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Keyphrases

Tubercidin analogs
Pyrrolo[2,3-*d*]pyrimidines—synthesis
pKa values—titration
TLC—separation
Proton magnetic resonance—identity
UV spectrophotometry—identity
NMR spectroscopy—identity
Cytotoxicity screening—tubercidin analogs

Alkaloids of *Peumus boldus*. Isolation of Laurotetanine and Laurolitsine

By D. W. HUGHES, K. GENEST, and W. SKAKUM

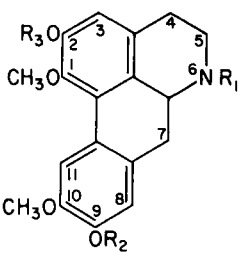
Two alkaloids, in addition to the six previously described, have been isolated from the leaves of *Peumus boldus* Molina. They were characterized by chromatographic and spectral data and shown to be the noraporphines, laurotetanine and laurolitsine.

DURING A chromatographic study of the alkaloids of the leaves of the South American shrub *Peumus boldus* Molina (*Monimiaceae*) (boldo leaves), the authors detected the presence of at least 17 alkaloids in a nonquaternary fraction obtained by chloroform extraction of the plant material after treatment with ammonia (1). The alkaloids were numbered 1–17 according to increasing R_f on thin-layer chromatography (TLC), and two were isolated and characterized as reticuline and the aporphine, isoboldine. Earlier, the aporphines boldine (I) (2), *N*-methyllaurotetanine (II), and isocorydine and the noraporphine, norisocorydine had been isolated (3). On the basis of paper chromatographic evidence the presence of sparteine has also been suggested (4).

This paper describes the isolation from boldo leaves and the characterization of two closely related noraporphines, laurotetanine (Alkaloid 6) (III) and laurolitsine (norboldine; Alkaloid 2) (IV). TLC examination of the crude alkaloid extract indicates that the leaves contain 0.005–0.007% laurotetanine and approximately 0.001% laurolitsine.

These alkaloids have been isolated from a number of species, particularly in the family *Lauraceae* (5, 6), sometimes together with boldine (5). A recent report describes the isolation of laurotetanine and *N*-methyllaurotetanine from another *Monimiaceae*: *Palmeria fengeriana* Perk (7).

Received February 27, 1968, from the Research Laboratories, Food and Drug Directorate, Ottawa, Ontario, Canada.
Accepted for publication June 4, 1968.
The authors thank Dr. D. B. MacLean (McMaster University, Hamilton, Ontario) and Dr. G. Neville for mass and nuclear magnetic resonance spectra, Dr. A. Rüegger (Sandoz Ltd., Basle, Switzerland) for a gift of *N*-methyllaurotetanine, and Dr. M. Kozuka (College of Pharmacy, Kyoto, Japan) for a gift of laurolitsine picrolonate.



I, $R_1 = CH_3$; $R_2 = R_3 = H$
II, $R_1 = R_3 = CH_3$; $R_2 = H$
III, $R_1 = R_2 = H$; $R_3 = CH_3$
IV, $R_1 = R_2 = R_3 = H$

EXPERIMENTAL

Isolation of Alkaloid 2—Alkaloids were extracted from 5 kg. boldo leaves and fractionated as described earlier (1) into four solutions (i, ii, iii, and iv). TLC examination of Solution i showed the presence of three main alkaloids (Nos. 1, 2, and 5). These were partially separated by column chromatography on silicic acid using chloroform–methanol mixtures as eluant. Fractions containing Alkaloid 2 were further resolved, first by rechromatography on silicic acid using benzene–methanol mixtures and then by preparative TLC. Alkaloid 2 was then found to be homogeneous by TLC, and was precipitated as an amorphous light brown solid with cyclohexane from ethanol solution. Yield 20 mg. (0.0004%); m.p. 128–134°.[1] Spectroscopic data

[1] Melting points were taken on a Kofler melting point apparatus and are uncorrected.

