

Anthocyanins — Prospective food colours

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Anthocyanins are the natural pigments responsible for blue to red coloration in many fruits and vegetables. These pigments show great promise as replacements for many of the now widely used synthetic coal tar based food dyes.

THE term anthocyanin is derived from the Greek words for flowers and blue, it was coined by Marquart¹ in 1835 to designate the blue of flowers. Anthocyanin pigmentation is almost universal in flowering plants providing the purple violet, mauve, magenta and nearly all the red hues appearing on flowers, fruits and vegetables. Chemically, anthocyanins belong to the flavonoid class of compounds and are glycosylated polyhydroxy and polymethoxy derivatives of 2-phenyl benzopyrilium (flavylium) salts.

In the past two to three decades there has been an increasing tendency in the food industry all over the world to replace synthetic coal tar dyes with natural colours. Anthocyanins have a great potential in replacing many of these dyes, especially the red dyes. Anthocyanins pose no threat to human health and have even been thought of as being dietarily beneficial in humans². According to Horowitz and Gentili³, these compounds are metabolized by the intestinal flora to carbon dioxide from the A ring and various aromatic acids from the B ring, none of which are harmful (see Figure 1). Work needs to be done on stabilizing anthocyanins in various food systems before they can be universally considered as synthetic dye replacements. This is necessary in view of the various factors which affect anthocyanin stability.

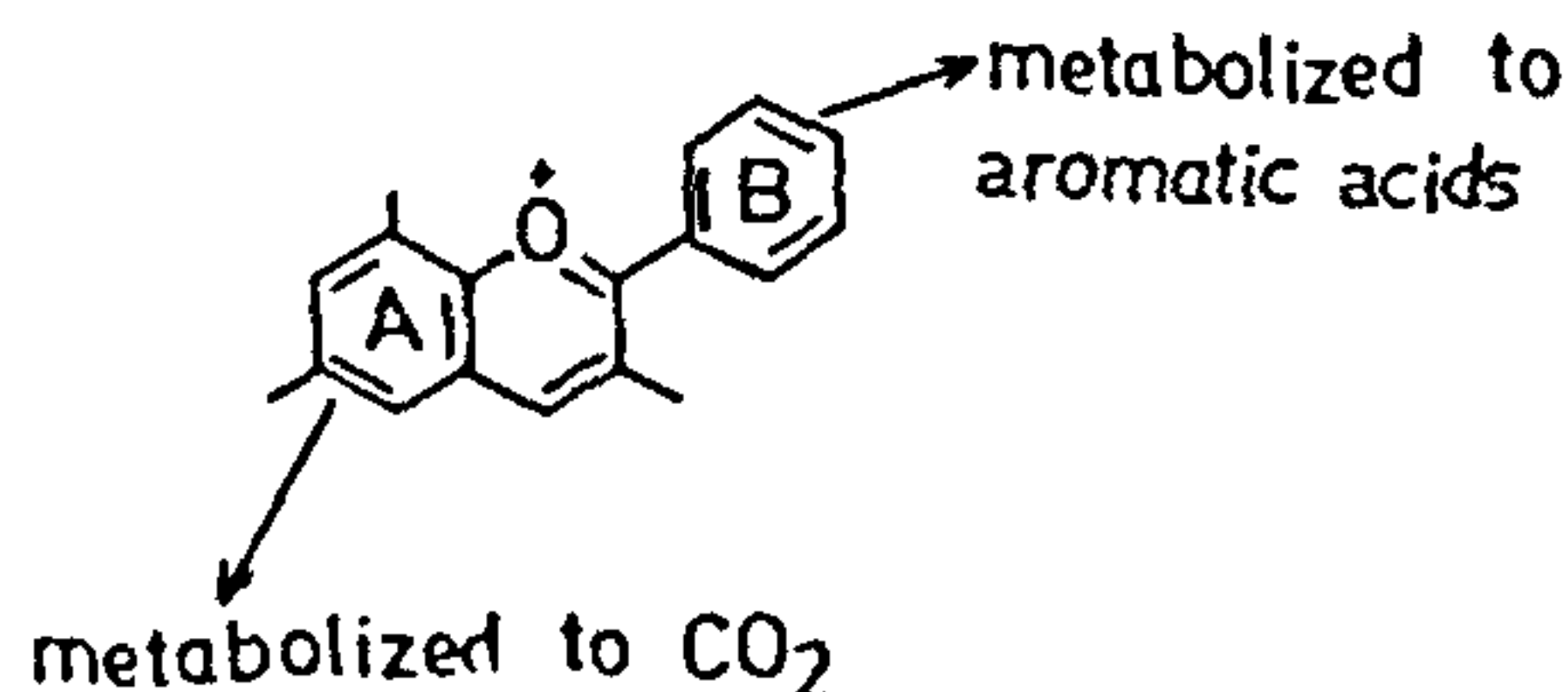


Figure 1. Metabolism of anthocyanins in humans.

Anthocyanin destabilizing factors

Enzymes

Huang⁴ showed that fungal glycosidases (anthocyanases) hydrolyse the glycosidic bonds of anthocyanins and yield anthocyanidins which are much more unstable and decolourize rapidly and enzymatically in the presence of catechol. Peng and Markakis^{4a} proposed a mechanism by which the orthoquinone formed by the enzymatic oxidation of catechol would in turn oxidize the anthocyanin (see Figure 2). Blom⁵ isolated an enzyme anthocyanin-glycosidase from *Aspergillus niger* and 'showed its catalytic effect in the hydrolysis of the glycosidic bond of anthocyanins. Wesche-Ebeling and Montgomery⁶ showed the role of polyphenol oxidase in combination with D-catechin in anthocyanin degradation of strawberries.

