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NSCG Neue Schweizerische Chemische Gesellschaft

Das Farbensymposium wird seit 1960 von deutschen und schweizerischen Farbenchemikern veranstaltet. Es setzt sich zum Ziel, anhand von Erkenntnissen und Entwicklungen die Bedeutung der Farbenchemie auf den verschiedenen Gebieten von Wissenschaft und Praxis darzustellen.

Die meisten Referenten (aber leider nicht alle) haben ein Manuskript zur Veröffentlichung eingesandt. Das vorliegende Heft gibt einen repräsentativen (wenn auch nicht vollen) Überblick über das Symposium.

Biosynthesis and Biodegradation of Natural Dyestuffs

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Structure and Colour-Development of Anthocyanins

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Flower colours, from red through purple to blue, are mostly anthocyanins. Although there are many colours in nature, only a few anthocyanins, chromophores of the pigments, have been found. The colour of the pigments is stable in flower petals but the extracted anthocyanins are unstable and quickly decolourized in a physiological condition. From early of this century, blue-colour development has been attracting many chemists with controversy between pH theory and metal chelation theory. Flower colour development and stability of anthocyanins being closely related to molecular association with anthocyanin itself and the other molecules have chemically been proved [1].

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The blue pigment, commelinin, from blue flower petals of *Commelina communis* is a metal-complex anthocyanin (metalloanthocyanin). Reconstruction of commelinin from the components gave pure pigment as single crystals. Recently, we determined the complete structure of commelinin [2], which is a self-assembled supramolecule, by X-ray crystallographic

