

IDENTIFICATION OF TERPENOIDS FROM THE LEAVES OF *PIPTOCARPHA PARADOXA* AND THEIR BIOLOGICAL ACTIVITIES

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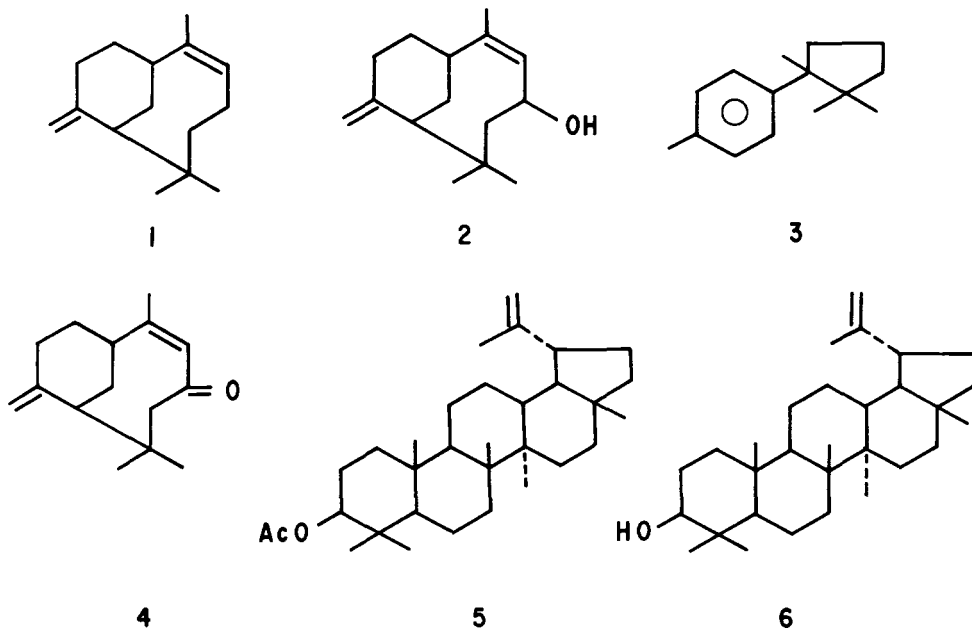
Bazzanene (1) and bazzanenol (2) are sesquiterpenes with novel carbon skeleton. The only reported source in nature of these compounds was from *Bazzanene pompeana* (Lac.) Mitt. (1). As far as is known, this is the first report of their existence in the Asteraceae (Compositae) family in Venezuela. It is also the first report of their biological activity.

RESULTS AND DISCUSSION

The structure of bazzanene was confirmed by its nmr and ir spectra and also by its conversion into the aromatic hydrocarbon cuparane (3); this reaction was reported earlier by Hayashi *et al* (1). Oxidation with $\text{Na}_2\text{Cr}_2\text{O}_7\text{-HOAc}$ (2) gave the ketone bazzanone (4). The elemental analysis of the hydrocarbon agreed well for $\text{C}_{15}\text{H}_{24}$.

The structure of bazzanenol (2) was determined by its ir and ms spectra and some chemical reactions. Oxidation with Jones Reagent (3) gave the ketone bazzanone (4), which was identical with that obtained from bazzanene. It also gave a monoacetate with acetic anhydride-pyridine (4). In addition, the pentacyclic triterpenes lupeol and lupenyl acetate were also isolated. The physical properties and the ir spectra of these compounds were identical with those of the authentic samples.

Analysis of the antimicrobial activity of bazzanene, bazzanenol, lupeol, lupenyl acetate, and one unknown compound (UC) were performed by the method of Kirby and Baur (5) against the following strains—*Enterobacter aerogens* (Kruse, 1896), *Micrococcus roseus* (Flügge, 1886), *Staphy-*



lococus aureus (Rosenbach, 1884), *Salmonella typhi* (Zopf, 1884), *Escherichia coli* (Migula, 1895), *Proteus rettigeri* (Hadley et al, 1918), *Streptococcus sp.* (Rosenbach, 1884) and *Candida sp.* (Berkhout). Only two of these above-mentioned compounds, namely, bazzanenol and the unknown compound (UC), showed activities against the strains (*Staphylococcus aureus* and *Candida sp.*, respectively). These compounds did not show any activity against other above-mentioned strains.

EXPERIMENTAL¹

PLANT MATERIAL.—The plant *Piptocarpha paradoxa* (Sch. Bip) Aristeguieta n. comb. was collected from the Islands of Caracas located in the State of Sucre, Venezuela, during the month of December 1975; a voucher specimen (No. BHAT 1044) is deposited in the herbarium of the Departamento de Biología of the Universidad de Oriente, Cumana.

The aerial part of the dried ground plant was extracted with petroleum ether (40–60°), Concentration (*in vacuo*) of the petroleum ether extract produced 90 g of extract. A portion of the extract was chromatographed over silica gel and eluted with the solvents petroleum ether, benzene, chloroform, and methanol.