Temperature of processing and storage

Anthocyanin degradation increases with temperature rise. Meschter⁷ was able to show a logarithmic relationship between anthocyanin colour retention in strawberry preserves and temperature over a large range covering both processing and storage temperature. Markakis *et al.*⁸ have recommended short-time high temperature heat processing for better pigment retention. Adams⁹ and Adams and Ongley¹⁰ showed that during high temperature sterilization of canned and bottled red fruits, the loss of pigment was negligible in comparison to that occurring during slow cooling and subsequent ambient temperature storage. In food processing along with degradation of the anthocyanins, degradation

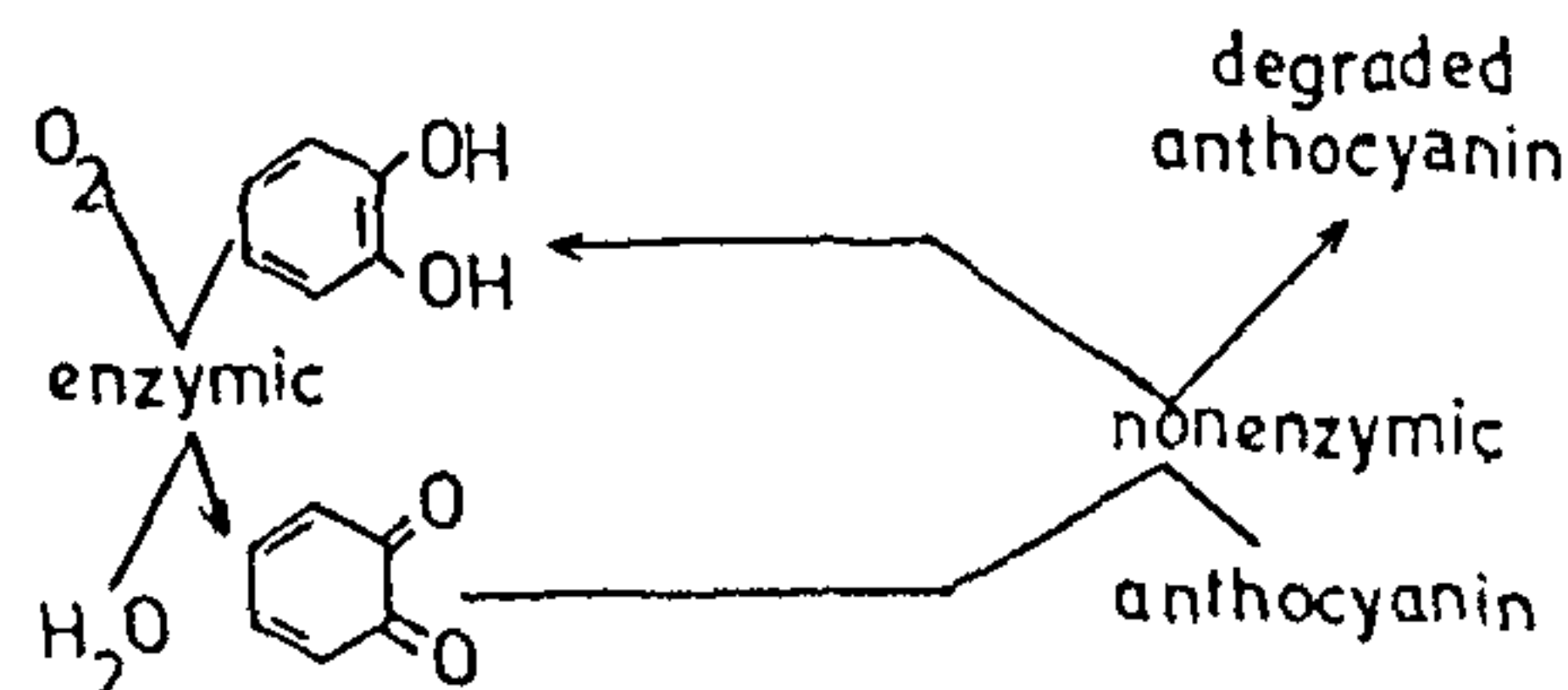


Figure 2. Anthocyanin degradation with enzymic catechol oxidation.

products of carbohydrates such as furfural and hydroxymethyl furfural are also formed; these react with anthocyanins to give dark brownish reaction products. Various condensation reactions between cyanidin and furfural have been proposed. The first among such was proposed by Tinsley and Bockian¹¹ (see Figure 3). Debicki-Pospisil *et al.*¹² proposed reaction between furfural and -OH groups of noncondensed side benzene cyanidin ring (see Figure 4). They also proposed the reaction of two molecules of cyanidin anhydrobase with furfural (see Figure 5). Nadolna and Kwasniewska¹³ confirmed Adams and Ongley's findings^{9,10} when they showed that losses in anthocyanin colour during manufacture of black currant beverage were approximately 3% in comparison to colour losses of 41 to 81% obtained during storage of the beverage at 18 to 20°C.

