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SHORT COMMUNICATION

THE STRUCTURE OF AURANTINIDIN

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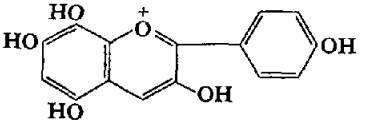
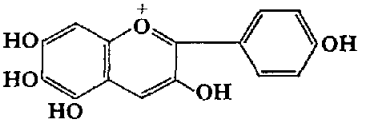
Abstract—Isomeric rearrangements during the synthesis and purification of 5,6,7- and 5,7,8-trihydroxyanthocyanidins are discussed and spectral evidence is presented in support of the 3,5,6,7,4′-pentahydroxyflavylium structure (II) for aurantinidin.

INTRODUCTION

AURANTINIDIN, a novel anthocyanidin which occurs[1] in the petals of *Impatiens aurantiaca* (*Balsaminaceae*), is a pentahydroxyflavylium salt which on reductive cleavage yields pyrogallol and *p*-hydroxyphenylpropane derivatives. On this basis aurantinidin has been formulated[2] as either 8-hydroxypelargonidin (I) or the isomeric 6-hydroxypelargonidin (II).



(I)



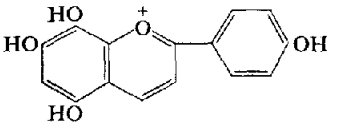
(II)

Attempts to distinguish between these two possible structures by synthesis, however, failed. Thus, it was found[2] that 6-hydroxypelargonidin (II), prepared by pyridinium chloride demethylation of 5,7-dimethoxy-3,6,4′-trihydroxyflavylium chloride, and 8-hydroxypelargonidin (I),[3] prepared by reductive acetylation[4] of herbacetin (3,5,7,8,4′-pentahydroxyflavone) and subsequent acid treatment of the reduced product, were completely indistinguishable from each other and from aurantinidin by any of the usual chromatographic and spectral criteria.

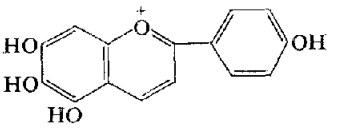
[1] S. CLEVENGER, *Can. J. Biochem.* **42**, 154 (1964).
[2] H. M. HURST and J. B. HARBORNE, *Phytochem.* **6**, 1111 (1967).
[3] This was the presumed structure of the reductive acetylation product. As subsequently indicated in the text it is now proposed that reductive acetylation and hydrolysis of herbacetin actually leads to isomerization and formation of 6-hydroxypelargonidin.
[4] H. G. C. KING and T. H. WHITE, *J. Chem. Soc.* 3901 (1957).

RESULTS AND DISCUSSION

Some years ago it was demonstrated[5] that in acid solutions 3-desoxyanthocyanidins undergo facile, reversible ring opening to the corresponding 2′-hydroxychalcones and under these conditions the 5,7,8,4′-tetrahydroxyflavylium salt (III) rapidly isomerizes to the 5,6,7,4′-tetrahydroxyflavylium salt (IV). Hydrolytic ring opening of flavylium salts has since been confirmed[6, 7] and, furthermore, evidence has been reported[8] which indicates that



(III)



(IV)

3-hydroxyflavylium salts, e.g. pelargonidin and cyanidin, also exhibit this property of reversible ring fission in aqueous solutions at pH < 7. The established methods for the synthesis and subsequent purification of anthocyanidins all involve prolonged exposure of the flavylium product to acid conditions and water or other polar solvents. The above observations suggest, therefore, that unambiguous verification of aurantinidin-type structures is not possible by the direct use of known synthetic procedures, since the initial flavylium product may undergo reversible ring fission to yield the more thermodynamically stable isomer. Thus, we now believe that the syntheses[2] designed to yield I and II almost certainly led to the formation of the *same* flavylium salt. Spectral considerations (*vide infra*) indicate that this is the 6-hydroxy isomer (II). Confirmatory evidence of facile ring fission and isomerization in this series is provided by the reductive acetylation of gossypetin (3,5,7,8,3′,4′-hexahydroxyflavone) and quercetagetin (3,5,6,7,3′,4′-hexahydroxyflavone). The flavylium salt obtained from the gossypetin reaction was identical in all chromatographic and spectral respects with that from the isomeric quercetagetin. The spectrum of this flavylium salt indicates that it is 6-hydroxycyanidin.

