

SAMPANGINE, A NEW ALKALOID FROM *CANANGA ODORATA*

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From the basic fraction of the  $\text{CHCl}_3$  extract of the stem bark of *Cananga odorata* Hook, F. and Thoms. (Annonaceae), Cave and co-workers (1) reported liriodenine, anonaine, roemerine, ushinine, and canangine, which was later identified as eupolauridine (2). The present paper reports the isolation and structural elucidation of two alkaloids, one of which is new, from the  $\text{CHCl}_3$  extract of the stem bark of the parent plant.

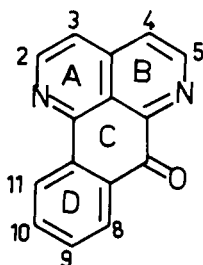
The powdered stem-bark was extracted first with hexane to remove waxes and then with  $\text{CHCl}_3$ . Examination of the  $\text{CHCl}_3$  extract by tlc showed two Dragendorff-positive spots, one major and the other minor. The two alkaloids A and B were isolated in pure form using chromatographic techniques. The alkaloid B was identified as the known compound, liriodenine (1).

Alkaloid A is new and named sampangine (1). The uv spectrum showed a complex pattern characteristic of a highly conjugated system. Acetylation and methylation failed, which indicated the tertiary nature of the nitrogen and the absence of hydroxyl groups; a lack of a bathochromic shift upon addition of base further confirmed the latter. Sampangine showed ir absorption at  $1680\text{ cm}^{-1}$  attributable to a highly conjugated ketone function. The low ratio of

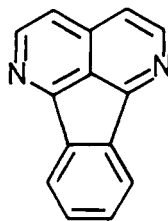
hydrogen to carbon suggested the presence of a condensed ring system.

The hrms indicated the molecular formula as  $\text{C}_{15}\text{H}_8\text{N}_2\text{O}$ . The molecular ion peak at  $m/z$  232 was also the base peak. Another strong peak in the high mass region appeared at  $m/z$  204 ( $\text{M}^+ - \text{CO}$ ) corresponding to the molecular ion of eupolauridine (2). The remainder of the spectrum was virtually similar for both the compounds, including the fragment ions at  $m/z$  177 and 150 corresponding to the ions formed as a result of the loss of one and two molecules of HCN, respectively, from the fragment ion at  $m/z$  204, characteristic of heterocyclic nitrogenous compounds (3). Thus, sampangine is closely related to eupolauridine but possesses a carbonyl group.

The position of the carbonyl group was determined by studying the  $^1\text{H}$ -nmr spectrum ( $\text{CDCl}_3$ ), which showed eight aromatic protons. Coupling constants are very useful in distinguishing the pyridine ring protons from other aromatic protons (4,5). The two doublets (each 1H,  $J=5$  Hz) at 8.90 and 9.14 corresponded to H-2 or H-5 ( $\alpha$  to N), and the other two doublets (each 1H,  $J=5$  Hz) at 7.94 and 7.71 corresponded to H-3 or H-4 ( $\beta$  to N). Two single-proton doublets of doublets ( $J_o=7.5$  Hz,  $J_m=2$  Hz) at 8.46 and 8.83 formed the MX part (H-8 and H-11, respectively) of an



1



2

ABMX system. The AB part (H-9 and H-10) was comprised of two doublets of doublets ( $J_o = 7.5$  Hz,  $J_m = 2$  Hz) at 7.86 and 7.80, respectively. This established that ring D was unsubstituted. A strong band at  $750\text{ cm}^{-1}$  in the ir spectrum was attributed to C-H out-of-plane deformation of these four aromatic protons (6). In ring-D, the H-11 was reported to appear usually at lower field relative to the other protons (7). On the basis of the spectroscopic evidence, sampangine was assigned the structure **1**. In the  $^1\text{H}$ -nmr spectrum of eupolauridine (**2**) (2), spectral simplification for the heterocyclic ring protons was observed as H-2 and H-5, H-3 and H-4 are isochronous; but in sampangine (**1**) the corresponding protons appeared as discrete doublets, and this was attributed to the presence of the carbonyl group in ring C.

### EXPERIMENTAL

**PLANT MATERIAL.**—The plant *C. odorata* was collected at Visakhapatnam, A.P., India. A voucher specimen is deposited in the Andhra University Herbarium, No. PNR-210 (AUH).

**EXTRACTION AND ISOLATION OF ALKALOIDS.**—The powdered stem-bark (2.5 kg) was extracted with n-hexane in a Soxhlet apparatus (10 syphonings). The defatted material was then extracted with  $\text{CHCl}_3$  (10 syphonings). The  $\text{CHCl}_3$  extract (25 g) was subjected to silica gel (500 g) column chromatography. The column was eluted with  $\text{C}_6\text{H}_6$ ,  $\text{C}_6\text{H}_6$ -EtOAc (9:1) and (4:1). Alkaloids A and B were eluted with  $\text{C}_6\text{H}_6$ -EtOAc (9:1) and (4:1), respectively. Yields: Alkaloid A, 25 mg; alkaloid B, 1.4 g.

**ALKALOID A.**—*Sampangine* (**1**).—Crystallized

from  $\text{C}_6\text{H}_6$  as bright yellow needles, mp  $210^\circ$  (dec.); uv (MeOH) 220, 252, 312, 326, 392 nm; ir (KBr) 1680, 1620, 1402, 1380, 1320, 1275, 1225,  $750\text{ cm}^{-1}$ ;  $^1\text{H}$  nmr (100 MHz,  $\text{CDCl}_3$ ) 7.71 (1H, d,  $J = 5$  Hz, H-3 or H-4), 7.80 (1H, dd,  $J = 7.5, 2$  Hz, H-10), 7.86 (1H, dd,  $J = 7.5, 2$  Hz, H-9), 7.94 (1H, d,  $J = 5$  Hz, H-3 or H-4), 8.46 (1H, dd,  $J = 7.5, 2$  Hz, H-8), 8.83 (1H, dd,  $J = 7.5, 2$  Hz, H-11), 8.90 (1H, d,  $J = 5$  Hz, H-2 or H-5), 9.14 (1H, d,  $J = 5$  Hz, H-2 or H-5); ms  $m/z$  232 (100), (Calcd for  $\text{C}_{15}\text{H}_8\text{N}_2\text{O}$  232.0636. Found 232.0630), 204 (92.4) (Calcd for  $\text{C}_{14}\text{H}_8\text{N}_2$  204.0673. Found 204.0673), 177 (17.5), 150 (23.9), 102 (31.3), 88.5 (15), 75 (51.7), 50 (26.5).

**ALKALOID B.**—*Liriodenine*.—Crystallized from  $\text{CHCl}_3$  as yellow needles, mp  $273^\circ$  (dec.); identical with liriodenine.

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