Light

Light favours biosynthesis of anthocyanins and also

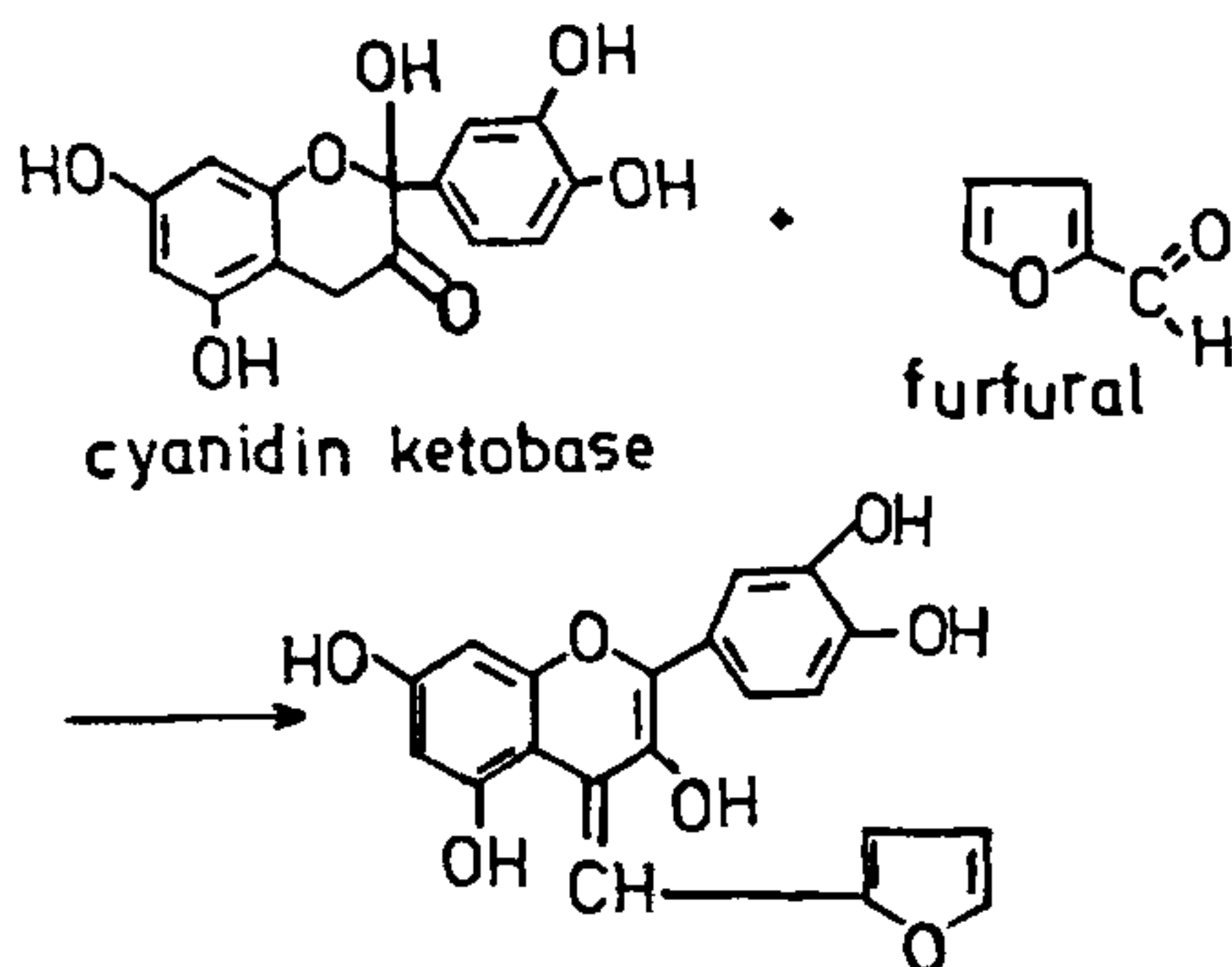


Figure 3. Condensation reaction of cyanidin ketobase and furfural.

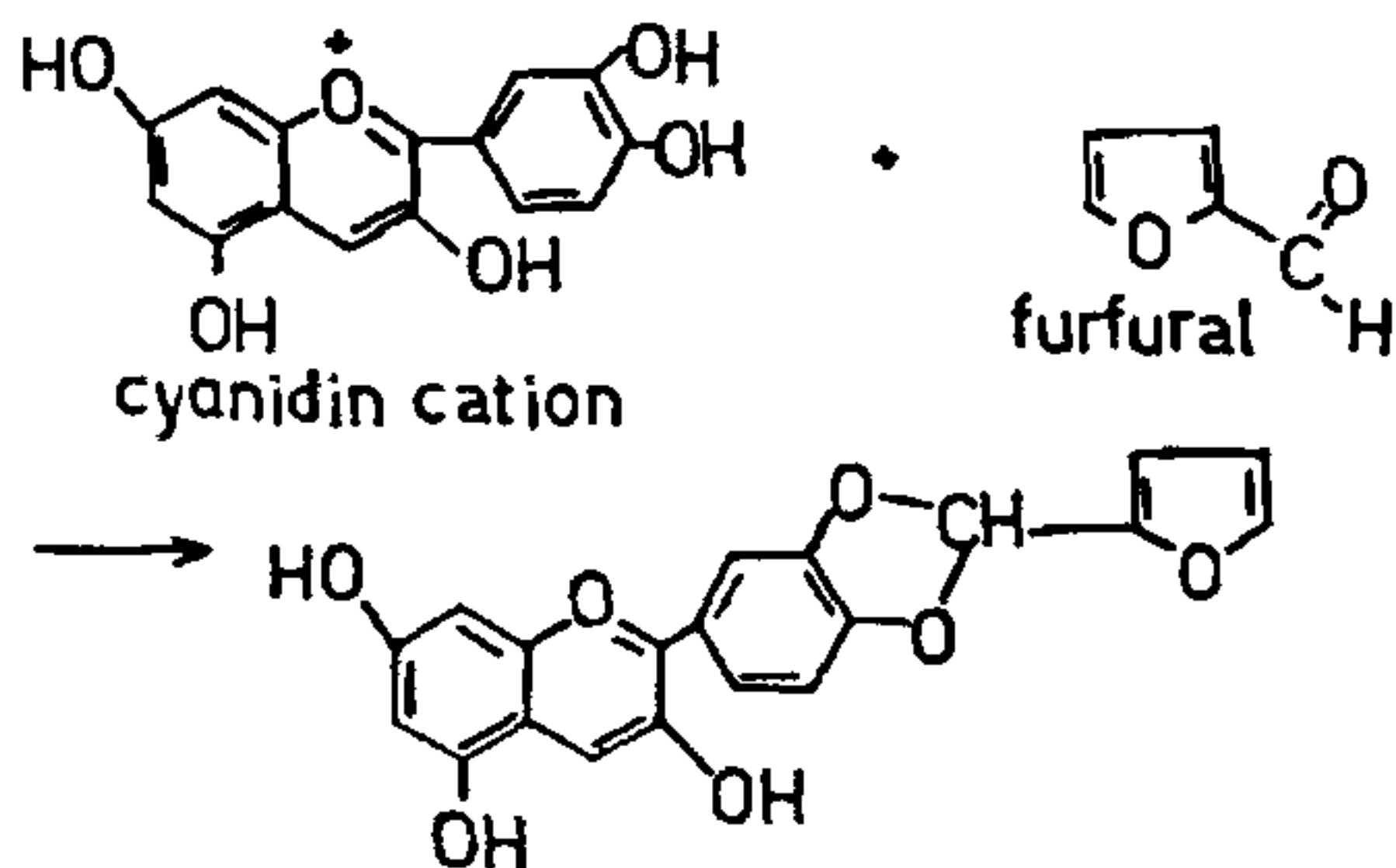


Figure 4. Condensation reaction of cyanidin and furfural.

