Impact of cell wall adsorption behaviours on phenolic stability under air drying of blackberry with and without contact ultrasound assistance

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Abstract

The physicochemical properties of blackberry cell walls under air drying with and without contact ultrasonication were analysed, and their ability to bind soluble phenolics was evaluated. Compared to air drying alone, ultrasound promoted cell wall shrinkage and reduced their specific surface area and water binding capacity. Meanwhile, the in-process ultrasound further increased the amount of water soluble pectin (WSP) and decreased protopectin. After drying, the cell walls of ultrasound-dried samples contained 11.6 % less protopectin (PP) than air-dried samples. Pectins in ultrasound-dried samples were also more aggregated with a reduced branching degree of Rhamnogalacturonan-I (RG-I). Most of these ultrasonic modifications of blackberry cell walls hindered their phenolics acquirement. The equilibrium adsorption capacities of cell walls from ultrasound-dried blackberries for 1 h were 33.5% (for catechin) and 21.8% (for phloretic acid) lower than the counterparts from air-dried samples for 8 h. Although the soluble phenolics absorbed by dried blackberry cell walls were more thermal-stable than those adsorbed by fresh blackberry cell walls, the overall protection provided by cell walls was still regarded as attenuated with drying due to the decline in the adsorption ability. Besides, it is believed that the higher retention of soluble phenolics in ultrasound dried samples is ascribed to the shortened thermal-drying time rather than the cell walls-phenolics interactions. These findings provide an in-depth understanding of the effect of ultrasound drying on phenolic stability.

Keywords: Blackberry, ultrasound, drying, cell walls, phenolics, stability.

1. Introduction

Bioactive phenolic compounds are broadly distributed in soluble and bound forms in fruits and vegetables (F&V) (Liu, Le Bourvellec, & Renard, 2020). Many studies have shown that phenolics can be degraded enzymatically or non-enzymatically (Nayak, Liu, & Tang, 2015; Zhu et al., 2022), as well as synthesised through isomerisation, polymerisation, and depolymerisation during F&V drying (Wang, Zhou, & Jiang, 2008). In the past decades, the effects of degradation and synthesis reactions on the stability of phenolics during food F&V processing have been extensively reported (Gancel, Feneuil, Acosta, Perez, & Vaillant, 2011; Mendez-Lagunas, Rodriguez-Ramirez, Cruz-Gracida, Sandoval-Torres, & Barriada-Bernal, 2017; Tan et al., 2021). On the other hand, some evidence shows that the cell walls can partially adsorb soluble phenolics released from plant cell vacuoles through hydrogen bonding, hydrophobic interactions and ionic interactions, which also affect the phenolic stability under food drying, extraction, fermentation, homogenization and other processing (Liu et al., 2020; Loo, Howell, Chan, Zhang, & Ng, 2020). Plant cell walls are extracellular matrices with a network structure composed of cellulose, hemicellulose and pectin (Hu, Zhang, Hamaker, & Miao, 2022). The modification of cell walls, including the surface structure, physical properties, and chemical composition (especially pectin), may occur in the F&V drying, affecting the cell wall's adsorption capacity for phenolic compounds (Liu, Lopez-Sanchez, Martinez-Sanz, Gilbert, & Gidley, 2019). Although the interactions between plant cell wall polysaccharides and phenolics *in vitro* have been well-studied (Ando et al., 2016; Deng, Wu, & Li, 2005; Liu et al., 2019), it is still unclear about

the progress of the interactions between the cell walls and phenolics and its influence on the phenolic stability in the given processing, i.e. drying, extraction, and homogenisation.

Owing to the mechanical forces exerted on food materials, ultrasound-incorporated air drying is a promising F&V dehydration method to shorten the drying time, alleviate quality deterioration and reduce energy consumption (Tao et al., 2021; Zhu et al., 2022). Many studies have shown that mechanical shearing and ultrasound cavitation can degrade pectin polysaccharides and reduce the branching degree of pectins, particularly RG-I (Ogutu & Mu, 2017; Wang et al., 2018). Under this circumstance, it is believed that changes in plant cell wall composition and structure under air drying simultaneously with ultrasonication differ from air drying alone. The protective effect of cell walls on soluble phenolics due to adsorption should also be affected by ultrasound. Considering the advantages of ultrasound in F&V drying and the knowledge gap about cell wall adsorption behaviour under novel drying methods, it is indispensable to understand the in-depth evolutions of the F&V cell walls throughout ultrasound-assisted air drying and evaluate the interactions between cell walls and soluble phenolics.

Our previous study reported that contact ultrasound-intensified air drying enhanced the retention of blackberry soluble phenolics, including catechin, phloretic acid, and rutin (Gong et al., 2021). Following this study, the evolutions of blackberry cell walls, including physical properties, surface structure and pectin components under ultrasound-assisted air drying, were intensively explored. Also, the adsorption behaviour of the blackberry cell walls on the representative phenolics at different drying stages was investigated.

Furthermore, the stabilities of the attached phenolics on cell walls extracted from ultrasound-dried blackberries were assessed under exposure to hot air. The outcome of this study provides a mechanistic understanding of the effect of ultrasound on cell wall modifications under air drying and the contribution of cell wall adsorption to the stability of soluble phenolics.

2. Materials and methods

2.1. Materials and chemicals

Fresh blackberry fruits (*Rubus americanus Britton*, cultivar: *Hull*) were obtained from the plantation in Lishui, Nanjing, belonging to the Institute of Botany, Jiangsu Province and the Chinese Academy of Science. Samples were stored at -20 ºC after reaching the laboratory in July 2021.

Monosaccharide standards (e.g. mannose, rhamnose, glucuronic acid, galacturonic acid, glucose, galactose, xylose, arabinose and fucose) and phenolic standards (e.g. catechin and phloretic acid) were received from Yuanye Bio-Technology Co., Ltd. (Shanghai, China). All the other chemicals were analytical-grade reagents.

2.2. Contact ultrasound-assisted air drying

Before each experiment, blackberries were thawed at 4 ºC for 12 h. Blackberries of similar sizes and weights were selected. Drying treatment was performed in a self-assembly hybrid dryer, including an ultrasound vibration probe and circulating hot air inside. The

configuration of this device can be referred to in our previous study (Tao et al., 2021). 9 g of blackberry fruits were loaded into the dryer, making them gently contact the ultrasound emitting probe. The samples were kept contacting with the ultrasound probe throughout drying by adjusting their height periodically. Ultrasonication was performed at 180.1 W/dm^2 in a pulsed mode (5 s on, 5 s off). The air velocity and humidity were 2.0 m/s and 0.08, respectively. Drying without sonication was performed as a control. The drying process was terminated when the water content decreased below 2 kg water/kg dry matter (DM). Based on our earlier studies, it took approximately 8 h for air drying (AD), and 1 h for contact ultrasound assisted with air drying (AD-US) to achieve this point (below 2 kg water/kg DM) (Gong et al., 2021). The samples dried for 0.5 h and at the end of drying were collected for the following analysis. All the treatments were conducted in triplicate.

2.3. Characterisation of blackberry cell walls

2.3.1. Preparation of cell walls from fresh and dried blackberries

Cell wall materials in the form of alcohol-insoluble residue (AIR) were prepared according to the method of Deng et al. (2018) with minor modifications. First, blackberries were mixed with 90% aqueous ethanol at a 20:1 (mL:g) solvent-to-solid ratio at different drying stages. The mixture was kept boiling for 10 min, cooled and then centrifuged. The residues were added to 70% ethanol at a 15:1 (mL:g) solvent-to-solid ratio, mashed in a mortar by hand and centrifuged. Then, the residues were washed again with fresh 70% ethanol for 20 min before centrifugation. This procedure was repeated more than five times

until the supernatant demonstrated negative in the anthrone sulfuric acid test. The final residue was mixed with acetone at a 10:1 (mL:g) solvent-to-solid ratio for 20 min. Lastly, the residues were collected and dried overnight at 40 °C to obtain AIR.

2.3.2. Surface morphology analysis by scanning electron microscopy (SEM)

Blackberry cell wall materials were mounted on SEM specimen stubs with conductive and double sticky carbon tape and then coated with 20 nm gold layers by ion sputtering (Cressington 108 Auto Sputter Coater, England) (He, Liu, Zhao, Li, & Wang, 2021). Subsequently, the samples were imaged using a scanning electron microscope (ZEISS EVO LS10, Germany) at an accelerating voltage of 10 kV under 500X magnification. For each sample, at least six images were collected.

2.3.3. Surface groups analysis by Fourier transform infrared spectroscopy (FTIR)

Blackberry cell wall materials were further analysed by FTIR (IR 200, NICOLET Co., Ltd., America). 1 mg cell wall sample was mixed with 100 mg potassium bromide, grounded and then tableted. The samples were scanned from 4000 to 400 cm^{-1} with an accumulation of 60 scans at a resolution of 4 cm^{-1}. Each spectrum was recorded against potassium bromide as the background, and each sample was analysed three times.

2.3.4. Water binding capacity (WBC)

The water binding capacity was measured by the filtration method (Liu, Renard, Rolland-Sabate, Bureau, & Le Bourvellec, 2021). Approximately 100 mg of blackberry cell wall materials were soaked in water (5 mL) for 1 h at room temperature, filtered and dried (103 °C, 12 h). The WBC was then calculated using the following Eq. (1).

$$\text{WBC } (g/g) = (w_1 - w_2)/(w_2 - w_3) \quad (1)$$

where w_1 is the total weight of filter and cell wall materials after filtration (g), w_2 is the total weight of filter and cell wall materials after drying (g), and w_3 is the weight of filter (g). Each sample was analysed in triplicate.

2.3.5. Determination of the internal structure

The specific surface area, total pore volume, and mean pore diameter of the cell wall materials were determined by nitrogen adsorption isotherms at -196 °C using the BELSORP-mini adsorption apparatus (Bel Japan Inc, Japan) (Tao et al., 2022).

2.4. Characterisation of pectin from blackberry cell walls

2.4.1. Fractionation of cell wall pectin

Following the reports of Keutgen and Pawelzik (2007) and Zioga et al. (2022), different pectin fractions were separated in the AIR. Approximately 20 mg AIR was mixed with 10 mL distilled water and shaken at 50 °C for 1 h. The filtrate was then collected, and the residue was extracted using the above procedures. The two filtrates were combined as the water soluble pectin (WSP) fraction and stored at 4 °C before further analysis.

