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CHIRAL STACKING OF CYANIN AND PELARGONIN --- SOLUBLE AND INSOLUBLE AGGREGATES AS DETERMINED BY MEANS OF CIRCULAR DICHROISM

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Abstract: CD of anthocyanidin 3,5-diglucosides show a negative exciton-type Cotton curve (A = -4∼-18) when dissolved in neutral aqueous solution. Pelargonin and cyanin show an unusual aging effect; insoluble particles of the anhydrobase gradually form to give a suspension, which shows a positive and unsymmetrical exciton-type CD curve (pelargonin: A = ca +45). Trace amounts of aluminum ions, if present in the buffer solution used, form aluminum chelate of cyanin, which gives a large positive exciton-type Cotton effect (A = ca +110).

Hoshino et al.[1,2] obtained evidence for self-association of anthocyanin anhydrobases in neutral solution by using circular dichroism as a sensitive probe for molecular association. Thus, the CD curves of peonin, delphin, hirsutin and malvin show a large exciton-type splitting with first negative and second positive Cotton effects ($A = \Delta\varepsilon_1 - \Delta\varepsilon_2 = -4 \sim -18$; conc 5 x 10^{-4}M) in the visible absorption band region when the anthocyanin chlorides are dissolved in a neutral buffer (pH 7.0) in a fairly high concentration, indicating that two or more anthocyanidin chromophores must stack vertically in a left-handed screw axis to cause this type of split bands.[2] The magnitudes of $\Delta\varepsilon$ in each of the anthocyanins are strongly intensified when the concentration is increased, indicating enhanced formation of stacked molecules in the more concentrated solutions.

As reported previously,[1] cyanin showed unusual properties, however; the positive exciton-type Cotton effect, whose sign was opposite to that of the case discussed above, increased gradually after cyanin chloride was dissolved in neutral buffer solution (0.1M phosphate). This aging lasted 60 min, when blue floccules precipitated out. The precipitate, on being redissolved in water, showed an exceptionally large positive exciton-type Cotton effect (A = ca +110), which was previously attributed to a very high self-association in a right-handed screw axis.[1] This unusual phenomenon was now disclosed to be that the cyanin floccules actually consisted of a metal chelate and not a simple self-association. Immediately after dissolution in neutral buffer, cyanin indeed showed a negative exciton-type Cotton effect of the magnitude (A = ca -10 at conc 5 x 10^{-4}M) similar to those of other anthocyanidin 3,5-diglucosides (Fig. 1). The electronic and CD spectra of the blue floccules of cyanin reported by Hoshino et al.[1] were identical with those of the aluminum complex (A = ca +110) of cyanin. Thus, the aging phenomenon of cyanin could be explained in terms of the slow

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formation of aluminum chelate with trace aluminum ions supplied from the phosphate buffer solution and/or the glass vessel used.

Pelargonin has no o-dihydroxy group and hence cannot form such a metal complex, but curiously it shows an aging effect and a positive exciton-type Cotton effect similar to those of cyanin. The CD curve, however, has an unsymmetrical shape; the first (positive) Cotton effect is large and the second (negative) Cotton effect is small (A = ca +45).[2] Reexamination disclosed that pelargonin chloride, when dissolved in a neutral buffer, first showed a small negative exciton-type Cotton effect similar to that of other anthocyanidin 3,5-diglucosides and then gradually formed a suspension of insoluble particles, which were responsible for the unsymmetrical positive exciton-type Cotton curve (Fig. 2). The supernatant obtained by centrifugation showed no Cotton effect, whereas the CD curve was restored by dispersing the precipitates again in water ultrasonically. Since the solubility of pelargonin anhydrobase in water is very low, highly aggregated insoluble particles would have been formed.

In the complete absence of di- or trivalent metal ions, cyanin chloride also formed in neutral buffer solution insoluble particles of a similar type which showed an unsymmetrical exciton-type CD curve with a first large positive and a second small negative sign (Fig. 1).

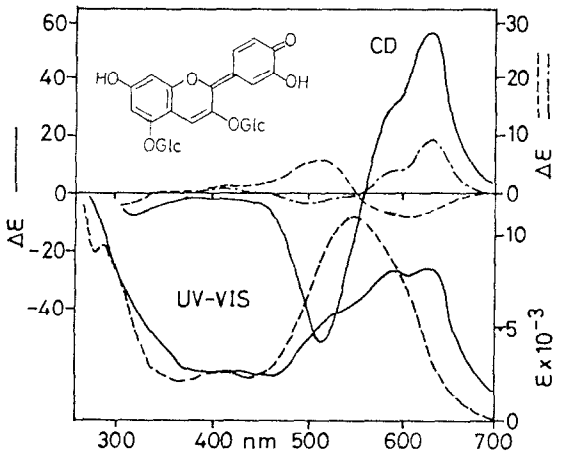

Fig. 1. Electronic and CD spectra of cyanin (5 x 10^{-4}M) in 0.1 M phosphate buffer at pH 7.0. CD: --- 2 min after dissolving without polyvalent metal ions; —— Al^{3+} added; -·- insoluble particles formed by aging without polyvalent metal ions (dispersed by ultra-sonification). UV-VIS: --- 2 min after dissolving; —— Al^{+3} added.

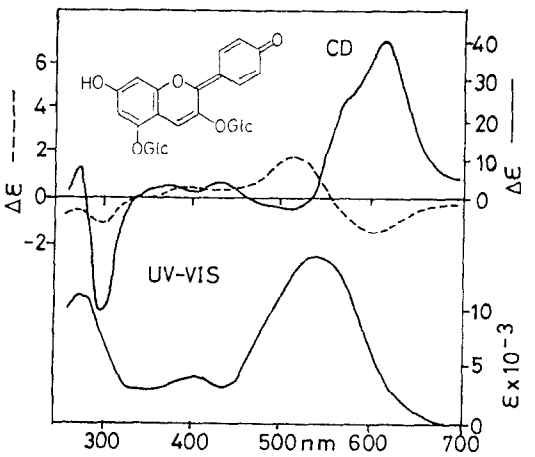

Fig. 2. Electronic and CD spectra of pelargonin (7 x 10^{-4}M) in 0.05 M phosphate buffer at pH 7.27 (path length 1 mm). CD: --- 2 min after dissolving; —— insoluble particles formed by aging (dispersed by ultrasonification). UV-VIS: —— 2 min after dissolving.

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