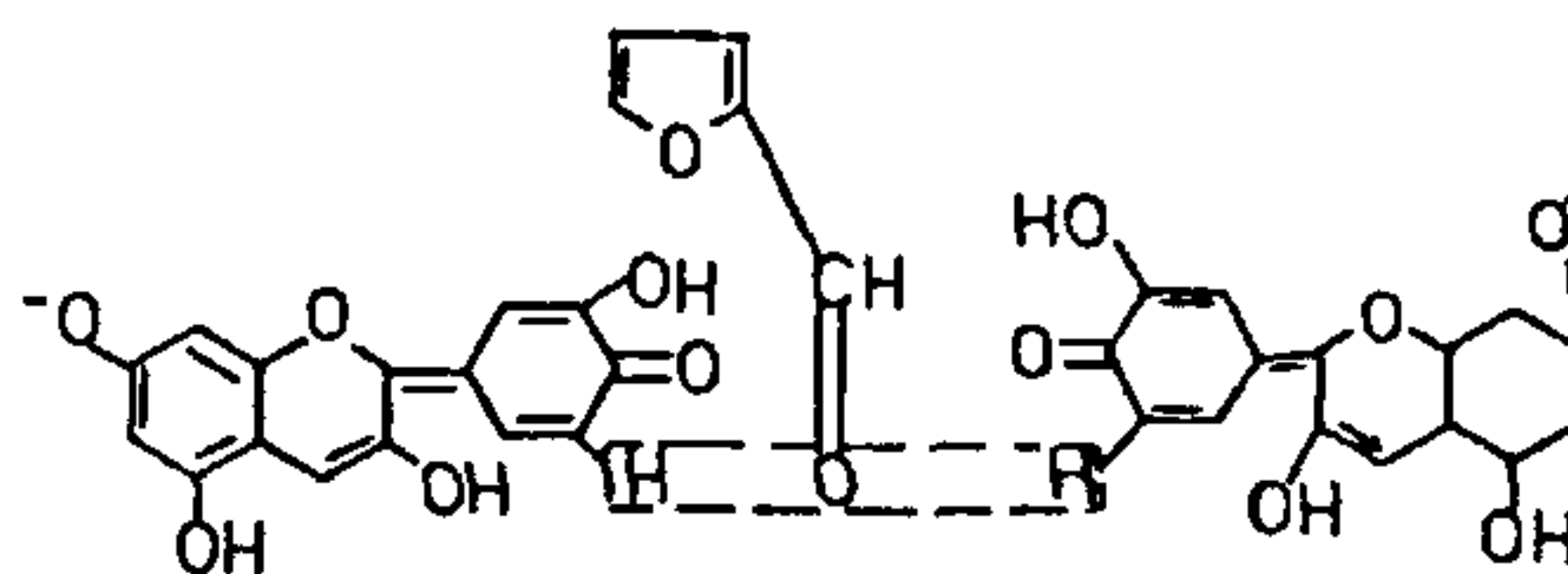


Figure 5. Condensation reaction of cyanidin anhydrobase and furfural.

accelerates their degradation. Tressler and Pederson¹⁴ noticed the adverse effect of light on the colour of bottled Concord grape juice. Palamidis and Markakis¹⁵ found that light accelerated the destruction of anthocyanins in a carbonated beverage coloured with anthocyanins extracted from grape pomace. Maccarone *et al.*¹⁶ studied the photolysis of anthocyanins and showed that anthocyanins diglycosylated at 3 and 5 positions are more stable than anthocyanins with monoglycosylation at 3 position which in turn are more photostable than the corresponding aglycones.

Oxygen and pH

The pH not only exerts a profound influence on the colour of anthocyanins but also affects their stability. Lukton *et al.*¹⁷ concluded that pH in the range 2 to 4 has little effect on the rate of anthocyanin breakdown during heat processing under anoxic conditions. However, oxygen greatly accelerated the anthocyanin degradation in the same pH range. Nebesky *et al.*¹⁸ found oxygen and temperature to be the most specific accelerating agents in the degradation of anthocyanins in fruit juices. Daravingas and Cain¹⁹ found a greater retention of anthocyanins in raspberries canned under nitrogen or vacuum than under air. Francis and Starr²⁰ and Clydesdale *et al.*²¹ also demonstrated the detrimental effects of oxygen on anthocyanins.

Vitamin C

Beattie *et al.*²² and Pederson *et al.*²³ observed the concurrent disappearance of ascorbic acid (vitamin C) and anthocyanins in stored fruit juices. They suggested a possible interaction between the two compounds. Shrikhande and Francis²⁴ found that copper ions accelerate and flavonoids (quercetin and quercetrin) diminish the destruction of both ascorbic acid and anthocyanin when they are simultaneously present. Ascorbic acid or vitamin C is present in most of the fruit products. This vitamin undergoes oxidation to form H_2O_2 , which reacts with anthocyanin to form colourless compounds, for example the conversion of malvin to malvone^{25,26} (see Figure 6). Jurd²⁷ reports the

