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学 位 論 文 要 旨
Dissertation Abstract

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学位論文題目：
Title of Dissertation

New food technology for the purification and utilization of anthocyanins by forming supramolecular complexes
（超分子複合体法によるアントシアニンの精製法の開発と利用）

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Anthocyanins, one group of flavonoids, widely occur in vascular plants. They have been used as natural food colorants. Moreover, they are receiving increased attention, not only as food colorants, but also as potential therapeutic components. Efficient separation and purification of anthocyanins will be desired when they expand the usages to food colorants and pharmaceutical chemicals because plant extractions contain foreign substances. Thus, the development of useful and practical techniques for anthocyanins isolation from plants is an important step for the further applications of anthocyanins as functional pigments.

In this study, we introduce the unique idea for isolation of anthocyanins with the combination of supramolecules formation and solid phase extraction (SPE) cartridges. Supramolecule is a stoichiometric self-assembled complex that consists of anthocyanins that have *ortho*-dihydroxyl groups on the B ring, specific flavonoids and metal ions. Supramolecules recognize the stereostructure of specific anthocyanins and flavonoids that may have great affinity and higher matching each other. To perform efficient purification of anthocyanins, we have to consider the separation techniques of the supramolecule to the fragment anthocyanins and flavonoids. SPE is, therefore, considered to be a useful method for isolation of anthocyanins. In this dissertation, I would like to describe the separation technique of anthocyanins and flavonoids that were used for the supramolecule formation and then introduce two typical examples of purification of anthocyanins.

In the second chapter, appropriate resins that will separate anthocyanins and flavocommelin (FC), one kind of flavonoids was looked for by using well-known supramolecules of natural pigments after dissociating the supramolecules by acid hydrolysis. As the results, Discovery DPA-6S made it possible to separate anthocyanidin 3,5-diglucosides from hydrophobic acylated anthocyanidin 3,5-diglucosides and FC. On the other hand, Discovery DSC-SCX made it possible to separate various anthocyanins from FC and other neutral plant impurities in electric charge.

In the third chapter, anthocyanidin 3-glycosides (An3G) that are common

pigments and rich in bilberry, some grapes and others were successfully formed the artificial supramolecules with FC and Al^{3+}. Bilberry pigment that contains 15 different An3G was tested to form the supramolecules-like complex formation of An3G with FC and Al^{3+}. As the results, pure An3G bearing *ortho*-dhydroxyl group on B ring was successfully separated from other An3G by choosing Al^{3+} as the metal ions. On the other hands, other metal ions (Mg^{2+}, Zn^{2+} and Fe^{3+}) were not formed the supramolecules. For example, complex blue pigment (CP, 1.30g) with Al^{3+} was formed from 1.86 g (1.5 mmol) of bilberry pigment, 1.82 g (3.0 mmol) of FC and 3 mL of 0.5 M aluminium chloride aqueous solution (1.5 mmol), yielding 40.2% recovery of An3G in the complex after precipitation by ethanol. The purity of An3G after purification with Sephadex G-10 and Discovery DPA-6S from CP was 96.9%, and the recovery rate of An3G was 90.6%. Additionally, the composition of An3G bearing *ortho*-dihydroxyl groups on the B ring was 99.1%. Furthermore, purified An3G was increased DPPH radical scavenging activity against the original bilberry pigment.

In the fourth chapter, Delaware grape anthocyanins, bearing *ortho*-dihydroxyl group on the B ring and/or *p*-coumaoly group as an ester were successfully formed the supramolecule and then isolated by ethanol precipitation. With the combination of metal complex formation and the Discovery DPA-6S column, the selective anthocyanins bearing *ortho*-dihydroxyl group on the B ring were isolated to be afforded to Cy3G (48.2% yield with 95.2% purity) and Cy3-*p*C·G (44.9% yield with 91.4% purity) without any preparative HPLC techniques. Isolated anthocyanins showed higher color values and great activities for antioxidant activity and radical scavenging activity.

In the fifth chapter, the structure of delphinidin 3-glucoside (Dp3G) complex with FC and Al^{3+} was determined by several physical analyses. Thus, the composition of Dp3G complex was determined to be one molecule each of Dp3G, FC and Al^{3+}; the molecular weight for Dp3G complex as [$C_{49}H_{49}AlO_{27}$] was 1097.2344.

Thus, we first found the supramolecular like complex consisting of anthocyanidin 3-glucoside, FC and Al^{3+}. Furthermore, our separation and purification technique for anthocyanins by combination with complex formation and SPE reveals the possibilities for one advanced technology to obtain some functional anthocyanins.