The remaining residue was then mixed with 10 mL hydrochloric acid (0.01 M), boiled for 1 h, and filtered. This process was repeated. The two filtrates were combined, pH adjusted to 7.0, and stored at 4 ^{o}C until further analysis. This fraction refers to the protopectin (PP) fraction.

2.4.2. Quantification of pectin fractions

Different pectin fractions obtained in Section 2.4.1 were quantified with the carbazole colorimetry method using galacturonic acid (Gal A) as standard (Keutgen & Pawelzik, 2007). Specifically, 0.5 mL PP (or WSP) fraction diluent was adequately mixed with 3 mL sulfuric acid (98%, w/w). The mixed solution was boiled for 10 min and cooled in an ice bath. Then, 0.25 mL carbazole ethanol solution (1.5 g/L) was added to the above solution and incubated at 25 ^{o}C for 1 h. The content of each pectin fraction was determined using a TU-1900 UV-vis spectrophotometer (Persee General Instruments Co., Ltd, Beijing, China) at 530 nm. The results were expressed as mg Gal A/g AIR. All measurements were performed in triplicate.

2.4.3. Characterisation of cell wall pectin nanostructure

Each pectin fraction extract solution was diluted to 10 μg/mL with distilled water, heated at 70 °C for 5 min and agitated with a vortex mixer (Deng et al., 2018). The nanostructures of WSP and PP from different drying treatments were characterised by atomic force microscopy (AFM) (Dimension Edge, Bruker Co., Ltd., Germany). The

imaging was operated in tapping mode with a scan speed of 2 Hz. The topographical mode images were collected simultaneously. For each sample, at least ten images were examined.

2.4.4. Analysis of neutral sugar composition of cell wall pectin

The neutral sugar composition of cell wall pectin was analysed using the precolumn derivatisation method described by Dai et al. (2010) with minor modifications. The WSP and PP fractions extract solution were mixed at a ratio of 1:1 (v/v). Then, 1 mL pectin mixed solution was hydrolysed with 1 mL of 4.0 M trifluoroacetic acid (TFA) at 120 °C for 2 h. The monosaccharide-rich filtrate was then collected. The excessive TFA in the filtrate was removed by evaporation with 1 mL methanol under a vacuum. This procedure was repeated three times. The hydrolysed cell wall pectin sample was dissolved in 100 μL milli-Q water and derivatised with 1-phenyl-3-methyl-5-pyrazolone (PMP) strictly following the method of Dai et al. (2010). Detailed derivatisation procedures can be found in this literature.

Monosaccharide-PMP derivative was further analysed using a Waters 1525 HPLC system coupled with a ZORBAX Eclipse XDB-C18 column (4.6 × 250 mm, 5 μm). The PMP derivatives elution was performed with a mixture of 0.1 M phosphate buffer (pH 6.8) and acetonitrile in a ratio of 83:17 (v/v) at a flow rate of 1 mL/min. The injection volume was set to 20 μL, and the column temperature was maintained at 35 °C. The detection wavelength was 245 nm. The standard of each monosaccharide was used to construct the calibration curve. The results are expressed as mg of each monosaccharide/g AIR.

2.5. Texture profile analysis of blackberry fruits

Texture analysis of blackberries under different drying treatments was performed by a compression test in a TLP texture analyser (Food Technology Co., Ltd., America). The operating parameters were: a test rate of 60.0 mm/min, trigger force of 0.1 N, two compressions intervals of 10 s and a deformation variable of 40% (Zhang et al., 2018). Hardness is defined as the maximum force during the first compression. The test was performed on six individual blackberry samples for each drying treatment.

2.6. Determination of pectinase activity

The pectinase activity was determined by the dinitrosalicylic acid (DNS) colorimetry method. First, fresh and dried blackberries were ground manually with a commercial solvent in the pectinase assay kit (70T/25S, BOXBIO Bio-Technology Co., Ltd., China) at a ratio of 1:10 (g/mL) in an ice bath. Then, the mixture was centrifuged at 10000 rpm for 10 min and the supernatant was collected to obtain the crude pectinase solution. After that, a portion of the crude pectinase solution was placed in a boiling water bath for 10 min and cooled to room temperature to prepare the inactivated crude pectinase solution. Pectinase activity was determined and calculated according to the methods described by the pectinase assay kit. One unit of the enzyme is defined as the enzyme amount required to catalyse the formation of 1 μmol of galacturonic acid per hour under 50 ^{o}C and pH 3.5. The results are expressed as U/g DM, and all measurements were performed in triplicate.

2.7. Capacity of blackberry cell walls to adsorb individual phenolics

Adsorption experiments were conducted according to the method described by Liu et al. (2019) with small modifications. Catechin and phloretic acid were used in this study. Based on our previous research, ultrasound promoted the retention of some soluble phenolics during drying, including phloretic acid and catechin (Gong et al., 2021). The phenolic standard was initially dissolved in ethanol and added to the citric acid/phosphate buffer (0.1 M, pH 3.8), making its concentration 10 mM. The ethanol content in the prepared phenolic solution was 10%. Then, the cell wall suspension was prepared by mixing AIR and citric acid/phosphate buffer at a 200:1 (mL:g) solvent-to-solid ratio. This cell wall suspension was then mixed with the prepared phenolic solution at a ratio of 4:1 (v/v) and incubated in an Erlenmeyer flask under orbital agitation at 150 rpm and 25 °C. The variation of phenolic content in the solution was monitored periodically until the adsorption reached equilibrium. The catechin and phloretic acid contents were determined using a TU-1900 UV-vis spectrophotometer (Persee General Instruments Co., Ltd, Beijing, China) at 278.8 and 275.3 nm, respectively. The adsorption capacity of the cell walls was quantified using the following Eq. (2).

$$Q_{A,t}=\frac{(C_{A,0}-C_{A,t})\times V_A\times 1000}{W} \quad (2)$$

where $C_{A,0}$ and $C_{A,t}$ are the phenolic concentrations in the solvent at 0 and t min of adsorption, respectively (mg/mL). V_A is the volume of mixed suspension (mL), and W is

the dry weight of the AIR used (mg). $Q_{A,t}$ is the adsorption capacity of cell walls at t min of adsorption (μg/mg AIR).

2.8. Thermal stability analysis of phenolics adsorbed on blackberry cell walls

The thermal stability of the phenolics adsorbed on the blackberry cell walls was analysed. Following the test in Section 2.7, the cell wall residuals loaded with phloretic acid or catechin were obtained by filtration. As a reference, the solutions of catechin (2.75 mg/mL) and phloretic acid (0.78 mg/mL) were also prepared following the same method in Section 2.7. The catechin and phloretic acid concentrations were set according to their contents in fresh blackberries (Gong et al., 2021). The cell wall materials containing adsorbed phenolics and the phenolic solutions were then placed in an oven at 65 °C for 30 min. After heat treatment, the residual phenolics in the cell wall materials were eluted twice using 50% ethanol (pH 3.5) (Gong et al., 2021). The phenolic content in the elutes and the above solution were then measured using the spectrophotometric method. The loss of phenolics was calculated, which represents their thermal stability. Experiments were carried out in triplicate.

2.9. Data analysis

One-way analysis of variance (ANOVA) was conducted in Statistix 9.0 (Analytical Software, Tallahassee, FL, USA) to compare the means of quality data of blackberry under different treatments. The Least Significant Difference (Fisher's LSD) test was applied, and

the significance was set at $p < 0.05$. Correlations between the studied data determined by Pearson's correlation method were conducted in SPSS 11.5 (SPSS Inc., USA), and a heatmap plot on the correlation coefficient was generated in Morpheus (https://software.broadinstitute.org/morpheus/). The AFM images were analysed offline using Nanoscope Analysis 1.50 (Analytical Software, Bruker Co., Ltd., Germany).

3. Results and discussion

3.1. Characterisation of blackberry cell walls under different treatments at different stages of drying with and without ultrasound assistance

3.1.1. Surface morphology

SEM was used to study the morphological structure of cell walls extracted from blackberry at different drying periods (Fig. 1 and Supplementary Fig. 1). Apart from some shallow depressions and protrusions, fresh blackberry cell wall preparations generally exhibited a flat and smooth appearance (Fig. 1a and 1b), similar to the surface morphology of cell wall components extracted from fresh apple (Liu, Renard, Rolland-Sabate, et al., 2021). Drying changed the surface morphology of blackberry cell wall preparations markedly. Compared with the counterparts from fresh blackberries, the cell wall preparations from all the dried blackberries exhibited wrinkled and compact morphology due to the water loss. Furthermore, contact ultrasonication promoted deforming blackberry cell wall components. After drying for 0.5 h, the cell wall preparations from the sonicated blackberry (Fig. 1d and Supplementary Fig. 1b) appeared to be more crumpled than the

non-sonicated samples (Fig. 1c and Supplementary Fig. 1a). In Fig. 1d and Supplementary Fig. 1b, some visible and irregular substructures are observed probably due to the cross-linking of cellulose microfibrils (Liu, Renard, Rolland-Sabate, et al., 2021). It is supposed that the ultrasonic impacts, including the series of compression and rarefaction induced by ultrasound and the generation of cavitation in the cytosol, may not only strengthen the water movement but promote changes in the cell wall structure. Besides, no obvious differences in the morphology can be recognised between the cell wall preparations extracted from ultrasound-treated (Fig. 1f and Supplementary Fig. 1d) and non-ultrasound treated (Fig. 1e and Supplementary Fig. 1c) blackberries at the end of drying. This phenomenon indicates that the deformation degree of the cell walls from ultrasound-dried blackberries for 1 h is comparable to samples dried only by hot air for 8 h, partly attributed to the synergistic effect of ultrasound and heat treatment on the blackberry cell walls.