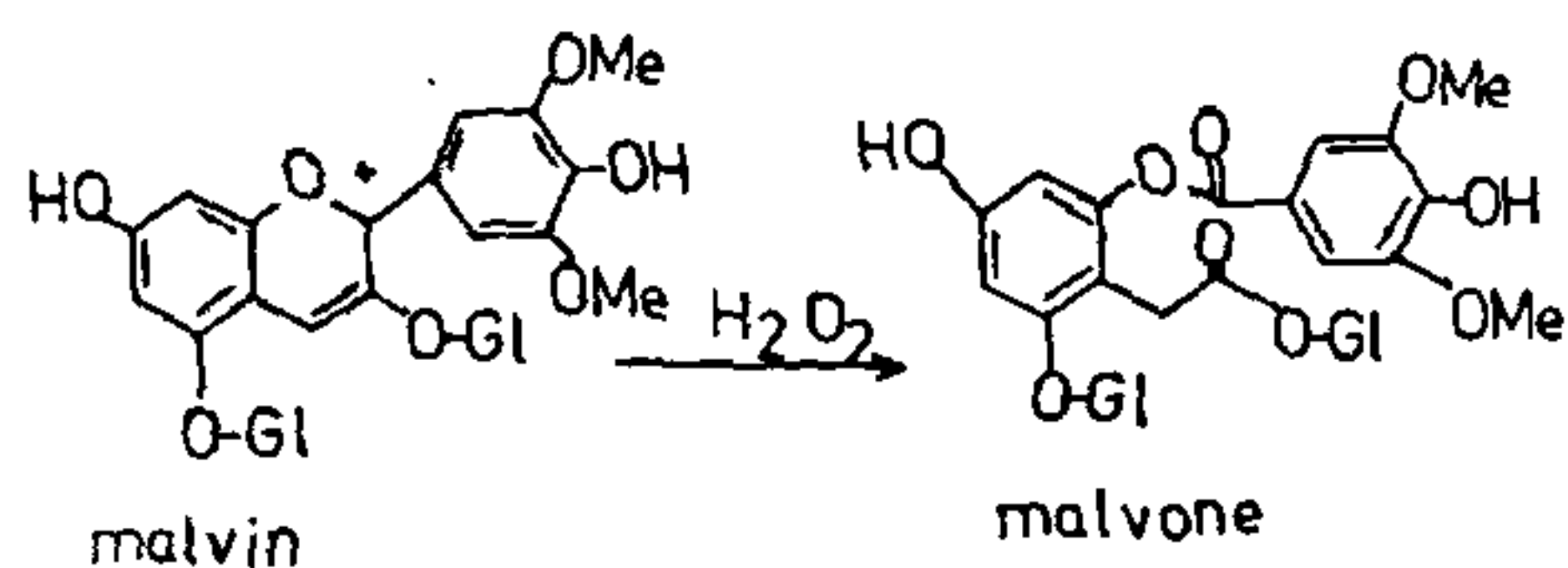


Figure 6. Malvin to malvone transformation by H_2O_2 from vitamin C oxidation.

formation of colourless flav-2-enes resulting from ascorbic acid (see Figure 7). Mikova *et al.*²⁸ studied the effect of ascorbic acid on anthocyanin contained elderberry juice and found a linear relationship between anthocyanin decomposition rate and ascorbic acid concentration. In addition to ascorbic acid Jurd²⁷ also considers the possibility of condensation reactions of anthocyanins with amino acids, phloroglucinol and other flavonoids of nucleophilic character to yield colourless 4-substituted flav-2-enes. For instance, the condensation product between anthocyanin and catechin (see Figure 8), and the condensation product of anthocyanin with phloroglucinol to form colourless flavnyl phloroglucinol (see Figure 9).

Carbohydrates

MacKinney *et al.*²⁹ and Meschter⁷ have noticed the accelerating effects of sugars on the degradation of chief

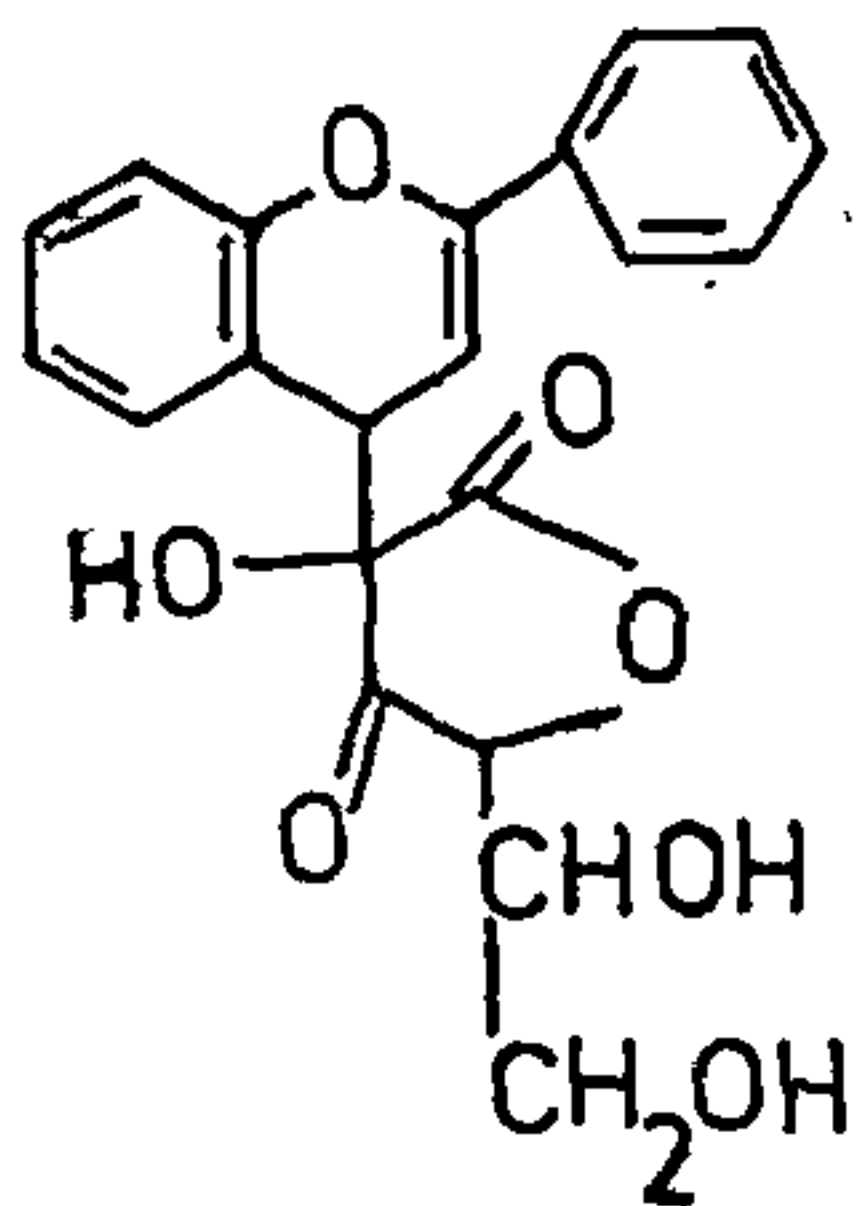


Figure 7. Flav-2-ene from reaction of vitamin C and anthocyanin.