BAZZANENE AND BAZZANENOL.—The petroleum ether fraction was chromatographed over AgNO₃ impregnated (10%) silica gel (6) and eluted with pure solvents and solvent mixtures of increasing polarity beginning with petroleum ether. Pentatriacontane [mp 71–72; Lit. (7) mp 75°], a saturated long chain hydrocarbon, was identified as the only constituent in the first 100 ml. of the eluent. Bazzanene was isolated as a colorless oil in the next 140 ml. of the solvent. It showed the following properties: bp 100–110° (bath)/1.6 mm; n_D²⁵ 1.4960; ir (CHCl₃): 1665, 1645, 1385, 1375, 889 and 835 cm⁻¹; nmr (CCl₄): 0.82 δ (3H, s -C-CH₃), 1.01δ (3H, s -C-CH₃), 1.66δ (3H, d -C=C-CH₃), 4.55δ (1H, s br -C=CH₂), 4.65δ (1H, s -C=CH₂) and 5.35δ (1H, m -C=CH₂). Oxidation with Na₂Cr₂O₇ -HOAc gave bazzanone; the ir (CHCl₃) gave 3010, 2970, 2930, 2860, 1700, 1650, 1375, 1385, 890 and 835 cm⁻¹. From the fraction eluted with petroleum ether-benzene (1:1), bazzanenol was obtained as colorless oil, bp 130–135° (bath)/0.8 mm;

ir (CHCl₃): 3650, 3400, 1650, 1385, 1365, 890 and 865 cm⁻¹. The identity of this compound was verified by preparation of its acetate which gave bands at (CHCl₃) 1730, 1260 and 865 cm⁻¹, identical as described by Hayashi *et al.* (2). Oxidation with Jones Reagent gave bazzanone, which had the following ir (CHCl₃) 1705, 1655, 1385, 1370, 898 and 820 cm⁻¹, and was identical with that obtained by oxidation of bazzanene.

LUPENYL ACETATE AND LUPEOL.—The benzene fraction was chromatographed over silica gel and eluted with solvents and solvent mixtures of increasing polarity. The fraction eluted by petroleum ether-benzene (1:4) yielded a solid which, after successive recrystallization from ethanol, gave colorless needles, mp 213–214°; ir (CHCl₃) 1730, 1648, 1460, 1385, 1375, 1200 and 896 cm⁻¹. The mp and mmp determination and comparative tlc with an authentic sample of lupenyl acetate indicated the identity of this compound to be lupenyl acetate 5.

The chloroform fraction when chromatographed over silica gel with solvents of increasing polarity yielded lupeol as the major component in the benzene fraction. The determination of the mp and mmp with an authentic sample, ir spectrum and comparative tlc with an authentic sample indicated it to be lupeol 6. Acetylation by means of the usual method gave lupenyl acetate, which analyzed for C₃₂H₅₂O₂. Oxidation with Jones reagent gave lupenone, which formed 2,4-dinitrophenylhydrazone (mp 144–145°).

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LITERATURE CITED

1. S. Hayashi, A. Matsuo and T. Matsuura, *Tetrahedron Lett.*, 1599 (1969). See also S. Hayashi, A. Matsuo and T. Matsuura, *Experientia*, **25**, 1139 (1969).
2. L. F. Fieser, *J. Am. Chem. Soc.*, **75**, 4377 (1953); *J. Am. Chem. Soc.*, **75**, 4395 (1953). See also *Org. Syn. Collec.*, **1**, 482 (1941).
3. Daniel J. Pasto and Carl R. Johnson, "Organic structure determination", Prentice-Hall Inc., 1969, p. 363.
4. Daniel J. Pasto and Carl R. Johnson, "Organic structure determination", Prentice-Hall Inc., 1969, p. 367.
5. A. W. Bauer, W. M. Kirby, J. C. Sherris and M. Turck, *Am. J. Clinical Pathology*, **45** (4), 439 (1966).
6. A. S. Gupta and Sukh Dev, *J. Chromatogr.*, **12**, 189 (1963).
7. Esterfield and Taylor, *J. Chem. Soc.*, **99**, 2305 (1911). See also, Clemmensen *Ber.*, **46**, 1842 (1913); Grun, Ulbrich and Z. Krezil, *Angew Chem.*, **39**, 421 (1926).

¹The elemental analyses were carried out by M-H-W Laboratories, Phoenix, Arizona, USA. The ir spectra were determined with a Perkin Elmer model IR 337 and IR 567 spectrophotometer. Nmr spectra were determined in CDCl₃ with a Varian T-60 instrument. The melting points were determined on a Thomas-Hoover capillary apparatus and are uncorrected. The authentic samples of lupeol and lupenyl acetate were obtained from K & K Laboratories.