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Influence of Polysaccharide Functional Groups on the Extraction Degree of Blackcurrant Anthocyanin Pigment

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Abstract

This article discusses the influence of anionic polysaccharides – kappa-carrageenan, agar-agar, sodium alginate, carboxymethyl cellulose and pectin on the extraction degree of anthocyanin pigment. It is demonstrated that all added anionic polysaccharides increase the extraction degree of blackcurrant anthocyanin pigment. It is established that the essence of polysaccharide functional groups is an important factor determining the extraction degree of anthocyanin pigment. The viscosity of systems with anionic polysaccharides and anthocyanin pigment is determined. It is demonstrated that addition of agar-agar, carrageenan and pectin anthocyanin pigment to the solution increases dynamic viscosity of the systems. On the contrary, addition to the carboxymethyl cellulose and sodium alginate solution of anthocyanin pigment decreases dynamic viscosity of the systems in comparison with their aqueous solutions. Antiradical activity of anthocyanin pigment-anionic polysaccharide complex has been determined. It is established that natural polysaccharides, such as sodium alginate, kappa-carrageenan and pectin, upon their addition to anthocyanin pigment increase its antiradical activity whereas chemically modified cellulose promotes its decrease. Addition of anthocyanin pigment with anionic polysaccharide upon production of vanilla cream makes it possible to obtain functional product with superior organoleptic properties.

Key words: anthocyanin pigments, polysaccharides, kappa-carrageenan, agar-agar, carboxymethyl cellulose, sodium alginate, pectin.

1. Introduction

Nowadays great attention is attracted to high quality food products combining superior organoleptic properties and perfect functional characteristics. Application of natural coloring agents enhances appearance and increases nutrition value of products. Most natural coloring agents in addition to pigments are comprised of vitamins, glycosides, organic acids, aromatic substances and microelements. The highest contribution to variety of colors is made by flavonoids, among them anthocyanins are more widely presented.

Application of anthocyanin pigments as coloring agents provides wide range of colors from red to purple as well as decreases the level of cholesterol, prevents formation of thrombi, improves elasticity of vessels, enhances wound healing, positively influences on vision, promotes prevention of oncological diseases [1; 2; 3; 4].

The sources of natural anthocyanins are flowers, fruits, vegetables and products of their processing. In terms of structure anthocyanins are glycosides containing hydroxy- and methoxy-substituted flavonoids (2-phenylchromenylium) as aglycone-anthocyanin [5].

Since application of anthocyanin pigments for food production is limited due to their instability during processing, such as long-term heating, heating and storage, the issue of development and improvement of their extraction is of great importance. Various techniques of extraction of anthocyanin pigments out of vegetable stock using various extracting agents are described [6; 7; 8; 9; 10; 11]. Previously [12] we demonstrated that anionic polysaccharide, carrageenan, can be successfully used as extracting agent, whereas cationic polysaccharide, chitosan, decreases the extraction degree of anthocyanin pigment. This work investigates into the influence of anionic polysaccharides and their functional groups on the extraction degree of blackcurrant anthocyanin pigment as well as possibility to use the combination of anthocyanin pigment-anionic polysaccharide as desserts.

2. Materials And Methods

2.1 Materials

Black currant berries (*Ríbes nígrum*) were used as a source of extraction of anthocyanin pigment. The extraction was carried out by aqueous solutions of polysaccharides. Anionic polysaccharides were used as extraction agents: kappa-carrageenan (MCS, Korea), agar-agar (Fodding, China), carboxymethyl cellulose (CMC) (MCS, Korea), sodium alginate (Foodchem, China) and pectin (Foodchem, China). The content of polysaccharides in the solution was 0.05 wt %.

2.2 Extraction

Smashed berries were mixed with aqueous solution of polysaccharides in the ratio of 6:100 and thermostated at 70°C in 1 h with subsequent filtration. Color intensity of the solution was determined by optical density using a SHIMADZU UV-1800 spectrophotometer (Japan) in the wavelength range of 400-800 nm.

