REFERENCES

1. Usubillaga, A., Seelkopf, C., Karle, J., Dale, J. and Witkop, B. (1970) *J. Am. Chem. Soc.* **92**, 700.
2. Usubillaga, A. (1973) *Rev. Latinoam. Quim.* **4**, 32.
3. Usubillaga, A., Zabel, V. and Watson, W. (1982) *Acta Crystallog.* **b38**, 966.
4. Usubillaga, A. (1984) *J. Nat. Prod.* **47**, 52.
5. Bird, G. J., Collins, D. J., Eastwood, F. W. and Exner, R. H. (1979) *Aust. J. Chem.* **32**, 797.
6. Shoolery, J. N. (1984) *J. Nat. Prod.* **47**, 226.
7. Tory, K., Seo, S., Terui, Y., Nishikawa, J. and Yasuda F. (1981) *Tetrahedron Letters* **22**, 2405.

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SIMPLEXINE (14-HYDROXY-4-METHOXY-13,14-DIHYDRONORSECURININE): AN ALKALOID FROM *PHYLLANTHUS SIMPLEX*

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Key Word Index—*Phyllanthus simplex*; Euphorbiaceae; alkaloids; simplexine; phyllanthine.

Abstract—From the whole plant of *Phyllanthus simplex* (Fam. Euphorbiaceae), two securinegia alkaloids, simplexine (**1**) and phyllanthine (**2**) have been isolated and their structures elucidated on the basis of spectroscopic data.

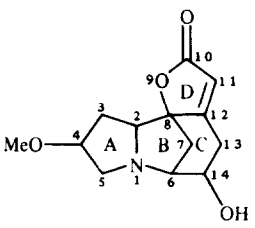
INTRODUCTION

Phyllanthus simplex's common Indian names are 'Bhuiaveli' in Marathi and 'Uchchiyusirika' in Telgu. Its fresh leaves are used as a wash for itch in children [1]. The plant has not been chemically investigated before. Our present investigation of the whole plant led to the isolation of a new alkaloid, the structure of which has been established as **1**.

RESULTS AND DISCUSSION

The alkaloid **1** showed a UV absorption at 255 nm and IR absorptions at 3622 cm^{-1} (OH), 1800 cm^{-1} (five-membered ring lactone), 1117 cm^{-1} (–OMe) and 1773 cm^{-1} (C=O) and 1642 cm^{-1} (olefinic bond). Its mass spectrum showed a molecular ion peak at *m/z* 251 and a base peak at *m/z* 207. On the basis of the mass and ^{1}H NMR spectra of this alkaloid, the position of a –OMe group in the ring A at C-4 and the position of a hydroxyl group in the ring C at C-14 were established. The mass fragmentation at *m/z* 68 confirmed the presence of a five-membered ring in the alkaloid. The fragment at *m/z* 100 showed the –OMe group is present in the ring A and the fragment at *m/z* 56 established the isolation of –OMe at C-4. This is further confirmed by its ^{1}H NMR spectrum which showed a singlet at δ3.22 corresponding to 3 protons for –OMe. Further it shows a one-proton triplet at δ5.67 due to the olefinic proton at C-11–C-12 coupled with two allylic protons at C-13 suggesting that the hydroxyl group in the alkaloid is located at C-14. Further a multiplet at δ4.48 was observed that corresponds to 1H, (>CHOH), and an exchangeable (in D_2O) proton at δ2.48 shows the presence of the additional oxygen as a secondary hydroxyl function in the alkaloid. The peak at *m/z* 207 was assigned to the ion formed by loss of CH_2=CHOH. The peak at *m/z* 44 indicated that the ion at 207 was not due to the loss of CO_2. Therefore, the position of the hydroxyl group could only be assigned at C-14–OH in the ring C of the alkaloid. From all these spectral data, the structure of a new alkaloid is established as simplexine (14-hydroxy-4-methoxy-13,14-dihydronorsecurinine) (**1**). Earlier, dihydronorsecurinine was isolated from *Securinegia virosa* [2].

