

The isolation of liriioresinol-B-dimethyl ether from the present source is of interest with regard to the chemotaxonomy of African species of *Fagara*. In a recent publication⁷ 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 liriioresinol-B-dimethyl ether, or related material, and this may indicate a further variation between these two taxa.

Key Word Index—*Fagara leprieurii*; Rutaceae; liriioresinol-B-dimethyl ether.

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CHLOROFORM-SOLUBLE ALKALOIDS OF *FAGARA VITIENSIS*

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Fagara vitiensis (A. C. Smith) A. C. Smith (Synonym; *Zanthoxylum vitiensis* A. C. Smith) is a small tree or shrub indigenous to Fiji.¹ 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.,² was established by reference to an authentic sample and by comparison of the UV, IR and PMR (C₆D₆) spectra with those obtained by the original workers. The mass spectrum was consistent with that for a protopine base.³

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°) 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).

The presence of nitidine and 2,3-10,11-dimethylenedioxyprotopine in the root bark was indicated by TLC (3 systems) but they were not present in sufficient quantities for isolation. Chelerythrine chloride (13 mg) was isolated by the technique described for the stem bark.

Chelerythrine. Isolated as the chloride ($C_{21}H_{18}O_4N^+Cl^-$), yellow needles m.p. 199–200° (EtOH–Et₂O) (TLC, IR, m.m.p.); λ_{max}^{EtOH} 227, 273, 281 (sh.), 320, 343 nm (log ϵ 4.25, 4.52, 4.46, 4.33, 4.14); Chelerythrine nitrate m.p. 234–236° (EtOH–2 N HNO₃).

Nitidine. Isolated as the chloride and purified as the nitrate ($C_{21}H_{18}O_4N^+NO_3^-$) green prisms m.p. 274° (EtOH–2N HNO₃) (TLC, IR, m.m.p.), λ_{max}^{EtOH} 231, 273, 281, 329 nm (log ϵ 4.35, 4.49, 4.48, 4.35).

2,3-10,11-Dimethylenedioxyprotopine. Isolated as the base. Found: M^+ 353.1254 $C_{20}H_{19}NO_3$ requires 353.1263, white prisms m.p. 205° (MeOH) (TLC, IR, PMR, m.m.p.), λ_{max}^{EtOH} 290 nm (log ϵ 3.98).

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Key Word Index—*Fagara vitiensis*; Rutaceae; chelerythrine; nitidine; 2,3-10,11-dimethylenedioxyprotopine.

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RUTACULTIN UND RUTAMARIN-ALKOHOL AUS DEN WURZELN VON *RUTA GRAVEOLENS**

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Nachdem 1967 mit dem Rutamarin (I, $R=COCH_3$) erstmalig ein C3-1', 1'-dimethylallyl-substituiertes Cumarin aus *Ruta graveolens* isoliert werden konnte,¹ zeigte ein eingehenderes Studium der Inhaltsstoffe dieser Pflanze, daß besonders in den Wurzeln zahlreiche Vertreter dieses neuen Cumarin-Typs enthalten sind.² Bei den laufenden Untersuchungen konnten nun zwei weitere derartige Cumarine isoliert werden, über deren Vorkommen in den Wurzeln von *Ruta graveolens* u.W. nichts bekannt war. Eine dieser Verbindungen ist mit dem Rutamarin-Alkohol (I, $R=H$) identisch, der bereits früher durch Verseifung des Rutamarins dargestellt werden konnte.¹ Unter dem Namen Chalepin wurde er als Inhaltsstoff der oberirdischen Teile von *Ruta chalepensis* L. beschrieben,³ während das isomere Heliectin (*Heliecta longifoliata* Britt.) optisch inaktiv ist.⁴ Das zweite neue Wurzel-Cumarin ist mit dem Rutacultin (II) identisch, welches von Steck *et al.*⁵ in Gewebekulturen von *Ruta graveolens* aufgefunden wurde (vgl.⁶). Die Isolierung des Rutamarin-Alkohols und des

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⁶ M. M. BALLANTYNE, P. H. MCCABE und R. D. H. MURRAY, *Tetrahedron* **27**, 871 (1971).