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## COUMARIN, ALKALOID AND FLAVONOID CONSTITUENTS FROM THE ROOT AND STEM BARKS OF *ZANTHOXYLUM AVICENNÆ*

FRANCIS FISH, ALEXANDER I. GRAY and PETER G. WATERMAN

Division of Pharmacognosy and Forensic Science, Department of Pharmaceutical Chemistry, University of Strathclyde, Glasgow G1 1XW, Scotland

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**Key Word Index**—*Zanthoxylum avicennae*; Rutaceae; flavanone; hesperidin; alkaloids; dihydroavicine; chelerythrine; nitidine; magnoflorine; candicine; tembetarine.

**Plant.** *Zanthoxylum avicennae* (Lam.) DC (syn. *Fagara avicennae* Lam.) [1]. *Voucher specimens*. S.P. Lau-STR.3 and S.P. Lau-STR.30 deposited at the herbarium of the Royal Botanic Garden, Edinburgh. **Source.** STR.3-Tsuen Wan, New Territory, Hong Kong; STR.30-Tai Tam Reservoir, Hong Kong. **Uses.** Used in Hong Kong as a remedy for sore throat and jaundice [2]. **Previous work.** Isolation and characterization of the flavonoids hesperidin and diosmin [2], the benzophenanthridine alkaloid avicine [3], and the pyranocoumarin avicennin, for which three isomeric structures were suggested [4]. **Plant parts.** Root bark of STR.30 (150 g) and root and stem barks of STR.3 (2.4 and 8.4 g, respectively).

**Present work.** The powdered barks were extracted separately in a Soxhlet apparatus successively with petrol (40-60°),  $\text{CHCl}_3$  and MeOH. The petrol extract of STR.30 gave, on concentration, yellow crystals (3.55 g). Their identification as the novel pyranocoumarin avicennol, and its correlation with avicennin has been reported elsewhere [5]. An aliquot of the  $\text{CHCl}_3$  extract yielded, on shaking with 3% HCl, a yellow-orange precipitate from which were separated, by column

chromatography [6], the benzophenanthridine alkaloids chelerythrine (25 mg) mp 198-200° (identical with an authentic sample by mmp, UV, IR and TLC) and nitidine (8 mg) mp 237-240° (identical with an authentic sample by mmp, UV, IR and TLC). The remainder of the  $\text{CHCl}_3$  extract yielded dihydroavicine (4 mg) mp 210-212° (lit. [3] 211-212.5°)  $\text{M}^+ 333.0999$ ,  $\text{C}_{20}\text{H}_{15}\text{NO}_4$  requires 333.1001. The MS breakdown pattern, with a major ion at  $m/e$  317 ( $\text{C}_{19}\text{H}_{11}\text{NO}_4$ ) for loss of H and Me, was very simple indicating the presence of two methylenedioxy groups as ring substituents and the concomitant absence of methoxyl groups, unlike chelerythrine and nitidine [7]. The MeOH extract, on concentration, gave hesperidin (1.4 g) mp 255-258° (identical with an authentic sample by mmp, UV, IR, TLC and hydrolysis to hesperetin). Examination of the MeOH extract, purified as previously described [8], by TLC and high voltage electrophoresis, showed the presence of small quantities of the quaternary alkaloids magnoflorine, tembetarine and candicine.

Similar examination of STR.3 revealed the presence of avicennol (20 mg from stem bark, 57 mg from root bark), hesperidin (50 mg from stem bark)

and all the previously mentioned alkaloids (identified by TLC only).

*Biological significance.* The report of a wide range of 1-benzyltetrahydroisoquinoline derived alkaloids from *Z. avicennae*, rather than the single benzophenanthridine alkaloid previously noted, brings it into line with our present chemotaxonomic concepts of *Zanthoxylum sensu lato* [9]. In particular, except for the continued absence of furroquinoline alkaloids, *Z. avicennae* now shows marked similarity in alkaloid, coumarin and flavonoid constituents to another Asian species, *Zanthoxylum ailanthoides* Sieb. et Zucc. [9] (in which we include *Z. inerme* sensu Koidz.) [1, 10].

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