3.1.2. Distribution of chemical groups on the cell wall surface

The FTIR spectra were used to investigate the changes in the surface groups of blackberry cell walls during drying. In Supplementary Fig. 2, the spectra of cell walls from blackberries with and without drying exhibited similar peaks and valley waveforms. The strong absorption peaks at 1630 cm^{-1} and 1020 cm^{-1} are due to antisymmetric stretching of the carboxyl group (COO-) in polygalacturonic acid and vibrations of the pectin backbone (C2-C3, C2-O2, C1-O1), respectively, implying that blackberry cell walls are acidic polysaccharides rich in pectin (Szymanska-Chargot & Zdunek, 2013). The absorption

peaks at 1740 cm^{-1} and 1440 cm^{-1} are correlated with the stretching vibrations of alkyl esters (C=O) and methyl esters (-OCH_3) from pectin, indicating the existence of some esterified uronic acids in cell wall polysaccharides (Canteri, Renard, Le Bourvellec, & Sylvie., 2019). Moreover, the weak absorption peak at 1370 cm^{-1} represents the bending vibrations of the C-H and CH_2 groups. The peak with weak absorption at 1150 cm^{-1} is due to glycosidic bond (O-C-O) vibrations. These groups are mainly derived from cellulose and hemicellulose (Szymanska-Chargot, Chylinska, Kruk, & Zdunek, 2015). Overall, the similar spectra of all the samples indicate there might be no new covalent bonds formed on the surface of cell wall components from blackberries under drying with and without sonication.

3.1.3. Water binding capacity, specific surface area and porous attributes of blackberry cell walls

The water binding capacity, specific surface area, total pore volume, and mean pore diameter of blackberry cell wall preparations at different drying stages are shown in Table 1. The water binding capacity of fresh blackberry cell wall components was 8.92±2.14 g/g, close to that of apple cell walls (7.8 g/g) and kiwifruit cell walls (5.6 g/g) (Liu, Renard, Bureau, & Le Bourvellec, 2021). Contact ultrasound-assisted drying led to the significant decline of the water binding capacity of blackberry cell walls. Also, the cell wall water binding capacity for the AD-US dried samples for 1 h was the lowest among all the samples (6.10±0.21 g/g). This could be because ultrasound can accelerate the disruption of the

ordered structure of blackberry cell walls. Thus the water molecules are not easily encapsulated by the microfibrous network (Li, Li, Xi, & Hua, 2002).

Regarding the porous attributes, drying with and without ultrasound did not affect the total pore volume and mean pore diameter of the cell wall components. It is deduced that cavitation generated inside the cells was insufficient to affect the interior cell structure during drying. Instead, compared with the cell walls of freshly prepared blackberry, the cell wall specific surface area of all the cell wall components prepared from dried samples decreased to varying degrees, owing to cell wall shrinkage during dehydration, as shown in Fig. 1. The cell wall specific surface areas decreased from 5.14 m^2/g to 1.47 m^2/g at the end of air drying alone, and 1.33 m^2/g at the end of contact ultrasound drying. These results of water binding capacity and specific surface area are consistent with the surface morphology of cell wall preparations described in Section 3.1.1.

3.2. Changes in the pectin content of blackberry cell walls and hardness and pectinase of blackberry fruits under drying

3.2.1. Contents of pectin fractions

The changes in the pectin composition from cell wall preparations may occur in the F&V drying. The WSP polymers are loosely bound to the cell wall by non-covalent and non-ionic bonds (Deng et al., 2018). In contrast, covalent and ionic bonds link PP to cell wall polysaccharides (Zhou et al., 2021). The WSP and PP contents in the cell walls from raw and dried blackberries are shown in Fig. 2a. Fresh blackberry cell walls were rich in

PP (106.55±12.18 mg/g AIR), accounting for about 79.7% of total pectin content, similar to the pectin composition of blackberry reported by Zhang, Xiong, Yang, and Wu (2019). There are significant changes in the content of each pectin fraction at the end of drying. The WSP contents in the samples dried by AD for 8 h and AD-US for 1 h were 22.7% and 45.3% higher than the fresh blackberry. Instead, the PP content decreased from 106.55±12.18 to 87.03±6.80 mg/g AIR after 8 h AD treatment and 76.91±7.95 mg /g AIR after 1 h AD-US treatment. These results agree with the variations of carrot (Lo, Grun, Taylor, Kramer, & Fernando, 2002) and hawthorn (Zhou et al., 2021) pectin composition under high-temperature treatments. The increment of WSP could be attributed to the thermos-solubilisation and β-eliminative depolymerisation of cell wall polysaccharides during thermal processing (Imaizumi et al., 2017), while the reduction of PP potentially results from their own enzymatic and non-enzymatic degradation, and the conversion of insoluble pectin fractions to WSP due to the severing of chemical bonds (Fan et al., 2018; Imaizumi et al., 2017).

It is noted that the WSP content in the blackberries treated by AD-US for 1 h (39.48±2.42 mg/g AIR) is significantly higher than the samples treated by AD for 8 h (33.35±1.03 mg/g AIR) (p <0.05) (Fig. 2a). Instead, the samples dried by AD-US for 1 h (76.91±7.95 mg/g AIR) possess less PP than the counterparts dried by AD for 8 h (87.03±6.80 mg/g AIR). These comparisons imply that the mechanical forces of contact sonication may strengthen the degradation of polygalacturonic acid polymer, leading to the accumulation of WSP at the end of air drying (Yan et al., 2021). Also, Zhang et al. (2013)

reported that ultrasound cavitation (20 kHz, 181 W/cm^2, 60 min, 25 ºC) lowered the apple pectin molar mass, causing a reduced polydispersity index from 2.20 to 1.89.

3.2.2. Pectinase activities

Pectinases are responsible for catalysing the decomposition of plant pectin, including polygalacturonase, pectinesterase and pectate lyase (John, Kaimal, Smith, Rahman, & Chellam, 2020). The pectinase activity in blackberry under drying is illustrated in Fig. 2b. The pectinase activity of the fresh sample was 1846.37±98.80 U/g DM, and its activity declined significantly to 1173.04±89.98 U/g DM after AD for 8 h and 1374.51±126.83 U/g DM after AD-US for 1 h. Similarly, Ortega, de Diego, Perez-Mateos, and Busto (2004) reported that thermal treatment at 70 °C in fruit juice clarification declined the activities of commercial polygalacturonase preparations by 22-57%. Furthermore, no significant differences in blackberry pectinase activity were observed between sonicated and non-sonicated samples, neither after drying for 0.5 h nor at the end of drying, indicating the simultaneous ultrasonic enhancement of heat and mass transfer during drying had an ignorable influence on pectinase. Some controversial observations about the ultrasonic enhancement and inactivation of enzymes during liquid-food processing have been reported (Dalagnol, Silveira, da Silva, Manfroi, & Rodrigues, 2017; Suo, Zhou, Su, & Hu, 2022). Also, Zhu et al. (2022) reported that airborne sonication had no obvious influences on apple PPO activity during air drying. Thus, it is assumed that the propagation of

ultrasound waves in a solid matrix has a weaker influence on food-derived enzymes than on liquids.

3.2.3. Hardness

Changes in pectin composition are partly responsible for the texture of fruits and vegetables (Moens, Huang, Van Loey, & Hendrickx, 2021). The blackberry hardness values before and after drying are plotted in Fig. 2c. Significant differences in hardness are observed between the fresh and dried blackberries (p <0.05). Water loss can result in the gradual hardening of fruits, including blackberries. At the same water content level, the samples dried by air alone were harder than ultrasound-dried samples. This result indicates that contact ultrasound can alleviate surface hardening by shortening the drying time (Xu et al., 2022).

3.2.4. Correlations among pectin and water contents, pectinase activity and hardness under drying with and without ultrasound

Since pectin and water contents, pectinase activity and fruit hardness are highly interlinked, the Person's correlation coefficients were then calculated among these data (Fig. 3). It can be observed that the correlations among the involved attributes differ with the drying methods. No significant correlations between the cell wall WSP content and other attributes are observed under air drying alone. In contrast, the cell wall WSP content is positively correlated with drying time and negatively correlated with water content

significantly under drying with contact sonication (p <0.05). It suggests that the intensification of water movement by contact sonication positively influences the accumulation of cell wall WSP in blackberries. Under both air drying treatments, pectinase is positively correlated with cell wall PP with significance (p <0.05) and negatively correlated with cell wall WSP. Thus, the decline of pectinase activity does not alleviate the loss of cell wall PP.

Moreover, the correlations between hardness and the pectin fractions are weaker than between hardness and time, regardless of the application of ultrasound (Fig. 3). Taking air drying alone, for example, the absolute correlation coefficients for hardness-WSP (0.651, p ≥0.05) and Hardness-PP (0.498, p ≥0.05) are lower than the values for hardness-time (0.966, p <0.05). Thus, although the two pectin fractions could affect the texture of fresh fruit, the drying time prolongs more to the hardening of blackberries. On the other hand, the correlation between cell wall WSP and hardness under contact sonication is significant (r=0.727, p <0.05), whereas the WSP-hardness correlation is insignificant (r=0.651, p ≥0.05) under air drying alone. However, the exact influence of cell wall polysaccharides evaluation on the fruit texture throughout drying still needs to be examined.

3.3. Characterisation of the structural morphology of cell wall pectins from blackberries under different drying treatments

The nanostructures of WSP and PP from the cell walls of blackberries with different treatments were observed by atomic force microscopy (AFM). The representative plane

AFM images of WSP and PP at different drying stages are presented in Fig. 4, respectively. From Fig. 4a, the WSP from fresh blackberry cell walls mainly shows long linear chains, with a small number of long branches and without any branches, as well as a few aggregates. This nanostructure is similar to fresh citrus's water soluble pectin structures (Zhang, Zhang, Liu, Ding, & Ye, 2015) and strawberry cell walls (Pose, Kirby, Mercado, Morris, & Quesada, 2012). A long linear chain noted as homogalacturonan is the main component of pectin (Zhou et al., 2021), and the aggregate structure is usually linked to intermolecular interactions (Pose et al., 2012). After AD for 0.5 h and AD-US for 0.5 h, the cell wall WSP exhibited short straight chains and aggregate structures, which might be attributed to heat-induced pectin degradation with long straight chains (Deng et al., 2005). Probably owing to the destructive effect of ultrasound on the biomacromolecules like polysaccharides and protein (Yan et al., 2021), the long-chain structures were not observed in the samples treated by AD-US for 0.5 h. At the end of drying with and without sonication (AD for 8 h and AD-US for 1 h), the WSP was mainly featured by aggregates and small particles without the chain structure.