Alkaloid **2** showed a UV absorption at 256 nm, characteristic of the securinine type skeleton and its IR spectrum showed absorption at 1775 cm^{-1} (six-membered ring lactone), 1118 cm^{-1} (–OMe) and 1642 cm^{-1} (C=O) [3]. Its ^{1}H NMR and mass spectra were also found to be the same as earlier reported for phyllanthine [4]. From the



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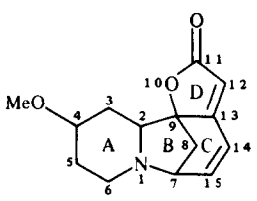

2

above spectral characteristics, its structure was confirmed as phyllanthine. This is the first report of its occurrence in *Phyllanthus simplex*. Phyllanthine was earlier isolated from *Phyllanthus discoides* [4].

EXPERIMENTAL

^{1}H NMR spectra were run in $CDCl_3$ and D_2O with TMS as int. standard. Analytical TLC was performed on silica gel using Me_2CO as solvent. The spots were detected on chromatograms by spraying with Dragendorff 's and Mayer's reagents.

Extraction and isolation of alkaloids. The whole plant of *Phyllanthus simplex* Retz, abundantly present in the Delhi locality [5], was collected in May 1986. The completely air-dried and coarsely powdered whole plant of *Phyllanthus simplex* (5 kg) was exhaustively extracted with EtOH (5 l) on a Soxhlet apparatus for 30 hr. It was acidified with an equal vol. of 10% aq. citric acid and the remaining EtOH distilled off under red. pres. on a rotary evaporator. After successive extraction with petrol and ether, the soln was made basic with NH_4OH and extracted exhaustively with $CHCl_3$. The $CHCl_3$ extract was evapd, yielding a brown gum (0.4 g) which contained alkaloids (Dragendorff's and Mayer's reagents). The total alkaloid extract showed two spots on TLC over silica gel (R_f 0.75 and 0.27) using MeOH as a solvent. PC also showed two spots R_f 0.56 and 0.36 using *n*-BuOH–HCO_2H–H_2O (12:1:7) as eluent. The crude alkaloid mixture (0.4 g) was separated on a silica gel column (Merck, type 60, 3 × 96 cm) using Me_2CO as eluting solvent. A total of 70 fractions were collected (each fraction contains 10 ml). Fractions 30–49 gave a single spot on TLC, R_f 0.75. Fractions 50–60 gave single spot, R_f 0.27 on TLC. Fractions 30–49 were combined and purified through repeated CC. The product, which did not crystallize (yield 0.17 g), was found to be a new alkaloid named as simplexine (**1**). Fractions 50–60 also combined and purified by the same method gave phyllanthine (**2**) [4] (yield 0.09 g)

Simplexine. Exhibited $[\alpha]_D^{20} - 20.4°$ (EtOH; *c* 0.2). Calcd for $C_{13}H_{17}NO_4$ (Found C, 61.9; H, 6.72; and N, 5.66% $C_{13}H_{17}NO_4$ requires C, 62.1; H, 6.77 and N, 5.57%). UV λ_{max}^{MeOH} (log ε): 255 (4.28), IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3622, 1800, 1773, 1642 and 1117. Its ^{1}H NMR (100 MHz, $CDCl_3$, TMS int. standard) showed characteristic proton signals at δ3.22 (3H, *s*, –OMe), δ5.67 (1H, olefinic), δ4.48 (1H, *m*, C<u>H</u>OH) exchangeable (in D_2O) proton at δ2.48. EIMS *m/z* (rel. int.%): 251 (M^+, 15), 207 (100), 100 (44), 68 (34), 56 (80), 44 (21).

Phyllanthine. Analysed for $C_{14}H_{17}NO_3$ (Found C, 66.8; H, 6.67; N, 5.56 requires C, 68.0; H, 6.8; N, 5.6%; UV λ_{max}^{MeOH} (log ε): 256 (4.20). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1775, 1642 and 1118.

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REFERENCES

1. Chopra, R. N. (1956) *Glossary of Indian Medicinal Plants*, p. 191.
2. Saito, S., Iwamoto, T., Tanaka, T., Matsumura, C., Sugimoto, N., Horii, Z. and Tamura, Y. (1964) *Chem. Ind.* 1623.
3. Mulchandani, N. B. and Hassarajani, S. A. (1984) *Planta Med.* **50**, 104.
4. Parello, J. (1968) *Bull. Soc. Chim. Fr.* **3**, 1117.
5. Maheshwari, J. K. (1963) *Flora of Delhi*, p. 319.