(UV, IR, NMR, and mass) were consistent with Alkaloid 2 being laurolitsine. This was confirmed by direct comparison (TLC, UV, and IR spectra) with an authentic sample of laurolitsine and by TLC identification of the product of *M*-methylation as boldine. Attempts to crystallize Alkaloid 2 or its picrate were unsuccessful.

Isolation of Alkaloid 6—TLC examination showed Alkaloid 6 to be present mainly in Solution iii, with smaller amounts in Solution iv and traces in Solution ii. The alkaloids in Solution iii were partially resolved by column chromatography on sodium hydroxide-treated silicic acid (1) using benzene–methanol mixtures as eluant. Fractions containing Alkaloid 6 in admixture with traces of boldine, isoboldine, and norisocorydine were combined. The alkaloid was then obtained chromatographically pure by preparative TLC and was precipitated from methanolic solution by *n*-hexane as a light brown solid. Attempts to crystallize it from other solvents were unsuccessful. Further amounts were obtained similarly from Solutions ii and iv. Yield 133 mg. (0.003%). The UV spectrum [$\lambda_{max.}^{ethano}$ 282, 303, 312 (inflection) mμ] was markedly similar to that of Alkaloid 2 and was typical of published spectra of aporphines unstrained by lack of substitution at Position 11 (8). The alkaloid was shown to be phenolic by color tests, chemical behavior, and bathochromic shift of the UV maxima in alkali. The NMR spectrum indicated that the compound was a noraporphine [No. 3 proton peak at 2.35–2.55 δ (9)] and an *O*-methyl derivative of Alkaloid 2. This was confirmed by *O*-methylation of each alkaloid with diazomethane to a common nonphenolic product (characterized by TLC). That Alkaloid 6 is laurotetanine was confirmed by the identical behavior on TLC of the product of *N*-methylation and an authentic sample of *N*-methyllaurotetanine. A picrate of Alkaloid 6 was prepared and crystallized from water as orange-yellow needles, m.p. 152–154° [lit. m.p. laurotetanine picrate 148° (10)].

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Keyphrases

Alkaloids—*Peumus boldus*
Laurotetanine—isolation, identification
Laurolitsine—isolation, identification
Column chromatography—separation
TLC—separation, identity
UV spectrophotometry—identity
IR spectrophotometry—identity
NMR, mass spectroscopy—structure

Polyamide Layer Chromatography of Organophosphorus Pesticides

By J. T. HUANG*, H. C. HSIU, T. B. SHIH, U. T. CHOU, K. T. WANG, and C. T. CHENG

Thin-layer chromatographic system and spray reagents are described for rapid differentiation of 11 organophosphorus pesticides.

THE USE of paper or thin-layer chromatography to determine and identify the organophosphorus pesticides had been widely studied and reviewed by Zweig (1). Recently, several workers used the formamide impregnated paper (2) and thin-layer (3) to separate organophosphorus pesticides. In previous reports (4, 5) better separation of opium alkaloids was obtained with polyamide layer, therefore, this method was applied to separate the organophosphorus pesticides. This note describes the results obtained.

EXPERIMENTAL

Material—Eleven organophosphorus pesticides, FDA standard were used. The solvents and chemicals are the reagent grade of Wako Pure Chemical Industries, Ltd., Osaka, Japan.

Thin-Layer Plates—All plates used were 15 × 15 cm. of polyamide layer sheet described by Wang (6).

Chromatographic Procedure—The standard techniques of ascending thin-layer chromatography (7) were employed.

Visualization—Four methods were employed: (*a*) iodine vapor exposing, (*b*) 5% alcoholic potassium hydroxide solution spraying, (*c*) iodoplatinate reagent spraying (8), (*d*) first spraying 5% alcoholic potassium hydroxide solution on the plate, allowing the plate to dry, then exposing the plate with iodine vapor for 5 min., followed by exposing ammonia vapor.

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Accepted for publication June 11, 1968.
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