Regarding the cell wall PP, their structural morphology in blackberries before and after drying is mainly displayed in the form of aggregates and small particles (Fig. 4b). It is deduced that PP is less liable to be affected by dehydration than WSP. Furthermore, it is worth noting that the size of the aggregates in both WSP and PP fractions from sonicated blackberries appeared to be larger than from blackberries dried by air alone. This phenomenon could be because ultrasound may promote the degradation of pectin

molecules, and the small pectin particles could aggregate more easily under ultrasound vibration (Zhang et al., 2015).

3.4. Monosaccharide composition of cell wall pectin from blackberries dried by different treatments

Galacturonic acids in the backbone of pectin and the neutral sugars of the pectin side chains in the blackberry cell wall preparations at different drying stages were then analysed (Fig. 5). The representative chromatographic plots for the monosaccharides of pectin in blackberry cell walls are shown in Supplementary Fig. 3. In summary, nine monosaccharide compounds were identified in blackberry pectin, including mannose, rhamnose, glucuronic acid, galacturonic acid, glucose, galactose, xylose, arabinose and fucose. In the fresh blackberries, xylose (167.67±24.70 mg/g AIR), arabinose (108.37±10.65 mg/g AIR) and galacturonic acid (91.33±10.21 mg/g AIR) were the three abundant monosaccharides (Fig. 5a). Herein, the observed high content of xylose is mainly attributed to the hydrolysis of pectin. Also, it is possible that a small amount of water-soluble hemicellulose may be hydrolyzed by acid during the extraction of protopectin as described in Section 2.4.1, leading to an over-estimation problem of xylose (Ciriminna, Fidalgo, Scurria, Ilharco, & Pagliaro, 2022). However, due to the relatively low acidic concentration of the solvent used for extraction, it is tentatively asserted that the observed xylose data can represent its content in blackberry pectin (Tsouko, Maina, Ladakis, Kookos, & Koutinas, 2020). The detected arabinose could be mainly derived from the hydrolysate

of the branch linked to RG-I fractions. The analysed level of galacturonic acid can be assigned primarily to the Homogalacturonan (HG) backbone (Sila et al., 2009).

As illustrated in Fig. 5a, the changes in pectin mannose, rhamnose, glucuronic acid and xylose contents during all the dehydration treatments are negligible. Instead, galacturonic acid, glucose, galactose, arabinose and fucose decreased to varying degrees under AD and AD-US. For example, the galacturonic acid contents in the samples processed by AD 8 h and AD-US 1 h were 15.7% and 22.4% lower than in the fresh samples (91.33±10.21 mg/g AIR), respectively. At temperatures above 60 °C, the β-eliminative cleavage and solubilisation of pectins can be triggered, leading to the decline of several monosaccharides in pectin (Lo et al., 2002). On the other hand, no obvious effect of contact sonication on the pectin monosaccharides can be observed except for arabinose. Specifically, after drying for 0.5 h, the arabinose content in cell wall preparations from the AD-US sample is 15.4% lower than the AD sample. Also, at the end of drying, the AD 8 h sample contains 22.2% more arabinose than the AD-US 1 h sample. Generally, arabinose is in the form of furanose, and the bonds involving furanose sugars are liable to be degraded (Liu, Renard, Rolland-Sabate, et al., 2021). It is proposed that ultrasound vibration emitted to the blackberry surface may promote the hydrolysis of glycosidic bonds between arabinoses by mechanical torque, thus accelerating the loss of arabinose during air drying (Larsen, van der Weem, Caspers-Weiffenbach, Schieber, & Weber, 2021; Renard, Crepeau, & Thibault, 1995).

Arabinose and galactose are important components of the RG-I backbone's side chains

attached to rhamnose residues. The (Ara+Gal)/Rha ratio is a representative characteristic for branching RG-I (Sila et al., 2009). Also, the ratios of Gal A/(Rha+Ara+Gal) and Gal A/Rha represent the linearity of pectin, and the contribution of homogalacturonans to pectin, respectively (Liu, Renard, Rolland-Sabate, et al., 2021). The ratios of Gal A/(Rha+Ara+Gal), Gal A/Rha, Ara/Gal and (Ara+Gal)/Rha, expressed in the form of mol%, are illustrated in Fig. 5b. The values of Gal A/(Rha+Ara+Gal), Gal A/Rha, Ara/Gal and (Ara+Gal)/Rha for fresh blackberries are 0.37±0.03, 1.97±0.10, 2.24±0.21 and 4.40±0.12, respectively. Compared with the neutral sugar composition in the cell wall pectin of apple, beet, carrot and kiwi (Liu, Renard, Rolland-Sabate, et al., 2021; Lo et al., 2002), it is tentatively deduced that blackberry cell wall pectin is a hetero-polysaccharide with low linearity and low contribution of homogalacturonic acid to pectin, followed by high RG-I branching and a high proportion of arabinose to galactose. Moreover, all drying treatments did not significantly affect the contribution of homogalacturonans to pectin and the linearity of pectin ($p \geq 0.05$). At the end of drying, both the ratios of (Ara+Gal)/Rha (3.81±0.10) and Ara/Gal (1.75±0.22) in the sonicated samples were significantly lower than the ratios in the samples dried by hot air alone (4.03±0.21 for (Ara+Gal)/Rha and 2.11±0.12 for Ara/Gal) ($p < 0.05$). This phenomenon suggests that dehydration reduced the branching degree of RG-I fractions by promoting arabinose degradation, and the in-process sonication further stimulated this reaction. Although ultrasound cavitation has been proven to induce the degradation of RG-I branches and consequently decline pectin molecular weight in the liquid medium (Ma et al., 2016; Munoz-Almagro, Montilla, Moreno, &

Villamiel, 2017), our results first demonstrate that the transmission of ultrasound waves in the solid medium can also lower the branching of cell wall pectin to some extent.

3.5. Adsorption capacity of phenolics by cell wall components of blackberry dried using different methods

To investigate the ability of blackberry cell walls to bind soluble phenolics under drying, the cell wall materials were first extracted from blackberries dried using different methods. Then, the adsorption capacities of phenolics by these cell wall materials *in vitro* were then analysed (Fig. 6). Herein, one flavanol (catechin) and one phenolic acid (phloretic acid) were selected as the representative adsorbates since both phenolics are rich in the studied blackberry cultivar and significantly declined under the indicated drying methods (Gong et al., 2021).

It can be noted that the adsorption is rapidly initiated, as indicated by the significant amount of adsorbed phenolics observed after 2.5 min of their contact with the cell wall components. All the adsorptions reached a plateau after incubation for about 30 min. These results agree with the adsorption behaviour between fruit cell walls and soluble phenolics reported by Liu, Martinez-Sanz, Lopez-Sanchez, Gilbert, and Gidley (2017) and Padayachee et al. (2012), verifying that the cell walls of both fresh and dehydrated blackberries can connect with soluble phenolics. Generally, the plant cell wall polysaccharides distribute some hydroxyl, hydrophobic and charged groups, which can

bind phenolics released from vacuole through hydrogen bonding, hydrophobic interactions or ionic interactions (Liu et al., 2020).

However, the adsorption capacities of blackberry cell walls can be markedly influenced by the blackberry drying treatments. In both cases of drying with and without contact sonication, the ability of blackberry cell walls to bind the selected phenolics was reduced to varying degrees compared with the cell walls from fresh blackberries (Fig. 6). For example, in the case of catechin, the adsorbed amount at equilibrium by the cell walls of fresh samples is 35.34±0.67 μg/mg AIR. In contrast, the equilibrium adsorption capacities by the cell walls of the samples dried by AD 0.5 h, AD 8 h, AD-US 0.5 h, and AD-US 1 h decreased to 33.04±1.04, 25.06±2.58, 29.73±2.03, and 16.66±3.99 μg/mg AIR, respectively. Similar results can be observed in the adsorption kinetic curves of phloretic acid. These findings are consistent with the study of Liu et al. (2019), where the capacity of apple cell walls to adsorb chlorogenic acid decreased from 141.23 μg/mg to 132.03 and 68.52 μg/mg after air drying and freeze-drying, respectively. As shown in Fig. 1 and Table 1, drying with and without ultrasound intensification markedly lowered the specific surface area of cell wall components, potentially accounting for the weakened ability to bind phenolics. Besides, it is assumed that the chemical bonds of the cell walls responsible for adsorbing phenolics, i.e. hydroxyl groups, may also be affected by dehydration, thus weakening the hydrogen bonding (Liu et al., 2017).

Notably, for phloretic acid and catechin, the adsorption capacity of cell walls from the sonicated samples is lower than without sonication. The adsorption kinetic curves of

blackberry cell walls from the samples dried by AD 0.5 h are always located above the curves of the cell wall components from the samples dried by AD-US 0.5 h. Also, at the end of drying, the maximum adsorption capacity of cell walls from the sonicated blackberries for catechin and phloretic acid is 33.5% and 21.8% lower than the counterparts from the samples processed by air drying alone, respectively. These observations can be explained as follows.

On the one hand, the relatively low content of PP in the cell walls of sonicated blackberries (Fig. 2a) is partly responsible for the low phenolic adsorption. Much literature demonstrates that insoluble pectin plays an important role in the interactions between phenolics and cell walls (Liu et al., 2020; Mamet, Ge, Zhang, & Li, 2018). Accordingly, the higher loss of PP under ultrasound drying probably contributes to a reduction in the adsorption of phenolics on cell wall polysaccharides due to the decline of binding sites (Bindon, Bacic, & Kennedy, 2012). On the other hand, the interactions between plant cell wall polysaccharides and soluble phenolics can be partly mediated by their physical properties. As shown in Table 1, ultrasound treatment further lowered the specific surface area and water binding capacity. Thus, the access of small molecules like phenolics into the cell walls can be restricted, causing a decrease in the phenolic adsorption amounts (Le Bourvellec, Watrelot, Ginies, Imberty, & Renard, 2012; Liu, Zheng, Wang, Jiang, & Li, 2010). Besides, pectin polysaccharide sidechains can modulate the interactions depending on their conformational flexibility (Watrelot, Le Bourvellec, Imberty, & Renard, 2013). According to Watrelot, Le Bourvellec, Imberty, and Renard (2014), the high branching of

RG-I pectin limits the interactions with phenolics due to low steric mobility. In the current study, contact sonication facilitated the degradation reactions of arabinose and further promoted the reduction in the degree of RG-I branching, as shown in Fig. 5. Instead, the binding capacity of blackberry cell walls from sonicated samples weakened. The detailed influence of ultrasonic modification of plant cell wall polysaccharide composition on their binding capacity with phenolics deserves a deep investigation in the future.

