A New Class of Flavone Pigments in the Palmae

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In the course of a chemotaxonomic flavonoid survey of monocotyledonous families related to the grasses [1], attention was turned to flavonoids in leaves of the Palmae. Many of the flavonoids present were readily identified as known pigments [2]. Thus, the flavonols, kaempferol and quercetin, and the flavones, apigenin and luteolin, were variously detected in glycosidic combination. Glycosylflavones based on apigenin and luteolin were also present. In one case, *Chamaerops humilis*, the rare flavone tricin, already known as a grass constituent, was found [2]. In addition, a series of apparently novel flavones were present; besides being very water-soluble, these pigments had markedly different chromatographic behaviour (very high R_fs in water, very low R_fs in butanol-acetic acid on paper) from the commoner constituents. An important clue to their identity came when it was discovered they were electrophoretically mobile in acid buffer (pH 2.2), carrying negative charges. The only charged flavonoids known are the anthocyanin pigment cations and the rare anionic flavonol, persicarin, the 3-potassium bisulphate of isorhamnetin. Persicarin was first found some years ago in several *Polygonum* species (Polygonaceae) [3, 4] and in *Oenanthe stolonifera* (Umbelliferae) [4] and more recently closely similar substances have been reported in two *Lasthenia* species (Compositae) [5]. Further studies have now revealed that the flavones present in the palms occur, like the flavonol persicarin, in conjugation with potassium bisulphate and thus they represent the first members of a new class of flavone pigments.

One of the novel flavones present in *Mascarena verschaffeltii* was isolated and analysed in more detail. Acid hydrolysis gave glucose, potassium, luteolin and sulphate (the latter moieties in equimolecular amount). Sulphate was recovered as $BaSO_4$ and weighed, the potassium being detected by flame photometry. Spectral and enzymic studies showed that the new compound could be formulated as the 7-potassium bisulphate salt of luteolin 3′-glucoside. Similar studies on the complex mixture of flavones present in leaves of *Washingtonia robusta* showed the presence of no less than eight charged flavones, including a luteolin 7-rhamnosylglucoside and derivatives of the glycosylflavones, vitexin and orientin, with bisulphate residues apparently attached either to the phenolic or the sugar hydroxyl groups.

The new class of compound is easily detected by electrophoresis, since ordinary flavones are immobile in an electric field. A survey showed that charged flavones were widespread in the palms, being found in 17 of 31 species examined. They were detected in *Chrysalidocarpus, Gaussia, Mascarena* (2 spp.), *Opsiandra* and *Rhopalostylis* of the subfamily Arecoideae; in *Caryota* (2 spp.) of the Caryotoideae; in *Butia* (2 spp.) of the Cocoideae; and in *Cocothrinax, Phoenix, Pritchardia, Sabal, Thrinas,* and *Washingtonia* (2 spp.) of the Coryphoideae.

The Palmae are widely recognised, both anatomically and morphologically, as being very isolated from other monocotyledonous groups [6]. It is not surprising, therefore, to find a distinctive chemical character, the flavone bisulphate, within this remarkable family. The variation in this character at the 50% level within the palms suggests it may prove of value as a taxonomic marker when more is known of its distribution. Their relatively widespread occurrence in palms suggests that the flavone bisulphates may have a special metabolic or other function in these plants. It has been suggested that the occurrence of the related flavonol derivatives, such as persicarin, in the dicotyledons is associated with adaptation to an aquatic habitat [7]. Such an explanation hardly holds for the Palmae and the ecological significance of flavone bisulphates in the palms must await further study.

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1 J. B. HARBORNE and H. T. CLIFFORD, Phytochem. **8**, 2071 [1969].

2 C. A. WILLIAMS, J. B. HARBORNE, and H. T. CLIFFORD, Phytochem. **10**, 1059 [1971].

3 R. KAWAGUCHI and K. W. KIM, J. pharm. Soc. Japan **57**, 108 [1937].

4 H. TATSUTA and Y. OCHII, Sci. Rep. Tohoku Univ. 1 **39**, 243 [1956].

5 N. A. M. SALEH, B. A. BOHM, and R. ORNDUFF, Phytochem. **10**, 611 [1971].

6 E. J. H. CORNER, "The Natural History of Palms", Weidenfeld and Nicolson 1966.

7 J. MCCLURE, in: "Phytochemical Phylogeny", (Ed. J. B. HARBORNE) p. 233, Academic Press, London 1970.