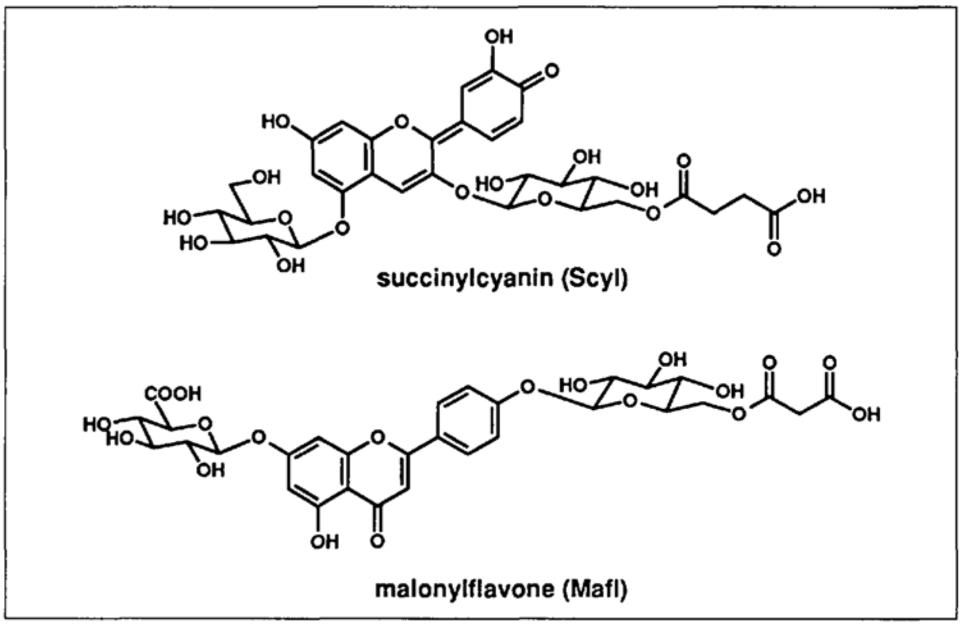

Fig. 1. *Composition of protocyanin*

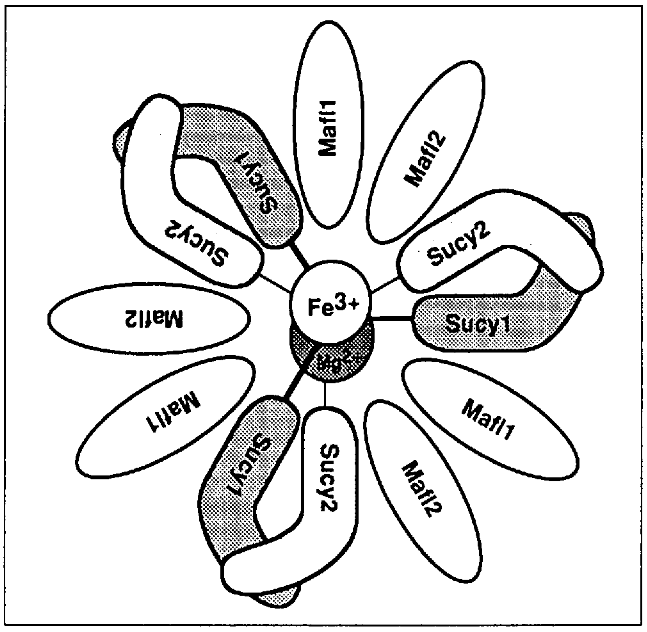

Fig. 2. *Proposed structure of protocyanin*

analysis combined with UV, CD and ^{1}H-NMR. In the molecule the organic components, malonylawobanin and flavocommelin are arranged by chiral self-association and copigmentation. The intermolecular hydrophobic interaction stabilizes the anthocyanin nuclei, which coordinate to Mg^{2+} to be a self-assembled metal-complex. Blue-colour development arises from 4'-oxoquinonoidal-3'-oxy anion form (anhydrobase anion) of delphinidin caused by Mg^{2+} chelation.

Protocyanin is a blue pigment isolated from blue petals of cornflower, *Centaurea cyanus*. Succinylcyanin (Sucy) and malonylflavone (Mafl) (*Fig. 1*) were elucidated to be the organic components of protocyanin by ^{1}H-NMR and FAB-MS. We could prepare pure protocyanin from the organic components with Mg^{2+} and controlled amount of Fe^{3+} by reconstruction. By ESI-MS the exact molecular weight was decided, thus the composition of protocyanin was established to be [$Sucy_6Mafl_6 Fe^{3+}Mg^{2+}$] [3]. For the further structural study protocyanin-like pigment was prepared from Al^{3+} instead of Fe^{3+}. Various ^{1}H-NMR measurements revealed that the arrangement pattern of the components of protocyanin (*Fig. 2*) is much similar to that of commelinin. MCD of protocyanin showed two peaks at 676 and 599 nm, thus the blue colour of protocyanin must be developed by LMCT interaction between anhydrobase anion of Sucy and Fe^{3+}.

The sepal colour of *Hydrangea macrophylla* occasionally changes from blue to violet or red to purple. Both red and blue sepals contained the same anthocyanin, delphinidin 3-glucoside(Dp 3-G) as pigment and the contents of Al^{3+} differed each other; the bluer the sepals were, the more Al^{3+} contained. Isolation of the blue pigment is difficult since it is much unstable than that of protocyanin. Reproducing study of sepals' blue colour revealed that Al^{3+} ion and isochlorogenic acid besides the anthocyanin is essential for the blue colour development. In the pigment Al^{3+} is existing in 1/3 equiv. of Dp 3-G [4]. CD Experiments showed that isochlorogenic acid self-assembles each other and stabilizes the colour. Therefore, the blue pigment might be a supramolecule composed from an anthocyanin, isochlorogenic acid and Al^{3+} ion.

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Natürliche Pteridin-Pigmente: Schmetterlings- und Augenfarbstoffe

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Abstract. Pteridine pigments are widely distributed in nature and are found as colouring matter especially in butterfly wings and insects. The butterfly pigments consists of relatively simple chemical structures but of unusual physical properties whereas the eye pigments from insects are composed of more complex structural arrangements. The biosynthesis of these pigments has been unravelled in detail and reveals a close structural relationship of the various types of compounds.

1. Einleitung

Die Entwicklung der Pteridin-Chemie geht auf *Frederick Gowland Hopkins* [1] zurück, der Ende des letzten Jahrhunderts erfolglos versuchte die gelben und farblosen Flügelpigmente aus heimischen Schmetterlingen in reiner Form zu isolieren. Dieses Unterfangen gelang dann erst in den Jahren 1925/26 *Clemens Schöpf* im Laboratorium von *Heinrich Wieland* [2] [3], wo er die Inhaltsstoffe der Schmetterlingsflügel des Kohlweisslings sowie des Zitronenfalters untersuchte.

Nach dem Vorkommen und der Farbe dieser Pigmente nannte er sie Leukopterin

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