It is also observed in Fig. 6 that the amount of catechin adsorbed by the cell walls is higher than phloretic acid, despite the drying method. Taking the cell walls from the blackberries dried by AD-US for 1 h, for example, the maximum adsorption capacity for catechin (16.66±3.99 μg/mg AIR) is 4.7 times higher than for phloretic acid (3.51±0.15 μg/mg AIR). Many studies also report that plant cell walls to have stronger binding abilities with flavonoids than phenolic acid due to the involvement of more hydroxyl groups in flavonoids (Liu et al., 2019; Padayachee et al., 2012).

3.6. Thermal stabilities of phenolics adsorbed by blackberry cell walls

The thermal stabilities of catechin and phloretic acid adsorbed by the cell walls from blackberries dried using different methods were analysed (Fig. 7). As can be seen, both the dissolved phenolics and phenolics adsorbed by blackberry cell walls are lost to varying degrees after exposing to hot air at 65 ºC for 30 min. Specifically, 22.7±1.1% of catechin and 35.7±4.3% of phloretic acid dissolved in the citric acid-phosphate buffer have been lost after the thermal treatment, and the losses of catechin and phloretic acid bound with

the cell wall components from fresh blackberries are 27.3±2.1% and 24.2±4.1%, respectively. The losses of catechin and phloretic acid attached to the cell walls of dried blackberries alleviate. For the thermal treatments of cell wall components extracted from dehydrated blackberries, the losses of catechin and phloretic acid are in the ranges of 19.3±1.8% - 20.7±1.1% and 18.1±1.8% - 19.7±4.3%, respectively. These results imply that phloretic acid and catechin adsorption on the dried blackberry cell walls can better protect against thermal degradation. Moreover, there are no significant differences in the loss of each phenolic compound among these four drying treatments. Nevertheless, the reasons for the difference in these phenolic losses between the fresh blackberry cell walls and cell walls from dried blackberries are still unknown.

Combining Fig. 6 and 7, it can be confirmed that the adsorption of soluble phenolics by the blackberry cell walls can enhance the thermal stability of phenolics to a certain extent, and the overall protections attenuate with drying due to the decline of adsorption ability of cell walls. Our previous study about ultrasound drying of blackberries confirmed that ultrasound promoted the retention of some soluble phenolics during drying, including phloretic acid and catechin (Gong et al., 2021). Considering the previous and current study outcomes, a key conclusion is that the shortening of the time exposed to hot air by ultrasound is the major contributor to the increment of retention of soluble phenolics rather than the protection provided by the interactions between soluble phenolics and cell wall components.

3.7. Proposed mechanism for the modifications and interactions of the blackberry cell walls with phenolics under ultrasound-intensified air drying

Considering the above-observed results, a schematic illustration of the effect of ultrasound-intensified air drying on the blackberry cell wall modification and the interactions with phenolics is shown in Fig. 8. Generally, the modifications of blackberry cell walls, including the surface structure, physical properties, and chemical composition (especially pectin) may occur in the F&V drying, which in turn affect the cell walls binding capacity with soluble phenolics (Liu et al., 2019). In the current study, compared with AD, the AD-US treatment promotes the shrinkage of cell wall components and further lowers their specific surface area and water binding capacity. For the cell wall pectin fractions, ultrasound vibration emitted to the blackberry surface further increases the WSP content. It decreases the PP content and promotes the aggregation of the short pectin chains. Also, the loss of arabinose and reduction in the branching degree of RG-I is promoted by ultrasound. Normally, plant cell walls with high specific surface area, high water binding capacity and pectin content favour binding more soluble phenolics (Liu, Renard, Bureau, et al., 2021). In contrast, the highly branched pectins have limited interactions with phenolics, probably due to steric hindrance (Watrelot et al., 2014). Consequently, the adsorption capacity of cell walls from the sonicated blackberries is lower than the samples without sonication, regardless of phloretic acid or catechin.

Apart from enzymatic and non-enzymatic degradation and potential synthesis, the behaviour of plant cell walls to adsorb soluble phenolics may affect the stability of soluble

phenolics in various food processes (Loo et al., 2020). From our data, it can be deduced that the attachment of phloretic acid or catechin on the dried blackberry cell walls can provide a better protective effect against thermal degradation. However, the overall protections attenuate with drying due to the decline in the adsorption ability of cell walls. Since the ultrasound-dried blackberries possess higher amounts of soluble phenolics, as shown by Gong et al. (2021), it is confirmed that the protection provided by the interactions between soluble phenolics and cell wall components has a weak contribution to the high retention of soluble phenolics under ultrasound-assisted air drying. Instead, the saving of the time exposed to hot air by ultrasound is the major contributor to the enhanced retention of soluble phenolics.

4. Conclusions

This study demonstrates that the in-process contact sonication during air drying of blackberries exerts a profound influence on the physicochemical properties of the cell walls. Ultrasound reduced water binding capacity, specific surface area and PP content and increased the WSP content. The ultrasound-intensified drying also affected the pectin structure, promoting the aggregation of short chains of pectin and decreasing the branching degree of RG-I pectin. These observed modifications under the ultrasonic field could significantly weaken the ability of blackberry cell walls to adsorb soluble phenolics (i.e. phloretic acid, catechin). Instead, phloretic acid and catechin adsorbed on the cell walls of dried blackberries were more thermal-stable than those attached to the fresh blackberry cell

walls. Due to the declined ability of the cell walls to bind soluble phenolics, it is believed that the protective effect against the thermal degradation of soluble phenolics provided by the blackberry cell walls weakened with drying. Besides, the higher retention of soluble phenolics under ultrasound-assisted drying is mainly due to the shortening exposure time to hot air rather than the protection of blackberry cell walls. However, investigations on the specific mechanism of the interactions between dried fruit cell walls and phenolics have not been attempted in-depth. More analytical studies are needed to explore the exact interactions between phenolics and fruit cell walls under drying processes.

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Table 1

Water binding capacity, specific surface area and porous attributes of cell walls from blackberry after different drying treatments

Treatments	Water binding capacity （g/g）	Specific surface area (m^2/g)	Total pore volume (cm^3/g)	Mean pore diameter (nm)
Fresh	8.92 ± 2.14^{a}	5.14	0.02	4.31
AD 0.5 h	8.69 ± 1.12^{a}	3.08	0.01	5.95
AD 8 h	7.76 ± 0.49^{ab}	1.47	0.01	4.42
AD-US 0.5 h	7.98 ± 0.85^{ab}	2.28	0.01	4.91
AD-US 1 h	6.10 ± 0.21^{b}	1.33	0.01	6.55

Note: Values followed by different letters in the second column indicate significant differences ($p < 0.05$). AD: air drying; AD-US: ultrasound-assisted with air drying. The time followed by the treatment means the sampling time.

Figure captions

Fig. 1 SEM images of blackberry cell walls with different drying treatments. Note: AD: air drying; AD-US: ultrasound-assisted with air drying. The time followed by the treatment means the sampling time.

Fig. 2 Changes in the blackberry cell wall WSP and PP contents (a), pectinase activity (b) and hardness (c) during drying. Note: AD: air drying; AD-US: ultrasound-assisted with air drying. The time followed above the treatment means the sampling time. Different capital (or lowercase) letters above each bar indicate significant differences among all the treatments (p <0.05).

Fig. 3 Correlations among pectin and water contents, pectinase activity, hardness and soluble phenolics under drying with and without sonication. Note: (a): Data from air drying without sonication (b): Data from contact ultrasound-assisted air drying. **: significant correlation (p <0.01)

Fig. 4 AFM images of WSP (a) and PP (b) in blackberry cell walls with different drying treatments. Note: Linear strands (Ls), short straight chains (Ss), small particles (Sp) and aggregates (Ag) structures. AD: air drying; AD-US: ultrasound assisted with air drying. The time followed by the treatment means the sampling time.

Fig. 5 Monosaccharide composition of cell wall pectin in blackberries dried using different treatments. Note: (a): Monosaccharide contents are calculated from individual sugar contents based on dry weights. (b): Ratios are calculated using the yields of monosaccharides expressed in mol%. Man: mannose, Rha: rhamnose, Glu A: glucuronic

acid, Gal A: galacturonic acid, Glu: glucose, Gal: galactose, Xyl: xylose, Ara: arabinose, Fuc: fucose. AD: air drying; AD-US: ultrasound assisted with air drying. The time followed by the treatment means the sampling time. Different letters above each monosaccharide indicate significant differences among the treatments (p <0.05).

Fig. 6 Adsorption kinetic curves of phenolics by the cell wall components of blackberry dried using different methods. Note: (a): adsorption of catechin; (b): adsorption of phloretic acid. AD 0.5 h and AD 8 h: air drying of blackberry for 0.5 h and 8 h, respectively; AD-US 0.5 h and AD-US 1 h: ultrasound assisted with air drying of blackberry for 0.5 h and 1 h, respectively.

Fig. 7 Thermal stability analysis of phenolics in the adsorbed state. Note: Free: dissolved phenolics in the unabsorbed state; Fresh: phenolics adsorbed by fresh cell walls; AD 0.5 h and AD 8 h represent the phenolics adsorbed by the cell walls of blackberries from air drying for 0.5 h and 8 h, respectively. AD-US 0.5 h and AD-US 1 h represent the phenolics adsorbed by the cell walls of blackberries from ultrasound combined with air drying for 0.5 h and 1 h, respectively. Different letters above each phenolic indicate significant differences among the treatments (p <0.05).

Fig. 8 The schematic illustrates the modifications and interactions of the blackberry cell walls with phenolics under ultrasound-intensified air drying.

