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ZANTHOMAMIDE: AN AROMATIC AMIDE FROM *ZANTHOXYLUM THOMENSE*

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Key Word Index—*Zanthoxylum thomense*; Rutaceae; aromatic amide; zanthomamide; benzophenanthridines.

Abstract—From the stem bark of *Zanthoxylum thomense* a new amide, zanthomamide has been isolated and characterized as *N*-methyl, *N*-cinnamyl-(3′,4′-methylenedioxy)-phenylethylamine. Other constituents identified are the known benzophenanthridines, decarine, norchelerythrine and angoline.

INTRODUCTION

The genus *Zanthoxylum* (including *Fagara*) is known to contain various components such as terpenes, lignans, amides and alkaloids [1]. We report here the examination of the stem bark of *Zanthoxylum thomense* (Engl.) A. Chev. *ex* Waterm. [2], a woody rutaceous plant indigenous to West Equatorial Africa.

RESULTS AND DISCUSSION

After preliminary defatting with petrol (bp 60–80°), the ground stem bark was extracted with chloroform, then with chloroform in an alkaline medium and finally with methanol. A total yield of 0.15% crude alkaloids was obtained.

From the concentrated petrol extract, the common triterpene lupeol crystallized, and the new amide, zanthomamide (**1**) was obtained by CC of the supernatant over silica gel, then by CC of eluates ($CHCl_3$) from the silica gel column over alumina.

From the neutral chloroform extract, three known benzophenanthridine alkaloids, decarine (**2**), norchelerythrine (**3**) and angoline (**4**) were successively separated by CC over silica gel then alumina. They were identified by direct comparison of their spectra (UV, MS, ^{1}H NMR) with those of authentic samples. Decarine (**2**) was the main alkaloid (55% of crude alkaloids).

The new amide, zanthomamide (**1**), was obtained only in an amorphous form. The EI mass spectrum showed a weak $[M]^+$ at *m/z* 309 ($C_{19}H_{19}O_3N$). In the UV spectrum (methanol) there is one maximum at 276 nm (log ε5.92); it is not modified by alkali. The IR spectrum exhibited an absorption band at 1650 cm^{-1}, characteristic of a tertiary amide [3], while the absence of absorption bands between 3200 and 3500 cm^{-1} confirmed the tertiary nature of the amide [3]. EI mass spectral fragmentation of the amide gave major ions at *m/z* 148 $[M-131-30]^+$, 131 (100%), 103 and 77. The latter three ions suggested that the acidic part of the amide was cinnamic acid. This argument was supported by the occurrence in the ^{1}H NMR (60 MHz, $CDCl_3$) spectrum of a broad signal for five aromatic protons at δ7.37 and, in the ^{1}H NMR (250 MHz, $CDCl_3$) spectrum, of an AB signal for two protons at δ7.73 and 6.88 (J = 15 Hz), characteristic of *trans*-cinnamic acid protons [4]. Alkaline hydrolysis [5] of **1** gave cinnamic acid, identified by direct comparison (TLC, mmp) with an authentic sample.

Further examination of the ^{1}H NMR spectrum of the amide showed that the amino part was a phenylethylamine substituted by an *N*-methyl group (3H, *s*, δ3.04) and by a methylenedioxy group on the aromatic nucleus

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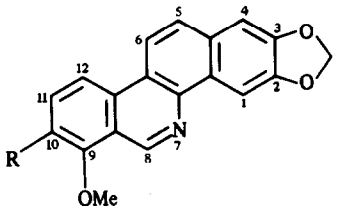
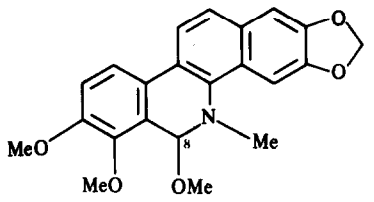


2 R = OH
3 R = OMe



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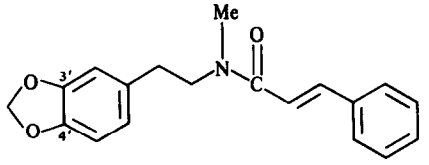

1

(2H, AB signal, $J = 1.5$ Hz at δ5.88 and 5.83). The methylenedioxy group may be assigned, on biogenetic grounds, to 3',4' [1]. Other signals were a broad singlet for the three aromatic protons at δ6.70, two triplets (each 2H) at δ3.70 and 2.78 ($J = 7$ Hz) typical for two closed non equivalent CH_2 groups [6]. These data lead to the assignment of structure **1** for zanthomamide.

Zanthoxylum thomense appears to be chemically typical of the genus. Both benzophenanthridines and aromatic amides come from the archaic pathway of tyrosine and are characteristic of this genus [7]. It is interesting that the three benzophenanthridines all belong to the chelerythrine type; angoline, 8-methoxychelerythrine, is known to be an artefact of chelerythrine [8]. The aromatic amide is formed by the condensation of a substituted tyramine with cinnamic acid. This type of substitution on the tyramine part is not rare in the genus *Zanthoxylum* [9] and zanthomamide is closely related to herclavine, another aromatic amide isolated from *Z. clava-herculis* [10].

EXPERIMENTAL

Plant material. Stem bark was collected in the Popular Republic of Congo during 1978 by Paul Sita. A voucher specimen (PS 3828) has been deposited at the herbarium of the Museum d'Histoire Naturelle in Paris, France.

Extraction and isolation. Extraction of 211.7 g of dried and ground stem bark was carried out in a Soxhlet apparatus. The concd petrol extract, after crystallization of lupeol, was subjected to CC on silica gel (Kieselgel 60); elution with $CHCl_3$ gave a mixture which was separated on alumina (activity II-III) by CC. Elution with $CHCl_3$ gave zanthomamide (**1**, 130 mg) in an amorphous form. The concd neutral $CHCl_3$ extract was subjected to CC on silica gel. Elution with $CHCl_3$–MeOH (99:1) gave, after crystallization from MeOH, decarine (**2**, 192 mg) and norchelerythrine (**3**, 35 mg). Elution with $CHCl_3$–MeOH (97:3) gave a mixture which was submitted to CC on alumina. Elution with $CHCl_3$ gave, after crystallization from MeOH, angoline (**4**, 66 mg). From alkaline $CHCl_3$, after CC on silica gel, an additional quantity of decarine (**2**, 66 mg) was obtained.

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