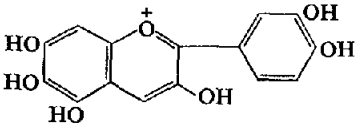
TABLE 1. VISIBLE SPECTRA OF MODEL FLAVYLIUM SALTS

Flavylium salt	MeOH–HCl λ_{max} (nm)	Difference
4′-Hydroxy	448	
3,4′,-Dihydroxy	473	25
4′-Hydroxy-8-methoxy	442	
3,4′,-Dihydroxy-8-methoxy	471	29
4′,7-Dihydroxy	470	
3,4′,7-Trihydroxy	505	35
4′,5,7-Trihydroxy	480	
3,4′,5,7-Tetrahydroxy	520	40

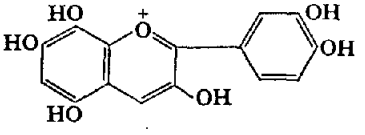
[5] L. JURD, *Chem. and Ind.* 1197 (1962); *J. Org. Chem.* **28**, 987 (1963).
[6] C. F. TIMBERLAKE and P. BRIDLE, *Chem. and Ind.* 1520 (1965); *J. Sci. Food Agr.* **18**, 473 (1967).
[7] K. A. HARPER and B. V. CHANDLER, *Australian J. Chem.* **20**, 731 (1967).
[8] C. F. TIMBERLAKE and P. BRIDLE, *Nature* **212**, 158 (1966).

Comparison of the spectra of aurantinidin (λ_{max} 499 nm in methanol–HCl) and a number of model flavylium salts (Table 1) provides strong support for the 6-hydroxypelargonidin structure (II) for this pigment. Thus, in methanol–HCl, the 3-desoxyflavylium salts (III) and (IV) have λ_{max} 432 nm and λ_{max} 467 nm respectively.[9] Examination of the spectra of the following pairs of flavylium salts reveals that addition of a 3-hydroxyl results in a 25–40 nm bathochromic shift of the λ_{max} of the corresponding 3-desoxyflavylium salt. For polyphenolic flavylium salts the shift is in the upper region (35–40 nm) of this range. If this figure is added to the measured λ_{max} (432 nm) of 5,7,8,4′-tetrahydroxyflavylium (III) then the predicted λ_{max} of 8-hydroxypelargonidin (I) will lie in the range 467–472 nm, which is 30 nm less than the λ_{max} of aurantinidin. On the other hand, if 35–40 nm is added to the measured λ_{max} (467 nm) of 5,6,7,4′tetrahydroxyflavylium (IV), the λ_{max} of 6-hydroxypelargonidin (II) is calculated to be 502–507 nm. This predicted spectrum is in excellent accord with the spectrum of aurantinidin and strongly indicates this structure for the pigment. Since the natural glycosides[2] of aurantinidin have λ_{max} 492–497 nm it follows that these compounds also have the 5,6,7-trihydroxy arrangement, i.e. aurantinidin is not an isomeric artefact resulting from a rearrangement during the acid hydrolysis of a natural 5,7,8,-trihydroxyflavylium glycoside.

It has been mentioned that reductive acetylation of gossypetin and quercetagetin apparently yields the same flavylium salt. The spectrum of the product (λ_{max} 518 nm) indicates that it is 6-hydroxycyanidin (V), and not the isomeric 8-hydroxy compound (VI). In support



(V)



(VI)

of this it is well known that addition of a 3′-hydroxyl to a flavylium salt results in a 15 nm bathochromic shift in its λ_{max}, e.g. 4′,7-dihydroxyflavylium (λ_{max} 469 nm), 3′,4′,7-trihydroxyflavylium (λ_{max} 485 nm); pelargonidin (λ_{max} 520 nm), cyanidin (λ_{max} 535 nm). If 15 nm is added to the calculated spectra of IV and III, it follows that 6-hydroxycyanidin (V) should have its absorption maximum at about 517–522 nm while 8-hydroxycyanidin (VI) is predicted to absorb at a much lower wavelength (482–487 nm). The predicted λ_{max} of V is identical with the measured λ_{max} of the gossypetin and quercetagetin product, and furthermore the synthetic pigment as prepared by Charlesworth and Robinson[10] by standard procedures has the same value (516–518 nm).

[9] Specimens of III and IV were kindly provided by the late Professor T. S. Wheeler.
[10] E. H. Charlesworth and R. Robinson, *J. Chem. Soc.* 1619 (1934).