Phytochemistry, 1972, Vol. 11, pp. 1527 to 1528. Pergamon Press. Printed in England.

RUTACEAE

LIRIORESINOL-B-DIMETHYL ETHER FROM THE BARK OF FAGARA LEPRIEURII

F. FISH and P. G. WATERMAN

Division of Pharmacognosy and Forensic Science, Department of Pharmaceutical Chemistry, University of Strathclyde, Glasgow, Scotland

(Received 30 October 1971)

Plant. Fagara leprieurii (Guill. et Perr.) Engl. (Synonyms; Zanthoxylum leprieurii Guill. et Perr.; Fagara angolensis Engl.). Source. Collected in Nigeria for the Tropical Products Institute, London; authenticated at source. Voucher samples of the bark FF 3 and FF 4 have been deposited at the Pharmaceutical Society Museum, University of Bradford. Uses. Used by the natives of Nigeria as a cure for toothache, colds and coughs¹ and as a vermifuge of rapid action.² Previous work. The isolation and characterization of skimmianine,³ 1-hydroxy-2,3-dimethoxy-N-methylacridan-9-one,⁴ chelerythrine, nitidine and 1-hydroxy-3-methoxy-N-methylacridan-9-one;⁵ the presence of several quaternary alkaloids has been indicated by TLC6 and high voltage electrophoresis.⁷

Discussion. In a previous communication⁵ we noted the presence of a non-alkaloidal fraction (105 mg) isolated during column chromatography of a light petroleum (b.p. 40–60°) extract from the root bark of Fagara leprieurii. The stem bark yielded a corresponding fraction (63 mg).

This material, empirical formula $C_{24}H_{30}O_8$, recrystallized from methanol (m.p. 120–121°), gave an IR spectrum in good agreement with that published for lirioresinol⁸ with the exception that the hydroxyl band was absent. The UV spectrum⁸ and the fragmentation pattern of the MS° were in agreement with previously published data for lirioresinol dimethyl ethers. PMR (CDCl₃) indicated 6 methoxy groups and that the steric form was that of lirioresinol B rather than the A or C analogues.¹⁰ The identity of this compound with lirioresinol-B-dimethyl ether [Lit.¹¹ m.p. 122–123°] was confirmed by measurement of the optical rotation [a]²⁴ +44·6 (c, 1·63 CHCl₃) [Lit.¹¹ +45·8° (c, 2·00 CHCl³)] and the preparation of the dibromo-derivative¹¹ m.p. 156° [Lit.¹¹ 157–157·5°].

This is the first report of this compound from the Rutaceae but a similar lignan, (\pm) -fagarol, has been isolated from two other African Fagara species, F. xanthoxyloides Lam. ¹² and F. viridis A. Cheval. ¹³

- ¹ B. OLIVER, Medicinal Plants of Nigeria, Nigerian College of Arts, Science and Technology (1960).
- ² S. KERERO and F. G. ADAM, Ann. Pharm. France 21, 773 (1963).
- ³ K. H. PALMER, Ph.D. Thesis, Univ. of Paris (1956).
- ⁴ L. Fonzes and F. Winternitz, Compt. Rend. 266, 930 (1968).
- ⁵ F. Fish and P. G. Waterman, Phytochem. 10, 3322 (1971).
- ⁶ F. Fish and J. M. CALDERWOOD, J. Pharm. Pharmac. 12, 119S (1966).
- ⁷ F. FISH and P. G. WATERMAN, J. Pharm. Pharmac. 23, 1325 (1971).
- ⁸ I. A. PEARL, D. L. BEYER and E. E. DICKEY, J. Org. Chem. 23, 705 (1958).
- ⁹ A M. Duffield, J. Heterocyclic Chem. 4, 16 (1967).
- ¹⁰ C. H. Briggs, R. C. Cambie and R. A. F. Couch, J. Chem. Soc. C, 3042 (1968).
- ¹¹ P. R. JEFFERIES, J. R. KNOX and D. E. WHITE, Austral. J. Chem. 14, 175 (1961).
- 12 B. CARNMALM, H. ERDTMANN and Z. PELCHOWICZ, Acta Chem. Scand. 9, 1111 (1955).
- ¹³ R. Paris and H. Moyse-Mignon, Ann. Pharm. Fr. 6, 409 (1948).

