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PEPTIDE ALKALOIDS FROM *ZIZYPHUS* SPECIES

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Key Word Index—*Zizyphus nummularia*; *Z. jujuba*; *Z. xylopyra*; Rhamnaceae; alkaloids; franguloline; amphibine-H; nummularine-K; nummularine-R.

Abstract—The isolation of cyclopeptide alkaloids, franguloline from *Zizyphus jujuba* and *Z. nummularia*, amphibine-H and nummularine-K from *Z. xylopyra* and nummularine-R, a new 13-membered cyclopeptide alkaloid, from *Z. nummularia* is reported. The structure of the new alkaloid was elucidated by spectroscopic methods and by chemical degradation.

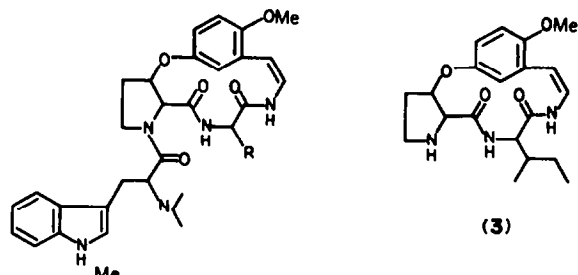
In continuation of our search for peptide alkaloids [1] from *Zizyphus* species we have re-examined the stem bark of, *Z. nummularia*, *Z. jujuba* and *Z. xylopyra*. Repeated CC and prep. TLC of the alkaloidal fraction resulted in the isolation of the cyclopeptide alkaloids, franguloline [2] from *Z. jujuba* and *Z. nummularia*; amphibine-H [3] and nummularine-K [4] from *Z. xylopyra* and nummularine-R (1) a new 13-membered cyclopeptide alkaloid from *Z. nummularia*.

The absorption bands in the IR and UV spectra and the mass fragmentation pattern of nummularine-R (1), mp 134–135°, $C_{33}H_{41}N_5O_5$, $[M]^+$ 587.3116) were exactly same as those reported for sativanine-E (2) [5]. The essential difference between the two was observed by acid and alkali hydrolysis. Acid hydrolysis of 1 with 6 N HCl furnished isoleucine whereas sativanine-E gave leucine. Hydrolysis of 1 with $Ba(OH)_2$ gave *N,N*-dimethyltryptophan. The attachment of isoleucine bound to the nitrogen of the styrylamine function in 1 was proved by partial hydrolysis after heating with HCl–HOAc–H₂O (1:1:1) when 1 furnished a major compound (3) which on further hydrolysis with 6 N HCl gave isoleucine. Based on these findings, the structure of nummularine-R is settled as 1 which differs from that of sativanine-E (2) in having a isoleucine unit instead of leucine as the amino acid bound to the nitrogen of the styrylamine function. Nummularine-R is thus a new member in the growing list of peptide alkaloids.

The structure of the known alkaloids was established by spectral evidence, hydrolysis and direct comparison with authentic samples. These alkaloids have not previously been reported from the above species.

EXPERIMENTAL

Plants were collected from Mirzapur District of Uttar Pradesh, India and identified by Prof. S. K. Roy, Dept. of Botany, Banaras Hindu University. The crude alkaloids were extd by usual methods [6]. Extensive chromatography and repeated prep. TLC of the crude bases of *Z. nummularia* (5 kg) with $CHCl_3$ –Me₂CO–MeOH (10:6:1) and $CHCl_3$ –MeOH (20:1) furnished franguloline (10 mg), mp 233–235°, and compound 1 (21 mg), mp 134–135°. 1 showed IR ν^{CHCl_3} 3385, 3251 (–NH), 2775 (–NMe), 1670 (amide), 1630 (C=C), 1592, 1490 (aromatic), 1040 and 1200 (aryl ether) cm^{-1} ; UV λ^{MeOH}_{max} 320, 268 nm^{-1} .



(1) $R = -CH(Me)-CH_2-Me$

(2) $R = -CH_2-CH(Me)_2$

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(characteristic of the styrylamine chromophore in the 13-membered cyclopeptide alkaloids), 290 sh, 280 sh, and 272 sh (tryptophan unit) [5]; MS, m/z 587.3116 ($[M]^+$, 6%), 457 (100), 401 (1.5), 400 (1), 374 (1.5), 373 (3), 372 (1), 304 (1), 259 (1), 233 (1.5), 216 (2), 187 (58), 181 (1), 165 (6), 144 (10), 130 (15), 96 (2), 86 (4), 68 (6).

Hydrolysis. Compound 1 (10 mg) was heated in a sealed tube with 1 ml of 6 N HCl for 20 h at 120°. The presence of isoleucine was confirmed by PC comparison with an authentic sample using *n*-BuOH-HOAc-H₂O (4:1:5) with ninhydrin as detection reagent. Compound 1 (10 mg) was heated with Ba(OH)₂ (60 mg) in 1 ml H₂O for 24 hr at 120°. The hydrolysate was neutralized with 2 N H₂SO₄, filtered, chromatographed over Whatman No. 1 and sprayed with Ehrlich's reagent [7]. *N,N*-Dimethyltryptophan was detected in the hydrolysate by comparison with an authentic sample.

Partial hydrolysis. Compound 1 (25 mg) was heated at 100° for 5 hr with 6 ml of conc HCl-HOAc-H₂O (1:1:1). The hydrolysis product after prep. TLC with CHCl₃-MeOH (50:1) gave one major compound 3 (5 mg) as a colourless amorphous solid; MS: m/z 373 ($[M]^+$) 304, 259, 233, 216, 181, 165, 96, 86. 3 on hydrolysis with 6 N HCl in a sealed tube for 20 hr at 120° gave isoleucine (co-PC with an authentic sample).

Repeated CC and prep. TLC of the crude base fraction of *Z. xylopyra* furnished amphibine-H (15 mg), mp 202–204° and nummularine-K (17 mg), mp 235–238°; *Z. jujuba* gave frangu-

foline (8 mg). The structure of these alkaloids was established by a study of the spectral data, hydrolysis and direct comparison with authentic samples (mmp and co-TLC).

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PICRASIDINE-T, A DIMERIC β -CARBOLINE ALKALOID FROM *PICRASMA QUASSIOIDES**

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Key Word Index—*Picrasma quassioides*; Simaroubaceae; β -carboline; β -carbolinium; dimeric alkaloid; (\pm)-picrasidine-T.

Abstract—A new β -carboline dimeric alkaloid, (\pm)-picrasidine-T was isolated from the bark of *Picrasma quassioides*. The structure was determined by spectral analysis and chemical evidence.

INTRODUCTION

In our previous studies [1, 2], we obtained three novel β -carboline dimeric alkaloids named (\pm)-picrasidines F [2], G and S [1] from the root bark of *Picrasma quassioides*

Bennet (Japanese name: Nigaki). Structures of the alkaloids were determined as racemic compounds by single crystal X-ray diffraction analysis [2] and spectral analysis [1].

We have recently isolated a new dimeric alkaloid named picrasidine-T from the bark of the plant. This paper deals with its structural elucidation by spectral analysis and chemical evidence of (\pm)-picrasidine-T hydrochloride (1).

* Part 10 in the series 'The alkaloids of *Picrasma quassioides*'. For Part 9 see ref. [1].