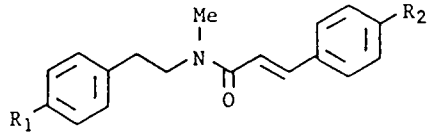
TYROSINE-DERIVED CONSTITUENTS OF ZANTHOXYLUM SPINOSUM

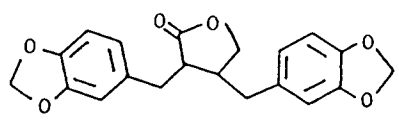
A. I. Gray* and K. M. Ng* , Department of Pharmacognosy, School of Pharmacy, Trinity College Dublin, 18 Shrewsbury Rd., Dublin, Ireland.
* present address, Phytochemistry Research Laboratories, Department of Pharmacy (Pharmaceutical Chemistry), University of Strathclyde, Glasgow Gl 1XW

Plants of the genus Zanthoxylum L. (fam. Rutaceae) are used in traditional medicine for the treatment of many ailments including circulatory diseases and pain (British Herbal Pharm. 1979). Phytochemical studies in the genus (Fish & Waterman 1973) have revealed its ability to synthesise a range of chemical types including alkaloids, coumarins, lignans and terpenoids. Among these the benzo(c)phenanthridine alkaloids fagaronine and nitidine have antileukaemic activity while chelerythrine (**7**) has anti-ACHE (Ulrichova et al 1983) and antifungal activity.

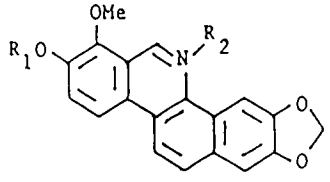
A stem bark sample of Zanthoxylum spinosum Swingle (500g, coll. Grand Cayman, Cayman Islands, Aug. 1981) was extracted with petrol (40-60), EtOAc and then MeOH. Chromatographic separation over Sigel 60 with petrol/EtOAc mixtures led to the isolation of several components which were identified as herclavin (1), isoherclavin (**2**), (+)-hinokinin (**3**), norchelerythrine (**4**), decarine (5), decarine acetate (**6**), chelerythrine (**7**), dihydrochelerythrine (**8**), 6-carboxymethyldihydrochelerythrine (**9**), 6-acetonyldihydrochelerythrine (**10**), β-amyrin, β-amyrin acetate and β-sitosterol.



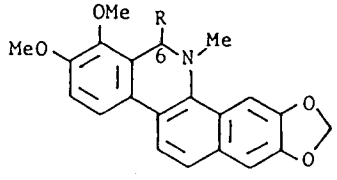
1 R_1=OMe, R_2=H; **2** R_1=H, R_2=OMe



3



4 R_1=Me, R_2=lone pair
5 R_1=H, R_2=lone pair
6 R_1=Ac, R_2=lone pair
7 R_1=Me, R_2=Me(+), Cl



8 R=H
9 R=CH_2COOH
10 R=CH_2COMe

Although the quaternary benzo(c)phenanthridine alkaloids such as (**7**) are common in Zanthoxylum s.l. the N-nor and 6-substituted dihydro types are not, the latter having been dismissed as artefacts (Fonzes & Winternitz 1968). We do not consider these alkaloid types as artefacts in this instance owing to the mild methods employed. To our knowledge this is the first report of (**2**), (**3**) and (**6**) from a natural source.

Acknowledgement: Prof. Brown (100MHz NMR), Dr. P. Caplan (MS) University College Dublin & Dr. P.G. Waterman (250MHz NMR & MS) University of Strathclyde.
British Herbal Pharmacopoeia (1979) Part 2, p. 229.
Fish, F. & Waterman, P.G. (1973) Taxon 22: 177.
Fonzes, L. & Winternitz, F. (1968) Phytochemistry 7: 1889.
Ulrichova, J. et al (1983) Planta Medica 48: 111.