

103.4 (C-10), 128.6 (C-1'), 128.5 (C-2',6'), 115.7 (C-3',5'), 157.7 (C-4'), 99.0 (C-1''), 71.10 (C-2''), 76.90 (C-3''), 67.95 (C-4''), 73.80 (C-5''), 62.90 (C-6''), 125.0, 125.2 (C-1''', 1'''), 130.0 (C-2''', 2''', 6''', 6'''), 115.2, 115.7 (C-3''', 3''', 5''', 5'''), 159.7, 159.8 (C-4''', 4'''), 113.9, 114.7 (C- $\alpha$ ,  $\alpha_1$ ), 144.4, 144.8 (C- $\beta$ ,  $\beta_1$ ) and 165.9, 166.2 (C-7''', 7''') ppm and were assigned on the basis of naringenin 7-O- $\beta$ -D-glucoside (6) and anisofolin-A (2).

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

#### ACKNOWLEDGMENTS

Two of the authors (LJMR and GNKK) are grateful to CSIR, New Delhi, for fellowships.

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Received 30 April 1984

#### ALKALOIDS FROM *ANNONA CHERIMOLIA* LEAVES

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In a previous work, the isolation of alkaloids from *Annona cherimolia* Mill. (Annonaceae) seeds (1) and twigs (2) was reported. In the present paper, we have isolated and identified eight alkaloids from the leaves. (+)-Isoboldine, (-)-stepholidine, (+)-corytuberine and (+)-normanténine have been reported for the first time from this source. (+)-Reticuline, (-)-anonaine, liriodenine, and lanuginosine were identified from seeds and twigs. Michelalbine, detected previously in *A. cherimolia* twigs (2), has not been detected in the leaves.

#### EXPERIMENTAL

**PLANT MATERIAL.**—Leaves of *A. cherimolia* used in this investigation were collected in January 1980, in Granada, Spain. An herbarium specimen (n° VF-10463) was deposited at the Department of Botany Herbarium, Faculty of Pharmacy, University of Valencia, Spain.

**EXTRACTION AND ISOLATION OF THE ALKALOIDS.**—Air-dried, finely ground leaves (15 kg) were exhaustively extracted with  $\text{CHCl}_3$ . The  $\text{CHCl}_3$  extract was concentrated in vacuo to a syrup and mixed with 5% HCl. The acidic extract was basified to pH 8 with  $\text{Na}_2\text{CO}_3$  and extracted with  $\text{CHCl}_3$ . The dried

( $\text{Na}_2\text{SO}_4$ )  $\text{CHCl}_3$  extract, filtered, and evaporated in vacuo, yielded the total bases (13.2 g, 0.09%). The organic solution was basified with 5%  $\text{NaOH}$ . The alkaline solution was acidified with dilute  $\text{HCl}$  and then basified with  $\text{NaHCO}_3$ . The liberated bases were extracted with  $\text{CHCl}_3$ , washed with  $\text{H}_2\text{O}$ , dried, and the solvent was removed to give alkaloidal mixture-A (phenolic bases: 4.6 g). The remaining organic solution was washed with  $\text{H}_2\text{O}$ , dried, and evaporated to give alkaloidal mixture-B (nonphenolic bases: 3.0 g).

**ALKALOIDAL MIXTURE A.**—Mixture A (4.6 g) was chromatographed on  $\text{SiO}_2$  (150 g). The column was successively eluted with  $\text{CHCl}_3$  and mixtures of  $\text{CHCl}_3$ - $\text{MeOH}$ , and elution was followed by tlc. Fractions were purified by preparative tlc on  $\text{SiO}_2$ . Four bases were isolated and identified by qualitative optical activity, ir, uv,  $^1\text{H}$  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  $\text{Al}_2\text{O}_3$  (120 g). The column was eluted successfully with  $\text{C}_6\text{H}_6$ ,  $\text{CHCl}_3$ , and mixtures of  $\text{CHCl}_3$ - $\text{MeOH}$ , and elution was followed by tlc. Fractions were purified by preparative tlc. Four bases were isolated and identified by qualitative optical activity, ir, uv,  $^1\text{H}$  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.

#### ACKNOWLEDGMENTS

The authors are grateful to Prof. Cavé and Leboeuf, Laboratoire de Pharmacognosie, Faculté of Pharmacie, Chatenay-Malabry, France, for authentic samples of alkaloids.

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Received 3 May 1984

### 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  $\gamma$ -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  $\text{CHCl}_3$  followed by  $\text{MeOH}$ . The dried  $\text{CHCl}_3$  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  $\text{MeOH}$  extract, upon treatment with hot  $\text{EtOH}$  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,  $^1\text{H}$  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.