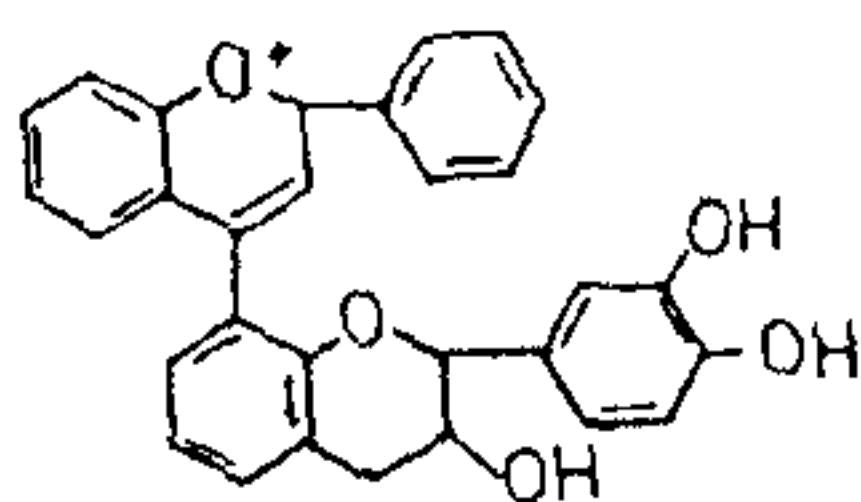


Figure 8. Condensation product of anthocyanin and catechin.

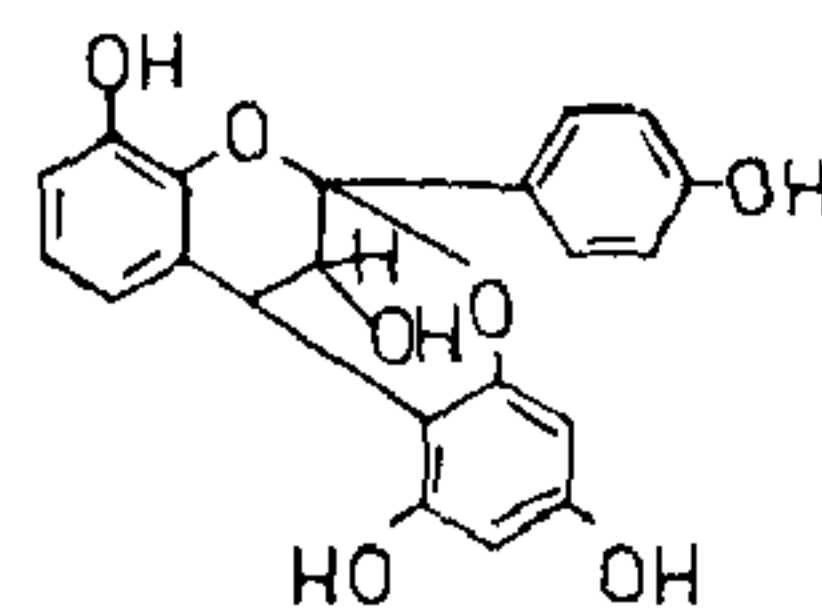


Figure 9. Condensation product of anthocyanin and flavnyl phloroglucinol.

anthocyanins of strawberries. Meschter related the effects of sugars on anthocyanins to sugar-degradation products, namely furfural and hydroxymethyl furfural. This has been borne out by the subsequent work of Tinsley and Bockian¹¹ and Debicki-Pospisil *et al.*¹².

Metals

The discoloration of anthocyanins in fruit products by reaction with tin of the cans has long been known to the fruit industry³⁰. In reaction with tin, anthocyanins can act as either cathodic depolarizers or as anodic depolarizers. As the former they are probably reduced by the nascent hydrogen formed in the acid-metal reaction³¹ (see Figure 10). Anodic depolarizers are usually anthocyanins with at least two $-\text{OH}$ groups in *ortho* positions. Stannous ions formed during corrosion initiation of the tin plate react with the anthocyanin *ortho* hydroxyl groups forming purplish compounds. Cichon and Kolek^{32,33} have studied the tin and iron contamination in processed strawberries, black currants and cherries in lacquered cans, and have presented relations between the levels of iron and tin and the levels of ascorbic acid and anthocyanins in the canned fruits.

Sulphur dioxide (SO_2)

Anthocyanins lose colour upon the addition of SO_2 . The bleaching of anthocyanins by SO_2 is frequently

