



# Constituents of *Zanthoxylum rugosum* St.-Hil & Tul

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## 1. Subject and source

*Zanthoxylum rugosum* St.-Hil & Tul. (syn. *Z. chiloperone* Martius ex Engler and *Fagara chiloperone* (Martius ex Engler) Engler), Rutaceae, is a tree up to 5–10 m high, growing in southeastern and southern Brazil and Argentina. Leaves and roots were collected in São Leopoldo, RS, Brazil. A voucher specimen (SPF 62982) is deposited at the herbarium of the Instituto de Biociências da Universidade de São Paulo, SP.

## 2. Previous work

Kuck et al. (1966,1967) described the isolation of the alkaloids candicine, tembetarine, magnoflorine, laurifoline, chelerythrine, and nitidine from the cortex of *Fagara chiloperone*, collected in Argentina. Other species of this genus produce furoquinoline,

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benzophenanthridine, aporphine and canthin-6-one alkaloids, among others (Fish & Waterman, 1971; Mester, 1973; Waterman, 1975; da Silva et al., 1988); some species also yielded coumarins (Murray et al., 1982) and amide derivatives (Mester, 1973).

### 3. Present study

Dried and powdered leaves and roots were slightly wetted with water and extracted with petroleum ether, then subsequently dried, alkalinized with dilute  $\text{NH}_4\text{OH}$  and extracted with  $\text{CH}_2\text{Cl}_2$ . The petroleum ether fraction from the leaves yielded a precipitated which was filtered, washed with petroleum ether, crystallized in cool  $\text{CHCl}_3$  and identified as anisocoumarin H (Ngadjui et al., 1989).

The concentrated  $\text{CH}_2\text{Cl}_2$  extract obtained from the leaves was partitioned into 0.2 M HCl and the aqueous layer was alkalinized ( $\text{NH}_4\text{OH}$ ) and partitioned with  $\text{CH}_2\text{Cl}_2$ . This extract was concentrated and submitted to preparative TLC eluting with  $\text{CHCl}_3 : \text{CH}_3\text{OH}$  (97 : 3) to give 5-methoxycanthin-6-one (Forgacs et al., 1982).

The petroleum ether fraction obtained from the roots gave a solid portion mixed with an oily fraction. Both fractions were submitted to silica gel column chromatography, eluting with  $n\text{-C}_6\text{H}_{12} : \text{CHCl}_3$  in mixture of increase polarities. The former yielded the alkaloids canthin-6-one (Forgacs et al., 1982) and 5-methoxycanthin-6-one and the coumarin *trans*-avicennol (Gray et al., 1975). The coumarin *trans*-avicennin (Gray et al., 1975) was isolated from the oily fraction.

The concentrated  $\text{CH}_2\text{Cl}_2$  extract obtained from the roots, by preparative TLC eluting with  $\text{CHCl}_3 : \text{CH}_3\text{OH}$  (95 : 5), gave the alkaloids chelerythrine (Krane et al., 1984) and skimmianine (Couillerot et al., 1994).

The compounds were identified by UV, IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR spectroscopy and MS spectrometry as well as by comparison with authentic samples (TLC).

### 4. Chemotaxonomic significance

All the classes of compounds reported in this work have been found in other species of *Zanthoxylum* (including *Fagara*) (Mester, 1973; Waterman, 1975; da Silva et al., 1988). Furoquinoline alkaloids are almost exclusively found in Rutaceae, being very common in *Zanthoxylum*. Benzophenanthridines are widespread in the genus but not in Rutaceae as a whole. The same is true to a lesser extent for canthinones but they are more common in the Simaroubaceae (Ohmoto & Koike, 1989). Avicennin type angular pyranocoumarins are rather unusual being based on a 5,7-dioxygenated coumarin prenylated at C-6 and C-8. These compounds were isolated from *Zanthoxylum avicennae*, *Z. elephantiasis* and *Z. dipetalum* (Gray et al., 1975; Murray et al., 1982), and from other rutaceous genera including *Eriostemon* (Ghisalberti, 1998). The unusual geranyl coumarin, anisocoumarin H, was previously found in *Clausena anisata* (Ngadjui et al., 1989), and more recently in the bark of *Zanthoxylum schinifolium* (Chang et al., 1997).

The data presented here reflect *Z. rugosum* to contain metabolites typical of the genus and suggest a relationship with other taxa such as *Z. elephantiasis* which share many of its metabolites.

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