

(Na_2SO_4) CHCl_3 extract, filtered, and evaporated in vacuo, yielded the total bases (13.2 g, 0.09%). The organic solution was basified with 5% NaOH . The alkaline solution was acidified with dilute HCl and then basified with NaHCO_3 . The liberated bases were extracted with CHCl_3 , washed with H_2O , dried, and the solvent was removed to give alkaloidal mixture-A (phenolic bases: 4.6 g). The remaining organic solution was washed with H_2O , dried, and evaporated to give alkaloidal mixture-B (nonphenolic bases: 3.0 g).

ALKALOIDAL MIXTURE A.—Mixture A (4.6 g) was chromatographed on SiO_2 (150 g). The column was successively eluted with CHCl_3 and mixtures of CHCl_3 - MeOH , and elution was followed by tlc. Fractions were purified by preparative tlc on SiO_2 . Four bases were isolated and identified by qualitative optical activity, ir, uv, ^1H nmr, and ms as (+)-reticuline (35 mg), (+)-isoboldine (125 mg), corytuberine (12 mg), and (-)-stepholidine (42 mg).

ALKALOIDAL MIXTURE B.—Mixture B (3.0 g) was chromatographed on neutral Al_2O_3 (120 g). The column was eluted successfully with C_6H_6 , CHCl_3 , and mixtures of CHCl_3 - MeOH , and elution was followed by tlc. Fractions were purified by preparative tlc. Four bases were isolated and identified by qualitative optical activity, ir, uv, ^1H nmr and ms as liriodenine (117 mg), lanuginosine (15 mg), (-)-anonaine (28 mg), and (+)-nornantenine (8 mg).

The structures were confirmed by comparison with authentic samples.

Full details of the isolation and identification are available on request to the senior author.

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LITERATURE CITED

1. A. Villar and J.L. Rios, *J. Nat. Prod.*, **46**, 438 (1983).
2. A. Urzua and B.K. Cassels, *Rev. Latinoamer. Quim.*, **8**, 133 (1977).

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CONSTITUENTS OF THE STEM-BARK OF *ZIZYPHUS JOAZEIRO*

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In our continuing study of the medicinal plants of northeastern Brazil, we investigated the stem-bark of *Zizyphus joazeiro* Mart. from which we report here the isolation of betulinic acid, oleanolic acid, and a saponin which furnished ebilin lactone (1) upon acid hydrolysis. Ebilin lactone is certainly an artifact arising from the acid hydrolysis of the saponin which, like jujuboside A, jujuboside B, hovenoside, and bacoside A, is probably a glycoside of jujubogenin (1,2) because, the saponin neither showed the characteristic uv absorption for a conjugated triene nor the strong ir band of γ -lactone shown by ebilin lactone.

EXPERIMENT

PLANT MATERIAL.—The plant material used in this study was collected from the interior of the State of Paraíba in April 1980, and the voucher specimen is deposited at the Herbarium of the Universidade Federal da Paraíba, João Pessoa, PB, Brazil.

EXTRACTION AND ISOLATION OF THE CONSTITUENTS.—Dried and ground stem-bark (2 kg) of *Z. joazeiro* was first extracted with CHCl_3 followed by MeOH . The dried CHCl_3 extract, after treatment with hexane, gave a residue that, upon column chromatography (cc), yielded betulinic acid (2.4 g), mp 290-292° and oleanolic acid (0.016 g), mp 300°. The dried MeOH extract, upon treatment with hot EtOH gave a white solid on standing, which afforded a homogeneous (tlc) substance upon cc on a Sephadex column. This material, mp 225-236° (dec.), upon acid hydrolysis furnished ebilin lactone.

The identification was done by comparison of the physical properties (mp, uv, ir, ms, ^1H nmr) of the compounds and their derivatives (Me-ester, acetate) with those given in the literature (1-6).

Full details of the isolation and identification of the compounds are available on request to the senior author.

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LITERATURE CITED

1. D.K. Kulshreshtha and R.P. Rastogi, *Phytochemistry*, **12**, 2074 (1973).
2. K. Kawai, T. Akiyama, Y. Ogihara, and S. Shibata, *Phytochemistry*, **13**, 2829 (1974).
3. J. Bhattacharyya, U. Kokpol, and D.H. Miles, *Phytochemistry*, **15**, 431 (1976).
4. S.C. Pakrashi, J. Bhattacharyya, S. Mookerjee, and H. Vorgbruggen, *Phytochemistry*, **7**, 461 (1968).
5. "Merck Index," 10th ed. Rahway, NJ: Merck & Co., Inc., 1983, p. 979.
6. R.A. Eade, J. Ellis, J.S. Shannon, H.V. Simes, and J.J.H. Sims, *Austr. J. Chem.*, **23**, 2085 (1970) and references cited therein.

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VINCADINE FROM THE LEGUMES OF *RHAZYA STRICTA*

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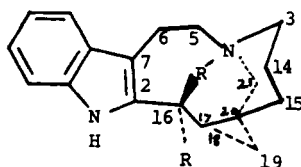
Rhazya stricta Decsne. (Apocynaceae) (1) is a small glabrous, erect shrub, widely distributed in Western Asia and abundantly found in Pakistan. It has long been used in the indigenous system of medicine for the treatment of various diseases (2-4). Some of its alkaloids also possess anticancer activity (5,6). In our continuing chemical analysis of the legumes of *R. stricta* (7), we report here the isolation of vincadine, identified on the basis of spectral studies. Vincadine has not previously been reported from this plant.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Spectra were recorded on JASCO A-302 ir spectrophotometer, Shimadzu UV-240 spectrophotometer, Finnigan MAT 312 mass spectrometer, and Bruker WP-100 SY nmr spectrometer.

PLANT MATERIAL.—The plant material was collected in the month of July 1982, from a small village near Karachi and was identified by the Botany Department of Karachi University where a voucher specimen is deposited.

The crude alkaloids (40 g) isolated by conventional procedures (8) from (10 kg) dried legumes (without seeds) were dissolved in 10% HOAc solution and subjected to selective pH separations after the stepwise basification with NH_3 . The fraction which was extracted into CHCl_3 at pH 2.7 (2 g) was subjected (0.7 g) to preparative tlc and afforded a faster running alkaloid (~10 mg) on silica gel (GF-254) plates (0.2 mm) with light petroleum (40°-60°): Me_2CO (8:2) as the solvent system, with an overall yield of $2.85 \times 10^{-4}\%$. The R_f value calculated was 0.80. The alkaloid thus obtained was crystallized with MeOH, mp 125°, $[\alpha]^{23}_{\text{D}} \pm 0$ (EtOH). The structure of this alkaloid was confirmed as vincadine (1) by comparison of its spectral data with those reported in the literature (9-13).



1

R=H
R'=COOCH₃