

g) was chromatographed over a Polyclar column using Egger solvent (CHCl<sub>3</sub>-MeOH-MeCOEt-Me<sub>2</sub>CO, 20:10:5:1) to give the three glucosides. For both columns, fractions were collected on the basis of monitoring the bands with uv light. All bands were further separated by paper chromatography (Whatman 3MM) using 15% HOAc and *t*-BuOH-HOAc-H<sub>2</sub>O (3:1:1). After purification over Sephadex LH-20 (MeOH) all compounds were identified by uv, <sup>1</sup>H nmr, ms, and color reactions (11).

#### ACKNOWLEDGMENTS

This work was supported by grants from the National Science Foundation (BSR-8402017) and the Robert A. Welch Foundation (F-130). The authors thank Douglas Gage and John Norris for collecting and identifying the plant material.

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Received 17 January 1986

#### ALKALOIDS OF *TABERNAEMONTANA VENTRICOSA*<sup>1</sup>

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*Tabernaemontana ventricosa* Hochst. ex A.DC. is a small tree occurring in montane forests in tropical Africa (2). In a current taxonomic revision of the genus *Tabernaemontana* by Leeuwenberg (3), this species was shown to possess several synonyms such as *Conopharyngia usambarensis*, *Conopharyngia ventricosa*, and *Tabernaemontana usambarensis*. No phytochemical investigations prior to the one presented here have been reported, although it has been mentioned that the plant was suitable for extraction of conopharyngine (4). In traditional medicine, the latex has been used for healing wounds (5,6).

The stem bark was extracted with EtOH. The extract was separated by l.c. Some of the first fractions yielded a large quantity of triterpenes. The later fractions, after an acid-base extraction and preparative tlc, gave the alkaloids. Table 1 lists the identified alkaloids, together with an indication of their relative abundance in the stem bark. No conopharyngine could be detected in the plant material investigated. Because of the co-occurrence of ibogan, aspido-spermatan, and corynanthean alkaloids, *T. ventricosa* clearly is a member of the genus *Tabernaemontana* (3). Remarkable in this species is the relatively large amount of strychnan alkaloids, a type which is otherwise rather rare in this genus (3).

<sup>1</sup>Part 18 in the series "Pharmacognostical Studies of *Tabernaemontana* Species." For part 17, see van der Heijden *et al.* (1).

TABLE 1. Alkaloids Isolated from the Stem Bark of *Tabernaemontana ventricosa*

Alkaloid	Relative abundance <sup>a</sup>	Identified by	Reference
10-Hydroxyheyneanine . . . . .	+++	uv, ms, <sup>1</sup> H nmr	(9)
16- <i>epi</i> -Isositsirikine . . . . .	++	uv, ms, <sup>1</sup> H nmr, co-tlc	(10-12)
Apparicine . . . . .	++	uv, ms, <sup>1</sup> H nmr, co-tlc	(10, 13)
Tuboraiwine . . . . .	+	uv, ms, <sup>1</sup> H nmr, co-tlc	(10, 13)
Norfluorocurarine . . . . .	+	uv, ms, <sup>1</sup> H nmr, co-tlc	(10, 14)
Akuammicine . . . . .	+++	uv, ms, <sup>1</sup> H nmr, co-tlc	(10)
Akuammicine N-oxide . . . . .	+	uv, ms, <sup>1</sup> H nmr, co-tlc	(10)
10-Hydroxycoronaridine . . . . .	+	uv, ms, <sup>1</sup> H nmr	(15)

<sup>a</sup>+++ = major component, ++ = minor component, + = trace component.

### EXPERIMENTAL

**PLANT MATERIALS.**—Materials were collected from a plant cultivated in the greenhouse of the Agricultural University of Wageningen, The Netherlands, and identified by Dr. A. J. M. Leeuwenberg. The seeds were originally collected in Cameroon. A voucher specimen has been deposited in the herbarium of the Laboratory for Plant Systematics, Wageningen.

**EXTRACTION, ISOLATION, AND IDENTIFICATION.**—The stem bark (530 g) was extracted for 21 h with 96% EtOH in a Soxhlet apparatus working under a pressure of 0.2 atm. The EtOH extract was taken to dryness under reduced pressure.

The crude extract (ca. 20 g) was, after pre-adsorption, chromatographed on a column of silica gel (ca. 400 g), packed in toluene, using toluene-absolute EtOH as the mobile phase. The percentage EtOH was increased from 0 to 64%. Some of the first fractions contained a mixture of triterpenes, identified by <sup>1</sup>H nmr, <sup>13</sup>C nmr, and ms (7, 8) as comprising  $\alpha$ -amyrin acetate,  $\beta$ -amyrin acetate, and lupeol acetate (relative amounts 4:1:1). Later fractions were combined appropriately after tlc monitoring. These were purified by acid-base extraction, followed by preparative tlc of the alkaloids. The isolated alkaloids (total amount ca. 0.01% of dry weight) were identified by means of their spectral data, color reactions and, if possible, by tlc comparison with authentic samples (Table 1).