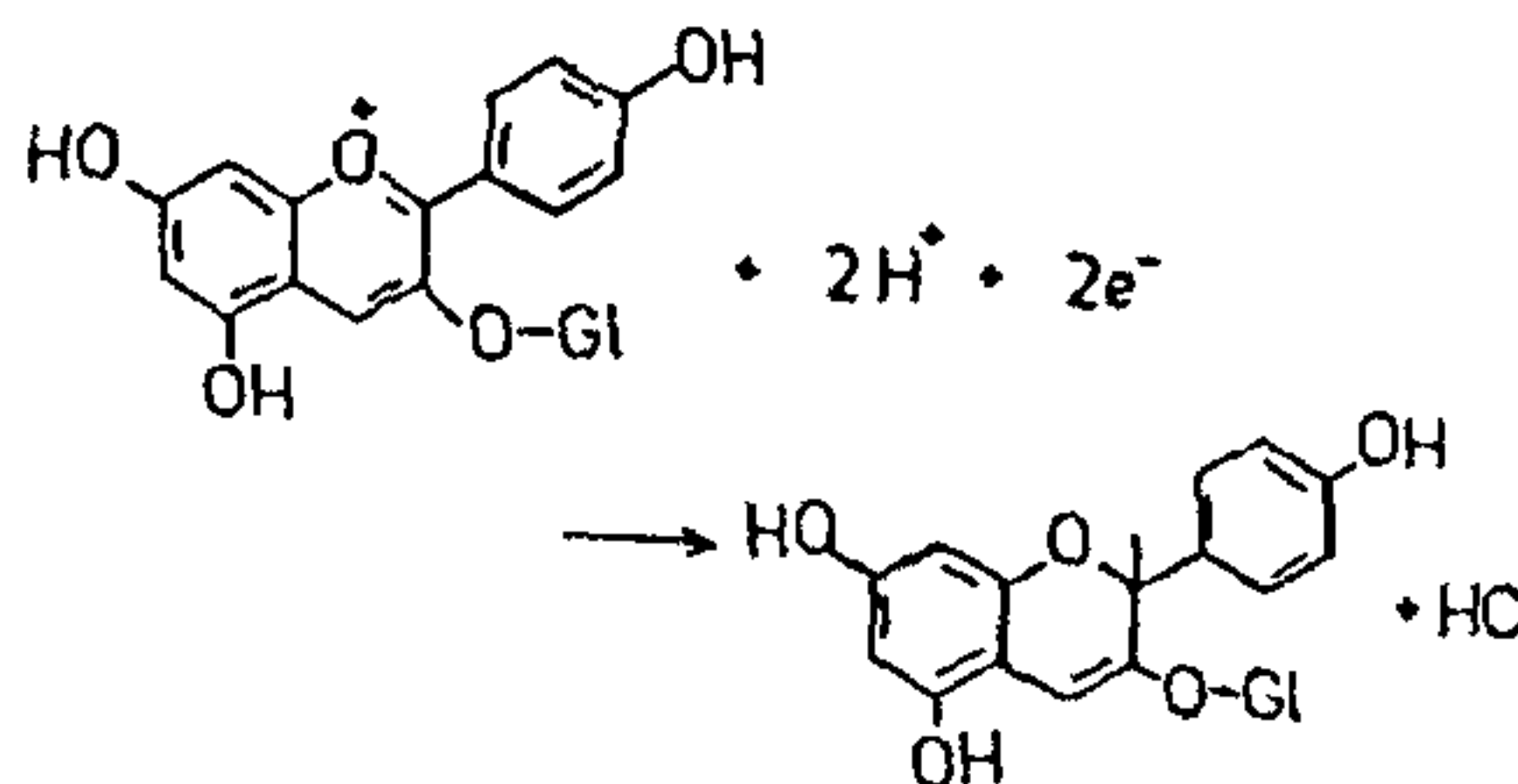


Figure 10. Reaction of anthocyanin as cathodic depolarizer in tin cans.

encountered in the fruit industry. The bleaching may be reversible or irreversible. Fruits and musts preserved by moderate amounts (500–2000 ppm) are desulfited before further processing and the anthocyanin colouration returns. Jurd³⁴ has proposed a scheme for the reversible reaction between SO_2 and anthocyanins according to which the coloured flavylum reacts with bisulphite ion to form colourless chromene-2 (or-4)-sulphonic acid (see Figure 11).

Applications as food colours

Anthocyanins for use as food colours may be extracted from the raw material, for example, black grape peels, strawberry, etc. by water^{35,36}, water containing SO_2 (ref. 37) and acidified alcohols³⁸. The quantitatively obtained extracts are usually concentrated under reduced pressure and marketed at room temperature. The oldest commercial anthocyanin preparation is 'Enocianina', a deeply coloured extract of red grapes marketed in Italy since 1879. This product was used originally to intensify the colour of red wines, but now has found application as a general food colourant. Garoglio³⁷ mentions the following composition for a liquid Italian 'Enocianina': Density, 1.04; alcohol, trace or absent; total acidity (as tartaric acid), 4.237%; volatile acidity, 0.130%; ash, 1.573%; pigments and tannin, 4.265%; sulphates as H_2SO_4 , 1.95%; free SO_2 , 320 ppm; total solids, 8.64%. Shewfelt and Ahmed³⁹ freeze-dried anthocyanin extracts from blue berries and cabbages and these displayed great colour stability in dry soft drinks. Lowry and Chen⁴⁰ reported that blue anthocyanin extracts from dried flowers of *Clitoria ternata* are used for colouring rice cakes in Malaysia. Jelly dyed vivid purplish, red violet and blue with *Clitoria* anthocyanins retained this colour unchanged

after 15 days of simulated storage⁴¹. Saito *et al.*⁴² found the anthocyanins of *Clitoria ternata* to be of remarkable stability in solution. The instability of anthocyanins in solution to light, pH and SO_2 can be avoided by reacting anthocyanins with carbonyl compounds like acetaldehyde to stabilize them. Acetaldehyde enhances the colour of anthocyanins and flavan-3-ols⁴³. This is attributed to the formation of highly coloured compounds in which anthocyanins and flavan-3-ols are linked by CH_3CH bridges. Multiglycosylated and acylated anthocyanins are more stable to light than simple monoglycosides or aglycones^{16,44}. Asen *et al.*⁴⁵ in 1979 made use of an acylated anthocyanin namely peonidin 3-dicaffeoyl sophoroside-5-glucoside from *Ipomea tricolor* (morning glory) flowers to colour foods and beverages in a pH range of 2 to 8. Kotake⁴⁶ in a Japanese patent stabilized anthocyanin food pigments by adding flavones like myricetin, quercetin or flavonols like kaempferol and phytic acid in the colour formulation. Another Japanese patent⁴⁷ mentions the stabilization of red cabbage anthocyanins by emulsifying the pigments in water containing surfactant with a hydrophile lipophile balance (HLB) value of about 3 at a pH of around 3.5 with an equal volume of salad oil. The above stabilized formulation was later used to give a highly stable purplish red colour to ice cream. Hasegawa⁴⁸ has shown that discoloration of anthocyanin food colour can be prevented by treatment with chlorogenic or caffeic acids. Maccarone⁴⁹ stabilized anthocyanin colouration in blood orange juice by addition of tannic acid.

