neutral and acidic fraction and the basic $CHCl_3$-soluble fraction separated into individual constituents by a combination of column chromatography with benzene, benzene-EtOAc, $CHCl_3$ and $CHCl_3$–MeOH.

Elution with $CHCl_3$ afforded a compound *A*. 4·8 mg (0·0006% root, fresh wt. not present in the aerial parts) mp 200–201° from EtOH (lit. [2] 196–198° from $CHCl_3$–MeOH), M^+ *m/e* 367, 111 ($C_{20}H_{17}NO_6$, found 367, 106) UV λ_{max}(EtOH) (log ε): 207 nm (4·56), 239 (4·46), 290 (4·38), 317 (4·35), UV λ_{max}(EtOH + 1N HCl). 245 nm, 297·5, 337, 380 (*Sh*). IR (KBr)ν_{max} cm^{-1}, 2945, 2880, 1685, 1625, 1590. NMR ($CDCl_3$, δ ppm) 2·39 (3H, S, N-Me), 2·50–3·50 (4H, *m*, $-CH_2-CH_2-$), 4·76, 5·16 (2H, each ABq, *J* 16 Hz, Ar–CH_2–O), 5·85 (2H, *s*, O–CH_2–O), 6·08 (2H, *s*, O–CH_2–O), 6·50, 6·60 (each 1H, *s*, aromatic proton), 6·83 (1H, *d*, *J* 8 Hz, aromatic proton) and 7·76 (1H, *d*, *J* 8 Hz, aromatic proton). Mass fragmentation: M^+ *m/e* 367 (7%), 352 (5%), 205 (5%), 190 (85%), 188 (77%), 178 (86%), 162 (78%), 151 (100%). R_f. 0·52 (C_6H_6–EtOAc = 2:1), 0·73 ($CHCl_3$–MeOH = 20:1) on silica gel H. These physical data showed *A* was identical with the isoquinoline alkaloid, corydalispirone* [2] and was confirmed by its identity with an authentic sample. This alkaloid has been previously reported only from *Corydalis incisa.*

Elution with benzene afforded pale yellow crystals, *B*, (aerial part 1·5 mg 0·00018% of fr. wt, root 15 mg 0·0018% of fr. wt.) mp 278–280° (decomp. from $CHCl_3$–EtOH), M^+ *m/e* 317, 067 ($C_{19}H_{11}O_4N$ found 317, 069), UV λ_{max}(EtOH) nm 215, 244, 282, 296, 329, IR (KBr)ν_{max} 2890, 1640, 1590, 1500, 1450, NMR (CF_3COOD, δ ppm), 6·22, 6·49 (2H, each *s*, O–CH_2–O), 7·41, 7·94 (1H, each *s*), 7·92 and 8·44 (1H, each *d*, *J* 8 Hz), 8·14 and 8·44 (1H, each *d*, *J* 8 Hz) and 9·50 (1H, *d*, *J* 8 Hz). Mass fragmentation; M^+ 317 (100%), 259 (7·1%), 202 (11·5%), 174 (5·3%), 158 (11·5%). These physical data for *B* agreed with those of authentic norsanguinarine isolated from the callus [3], and this base was identified by comparison with an authentic sample. Later this base has been isolated from a papaveraceous plant, *Argemone albiflora* [4].

Elution with $CHCl_3$ afforded plates, *C*, 4·5 mg (0·00054% fr. wt aerial part, not identified in root) mp 184–185·5° (from EtOH), NMR spectrum ($CDCl_3$, δ ppm), 2·54 (3H, *s*, N–Me), 3·70 (3H, *s*, OMe), 3·92 (6H, *s*, OMe), 6·70 (1H, *s*, aromatic), 6·84 (2H, *s*, aromatic) and 8·80 (1H, *s*, OH, disappeared after D_2O exchange), these values were almost same with authentic isocorydine [5]. Mass fragmentation M^+ 341 (60%), 326 (M^+ − 15, 100%), 310 (M^+ − 31, 49%), 298 (M^+ − 43, 4·4%) were identical with those of an authentic sample.

The $CHCl_3$–MeOH fraction was purified by preparative TLC (Si gel, benzene–MeOH = 3:2), followed by recrystallization from EtOH affording colorless prisms, *D*, mp 166–168° (macro) (172–173° micro, lit. [6] 169–171°). A mixed melting point with an authentic sample of α-allocryptopine mp 155–157° (macro) (161–163° micro) gave 164–166° (macro). The IR absorption spectrum of the base *D*, showed some minor differences to that of α-allocryptopine in KBr preparation, but gave identical spectra in $CHCl_3$. The NMR and mass fragmentation pattern were identical with α-allocryptopine, on the basis of the above results therefore *D* may be the so-called β-allocryptopine [6].

In addition, protopine, α-allocryptopine, dihydrosanguinarine, sanguinarine, oxysanguinarine and chelerythrine, and megnoflorine (from the quaternary base fraction) were identified by direct comparison (NMR, MS, TLC etc.) with authentic samples in a similar manner as reported previously [3, 7]. These alkaloids were identified in both parts of the plant.

The isolation and identification of all these alkaloids, except protopine and α-allocryptopine are first report from this species.

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* Corydalispirone was reported recently by G. Nonaka and I. Nishioka [2].

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ALKALOIDS AND COUMARINS FROM *ZANTHOXYLUM FLAVUM*: DIHYDRORUTAECARPINE, A NOVEL β-INDOLOQUINAZOLINE ALKALOID*

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Key Word Index—*Zanthoxylum flavum*; Rutaceae; alkaloids; β-indoloquinazoline; dihydrorutaecarpine; canthin-6-one; benzophenanthridine; chelerythrine; nitidine; furanocoumarin; imperatorin; chemotaxonomy.

