peak): 388 (83·7, M^+), 373 (100, M^+–Me from 6–OMe), 226 (0·3, M^+–162, RDA of γ-pyrone ring), 211 (12·5, 226–Me), 183 (8·1, 211–CO), 162 (2·7, M^+–226). Nobiletin was fully demethylated [3] to the corresponding hexahydroxy compound, when refluxed with Ac_2O–HI (1:2) for 1 hr, crystallizing from EtOH in yellow needles, m.p. 320° (lit. [3] 310–314°); hexaacetate (M^+ 570), m.p. 220–222° (lit. [3] 226–228°).

The later C_6H_6 and earlier C_6H_6–$CHCl_3$ (1:1) eluates afforded a solid showing single spot in TLC which on exhaustive rechromatography on silica gel yielded a further quantity of nobiletin, and tangeretin (yield 0·04%), crystallized from light petrol–$CHCl_3$ as needles, m.p. 150–151°; IR: ν_{max}^{KBr} 1656 cm^{-1}; PMR (60 MHz, $CDCl_3$ showed expected signals [9] MS *m/e* (base peak): 372 (37, M^+), 357 (100, M^+–Me), 240 (0·8, M^+–132, RDA of γ-pyrone ring), 225 (6·7, 240–Me), 197 (12·3, 225–CO), 132 (6·5, M^+–240). Treatment of (**2**) with anhydrous $AlCl_3$ in dry Et_2O (R.T., 24 hr) afforded the corresponding 5-desmethyl derivative, m.p. 175° (lit [10] 176°); IR: ν_{max}^{KBr} 1642 cm^{-1}; PMR (60 MHz, $CDCl_3$, δ): 7·89 *d* and 7·02 *d* (4H, A_2B_2 *q*, *J* 8·5 Hz, H–2′, H–3′, H–5′ and H–6′), 6·58 (1H, *s*, H–3), 4·01 (3H, *s*), 3·96 (6H, *s*) and 3·88 (3H, *s*) for four OMe groups; acetate prepared by Ac_2O-pyridine method had m.p. 161°. The completely demethylated derivative, 5,6,7,8,4′-pentahydroxyflavone, m.p. 320° *d*. (lit [9] 316–318°), was prepared by refluxing with Ac_2O–HI for 1 hr. The final C_6H_6–$CHCl_3$ (1:1) and $CHCl_3$ eluted fractions on rechromatography afforded 5,7,8,3′,4′-pentamethoxyflavone (**3**) (yield 0·016%) crystallized from light petrol–$CHCl_3$ as needles, m.p. 200° (lit [6], 197–198°); IR: ν_{max}^{KBr} 1653 cm^{-1}; PMR (60 MHz, $CDCl_3$, δ) identical with that reported earlier [11] MS *m/e* (% base peak): 372 (100, M^+), 357 (81, M^+–Me from 8–OMe), 210 (4, M^+–162 RDA of γ-pyrone ring), 195 (11·5, 210–Me), 167 (31, 195–CO), 162 (5·5, M^+–210).

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ALKALOIDS AND TRITERPENES FROM *ZANTHOXYLUM PARVIFOLIOLUM*

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Key Word Index—*Zanthoxylum parvifoliolum*; Rutaceae; alkaloids; chelerythrine; nitidine; triterpenes; lupeol; sitosterol.

Plant. Zanthoxylum parvifoliolum A. Chev. (syn. *Fagara parvifoliola* A. Chev. *ex* Keay)[1]. *Voucher specimens.* Enti 518a and Enti 518b have been deposited with the herbarium of the Royal Botanic Garden, Edinburgh. *Source.* Enti 518a from the Bombiri Forest Reserve, Juasso, Ghana and Enti 518b from the Kade Agricultural Research Station, Ghana. *Previous work.* None on this species. Other species of the *Zanthoxylum/Fagara* complex are known to yield a wide range of interesting secondary metabolites [2]. *Plant parts.* Stem bark and root bark from Enti 518a and 518b, wood, leaves and cork separated from the root bark of Enti 518b.

Present work. The powdered plant materials were extracted in a Soxhlet apparatus with light petrol (40–60°) and then $CHCl_3$. The light petrol extract from the root bark of Enti 518b (825 g)

gave, on concentration under reduced pressure, lupeol (5·21 g) m.p. 217° from $(Me)_2CO$, M^+ 426·3883, $C_{30}H_{50}O$ requires 426·3861, $[\alpha]_D^{21.5}$ + 27·5° (*c* 1, $CHCl_3$). Co-comparison of m.m.p. and IR and the preparation of both lupeol acetate m.p. 217° from EtOH, and lupenone, m.p. 170° from Et_2O, confirmed the identification.

On shaking with 10% HCl the $CHCl_3$ extract gave a yellow precipitate which after collection gave, on recrystallization from EtOH, nitidine (90 mg) m.p. 238–240° (identical with an authentic sample by m.m.p., UV, IR and TLC). Reduction with $NaBH_4$ yielded dihydronitidine m.p. 208° from MeOH (lit [3]. 208–211°). On further concentration the supernatant solution yielded chelerythrine (20 mg) m.p. 199–201° from EtOH (identical with an authentic sample by m.m.p., UV, IR and TLC). Reduction with $NaBH_4$ yielded dihydrochelerythrine m.p. 164–166° from MeOH (lit [4]. 164–165°).

Investigation of the extracts of stem bark of Enti 518b and of stem and root barks of Enti 518a revealed the presence of lupeol, chelerythrine and nitidine; identified as previously described. It was found that, in all cases, the quantity of lupeol isolated was greatly in excess of that of the alkaloids; of the latter, nitidine always occurred in greater concentration than chelerythrine.

From the light petrol extract of the wood lupeol was again isolated together with significant quantities of sitosterol, m.p. 136–140° from *n*-hexane (identical with an authentic sample by m.m.p., IR, MS and TLC). A trace of sitosterol was also detected, by TLC only, in the light petrol extract of the leaf.

Interesting observations were made on the extractives of the cork from the root bark of Enti 518b; it formed a very thick layer, up to 1 cm deep, which could be peeled easily from the supporting phloem. From the $CHCl_3$ extract of the cork (150 g) chelerythrine (1·4 g) was isolated and identified as before. Further extraction of the cork with MeOH gave, on concentration, nitidine (4·0 g) identified as before.

Biological significance. Z. parvifoliolum is the first African species of the genus, so far examined, to apparently lack the ability to produce alkaloids derived from anthranilic acid. However the occurrence of large quantities of benzophenanthridine alkaloids is typical of that genus. The distribution of the benzophenanthridine alkaloids, predominating largely in the cork, is unusual and of considerable interest. It has been shown that the benzophenanthridine alkaloids sanguinarine and chelerythrine are capable of completely inhibiting the growth of the root-rot fungus *Phymatotrichum omnivorum* (Shear) Dugger in very low concentrations [5]. Furthermore, an aqueous solution obtained by boiling the root bark of *Z. hamiltonianum* Wall. *ex* Hook. *f.* (in which the only reported alkaloid is nitidine) has been found to have considerable larvicidal activity [6]. It seems plausible, therefore, that high concentrations of water soluble chelerythrine and nitidine in the cork of the root bark of *Z. parvifoliolum* could present a considerable natural barrier to fungal and larval attack.

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