Phytochemistry, 1973, Vol. 12, p. 2546. Pergamon Press. Printed in England.

CAFFEOYLPUTRESCINE FROM *PENTACLETHRA MACROPHYLLA*

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(*Received* 20 *April* 1973. *Accepted* 5 *June* 1973)

Key Word Index—*Pentaclethra macrophylla*; Leguminosae; alkaloid; caffeoylputrescine; cinnamamide; paucine.

Plant. Pentaclethra macrophylla Benth. (Ibo name 'ugba' seeds; sometimes named in literature 'owala seeds' or 'pauco nuts'.) *Source.* Market in Nsukka, Nigeria. *Use.* In food, especially as *hors d'oeuvre*; in many parts of E. Central State of Nigeria, it is a major dietary component. *Previous work.* See Refs. 1, 2.

Merck[3,4] reported isolation of an alkaloid 'paucine' from seeds of this plant, without giving details of procedure or yield, but recently Hollerbach and Spiteller[2] have established the presence of caffeoylputrescine in Merck's original preparations. Caffeoylputrescine has also been found in *Nicotiana*.[5,6]

Present work. This was undertaken to ascertain whether caffeoylputrescine occurs as such in the *fresh* seeds. Seed endosperm on extraction and fractionation[5] yielded 1·4% of its dry matter as caffeoylputrescine hydrochloride dihydrate, which was identified with synthetic material by MS,[2] PMR,[5] UV[5] and by behaviour in the various electrophoretic and chromatographic procedures. It appeared to be the principal fluorescent and ninhydrin-positive component of the extract.

EXPERIMENTAL

All fractionations were monitored by high-voltage filter-paper electrophoresis in pyridine–HOAc–H_2O buffer (pH 6), in which caffeoylputrescine gave a blue-fluorescent, ninhydrin-purple zone having cationic migration 0·45 that of lysine.

Isolation. Endosperm was extracted[7] and the resulting aq. phase fractionated in an HOAc gradient on Amberlite CG-50[5] followed by *n*-BuOH–HOAc–H_2O (14:1:5) chromatography[5] on Kieselguhr. The zone collected ($\alpha = 2{\cdot}4$)[8] on evaporation and treatment with HCl was crystallized from H_2O.

Synthesis. The aminolytic[6] procedure gave a better yield than the alk. saponification procedure[5] though still $< 10\%$ on the basis of the *OO'*-diacetylcaffeoyl chloride taken. The $CHCl_3$-insoluble reaction product was purified as above.

Low-resolution MS were observed on an AEI MS902 mass spectrometer (direct-insertion probe, source temp. 200°, ionization energy 70 eV). The MS of both the natural and synthetic hydrochlorides, obtained in the present work, closely resemble the MS obtained by Hollerback and Spiteller.[2] However, the pyrocatechol line ($m/e = 110$), formed by thermal decomposition in the spectra of these workers,[2] was greatly reduced in the spectra obtained in the present study.

Acknowledgements—I am grateful to Dr. J. G. Buta and Professor S. Mizusaki for samples of synthetic caffeoylputrescine, to Mr. W. M. Laird, Mrs. Janice J. Sexton and Dr. R. L. M. Synge for useful advice and help, to Messrs. J. Eagles and R. Self for MS, to Dr. D. T. Coxon for PMR, to Dr. A. U. Ogan for suggesting this work and to the Federal Nigerian Government for a research grant.

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