenging activity, (B) FRAP, (C) DPPH· scavenging activity, (D) MCC. N–C: non-experimental statistical average of combined pomace, M–C: measured value of combined pomace. The other legends in Fig. 5 are the same as those in Fig. 2 and 3.

antioxidant for use in foods. If this technology can be adopted, the processing cost will be minimized also SBP products with balanced nutrition and strong antioxidant activity will be manufactured, and thus economic feasibility can be obtained.

Ethics Statements

There were no human subjects and mammalian animal experiments in our research.

Data availability statement

The metabolome raw data are deposited the in the Metabolights under accession number MTBLS8923. The data that support the results presented in this paper are available from the corresponding author, upon reasonable request.

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Additional information

No additional information is available for this paper.

CRediT authorship contribution statement

Xinkun Wang: Data curation, Formal analysis, Investigation, Methodology, Writing – original draft, Conceptualization, Project administration, Software, Visualization. **Peng Deng:** Investigation, Methodology, Writing – original draft, Writing – review & editing. **Anwei Cheng:** Investigation, Methodology, Funding acquisition. **Sujun Sun:** Methodology, Resources. **Kaining Sun:** Formal analysis, Investigation. **Zhou Sun:** Investigation, Validation. **Xiaoguang Zhan:** Resources, Software. **Congjing Zhang:** Formal analysis, Methodology. **Xiaodan Dong:** Investigation, Software. **Lizeng Peng:** Conceptualization, Data curation, Formal analysis, Funding acquisition, Resources, Supervision, Validation, Writing – review & editing. **Chune Peng:** Conceptualization, Data curation, Funding acquisition, Investigation, Methodology, Project administration, Resources, Software, Supervision, Validation, Visualization, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.heliyon.2023.e22623.

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