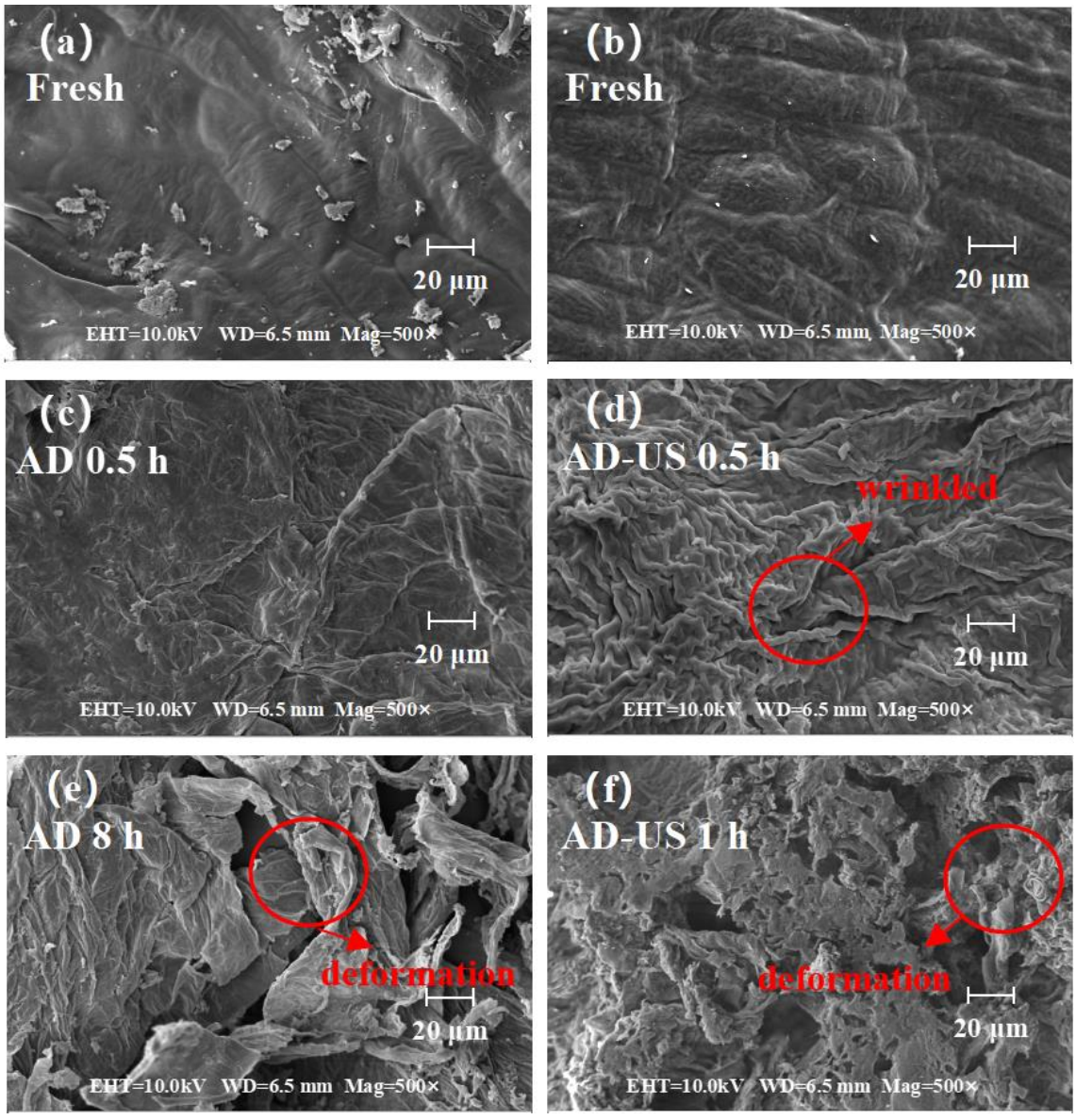
(a)
Fresh
20 μm
EHT=10.0kV WD=6.5 mm Mag=500×
(b)
Fresh
20 μm
EHT=10.0kV WD=6.5 mm Mag=500×
(c)
AD 0.5 h
20 μm
EHT=10.0kV WD=6.5 mm Mag=500×
(d)
AD-US 0.5 h
wrinkled
20 μm
EHT=10.0kV WD=6.5 mm Mag=500×
(e)
AD 8 h
deformation
20 μm
EHT=10.0kV WD=6.5 mm Mag=500×
(f)
AD-US 1 h
deformation
20 μm
EHT=10.0kV WD=6.5 mm Mag=500×

Fig. 1

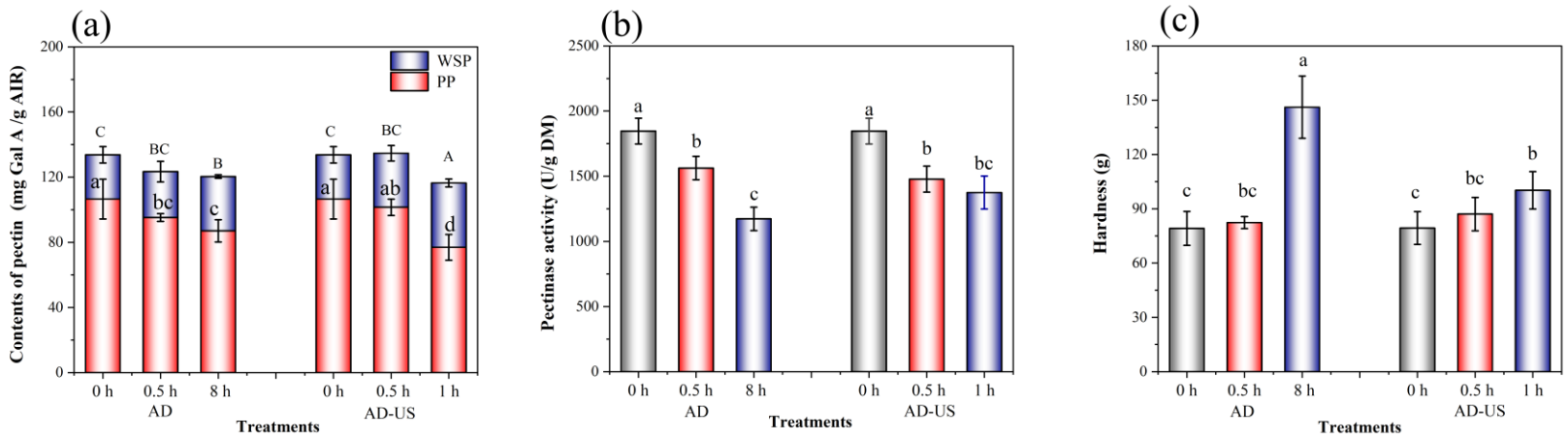
(a)
Contents of pectin (mg Gal A /g AIR)
WSP
PP
C
BC
B
C
BC
A
a
bc
c
a
ab
d
0 h
0.5 h
8 h
0 h
0.5 h
1 h
AD
AD-US
Treatments
(b)
Pectinase activity (U/g DM)
a
b
c
a
b
bc
Treatments
(c)
Hardness (g)
c
bc
a
c
bc
b
Treatments

Fig. 2

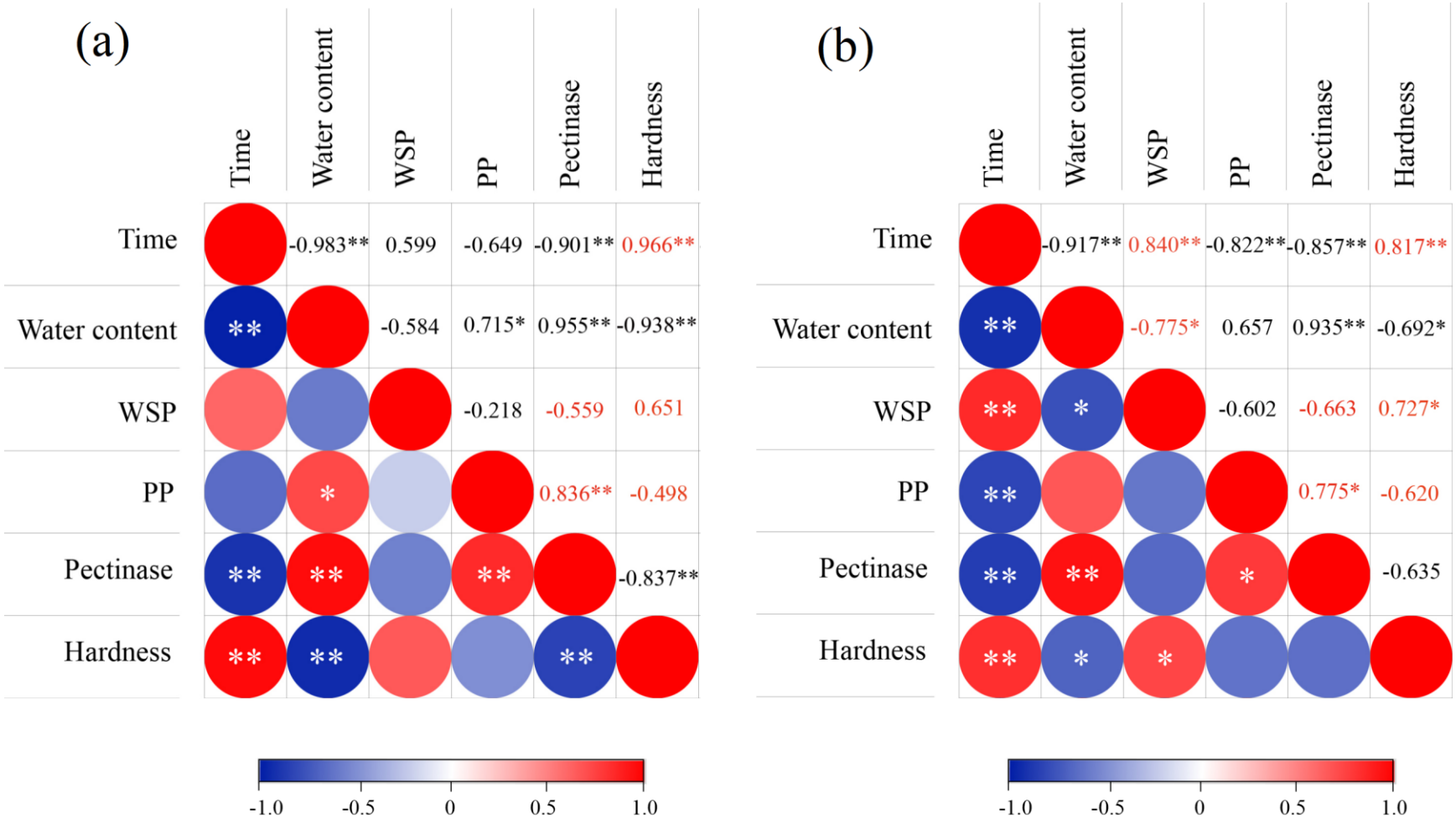
(a)
Time
Water content
WSP
PP
Pectinase
Hardness
Time -0.983** 0.599 -0.649 -0.901** 0.966**
Water content ** -0.584 0.715* 0.955** -0.938**
WSP * -0.218 -0.559 0.651
PP * 0.836** -0.498
Pectinase ** ** ** -0.837**
Hardness ** ** ** **
-1.0 -0.5 0 0.5 1.0
(b)
Time
Water content
WSP
PP
Pectinase
Hardness
Time -0.917** 0.840** -0.822** -0.857** 0.817**
Water content ** -0.775* 0.657 0.935** -0.692*
WSP ** * -0.602 -0.663 0.727*
PP ** 0.775* -0.620
Pectinase ** ** * -0.635
Hardness ** * *
-1.0 -0.5 0 0.5 1.0

