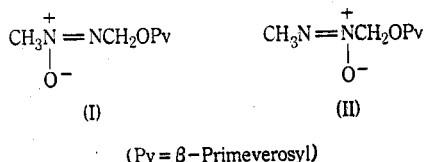


THE OCCURRENCE OF MACROZAMIN IN THE SEEDS OF CYCADS*

By N. V. RIGGS†

Macrozamin was shown by Cooper (1940) to be the toxic principle of *Macrozamia spiralis* Miq., a New South Wales cycad. It was later obtained from the Western Australian *M. reidleyi* C. A. Gard. (Lythgoe and Riggs 1949) and shown to be I or II (Langley, Lythgoe, and Riggs 1951).



The family Cycadaceae is more widely distributed in Queensland where it is represented by the genera, *Cycas* (tribe Cycadeae), and *Bowenia* and *Macrozamia* (tribe Encephalartaeae).

Experimental

The seeds of a representative of each genus, namely *C. media* R.Br., *B. serrata* F. M. Bail., and *M. miquelii* F. Muell. have now been examined by the method previously employed (Lythgoe and Riggs 1949), and a pseudo-cyanogenetic compound isolated from each in yields of 0.4–0.6% of the moist kernels.‡ It was identified as macrozamin by its m.p., 199–200 °C (decomp.), optical rotation, and elementary analysis, and by the preparation of an acetyl derivative which had m.p. 143–145 °C, undepressed in admixture with authentic hexa-acetylmacrozamin. Macrozamin has $[\alpha]_D^{16} -70^\circ$ (c, 0.4 in water) (Found for macrozamin from *C. media*: C, 40.8; H, 6.5; N, 7.3%, $[\alpha]_D^{18} -73^\circ$ (c, 0.4 in water); *B. serrata*: C, 41.0; H, 6.3; N, 7.1%, $[\alpha]_D^{18} -76^\circ$ (c, 0.7 in water); *M. miquelii*: C, 40.8; H, 6.5; N, 7.3%, $[\alpha]_D^{18} -78^\circ$ (c, 0.4 in water). Calc. for $\text{C}_{13}\text{H}_{24}\text{O}_{11}\text{N}_2$: C, 40.6; H, 6.3; N, 7.3%).

The material extracted by methanol from the crude macrozamin from *B. serrata* seeds was acetylated with acetic anhydride and pyridine, and the product chromatographed on neutral alumina from benzene solution. The eluate yielded sequoyitol acetate, m.p. 199–200 °C, hydrolysed by methanolic sodium hydroxide to sequoyitol, m.p. 236–238 °C, alone or in admixture with sequoyitol from *M. reidleyi* (Riggs 1949). Hexa-acetylmacrozamin was subsequently eluted from the alumina by chloroform. Similar chromatography of the other crude acetyl derivatives yielded to benzene traces of material, m.p. 190–194 °C, in insufficient quantity for identification.

Aqueous extracts of the seeds of *M. moorei* F. Muell., *M. paulo-guilielmi* F. Muell., *M. douglasii* W. Hill, *M. hopei* W. Hill, and *B. spectabilis* Hook. were concentrated, freed of starch and protein

* Manuscript received July 30, 1953.

† Division of Industrial Chemistry, C.S.I.R.O., Melbourne; present address: University of New England, Armidale, N.S.W.

‡ Professor B. Lythgoe states that he has also isolated macrozamin from the African cycad, *Encephalartos barkeri* Carruth.

by precipitation with ethanol, and boiled with sodium hydroxide and ferrous sulphate. The strong Prussian blue colours or precipitates formed showed that the seeds probably contained macrozamin. Seeds of *M. denisoni* C. Moore from four different localities gave negative tests in this way.

Mr. L. J. Webb, Division of Plant Industry, C.S.I.R.O., is thanked for the collection of the seeds examined in this survey.

References

- COOPER, J. M. (1940).—*J. Roy. Soc. N.S.W.* **74**: 450.
LANGLEY, B. W., LYTHGOE, B., and RIGGS, N. V. (1951).—*J. Chem. Soc.* **1951**: 2309.
LYTHGOE, B., and RIGGS, N. V. (1949).—*J. Chem. Soc.* **1949**: 2716.
RIGGS, N. V. (1949).—*J. Chem. Soc.* **1949**: 3199.