Phytochemistry, 1974, Vol. 13, pp. 1557 to 1559. Pergamon Press. Printed in England.

# DISTRIBUTION OF CHARGED FLAVONES AND CAFFEYLSHIKIMIC ACID IN PALMAE

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(*Received* 27 *November* 1973)

**Key Word Index**—*Arecastrum romanzoffianum*, *Butia capitata*, etc., Palmae, flower flavonoids, charged flavones, *C*-glycosylflavones, isorhamnetin 3,4'-diglucoside, quercetin 3,7-diglucoside, caffeylshikimic acid

**Abstract**—Identification of the phenolic constituents in flowers of nine palm species has revealed that charged *C*-glycosylflavones and caffeylshikimic acid are characteristically present. Flavonol glycosides are also common, the 3-glucosides, 3-rutinosides and 3,4'-diglucosides of quercetin and isorhamnetin and the 7-glucoside and 3,7-diglucoside of quercetin are all variously present. Tricin 7-glucoside, luteolin 7-rutinoside and several uncharged *C*-glycosylflavones were also detected. Male flowers of *Phoenix canariensis* differ from female flowers in having flavonol glycosides. As expected, in most species studied, flavonoid patterns in the flowers vary considerably from those found in the leaves.

## INTRODUCTION

A RECENT survey of 125 species of the Palmae for their leaf flavonoids revealed the frequent presence of a new type of flavone conjugate, flavone bisulphates, in some 50% of the samples. Other leaf constituents include tricin and luteolin glycosides and a range of *C*-glycosylflavones.[1,2] Flavone bisulphates appear to be rare in the plant kingdom, having only been detected subsequently in *Saccharum* and some related genera in the Gramineae[3] and in *Bixa orellana* (Bixaceae).[4] The corresponding flavonol bisulphates have a wider distribution, having been reported in the Compositae, Frankeniaceae, Polygonaceae, Tamaricaceae and Umbelliferae,[5] as well as in the Palmae.[2]

The flowers of palms are enormously varied in the diversity of their structures and provide many of the characters that are used in classification of the family.[6] It was therefore of interest to see if the characteristic leaf bisulphates also occurred in these organs. The present paper is therefore a report of flavonoids found in some representative palm flowers. Such tissues have not apparently been examined before for their flavonoid pigments.

[1] HARBORNE, J. B. and WILLIAMS, C. A. (1971) *Z. Naturforsch* **26b**, 5
[2] WILLIAMS, C. A., HARBORNE, J. B. and CLIFFORD, H. T. (1973) *Phytochemistry* **12**, 2417
[3] WILLIAMS, C. A., HARBORNE, J. B. and SMITH, P. (1974) *Phytochemistry*, in press
[4] HARBORNE, J. B., *Chemistry in Botanical Classification* (BENDZ, G. and SANTESSON, J., ed.) pp. 103–115, Academic Press, New York
[5] For review, see HARBORNE, J. B. and WILLIAMS, C. A. (1974) *The Flavonoids* (HARBORNE, J. B. and MABRY, T. J., ed.) Chapman & Hall, London
[6] MOORE, H. E. (1961) *Am. Hort. Mag.* **40**, 17

## RESULTS AND DISCUSSION

Palm plants only flower for relatively short periods during the year and even when in flower, the inflorescences are often inaccessible for study. Specimens are therefore difficult to collect and the present survey has inevitably been based on a relatively small sample. These were plants growing in Uruguay, in and around Montevideo, which could be taxonomically verified.

The results of the analyses of the flowers of nine species are presented in Table 1. There are four main points of interest.

TABLE 1. FLAVONOID GLYCOSIDES OF PALM FLOWERS

| Palm species | Ordinary flavonoids* | Negatively charged flavonoids* |
|---|---|---|
| *Arecastrum romanzoffianum* var. *australe* Becc. | Qu-7-G, Lucenin 7-G, Cfs. | Or |
| *Butia capitata* Becc. | Tricin 7-G, IOr, Cfs | Absent |
| *Chamaerops humilis* L. | Qu-3-RG, IRh 3-RG, IRh 3-G, Cfs | Absent |
| *Jubaea chilensis* (Molina) Baillon | Unidentified flavonol glycosides, Cfs | Unidentified flavonol glycosides |
| *Livistona chinensis* (N. J. Jacquin) R. Brown ex Martius | Qu-3-G, Flavone *C*-glycoside, Cfs | Flavone *C*-glycoside |
| *Phoenix canariensis* Hort. ex Chabaud (female flower) | Luteolin 7-RG, Cfs | Or 7-G, IOr 7-G, Vit 7-G, Apigenin 7-G |
| *Phoenix canariensis* Hort. ex Chabaud (male flower) | Qu-3-G, Q 3,4′-diG, IRh 3,4′-diG, IRh triglyc, Cfs | Or, IOr, Vit, IVit |
| *Phoenix roebolenii* O'Brien | Luteolin *C*-glycosides, Cfs | Luteolin *C*-glycosides |
| *Sabal minor* (N. J. Jacquin) Persoon | Flavone *C*-glycosides, Cfs | Flavone *C*-glycosides |
| *Sabal blackburniana* Glazebrook ex J. A. et J. H. Schultes | Qu 3,7-diG, Or, IOr, Vit, IVit, Vit 7-G, Cfs | Or, Or 7-G, IOr 7-G, Vit 7-G, IVit 7-G |

*Abbreviations: Cfs, caffeylshikimic acid; Or, orientin; IOr, iso-orientin; Qu, quercetin; IRh, isorhamnetin; Vit, vitexin; IVit, isovitexin; G, glucose; RG, rutinoside.