2.3. Measurements of viscosity

Dynamic viscosity was determined using an Expert R viscometer, 100–40000000 cP, Fungilab (US).

2.4. DPPH assay

Antiradical activity of blackcurrant anthocyanin pigment and anthocyanin pigment–anionic polysaccharide complex was studied according to DPPH method (2,2-Diphenyl-1-picrylhydrazyl) [13; 14]. The method is based on interaction of antiradicals with stable chromogene radical. Standard DPPH solution (5×10^4 M) in ethanol acidified by acetic acid was diluted by ethanol in the ratio of 1:10 in order to produce working solution. 50 cm^3 of the considered extracts were added to 5 cm^3 of DPPH working solution, mixed, then the kinetics of decrease in optical density of the solution was recorded using a SHIMADZU UV-1800 spectrophotometer (Japan) in 30 min at the wavelength of 517 nm. Trolox solutions (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid) of various concentrations were used as reference.

2.5. Preparation of vanilla cream

Preparation of vanilla cream was comprised of two main stages. At the first stage heavy cream was foamed. Cream with the fat content of 33% was cooled to 18°C and whipped. After 1.5-fold increase in the cream bulk some droplets of vanilla extract and powdered sugar were added. Simultaneously liquid complex of blackcurrant anthocyanin pigment and sodium alginate was prepared. The amount of complex forming agent was taken as per 2% of gelatin of the weight of finished product. Content of anthocyanin pigment in the complex was in the range from 2 to 10%. Finished product in a fine stream was added while whipping to the whipped cream. After formation of homogeneous fluffy structure of the whipped product it was batched into preliminary cooled molds and cooled to 0-4°C up to formation of steady porous jellified structure of cream.

3. Results And Discussion

3.1. Extraction of anthocyanin pigment in the presence of anionic polysaccharides

Since polysaccharide type and its functional groups can influence significantly the extraction degree of blackcurrant anthocyanin pigment, we investigated into the extraction degree of anthocyanin pigment as a function of added polysaccharide and essence of its functional groups.

Extraction degree of blackcurrant anthocyanin pigment as a function of anionic polysaccharides in aqueous solution is illustrated in Fig. 1. Content of anionic polysaccharides in the solution was 0.05 wt %. Solution of blackcurrant anthocyanin pigment without polysaccharides was used as reference.

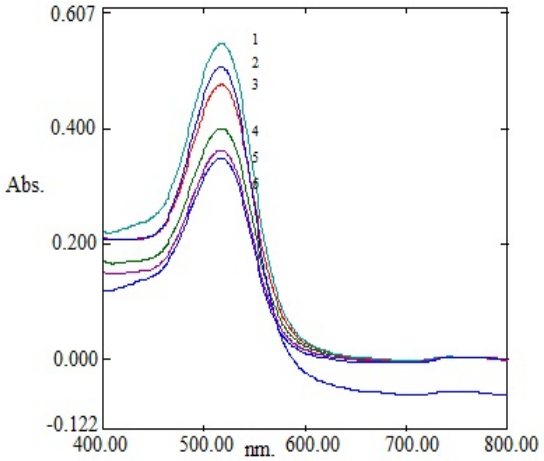

Fig. 1. Extraction degree of blackcurrant anthocyanin pigment as a function of anionic polysaccharides in aqueous solution: *1.* kappa-carrageenan, *2.* agar-agar, *3.* CMC, *4.* sodium alginate, *5.* pectin, *6.* anthocyanin pigment extracted w/o polysaccharides.

The presented results demonstrate that all added anionic polysaccharides increase the extraction degree of blackcurrant anthocyanin pigment. Probably, stable oxonium complexes are formed between anionic polysaccharides and cationic anthocyanins due to oxygen contained in anthocyanin heterocyclic ring which can electrostatically interact with negatively charged polysaccharide functional groups.

