



Research Article

Chemical constituents of *Zizyphus joazeiro*

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ABSTRACTS

A cyclopeptide alkaloid nummularine-M and one flavonoid – Kaempferol-7-methyl ether has been isolated from the root bark of Zizyphus joazeiro and their structures were established by spectral evidences. This is the first report of these compounds in Z. joazeiro.

Keywords: Zizyphus joazeiro – cyclopeptide alkaloids and flavonoids..

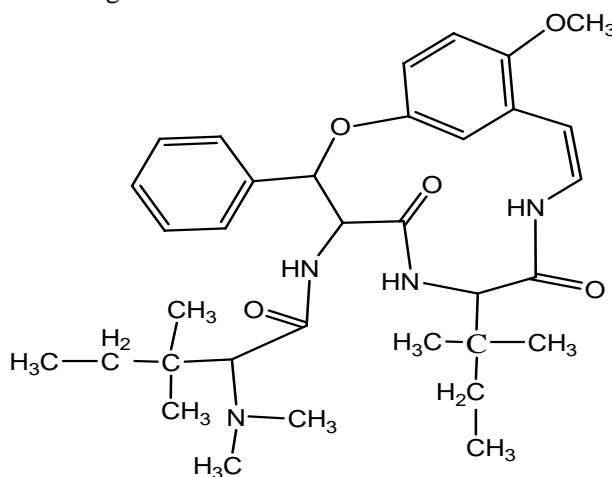
INTRODUCTION

The plant *Zizyphus joazeiro* Mart (Family: Rhamnaceae) is widely distributed in the dry regions of Brazil's north-east¹. The bark is locally used as detergent in the form of savings of powder. From the crust of *Zizyphus joazeiro* the saving of which on account of its 10% saponin content are sometimes used as soap substitute^{2,3}. Aqueous and ethanolic extracts of *Zizyphus joazeiro* had been reported for high toxicity, cardio respiratory and spasmogenic activity⁴. The stem barks of this plant is to be found quite rich in saponins⁵ and some alkaloids. We report here in the isolation and identification of a flavonoid and a cyclopeptide alkaloid namely kaemferol-7-methyl ether and nummularine-M which has not earlier been reported from this plant.

EXPERIMENTAL

Dried and powdered root barks of *Z. joazeiro* (8.00 kg) were extracted mechanically several times with mixtures of Benzene-Ammonium hydroxide-Methanol (100:1:1). The total extract was concentrated under reduced pressure and then extracted with 7% aqueous citric acid. The acidic solution was basified with ammonia and extracted thoroughly with chloroform. The CHCl₃ fraction was evaporated to dryness which furnished a brown semi-solid crude base fraction (4.00 g). The crude base fraction was chromatographed over SiO₂ gel column eluting with a mixture of CHCl₃ and MeOH. The eluants collected from CHCl₃-MeOH (2:1) on evaporation followed by crystallization from methanol furnished the cyclopeptide alkaloid nummularine-M⁶ (8 mg) (**1**) as amorphous powder. The C₆H₆-NH₄OH-MeOH fraction left after extraction of bases was chromatographed over silica gel column and eluted with chloroform. The chloroform eluants were mixed according to TLC and on crystallization with methanol afforded a flavonoid kaemferol-7-methyl ether^{7,8} (15 mg) (**2**) as yellow granules, m.p. 218-21°C.

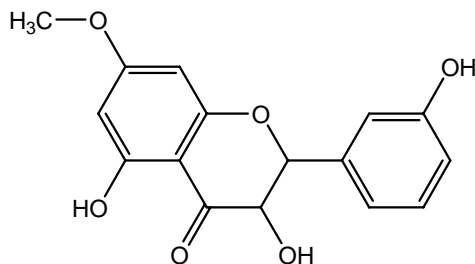
Compound (1): It exhibited UV λ_{\max} (MeOH) nm: typical strong absorption and shoulder at 150 and 280, characteristic styrylamine chromophore in 14-membered ring containing cyclopeptide alkaloid. IR ν_{\max} (KBr) cm^{-1} : 3300 (-NH), 2790 (-NCH₃), 1240 (phenol ether), 1685 and 1635 (sec-amino group) MS: m/z 534.3174 ($[M]^+$), HRMS, calcd for C₁₃H₄₂N₄O₄, 534.3160) 519, 505, 477, 421, 419, 378, 337, 274, 244, 229, 224, 216, 201, 135, 131, 114.126 (C₇H₁₆N, base peak), 103, 85, 86. Hydrolysis of **1** with 6 HCl in a sealed tube for 20 hour at 120°C furnished two ninhydrin positive spots in the hydrolysate identified as N,N-dimethylisoleucine and isoleucine by comparison with reference compounds. All the spectral data of **compound-1** tallies with the reported data of nummularine-M having a structure as below.



Compound- 1

The structure was further confirmed by direct comparison with authentic sample (mmp, co-TLC and superimposable IR). Nummularine-M has been previously isolated from *Z. nummularia* but this is first report of the nummularine-M in *Z. joazeiro*.

Compound (2): UV λ_{\max} (MeOH): 253, 266, 320 and 363 nm (log 4.25, 4.29, 4.13, 4.38) - flavonoid nature⁹ of the **2**. IR ν_{\max} (KBr) characteristic absorption band at 3150-3550 cm^{-1} broad and 1660 cm^{-1} strong (phenolic-OH) and chelated-carbonyl groups. 90 MHz ¹HNMR (DMSO-d₆) δ 3.70 (3H, s, - OMe), 6.11 (1H, d, J, 2.0 Hz, H-6), 6.46 (1H, d, J 2.0 Hz, H-8), 6.67 (1H, d, J 8.0 Hz, H-3', H-5'), 7.74 (1H, d, J 8.0 Hz H-2', H-6') 9.11, (1H, br s, exchangeable with D₂O, OH), 9.70 (1H, br s, exchangeable with D₂O, OH), 11.98, br s, exchangeable with D₂O, -OH). HRMS m/z 300 ($[M]^+$ calcd for C₁₆H₁₂O₆). The other significant ion peaks are 272, 257, 229, 176, 138, 134.



Compound 2: 3,5-dihydroxy-2-(3-hydroxyphenyl)-7-methoxy-2,3-dihydrochromen-4-one

Compound **2** on methylation with CH_2N_2 gave trimethyl derivative, m.p. 152-154°C. $^1\text{H-NMR}$: δ 3.93, 3.85, 3.83 for three more $-\text{OCH}_3$ groups. The structure of **compound 2** was supported by a study of the UV with shift reagents and direct comparison with authentic sample (m.m.p.; co-TLC and superimposable IR).

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