



transformations and not on spectral measurements.⁴ No direct comparison was possible but the identification of our material as VI was further supported by the following spectral data: $\nu_{\text{max}}^{\text{KBr}}$ (cm^{-1}) 3350, 1090, 1060 ($-\text{CH}_2\text{OH}$ and $=\text{CHOH}$), 1635, 990, 902 ($-\text{CH}=\text{CH}_2$) 850 ($-\text{CH}=\text{C}=\text{C}-$), and δ 0.78 (s, 10- CH_3), 0.81 (s, 4- CH_3), 0.99 (s, 13- CH_3), 3.40 (AB q, $J = 10.5$ Hz, 4- CH_2OH), 3.60 (broad t, $J = 6.0$ Hz, 3 α -H), 3.98 (OH), ABX system at 4.78, 4.80, 5.68 ($J_{\text{AX}} 18.0$, $J_{\text{BX}} 9.7$, $J_{\text{AB}} 2.0$ Hz, $-\text{CH}=\text{CH}_2$), 5.15 (s, 14-H).

Acknowledgements—We are grateful to Profs. Y. Kitahara and I. Murata, and Dr. M. Funamizu, Tohoku University, for measurements of mass and NMR spectra and elemental analyses. We are indebted to Mr. K. Komatsu and Hokushu Mokuzai Co. for supplying sawdust of the plant.

⁴ R. A. LAIDLAW and J. W. W. MORGAN, *J. Chem. Soc.* **1963**, 644.

Key Word Index—*Juniperus rigida*; Cupressaceae; diterpene; 3 β -hydroxysandaracopimaric acid.

Phytochemistry, 1972, Vol. 11, pp. 842 to 843. Pergamon Press. Printed in England.

CYCADACEAE

(ZAMIACEAE)

THE DETECTION OF C-GLYCOSYLFLAVONES IN *DIOON SPINULOSUM*

J. L. CARSON and J. W. WALLACE

Department of Biology, Western Carolina University, Cullowhee, N.C. 28723, U.S.A.

(Received 13 August 1971)

THE ONLY flavonoids that have been reported from the Cycadales¹ are biflavones; these have been identified in *Cycas revoluta* Thumb² and *Zamia angustifolia* Facq.³ The present report concerns the identification of C-glycosylflavones in *Dioon spinulosum* Dyer ex Eichl.

Orientin and an apigenin 8-C-glycoside, probably vitexin, were identified by standard

¹ L. A. S. JOHNSON, *Proc. Linnean Soc. N.S. Wales* **84**, 64 (1959).

² N. KAWANO and M. YAMADA, *J. Pharm. Soc. Japan* **80**, 1576 (1960).

³ B. K. HANDA, K. K. CHEXAL, R. RAHMAN, M. OKIGAWA and N. KAWANO, *Phytochem.* **10**, 436 (1971).

procedures.⁴⁻⁶ These C-glycosylflavones were minor constituents, the major flavonoids being as yet uncharacterized biflavones. This is the first report of C-glycosylflavones in the cycads.

EXPERIMENTAL

The plant material was furnished by the Fairchild Tropical Gardens, Miami, Florida, U.S.A. (accession Nos. 58545 and 59958). The air dried leaflets were thoroughly extracted with 80% EtOH. The extract was concentrated, filtered through celite, and the aqueous filtrate was exhaustively extracted with EtOAc. The EtOAc was removed under vacuum, the residue dissolved in a small amount of MeOH and chromatographed on a polyamide column (H₂O, 80% MeOH, and MeOH); each fraction was chromatographed one dimensionally on paper (15% HOAc); finally, each 1-dimensional band was purified by 2-dimensional chromatography on paper (TBA and 15% HOAc). UV-visible spectra were determined according to Mabry *et al.*⁴ The compounds were refluxed in acid according to Wallace *et al.*⁶ and the products were chromatographed on 0.25 mm Avicel (TG-101) plates using TBA and 15% HOAc. Cochromatography was on Avicel plates using 80% isopropyl alcohol; 1% HOAc; 15% HOAc; BAW, TBA; and Benz: HOAc: H₂O (6:7:3; organic phase).

⁴ T. J. MABRY, K. R. MARKHAM and M. B. THOMAS, *The Systematic Identification of Flavonoids*, Springer-Verlag, New York (1970).

⁵ J. W. WALLACE, T. J. MABRY and R. E. ALSTON, *Phytochem.* 8, 93 (1969).

⁶ J. W. WALLACE and T. J. MABRY, *Phytochem.* 9, 2133 (1970).

Key Word Index—*Dioon spinulosum*; cycadales; flavone-C-glycosides.

Phytochemistry, 1972, Vol. 11, pp. 843 to 846. Pergamon Press. Printed in England.

ANGIOSPERMAE DICOTYLEDONAE

APOCYNACEAE

ALCALOÏDES DES FEUILLES D'*HOLARRHENA MITIS**

M. LEBOEUF†, A. CAVÉ‡, G. P. WANNIGAMA§ et R. GOUTAREL‡

(Reçu le 4 juin 1971)

Holarrhena mitis est une espèce endémique dans l'île de Ceylan où elle est connue sous les noms de kiri-walla et kiri-mawara;^{1,2} on la trouve dans les régions sèches jusqu'à une altitude de 500 m. L'écorce, vendue sous le nom de 'kalinda' est utilisée en médecine locale dans le traitement des fièvres et de la dysenterie.

C'est un arbre grand et frêle, à écorce lisse et blanchâtre; les rameaux sont grêles, lisses, de couleur pourpre. Les feuilles, courtement pétiolées, mesurent de 4 à 9 cm; elles sont oblongues-lancéolées, glabres, minces. Les fleurs apparaissent en Avril en corymbes peu

* Partie CXXXIII dans la série "Alcaloïdes Stéroïdiques". Pour Partie CXXXII J. EINHORN, C. MONNERET et Q. KHUONG-HUU (sous presse).

† Laboratoire de Matière Médicale, Faculté de Médecine et de Pharmacie, 25-Besançon.

‡ Institut de Chimie des Substances Naturelles du C.N.R.S., 91-Gif s/Yvette.

§ Université de Ceylan, Peradeniya.

¹ TRIMEN, *A Handbook to the Flora of Ceylon* Part III, p. 131, Dulau, London (1895).

² KIRTIKAR et B. D. BASU, *Indian Medicinal Plants* (edited by L. M. BASU), Vol. II, p. 1573, Allahabad, India (1935).