Maximum extraction degree is that of anthocyanin pigment extracted in the presence of kappa-carrageenan. Optical density of the solution containing anthocyanin pigment and kappa-carrageenan is 0.550. Minimum extraction degree is that of anthocyanin pigment extracted in the presence of pectin substances (0.350).

It can be seen that the essence of polysaccharide functional groups is a significant factor determining the extraction degree of anthocyanin pigment. More complete extraction of anthocyanin pigment is promoted by kappa-carrageenan and agar-agar sulfate groups. The extraction degree of anthocyanin pigment in the presence of kappa-carrageenan and agar-agar increases by 1.8 and 1.6 times, respectively. Since sulfate groups in kappa-carrageenan and agar-agar molecules are more reactive [15], this probably leads to formation of steady complexes of anthocyanin pigment-polysaccharide, hence, to more complete extraction of the pigment.

Addition of CMC, sodium alginate and pectin substances to the system decreases the extraction degree of the pigment. Increase in the extraction degree of anthocyanin pigment in the presence of CMC, sodium alginate and pectin substances is 1.5, 1.3, 1.1, respectively. Probably, the carboxymethyl groups in CMC molecule promote higher extraction degree of anthocyanin pigment than the presenting sodium alginate acid in the molecule. Pectin substances are characterized by the lowest extracting abilities. Carboxyl groups in molecules of pectin substances gives them weak acidic properties.

3.2 Determination of viscosity

Since upon production of jellified items, polysaccharides perform as gelling agents, we analyzed viscosity of the systems containing anionic polysaccharide and anthocyanin pigment. Dynamic viscosities of the systems with anionic polysaccharide and anthocyanin pigment with 0.05 wt % of polysaccharides are illustrated in Fig. 2. Aqueous 0.05 wt % polysaccharide solution was used as reference.

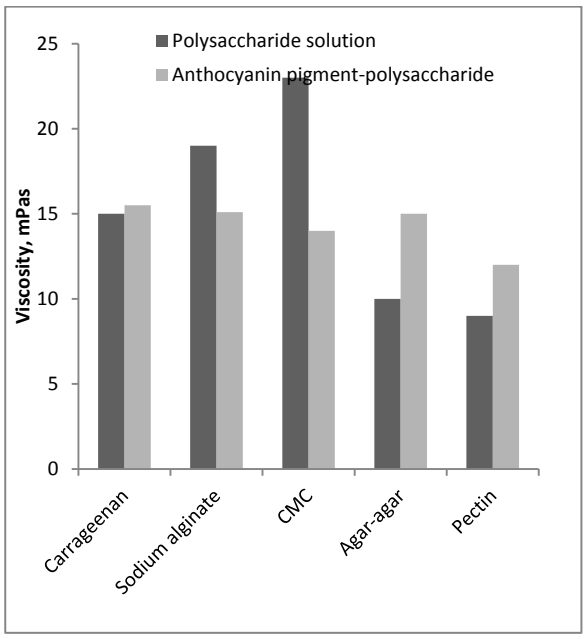

Fig. 2. Dynamic viscosity of systems with anionic polysaccharides and anthocyanin pigment at polysaccharide content of 0.05 wt % in the solution.

It can be seen that addition of anthocyanin pigment to the solution of anionic polysaccharides varies its viscosity differently. It was established that addition of anthocyanin pigment to the solutions of agar-agar, carrageenan and pectin increases dynamic viscosity in comparison with aqueous solutions of polysaccharides. Maximum increase in the viscosity by 1.5 times is observed in the system with agar-agar and anthocyanin pigment. Viscosity of the systems with kappa-carrageenan-anthocyanin pigment and pectin-anthocyanin pigment increases by 1.1 and 1.2 times, respectively. Probably, formation of steady complexes between anthocyanin molecules and sulfate groups of agar-agar and kappa-carrageenan increases viscosity of the system. Increase in viscosity of the system with pectin-anthocyanin pigment can be probably attributed to chemical composition of the applied berries. There are published data that blackcurrant berries contain 0.8-2.5% of pectin substances [16] which can influence significantly on increase in viscosity of pectin-anthocyanin pigment.