Data not previously recorded in the literature are given below. *10-Hydroxyheyneanine*: tlc (10) hRf in system S1:8, S2:12, S3:35, S4:60; Fe<sup>3+</sup>, purple; Ce<sup>4+</sup>, purple. *Norfluorocurarine*: <sup>1</sup>H nmr  $\delta$  10.31 (bs, NH), 9.35 (s, H-17), 7.30 (dd,  $J=7.8$  and 1 Hz, H-12), 7.21 (ddd,  $J=7.4$ ; 7.8 and 1 Hz, H-10), 6.98 (ddd,  $J=7.4$ ; 7.8 and 1 Hz, H-11), 6.92 (dd,  $J=7.8$  and 1 Hz, H-9), 5.41 (m, H-19). *Akuammicine*: <sup>1</sup>H nmr  $\delta$  8.98 (bs, NH), 7.41 (dd,  $J=7.4$  and 1 Hz, H-12), 7.19 (ddd,  $J=7.7$ ; 7.5 and 1 Hz, H-10), 6.95 (ddd,  $J=7.7$ ; 7.4 and 0.8 Hz, H-11), 6.84 (dd,  $J=7.5$  and 0.8 Hz, H-9), 5.54 (bq,  $J=6.9$  Hz, H-19), 4.46 (bs, H-3), 4.14 (bd,  $J=15.0$  Hz, H-21a), 4.03 (bs, H-15), 3.67 (ddd,  $J=12.0$ ; 13.2 and 5.6 Hz, H-5a), 3.17 (d,  $J=15.0$  Hz, H-21b), 3.14 (dd,  $J=12.0$  and 6.8 Hz, H-5b), 2.60 (ddd,  $J=13.1$ ; 13.2 and 6.8 Hz, H-6a), 2.51 (ddd,  $J=14.7$ ; 3.8 and 2.2 Hz, H-14a), 2.02 (dd,  $J=13.1$  and 5.6 Hz, H-6b), 1.66 (d,  $J=6.9$  Hz, H-18), 1.40 (ddd,  $J=14.7$ ; 1 and 1 Hz, H-14b). *Akuammicine N-oxide*: ms  $m/z$  (rel. int.) 338 (M<sup>+</sup>, 2), 322 (89), 263 (15), 252 (13), 234 (10), 220 (11), 216 (26), 121 (100); <sup>1</sup>H nmr  $\delta$  8.93 (bs, NH), 7.95 (d,  $J=7.5$  Hz, H-12), 7.26 (dd,  $J=7.5$  and 7.5 Hz, H-10), 7.06 (dd,  $J=7.5$  and 7.5 Hz, H-11), 6.87 (d,  $J=7.5$  Hz, H-9), 5.81 (m, H-19), 5.16 (bs, H-3), 4.16 (bs, H-15), 1.73 (d,  $J=5.7$  Hz, H-18). *10-Hydroxycoronaridine*: tlc (10) hRf in system S1:12, S2:22, S3:41, S4:71; Fe<sup>3+</sup>, purple; Ce<sup>4+</sup>, purple.

### ACKNOWLEDGMENTS

We wish to thank Dr. A. J. M. Leeuwenberg for the botanical identification, Mr. J. J. van Houste and Mr. E. van der Heeft for recording the mass spectra, Dr. C. Erkelens for instruction and assistance in recording the <sup>1</sup>H-nmr spectra, and Mr. F. Lefeber for recording the <sup>13</sup>C-nmr spectra.

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Received 3 February 1986

## CACTUS ALKALOIDS, LXI. IDENTIFICATION OF MESCALINE AND RELATED COMPOUNDS IN EIGHT ADDITIONAL SPECIES USING TLC AND MS/MS

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The well-known cactus alkaloid mescaline (3,4,5-trimethoxy- $\beta$ -phenethylamine) is present in *Lophophora* and some species of *Trichocereus* in sufficient concentrations to impart hallucinogenic activity upon ingestion by humans (1). It is less well known that additional cactus species, representing all three cactus subfamilies, can also contain this hallucinogen although in lesser concentrations (2). In this paper we report the detection of small traces of mescaline in eight additional species (Table 1), using a combination of tlc (3) and mass spectrometry (ms/ms) (4). Quantitative tlc estimated the maximum concentration in the richest of these species (*Stenocereus stellatus*) to be at the level of 0.01% of the dry weight, an insufficient amount to cause hallucinations upon ingestion. This is the first report of the detection of mescaline in *Polaskia*, *Pterocereus*, and *Stenocereus*. *Neoraimondia macrostibas* is an ingredient, with *Trichocereus pachanoi* and several noncactaceous plant species, of the Peruvian hallucinogenic drink, "cimora" (1); the absence of mescaline in *Neoraimondia arequipensis* var. *roseiflora*, formerly treated as a variety of *N. macrostibas* (5), leaves unexplained this folkloric use.

The presence of the biosynthetically-related compounds (6), 3,4-dimethoxy- $\beta$ -phenethylamine and 3,5-dimethoxy-4-hydroxy- $\beta$ -phenethylamine, was simultaneously determined. The tlc separation of mescaline and the former compound was difficult (7), but their separation by ms/ms and detection in the alkaloid extract was facile because the protonated molecules of each yielded characteristic daughter ion spectra. Ms/ms can thus be a rapid means of direct screening of crude extracts for series of trace compounds, including the detection of minute amounts of biosynthetic precursors.