

## CYCADACEAE

OCCURRENCE OF BISFLAVONES IN *ZAMIA*

B. K. HANDA, K. K. CHEXAL and W. RAHMAN

Department of Chemistry, Aligarh Muslim University, Aligarh, India  
and

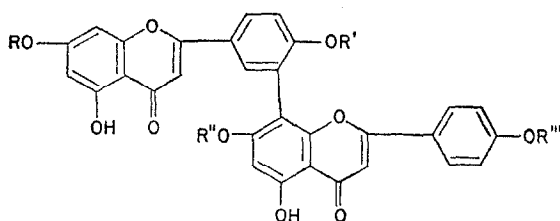
M. OKIGAWA and N. KAWANO

Faculty of Pharmaceutical Sciences, Nagasaki University, Nagasaki, Japan

(Received 16 March 1970)

CYCADS and the ginkgo are the only surviving types of ancient, primitive seed plants. These 'living fossils' clearly represent the last vestiges of formerly diversified and widely distributed type of gymnosperm. Because of the phylogenetic interest in these plants, the chemical investigation of *Zamia angustifolia* Facq. (*Z. floridana* A. DC.), Cycadaceae was undertaken. We now report the isolation and characterization of amentoflavone (I), bilobetin<sup>1</sup> (IIa), sequoiaflavone<sup>2</sup> (IIb), ginkgetin<sup>1</sup> (IIIa), sciadopitysin<sup>3</sup> (IV) and 7,7'',4',4'''-tetra-*O*-methyl-amentoflavone<sup>4</sup> (V) from *Z. angustifolia*.

Extraction of fresh leaves followed by solvent fractionation, column chromatography and preparative TLC gave six components. All gave the same hexamethyl ether which was identical with an authentic sample of amentoflavone hexamethyl ether. The results of NMR studies of the acetates of each component characterized the six individual bisflavones as mentioned above. These compounds form a sequential series of mono-, di-, tri- and tetra-methyl ethers of amentoflavone. It is possible that the methylation of amentoflavone in plant proceeds in the order: 4' or 7-(7,4')-4'''-7'' positions.



	R	R'	R''	R'''
I	H	H	H	H
IIa	H	Me	H	H
IIb	Me	H	H	H
IIc	H	H	Me	H
IIIa	Me	Me	H	H
IIIb	H	Me	H	Me
IV	Me	Me	H	Me
V	Me	Me	Me	Me

<sup>1</sup> W. BAKER, A. C. M. FINCH, W. D. OLLIS and K. W. ROBINSON, *J. Chem. Soc.* 1477 (1963).

<sup>2</sup> H. MIURA and N. KAWANO, *J. Pharm. Soc. Japan* **88**, 1489 (1968).

<sup>3</sup> N. KAWANO, *Chem. Pharm. Bull. Tokyo* **7**, 698; 821 (1959).

<sup>4</sup> R. HODGES, *Aust. J. Chem.* **18**, 1491 (1965).

Sotetsuflavone (IIc) has been reported as the sole bisflavone of *Cycas revoluta* Thunb.<sup>5</sup> However, reinvestigation of this plant revealed that the reported sotetsuflavone is a mixture, major part of which is amentoflavone and minor components are methyl ethers of amentoflavone. Details will be reported later.

Bilobetin (IIa), ginkgetin (IIIa), isoginkgetin (IIIb) and sciadopitysin (IV) have previously been isolated<sup>1,6</sup> from the leaves of *Ginkgo biloba* L. Thus, this cycad and the ginkgo resemble one another not only in many details of their reproductive structures but also in their ability to synthesize bilobetin, ginkgetin and sciadopitysin.

*Acknowledgement*—Two of us (BKH and KKC) thank the Department of Atomic Energy (Govt. of India) for the financial assistance.

<sup>5</sup> N. KAWANO and M. YAMADA, *J. Pharm. Soc. Japan* **80**, 1576 (1960).

<sup>6</sup> H. MIURA, T. KIHARA and N. KAWANO, *Chem. Pharm. Bull. Tokyo* **17**, 150 (1969).

Phytochemistry, 1971, Vol. 10, pp. 437 to 439. Pergamon Press. Printed in England.

## ANGIOSPERMAE (DICOTYLEDONAE)

### APOCYNACEAE

#### MACRALSTONINE FROM *ALSTONIA MUELLERIANA*\*

J. M. COOK and P. W. LE QUESNE

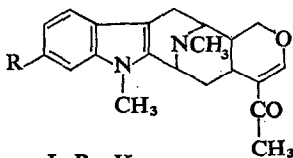
Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48104, U.S.A.

(Received 16 June 1970)

**Abstract**—Macralstonine has been isolated from the alkaloidal fraction of *Alstonia muelleriana*. This supports the close phytochemical relationship between this species and *A. macrophylla* inferred in other recent work.

#### INTRODUCTION

THE RECENT establishment<sup>1</sup> of structure (I) for alstonerine, a constituent of the alkaloidal fraction of *A. muelleriana*,<sup>2</sup> has emphasized the close relationship between *A. muelleriana*



I; R=H

III; R=OCH<sub>3</sub>

\* We thank Professor James P. Kutney and Mr. G. Eigendorf for assistance with mass spectra. This work was supported by a Faculty Research Fellowship and Research Grant from the Horace H. Rackham School of Graduate Studies, University of Michigan (to P. W. Le Q.), and by a NASA Fellowship (to J.M.C.).

<sup>1</sup> J. M. COOK, P. W. LE QUESNE and R. C. ELDERFIELD, *Chem. Commun.* 1306 (1969).

<sup>2</sup> (a) R. C. ELDERFIELD, *Am. Scientist* **48**, 193 (1960); (b) R. C. ELDERFIELD and R. E. GILMAN, *Phytochem.* in press.