Preparation of nodakenetin (VI). Nodakenetin acetate (IV) (40 mg) was refluxed with 5% methanolic KOH (6 ml) for 35 min on an H_2O bath. The reaction mixture was cooled, diluted with H_2O (10 ml), neutralized with 1 N HCl and extracted with $CHCl_3$. The $CHCl_3$ layer was washed with H_2O and dried. The solid obtained after the removal of the solvent crystallized from light petrol.–$CHCl_3$ in needles, m.p. 186–187° (lit.[10] 192°), $[\alpha]_D$ −26·9° (*c* 1·19, $CHCl_3$) (lit.[10] −25·4°), IR superimposable with its optical antipode marmesin.[7,9]

Conversion of nodakenetin acetate to anhydronodakenetin (VII) (= *anhydromarmesin*). To a solution of IV (25 mg) in HOAc (1 ml), $HClO_4$ (72%, 0·5 ml) was added. The clear solution was warmed on an H_2O bath for 3–4 min and then kept at room. temp. (1 hr). The reaction mixture was diluted with H_2O (10 ml), neutralized with $NaHCO_3$ and the precipitated solid was taken up in $CHCl_3$. The $CHCl_3$ layer was washed with H_2O, dried and the residue obtained after removal of the solvent was chromatographed. The earlier C_6H_6–$CHCl_3$ (1:1) eluates afforded anhydronodakenetin (VII), crystallizing from light petrol. as colourless needles (9 mg), m.p. 137–138°. This was identified by direct comparison (m.m.p., IR) with an authentic sample of the same prepared by dehydration of marmesin with P_2O_5 in dry C_6H_6.[9]

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FAGARIDINE: A PHENOLIC BENZOPHENANTHRIDINE ALKALOID FROM *FAGARA XANTHOXYLOIDES*

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Key Word Index—*Fagara xanthoxyloides*; Rutaceae; alkaloid; phenolic benzophenanthridine; fagaridine.

Previous investigations[1–5] have established the occurrence in *Fagara xanthoxyloides* of the alkaloids chelerythrine, dihydrochelerythrine, 3-dimethylallyl-4-methoxy-acridan-9-one, fagaramide and skimmianine. Indications have also been obtained[5] of the possible occurrence of the quaternary alkaloids tembetarine, magnoflorine, *N*-methylcorydine and/or *N*-methylisocorydine. We have investigated a red basic material, isolated from the root bark of *F. xanthoxyloides* by the method of Paris and Moyse–Mignon, who presumed it to be a single alkaloid and named it fagaridine. From our material, shown by TLC to be a mixture of at least four components, we have isolated a new phenolic benzophenanthridine alkaloid which has structure I.

[1] PARIS, R. and MOYSE-MIGNON, H. (1947) *Ann. Pharm. Fr.* **5**, 410.
[2] TORTO, F. G., SEFCOVIC, P., DADSON, B. A. and MENSAH, I.A. (1969) *Ghana J. Sci.* **9**, 3.
[3] TORTO, F. G., SEFCOVIC, P. and DADSON, B. A. (1966) *Tetrahredron Letters* 181.
[4] TAYLOR, D. A. H. and ESHIETT, I. T. (1968) *J. Chem. Soc.* 481.
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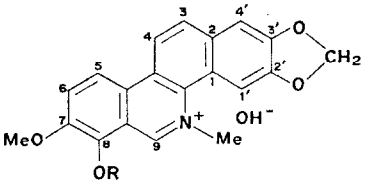
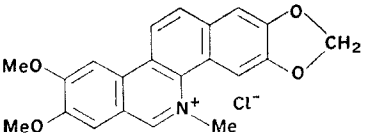


(I) R = H Fagaridine
(II) R = Me Chelerythrine



(III) Nitidine chloride

RESULTS AND DISCUSSION

In view of the small amount of material available (50 mg from 13 kg of dried root bark) the structure of the alkaloid was determined mainly by spectroscopic methods. Elemental analysis gave a molecular formula of $C_{20}H_{17}O_5N$ ($C_{20}H_{16}O_4N^+$ OH^-). The MS showed a relatively weak $C_{20}H_{16}O_4N^+$ (M^+) peak at *m/e* 334; in keeping with the behaviour of many quaternary bases there was a more prominent M^+-1 peak at 333·1024 ($C_{20}H_{15}O_4N$ requires: 333·1000). Other significant peaks, for which the corresponding molecular formulae were determined by high resolution measurements were at 319 (M^+-Me), 318 (M^+-1- Me) and 304 (318-Me).

The UV with λ_{max} 228, 284, 322(sh) nm (log ϵ 4·55, 4·65, 4·14), λ_{min} 252 nm (log ϵ 4·16), indicated the benzophenanthridine nucleus.[6] The presence of a phenolic hydroxyl group was indicated by a red colouration with $FeCl_3$, and confirmed by a broad band at 3420 cm^{-1} in the IR (KBr).

The 100 MHz PMR spectrum in CF_3COOH showed peaks for one OMe (δ 4·29 ppm, *s*), $\equiv\overset{+}{N}$–Me (5·05*s*), O–CH_2–O (6·21*s*), 9-position proton (9·77*s*), *ortho* protons 3,4 (*AB* quartet with two doublets centred at 8·21, 8·57, *J* 9 Hz), *ortho* protons 5,6 (*AB* quartet with two doublets cetnred at 8·08, 8·59, *J* 9 Hz). Virtually, the only difference between this spectrum and that of chelerythrine is that the latter has a second OMe peak at 4·14.

