

ALCALOÏDES DE L'UMBELLULARIA CALIFORNICA

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Umbellularia californica Nutt., Lauracée Cinnamominée de l'Oregon et de la Californie a des feuilles aromatiques utilisées concurremment à celles du *Laurus nobilis* L. et de *Pimenta racemosa* (Mill) J. W. Moore pour l'obtention du "laurel bay oil" (1). Lors d'une étude comparative avec *L. nobilis* nous avons isolé trois alcaloïdes aporphiniques des feuilles: domesticine, nor-domesticine et isoboldine. Les écorces de tronc renferment une quantité notable d'hydroxy-5 N-N-diméthyl tryptamine (bufoténine). Si la présence d'aporphines est habituelle chez les Lauracées (2) celle de la bufoténine n'avait jamais été signalée dans cette famille mais des dérivés voisins existent chez *Nectandra megapotomica* (Sprg.) C. et H. et *Persea americana* Mill. (3).

PARTIE EXPÉRIMENTALE

MATÉRIEL VÉGÉTAL.—Les échantillons étudiés proviennent d'un spécimen acclimaté à l'Arboretum Gaston Allard et ont été récoltés en novembre 1981.

EXTRACTION ET ISOLEMENT DES ALCALOÏDES.—Feuilles et écorces séchées en étuve ventilée à 40° sont extraites par la méthode standard et fournissent 0,36 et 0,50% d'alcaloïdes totaux. Les alcaloïdes aporphiniques isolés sont identifiés par leurs constantes (PF, $[\alpha]_D$, et caractéristiques spectrales (rmn, uv, ir, sm). La bufoténine, amorphe, purifiée par CCM préparative est comparée à un échantillon authentique (Rf dans trois solvants).

*Bufo*ténine.—Ms, uv, ir conformes à la littérature, pmr 360 MHz (CDCl_3 , 1 mg, δ ppm): s 2,38, 6H (2 x N- CH_3); 2 m 2,71 et 2,95; 2 x CH_2 ; dd 6,77, $J_o=8,5$, $J_m=2,1$: H₆; d 6,91, $J_m=2,1$: H₄; d 6,98, $J=2$: H₂; d 7,19, $J=8,5$: H₇; s 7,84: N-H.

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CHEMICAL CONSTITUENTS OF SAURAUIA EXCELSA

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As a part of a research program dealing with alkaloids extracted from Venezuelan flora, we examined *Sauraia excelsa* W. This species is a tree native to Venezuela and belongs to the family Actinidiaceae (1). It has been reported that species of this family contain actinidine (2-4) and several monoterpene lactones (2, 4, 5). We wish to report the isolation of *n*-tricosyl alcohol and β -sitosterol from a petroleum ether extract and anabasine from the ethanolic fraction. This is the first time anabasine has been reported in the genus *Sauraia*.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Melting points were determined on a Uni-melt apparatus. Spectra were recorded with the following instruments: ir, Perkin-Elmer model 753 and nmr, Varian T-60.

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PLANT MATERIAL.—*S. excelsa* was collected in August 1978, on the road between Colonia Tovar and El Limón (Estado Aragua), about 40 km southwest of Caracas, Venezuela. Voucher specimens are deposited at the Herbarium of the Botanic Gardens, Caracas, Venezuela.

—Air-dried leaves of *S. excelsa* (10.0 kg) were milled to a powder and extracted with light petroleum ether (40–60°) to afford a residue (190.5 g). The crude extract (10.0 g) was chromatographed on silica gel (320 g) column ($C_6H_6\text{-CHCl}_3$, 2:1 eluant). Fractions 18–25 (50 ml each) yielded *n*-tricosyl alcohol (2.59 g, 0.03%), which was identified from its mp, ir, nmr, microanalysis, and phenylisocyanate derivative. The chromatography fractions 43–114 yielded β -sitosterol (2.86 g, 0.03%), which was identified from its mp, optical rotation, ir, nmr, and by direct chromatographic comparison with an authentic sample.

Leaves were extracted with EtOH, providing 1.23 kg of dark green solid. This was processed to yield anabasine (80 mg, 0.001%), identified by physical and spectral data, and authentic sample comparison (from FLUKA, AG.).

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FLINDERSINE FROM FAGARA HEITZII

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During our work on irritant timbers, we chemically investigated the heartwood of a central African (Gabon) plant *Fagara heitzii* Auber and Pellegr (1, 2). The petroleum-ether extract of the heartwood yielded the known alkaloid flindersine.

EXPERIMENTAL

EXTRACTION AND ISOLATION OF FLINDERSINE.—The ground heartwood of the timber *F. heitzii* (14 kg) was continuously extracted with petroleum ether (60–80°) for 48 h. After evaporation of the solvent under reduced pressure, a thick oil was obtained, which crystallized from MeOH (9.0 g) as colorless needles mp 199–201° (decomp.) (Lit [4] 185–186° decomp.). Ir ν max (Nujol) cm^{-1} 1660, 1603. Uv λ max nm (MeOH) 235, 333, 348, 365 ($\log \epsilon$ 4.45, 3.92, 4.02, 3.83). Pmr ($CDCl_3$) δ 1.53 (6H, s); 5.57 (1H, d, $J=10$ Hz), 6.87 (1H, d, $J=10$ Hz); 7.92 (1H, d, $J=7$ Hz); 7.10–7.53 (3H, m); 12.70 (1H, br. s). Found: C, 74.04; H, 5.71; N, 5.88 calculated for $C_{14}H_{13}NO_2$; C, 74.0; H, 5.77; N, 6.16%. Treatment of flindersine with methyl iodide gave N-methylflindersine, while hydrogenation gave dihydroflindersine. The spectral data of both the derivatives were found to be identical to the known data (3, 4). Finally, the natural product on direct comparison with an authentic specimen of flindersine was found to be identical in all respects (ir, uv, nmr).

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