Plant. Zanthoxylum flavum Vahl. (syn. *Fagara flava* Krug. *et* Urb.) [1]. *Voucher.* Jimenez 5980 has been deposited at the herbarium of the Royal Botanic Garden, Edinburgh. *Source.* Hill sides above La Cuesta, Santiago

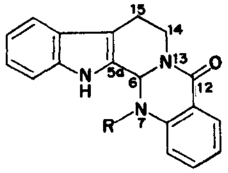
Province, Dominican Republic. *Uses.* The wood, known commercially as Jamaican Satinwood, is a timber of high quality [2]. *Previous work.* The coumarins xanthotoxin, psoralen and suberosin [3] and uncharacterised alkaloids [4] from the wood. *Plant parts examined.* Root and stem barks.

Present work. Soxhlet extraction of the stem bark (200 g) with petrol (40–60°), concn of the extract and column chromatography over Al_2O_3, eluting with EtOAc, gave imperatorin (75 mg) mp 101° (lit. [5] 102–103°). Found M^+ 270.0899, $C_{16}H_{14}O_4$ requires 270.0892. UV, IR, MS, PMR, were all in close agreement with published data [5–7]. No other compounds were isolated from petrol or MeOH extracts of the stem bark but traces of alkaloid were detected.

The root bark (100 g) was similarly extracted with petrol, then $CHCl_3$, then MeOH. On shaking with 1N HCl the concn. petrol extract gave a yellow ppt. of chelerythrine chloride (14 mg) mp 200°, identical in all respects (UV, IR, TLC, mmp) with an authentic sample. Basification of the acid layer with NH_4OH and re-extraction into CH_2Cl_2 gave canthin-6-one (6 mg) mp 165°, identical in all respects (UV, IR, TLC, mmp) with an authentic sample.

Similar treatment of the $CHCl_3$ extract gave, on addition of HCl, a yellow–green ppt. of nitidine chloride (46 mg) mp 220°, identical in all respects (UV, IR, TLC, mmp) with an authentic sample.

Re-examination of the original petrol extract from the root bark revealed the presence of a further alkaloid which was purified by column chromatography over Si gel, eluting with $CHCl_3$, to give white needles (13 mg) mp 168°. $[\alpha]_D^{25}$ −21 ($CHCl_3$; *c* 0·1). Found M^+ 289·1218, $C_{18}H_{15}N_3O$ requires 289·1215. UV $\lambda_{max}^{(EtOH)}$ nm (log ϵ): 275(3·89), 292(3·76), 304*sh*(3·45), 316(3·24). IR ν_{max} (KCl) cm^{-1}: 3350–3320 (NH), 1680 (CO), 1610, 1470, 1375. PMR (60 MHz, $CDCl_3$): δ 3·28 (2H, *t*, *J* 7Hz, CH_2-14), 4·30 (2H, *t*, *J* 7Hz, CH_2-15), 6·90 (1H, d, *J* 2Hz, H-6), 7·30–8·60 (8H, *m*, 8 × H-Ar), >10·00 (2H, both replaceable by D_2O, 2 × N-H). MS: *m/e* 289(14%), 288(2), 287(0·6), 170(0·4), 169(1·0), 159(1·5), 147(3·3), 146(1·4), 143(100), 142(8·3), 130(33), 119(0·4), 115(5·6). The occurrence of 3 × *N* in the molecule suggested the alkaloid was of the rare *β*-indoloquinazoline class known only from the Rutaceae [8]. This assumption was sustained by examination of IR (CO and NH) and MS. The complex fragmentation pattern of the latter can be rationalised by postulating fission of the *β*-indoloquinazoline nucleus between C_6-N_7 and C_{12}-N_{13} or between C_{5a}-C_6 and either N_{13}-C_{14} or C_{14}-C_{15}. The occurrence of the indolic fragments at *m/e* 143 and *m/e* 130 as major ions is in accord with findings for similar compounds [9,10]. The PMR confirmed both the presence of the $\geqslant C–CH_2–CH_2–N<$ moiety [11] and the lack of any substitution on the molecule. The combined spectral data thus suggested that this was a novel member of the *β*-indoloquinazoline class of alkaloids in which the empirical formula $C_{18}H_{15}N_3O$ had been previously unknown. From the lack of substituents, presence of 2 × NH, optical activity and UV, in which λ_{max} is in close agreement with evodiamine (**1**), it seems that this new alkaloid must be dihydrorutaecarpine (**2**).



(**1**) R = Me
(**2**) R = H

Direct evidence for structure (**2**) was obtained by reduction with $LiAlH_4$ in dry Et_2O [12,13]. Refluxing for 10 hr gave, on recrystallisation from EtOH, indolo-[2′,3′:3,4]-pyrido-2, 1*b*-quinazoline, mp 162° (lit. [12] 161–163°), identical in all respects (UV, IR, mmp) with material obtained on reduction of rutaecarpine by the same method. Further evidence for structure (**2**) was obtained from methylation with MeI in boiling MeOH. A mixture was obtained the major component of which was identical (TLC-3 systems) with evodiamine.

Examination of the partially purified MeOH extract of the root bark by methods previously described [14] revealed the presence of small amounts of quaternary alkaloids of which one was tembetarine (TLC, UV).

Biological significance. Whilst the type and distribution of alkaloids in *Z. flavum* appears typical of the genus [8,15] the presence of canthin-6-one and dihydrorutaecarpine may have additional systematic significance. Certainly the recent suggestion [16] that a close biochemical relationship exists between Central American and South East Asian species is supported by the isolation of a *β*-indoloquinazoline from *Z. flavum.*

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* Part 7 in the series "Chemosystematics in the Rutaceae". For Part 6 see ref. [8].