Fig. 3

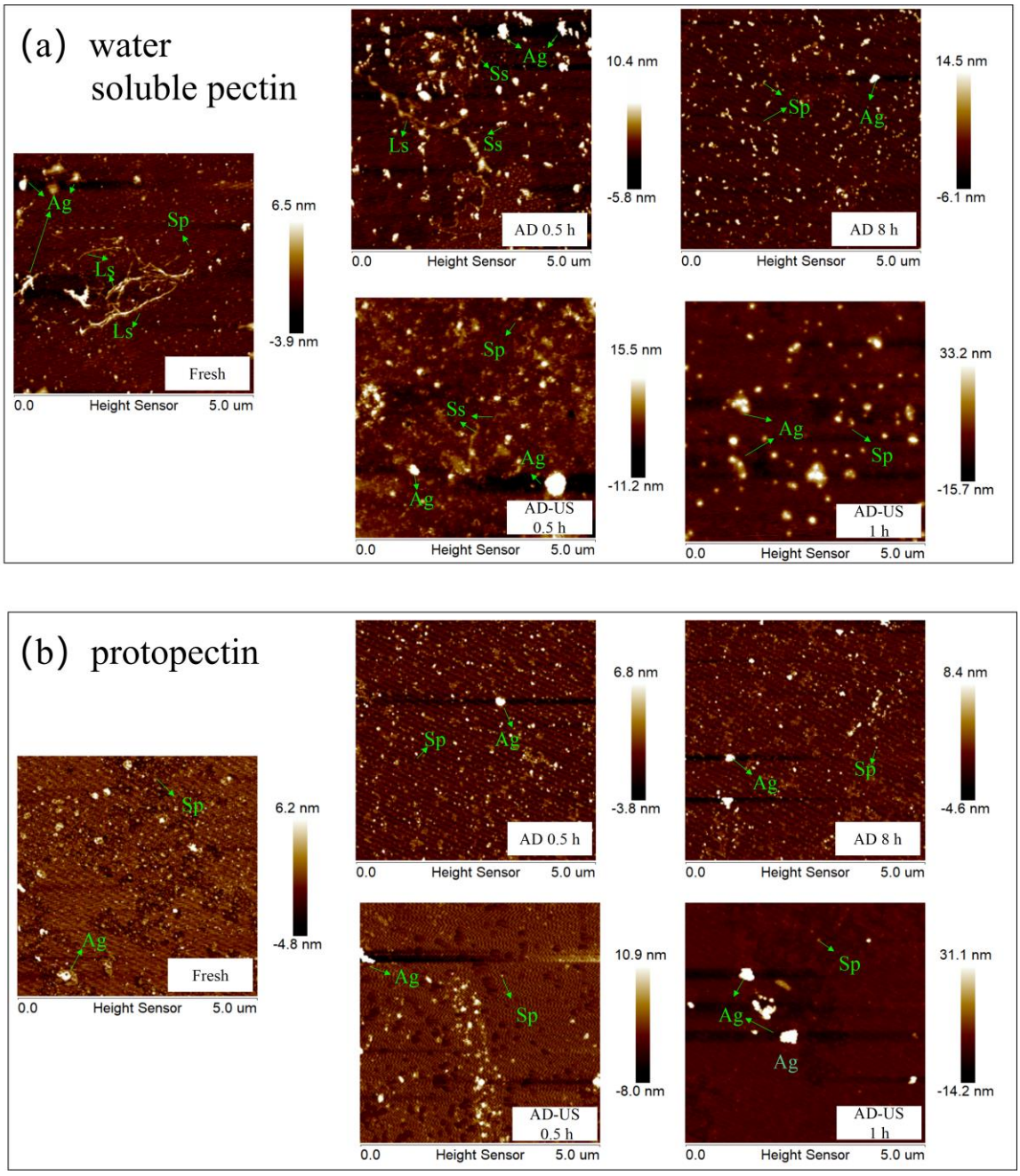
(a) water soluble pectin
Ag
Sp
Ls
Ls
Fresh
6.5 nm
-3.9 nm
0.0 Height Sensor 5.0 um
Ag
Ss
Ls
Ss
AD 0.5 h
10.4 nm
-5.8 nm
0.0 Height Sensor 5.0 um
Sp
Ag
AD 8 h
14.5 nm
-6.1 nm
0.0 Height Sensor 5.0 um
Sp
Ss
Ag
Ag
AD-US 0.5 h
15.5 nm
-11.2 nm
0.0 Height Sensor 5.0 um
Ag
Sp
AD-US 1 h
33.2 nm
-15.7 nm
0.0 Height Sensor 5.0 um
(b) protopectin
Sp
Ag
Fresh
6.2 nm
-4.8 nm
0.0 Height Sensor 5.0 um
Sp
Ag
AD 0.5 h
6.8 nm
-3.8 nm
0.0 Height Sensor 5.0 um
Ag
Sp
AD 8 h
8.4 nm
-4.6 nm
0.0 Height Sensor 5.0 um
Ag
Sp
AD-US 0.5 h
10.9 nm
-8.0 nm
0.0 Height Sensor 5.0 um
Sp
Ag
Ag
AD-US 1 h
31.1 nm
-14.2 nm
0.0 Height Sensor 5.0 um

Fig. 4

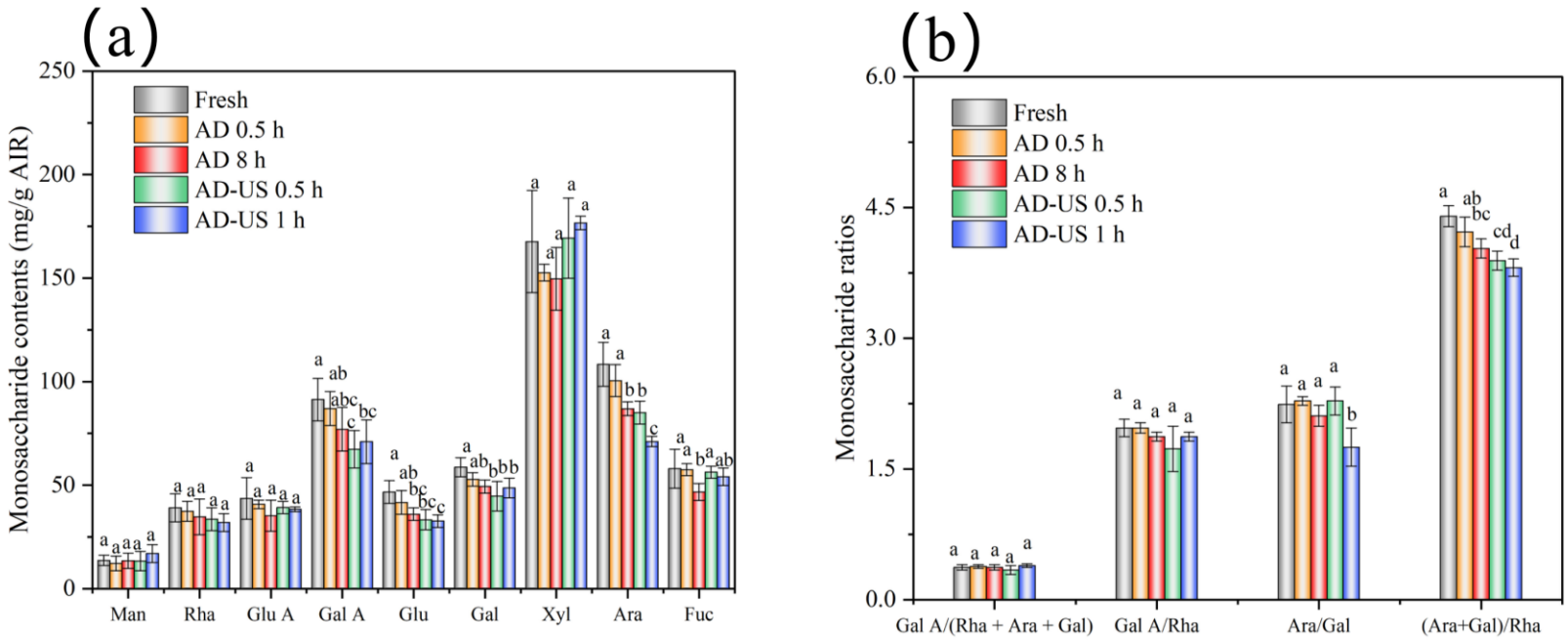
(a)
Monosaccharide contents (mg/g AIR)
Fresh
AD 0.5 h
AD 8 h
AD-US 0.5 h
AD-US 1 h
Man
Rha
Glu A
Gal A
Glu
Gal
Xyl
Ara
Fuc
(b)
Monosaccharide ratios
Gal A/(Rha + Ara + Gal)
Gal A/Rha
Ara/Gal
(Ara+Gal)/Rha