The isolation of lirioresinol-B-dimethyl ether from the present source is of interest with regard to the chemotaxonomy of African species of Fagara. In a recent publication some minor differences in the alkaloid patterns of F. leprieurii and the closely related F. rubescens (Planch. ex Hook. f) Engl. (syn. $Zanthoxylum\ rubescens$ (Planch. ex Hook. f) were discussed: an investigation of one sample of F. rubescens has failed to yield any trace of lirioresinol-B-dimethyl ether, or related material, and this may indicate a further variation between these two taxa.

Key Word Index-Fagara leprieurii; Rutaceae; lirioresinol-B-dimethyl ether.

Phytochemistry, 1972, Vol. 11, pp. 1528 to 1529. Pergamon Press. Printed in England.

CHLOROFORM-SOLUBLE ALKALOIDS OF FAGARA VITIENSIS

F. FISH and P. G. WATERMAN

Division of Pharmacognosy and Forensic Science, Department of Pharmaceutical Chemistry, University of Strathclyde, Glasgow, Scotland

(Received 30 October 1971)

Fagara vitiensis (A. C. Smith) A. C. Smith (Synonym; Zanthoxylum vitiensis A. C. Smith) is a small tree or shrub indigenous to Fiji. Hitherto no ethnobotanical or chemical data have been available on this plant but a knowledge of the alkaloids is of interest in relation to the chemotaxonomy of the Fagara-Zanthoxylum complex. Extraction of the root bark has yielded the two benzophenanthridine alkaloids chelerythrine and nitidine together with a third tertiary base belonging to the protopine group. The identity of the latter as 2,3-10,11-dimethylenedioxyprotopine, recently isolated for the first time from Zanthoxylum conspersipunctatum Merr. & Perr., was established by reference to an authentic sample and by comparison of the UV, IR and PMR (C_6D_6) spectra with those obtained by the original workers. The mass spectrum was consistent with that for a protopine base.

EXPERIMENTAL

Plant material. Dried root and stem bark of Fagara vitiensis supplied by the Tropical Products Institute, London, was authenticated at source. Voucher samples FF 14 (root bark) and FF 15 (stem bark) have been deposited with the Pharmaceutical Society Museum, University of Bradford.

Extraction. Samples of root bark (50 g) of Fagara vitiensis and of stem bark (scraped free of adhering epiphytes, 400 g) were powdered, then separately extracted in Soxhlets (48 hr), first with light petroleum (b.p. $40-60^{\circ}$) followed by CHCl₃. The petrol. and CHCl₃ extracts of stem bark were separately concentrated under reduced pressure and on examination by TLC were found to contain 3 identical bases. Both concentrates were extracted with 1 N HCl (3 × 50 ml) and the total acid extract combined. On standing, a yellow precipitate was formed in the aqueous acid layer; this was filtered to give 145 mg of mixed chelerythrine and nitidine chlorides. The precipitate was subsequently chromatographed on a column (Woelm Alumina, activity II, 20 g) packed in CHCl₃-MeOH 49:1. Elution with the same solvent gave chelerythrine (33 mg), crystallized as the chloride, followed by nitidine (51 mg), crystallized as the nitrate. The acid extract was made alkaline with 0.88 NH₄OH and extracted with CHCl₃. Column chromatography (Woelm Alumina, activity I, 10 g) using CHCl₃-cyclohexane (7:3), gave 2,3-10,11 dimethylenedioxyprotopine (65 mg).

¹ A. C. SMITH, J. Arn. Arbr. 32, 226 (1951).

² S. R. Johns, J. A. Lamberton, H. J. Tweedale and R. I. Willing, Austral. J. Chem. 22, 2233 (1969).

³ L. Dolejs, V. Hanus and J. Slavik, Colln. Czech. Chem. Commun. 29, 2479 (1964).