Upon treatment with diazomethane, a specimen of fagaridine gave a product whose PMR was identical with that of chelerythrine. It may be concluded, therefore, that fagaridine differs from chelerythrine only in having an OH instead of an OMe in either the 7 or 8 position. The choice of the 7-position for the OMe, and hence of the 8-position for the OH, was based on a comparison of the chemical shifts of the OMe groups in fagaridine, chelerythrine and nitidine chloride, III, in the same solvent (Table 1). The single OMe in fagaridine corresponds to the 7-position OMe that is present in both chelerythrine and nitidine.

TABLE 1. CHEMICAL SHIFTS OF OMe IN VARIOUS ALKALOIDS

	Fagaridine	Chelerythrine and Fagaridine treated with CH_2N_2	Nitidine
6-OMe	—	—	4·19
7-OMe	4·29	4·34	4·31
8-OMe	—	4·14	—

This is the first benzophenanthridine alkaloid, as far as we can ascertain, with an OH group in one of the terminal rings. The possibility that it is an artefact, formed during the

[6] SANGSTER, A. W. and STUART, K. L. (1965) *Chem. Rev.* **65**, 69.

isolation by demethylation of chelerythrine, a major alkaloid of the bark, can be dismissed because it was shown by TLC that fagaridine was present in a specimen of crude alkaloids isolated from the bark by benzene extraction, and precipitation as the hydrochlorides by treatment of the extract with cold dilute hydrochloric acid. Under these conditions demethylation of chelerythrine could not have taken place.

EXPERIMENTAL

Following the procedure used in previous investigations,[1,2] a red material corresponding to the 'fagaridine' of Paris and Moyse-Mignon was obtained from dried root bark. It was resolved by TLC on silica gel with cyclohexane–$CHCl_3$–$NHEt_2$ (5:4:1) into four components. The major component, the second slowest moving, was isolated by preparative TLC. Recrystallized from MeOH it formed yellow crystals m.p. 269–270° (Found: C, 68·1; H, 4·6; N, 4·2. $C_{20}H_{17}O_5N$ requires: C, 68·4; H, 4·8; N, 4·0%) ν_{max} (KBr) 3420 (broad), 3040, 2915, 2870, 1610, 1550, 1485, 1350, 1280, 950, 725 cm^{-1}. UV absorption, quoted above, was determined in ethanol solution, and NMR in trifluoroacetic acid with tetramethylsilane as standard.

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FLAVONE AUS *DIGITALIS FERRUGINEA**

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(*Eingegangen* 12. *April* 1973. *Angenommen* 1. *Mai* 1973)

Key Word Index—*Digitalis ferruginea*; Scrophulariaceae; flavonoids; luteolin, hispidulin (dinatin), a scutellarein dimethyl ether.

Pflanze und Herkunft. Digitalis ferruginea L.; gesammelt im Juli 1969 in der Nähe von Demirköy, Osttrazien-Türkei.

Isolierung und Identifizierung. Die getrocknete Blätter wurden mit 80% igem EtOH extrahiert. Nach Entfernung von EtOH wurde der wässrige Rückstand zuerst mit Petrol., dann mit C_6H_6 und schliesslich mit Et_2O extrahiert. Laut Polyamid-DC (MeOH) enthielt nur der Et_2O-Extrakt 3 Flavon-Verbindungen: DF–F_1 (R_f = 0,17), DF–F_2 (0,32), DF–F_3 (0,39). Sie konnten durch mehrmalige Polyamid-SC (MeOH–H_2O) in folgenden Ausbeuten isoliert werden: 16 mg; 29 mg; 13 mg (ausgehend von 1,5 kg trockenem Blattmaterial).

DF–F_1 (=*Luteolin*). Die Identifizierung erfolgte durch Mischschmp. mit auth. Substanz, Cochromatographie, UV- und IR-Spektroskopie.

DF–F_2 (=*Hispidulin, Dinatin*). Hellgelbe Nadeln aus MeOH. Schmp. 287–289° (Lit.[1,2] 291–292°, 289–290°). UV: (MeOH)λ_{max} (log ϵ) 275 (4,09), 337 (4,31). IR: (KBr) Hydroxyl 2570–3560 cm^{-1}, Carbonyl 1650 cm^{-1}. NMR: (DMSO) δ = 3,79 (3H, *s*, $-OCH_3$), δ = 6,58 (1H, *s*, H-8), δ = 6,74 (1H, *s*, H-3), δ = 6,93 (2H, *d*, H-3′ u. H-5′, *J* 8,5), δ = 7,92 (2H, *d*, H-2′ u. H-6′, *J* 8,5), δ = 12,75 (1H, *s*, C_5-OH). $C_{16}H_{12}O_6$ ber. 64,00% C u. 4,03% H; gef. 63,55% C u. 4,70% H. Acetylierung mit Essigsäureanhydrid und Natriumacetat lieferte ein Triacetat: Farblose Nadeln aus MeOH. Schmp. 166–168° (Lit.[1,2] 168–170°, 168–169°). $C_{22}H_{18}O_9$ ber. 61,97% C u. 4,25% H; gef. 62,19% C u. 4,32% H.

* Mitt. VIII über "Flavon-und Anthrachinon-Farbstoffe der Digitalis-Arten".

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[2] PHADKE, P. S., RAMA RAO, A. V. und VENKATARAMAN, K. (1967) *Indian J. Chem.* **5**, 131.