There has been a rise in commercial interest in elaborating anthocyanins in plant tissue culture due to their potential application as colourants in the food industry. The acylated cyanidin triglycoside of carrot cells namely cyanidin 3-(sinapylxylosylglucosylgalactoside) is advantageous because of the high yields in which it can be obtained in carrot cell suspension cultures⁵⁰. A Japanese patent describes the manufacture of anthocyanins from *Hibiscus subdariffa* calluses⁵¹. Saquet-Barel and Crouzet⁵² have given an industrial process for the manufacture of anthocyanin food colour.

Prognosis

With reference to food elements, there is nowadays an awareness for everything 'natural' in preference to 'synthetic'. The food industry has now become increasingly aware of the possibilities of making use of natural vegetable colours. Given the present pace of research in stabilizing anthocyanins in various food systems along with the efforts put into producing anthocyanin-rich plant tissue cultures the day is not far off when these pigments will universally replace synthetic red food colours.

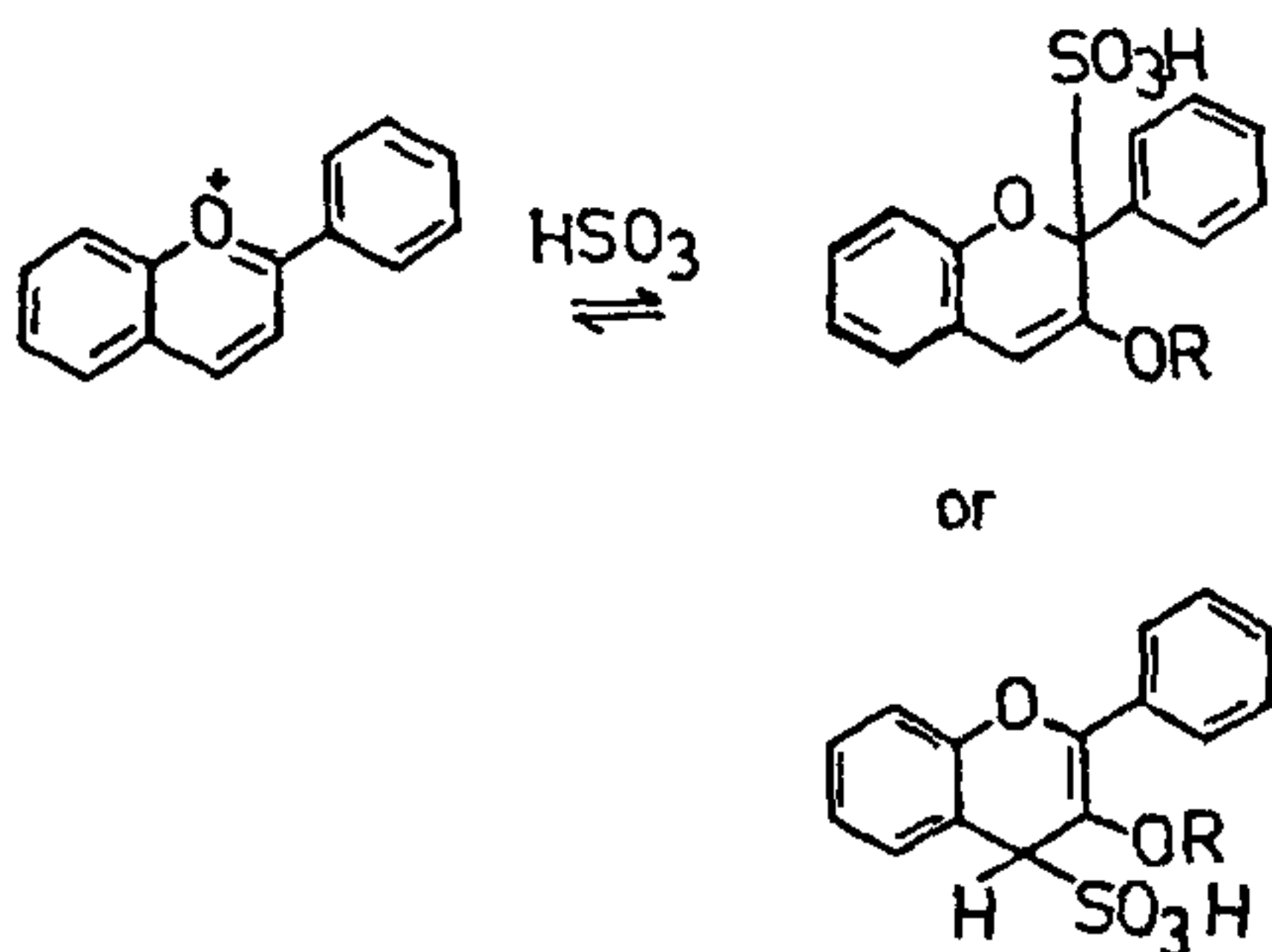


Figure 11. Jurd's scheme for reversible reaction between SO_2 and anthocyanin.

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High latitude–low latitude ionosphere coupling

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This article examines the strong electrodynamic coupling between the high, middle and low latitude ionospheres using interplanetary magnetic field data together with the electric fields obtained from the Doppler frequency variations of the coherent VHF backscatter signals at Trivandrum, plasma drift measurements in the F region from the incoherent scatter radar, ground-based magnetograms from high, middle and low latitudes including

the equatorial region. The virtual height variations obtained from ionograms during the post-midnight sector are used to show that the global convection models reproduce a number of characteristics of low latitude and equatorial electric fields associated with changes in the polar cap potential drop. In addition, we highlight several areas of substantial disagreement between the electric field data and the theoretical results.

DURING the last two decades, significant progress has been made in elucidating the magnetosphere-ionosphere-

thermosphere coupling processes at high latitudes¹. One of the important features of the dynamic