On the contrary, addition of anthocyanin pigment CMC and sodium alginate solution decreases dynamic viscosity of the system in comparison with their aqueous solution. Viscosity of these systems decreases by 1.6 and 1.2 times.

3.3. Antioxidant activity

Aiming at further application of the systems containing anionic polysaccharides and anthocyanin pigment for production

of jellified items as well as for improvement of their nutrition value, we studied antiradical activity of anthocyanin pigment-anionic polysaccharide complex. Antiradical activities of the systems containing anionic polysaccharides and anthocyanin pigment are illustrated in Fig. 3. Antiradical activity of solution of anthocyanin pigment extracted out of blackcurrant was used as reference.

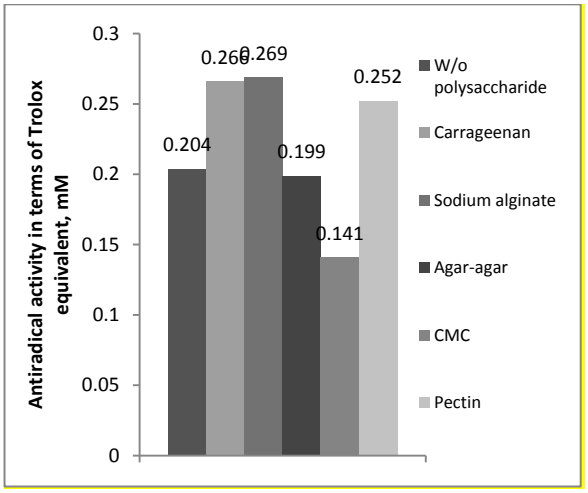

Fig. 3. Antiradical activity of systems with anionic polysaccharides and anthocyanin pigment.

It has been experimentally established that the solution of anthocyanin pigment extracted out of blackcurrant possesses antiradical activity (0.204 Trolox equivalent, mM). Addition of anionic polysaccharides: kappa-carrageenan, sodium alginate and pectin to the solution of anthocyanin pigment increases antiradical activity of the systems. Antiradical activity of these systems increase by 1.3, 1.3 and 1.2 times, respectively. Addition of agar-agar to anthocyanin pigment does not influence significantly its antiradical activity. On the contrary, addition of CMC to the solution of anthocyanin pigment decreases antiradical activity by 1.5 times. Probably, chemical modification of cellulose promotes decrease in antiradical activity.

The obtained data agree with the results by other researchers [17; 18; 19] demonstrating that natural polysaccharides are characterized by antiradical activity. Probably, this can be attributed to the fact that in the areas of extraction, polysaccharides are closely related with polyphenols possessing their intrinsic antiradical activity. Such complexes are very stable and can preserve their structure upon extraction of polysaccharides.

3.4. Anthocyanin pigment-anionic polysaccharide for production of jellified desserts

Taking into account that anthocyanin pigments on the basis of berries were extracted using polysaccharides possessing structure forming properties, we proposed to apply coloring and jellifying ability for production of jellified desserts. The studies were performed on vanilla cream prepared according to standard technology [20], in its recipe coloring and jellifying agents were substituted for anthocyanin pigment-polysaccharide complex. The content of anthocyanin pigments in the system was from 2 to 10 vol %, and initial gelatin was substituted for sodium alginate. Coloring intensity varied as a function of content of added anthocyanin pigment. The most agreeable mild pink color and sweet-sour taste of blackcurrant were observed in the cream containing 8 vol % of anthocyanin pigment. Substitution of initial constituents of the cream with anthocyanin-polysaccharide complex makes it possible to obtain functional product with superior organoleptic properties.

4. Conclusion

Extraction of anthocyanin pigment is the most efficient in the presence of anionic polysaccharides. The essence of functional polysaccharide groups is a significant factor which determines the extraction degree of anthocyanin pigment. It is proposed to apply combination of anthocyanin pigment with anionic polysaccharide as structure forming agent and natural coloring matter.

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