Fig. 5

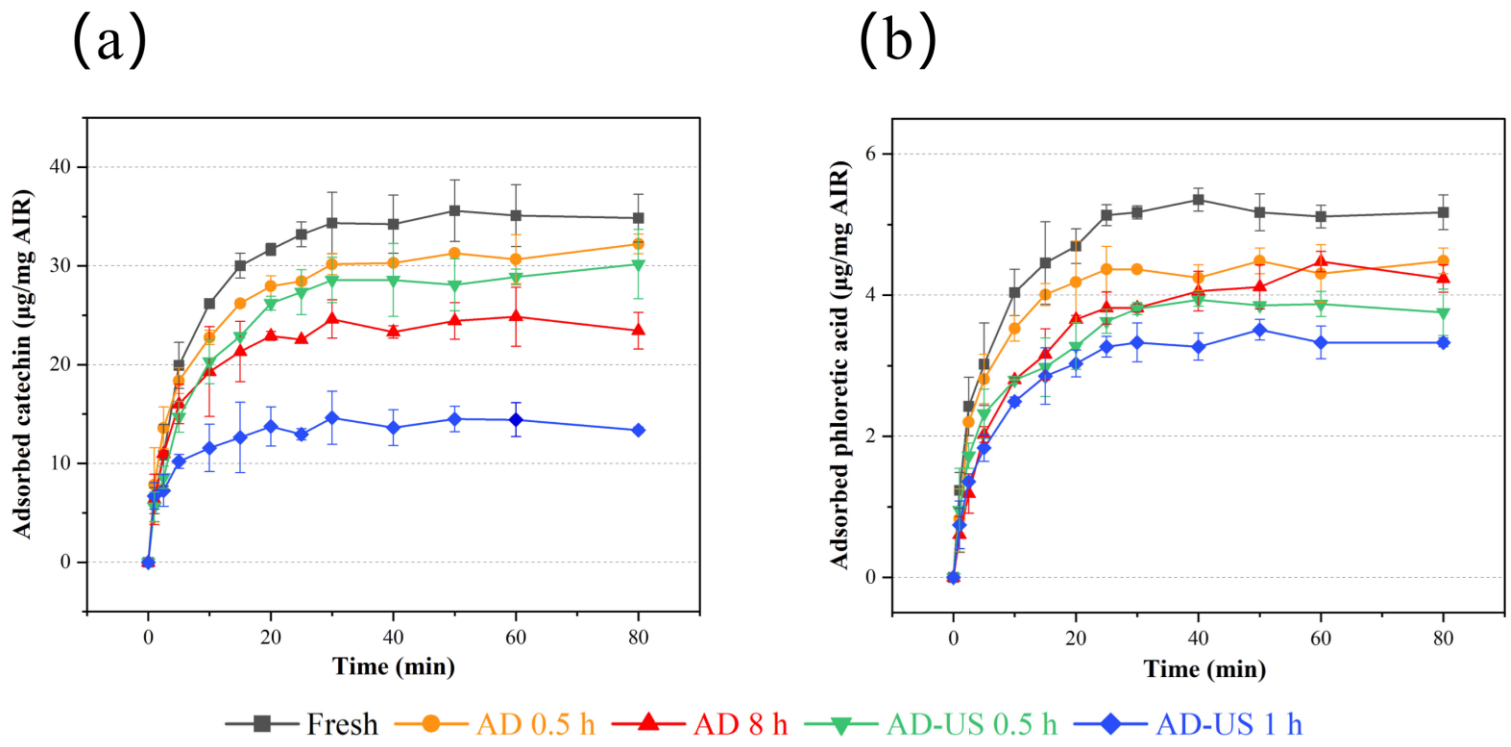
(a)
(b)
Adsorbed catechin (μg/mg AIR)
Adsorbed phloretic acid (μg/mg AIR)
Time (min)
Time (min)
Fresh
AD 0.5 h
AD 8 h
AD-US 0.5 h
AD-US 1 h

Fig. 6

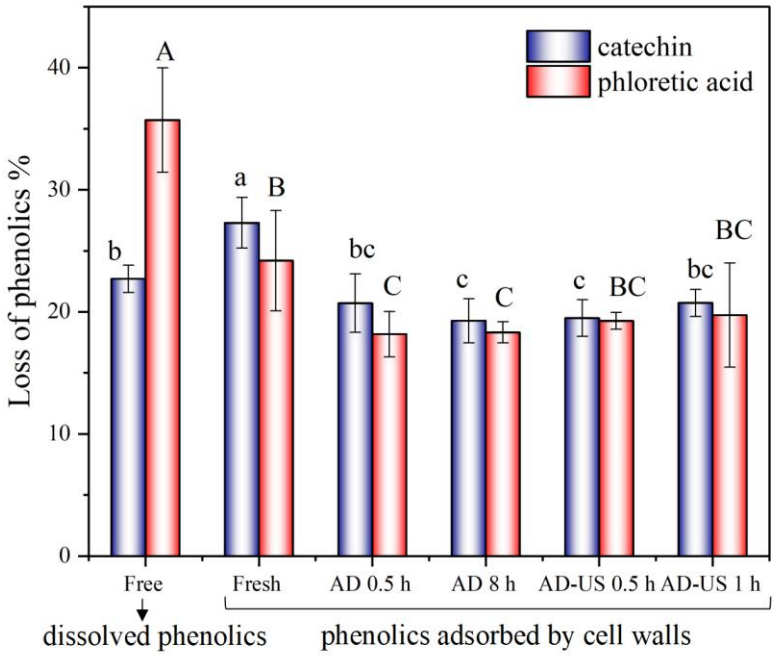
catechin
phloretic acid
Loss of phenolics %
40
30
20
10
0
A
B
a
b
bc
C
c
C
c
BC
bc
BC
Free
Fresh
AD 0.5 h
AD 8 h
AD-US 0.5 h
AD-US 1 h
dissolved phenolics
phenolics adsorbed by cell walls

Fig. 7

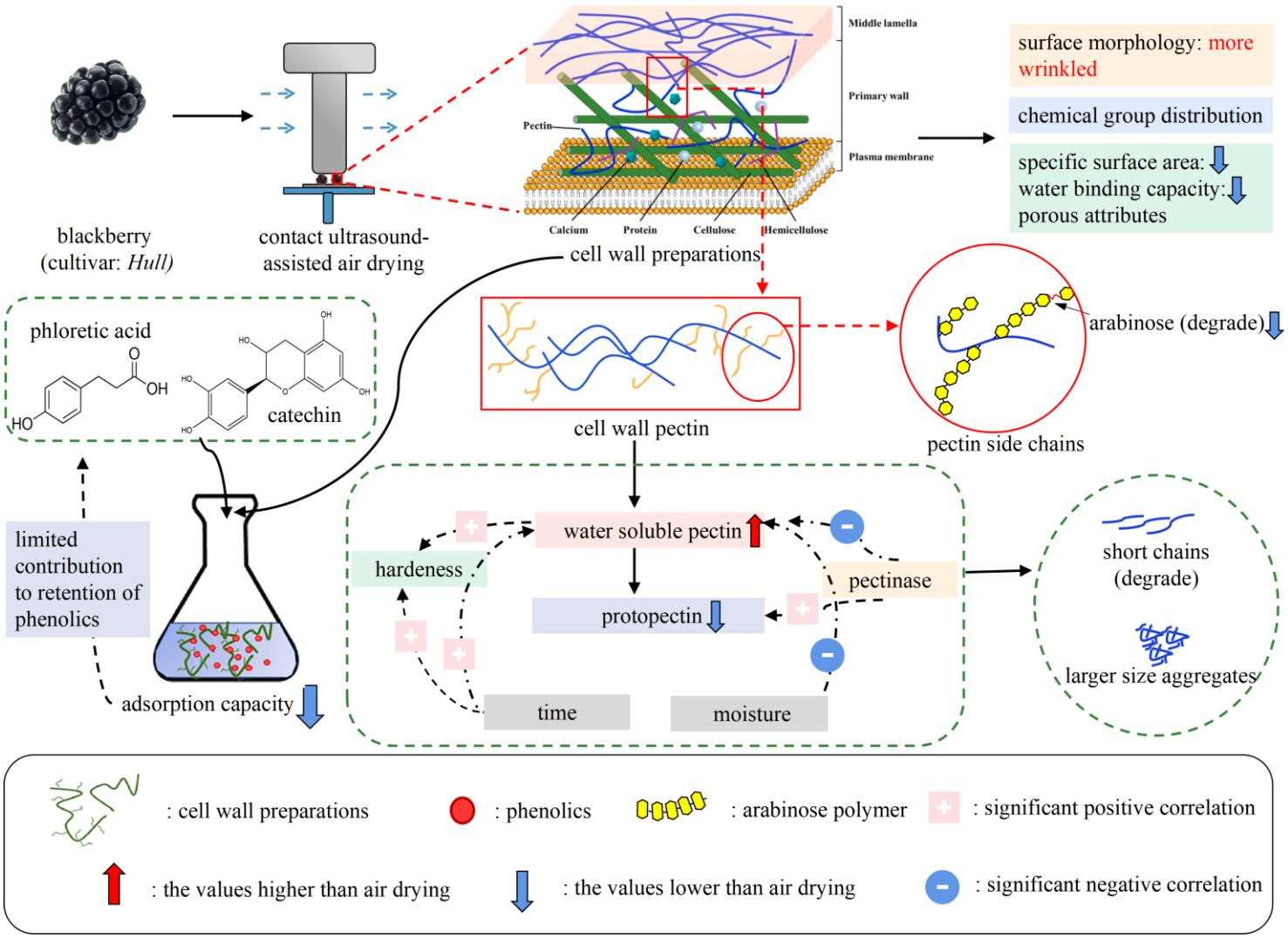
blackberry
(cultivar: *Hull*)
contact ultrasound-assisted air drying
Middle lamella
Primary wall
Plasma membrane
Pectin
Calcium
Protein
Cellulose
Hemicellulose
surface morphology: more wrinkled
chemical group distribution
specific surface area:
water binding capacity:
porous attributes
cell wall preparations
phloretic acid
catechin
cell wall pectin
arabinose (degrade)
pectin side chains
limited contribution to retention of phenolics
adsorption capacity
water soluble pectin
hardeness
protopectin
pectinase
time
moisture
short chains (degrade)
larger size aggregates
: cell wall preparations
: phenolics
: arabinose polymer
: significant positive correlation
: the values higher than air drying
: the values lower than air drying
: significant negative correlation

Fig. 8