Firstly, 7 out of the 9 taxa have charged flavones, which is a higher percentage than that (50%) found in the leaves.[2] However, the difference is probably a matter of sampling, since charged flavones occur mainly in the flowers of those species which have them in the leaves. The only exception is *Butia capitata*, where the conjugates occur in the leaf[2] but not the flower (see Table 1).

Secondly, flavonol glycosides are more frequent in the flowers than in the leaves, relative frequencies being 55 and 25%. Glycosides not found previously in the leaf survey include the 7-glucoside and 3,7-diglucoside of quercetin and the 3,4′-diglucosides of quercetin and isorhamnetin. These latter two pigments are rather uncommon in nature, but have been previously detected in monocotyledons in the pollen of *Dactylis glomerata*, *Phleum pratense* (Gramineae) and *Crocus* (Iridaceae)[7,8] and in the bulb of *Allium* (Liliaceae).[9]

[7] INGLETT, G. E. (1957) *J. Org. Chem.* **22**, 189.
[8] KUHN, R. and LOW, I. (1944) *Chem. Ber.* **77b**, 196.
[9] HARBORNE, J. B. (1965) *Phytochemistry* **4**, 107.

A third point of interest relates to the differences in flavonoids between male and female flowers of *Phoenix canariensis*. There are striking differences both in charged flavones and also in the uncharged flavonoid fraction (see Table 1). Earlier work[2] has shown that the leaf of this species has a wider range of flavonoids than either male or female flower; tricin, detected in the leaf, was not found in flowers of either sex. This is not really surprising since although tricin is a characteristic leaf compound, it does not appear often in the flowers. Indeed, in the present survey (Table 1), there is a single record in *Butia capitata*.

Fourthly, a major phenol in palm flowers, often occurring in greater amount than any of the flavonoids, is 3-caffeylshikimic acid. This compound has previously been characterized in the fruits of the date palm, *Phoenix dactylifera* L. and of four other palm species[10,11] and is clearly very rare outside the palms, there being a single report of it in a gymnosperm, in *Tsuga canadensis* Carr.[12] Its universal occurrence in palm flowers is therefore of considerable interest and suggests that it may be a distinctive taxonomic marker for the family. However, in the leaf, it is apparently much less frequent. In a survey of 15 representative species, it was found in only three, one had the related *p*-coumarylshikimic acid and the remainder contained the much more common quinic ester of caffeic acid, namely chlorogenic acid.[13]

In summary, from a limited survey, it appears that the flowers of palms are relatively rich in flavonoid pigments and that each species has a characteristic flavonoid pattern. The flavonoids present are similar to those found in the leaf, but the frequencies of their distribution are significantly different from those in the leaf. Finally, it is apparent that palm flowers are characterized by having charged flavones and large quantities of caffeylshikimic acid in their tissues. The ecological significance of these findings remains to be determined.

## EXPERIMENTAL

*Plant material* Fresh flowers were collected by P M during 1972 and early 1973 from palm specimens, which were taxonomically identified by the staff of the Botany Department, University of Montevideo The fresh tissues were extracted with hot EtOH and the concentrated extracts sent to the U K by airmail for further analysis

*Phenolic identifications* Flavonoids were separated and identified by standard procedures Confirmation was by spectral and chromatographic comparison with authentic samples, most of which were available from the earlier studies of leaf flavonoids in the same family [2] The sample of isorhamnetin 3,4′-diglucoside (dactylin) was kindly provided by Dr G Inglett, that of quercetin 3,4′-diglucoside was previously isolated from *Allium cepa* Caffeylshikimic acid was identified by its hydrolysis to give caffeic and shikimic acids, and by co-chromatography and spectral comparison with an authentic specimen, kindly provided by Dr V P. Maier

*Acknowledgements*—The authors are grateful to members of staff of the Botany Department, University of Montevideo for their assistance in collecting and identifying the plants used in this study P M thanks Miss Graciela Galante for technical assistance and the Chemical Society and the Forge Foundation for financial support

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[11] MAIER, V P (1963) *Proc Third Ann Symp Plant Phenolics Group N America*, p 53
[12] GOLDSCHMID, O and HERGERT, H L (1961) *Tappi* **44**, 858
[13] WILLIAMS, C A, unpublished results