

JUNOSIDINE: A NEW LINEAR PYRANOACRIDONE ALKALOID FROM
CITRUS JUNOS TANAKA¹

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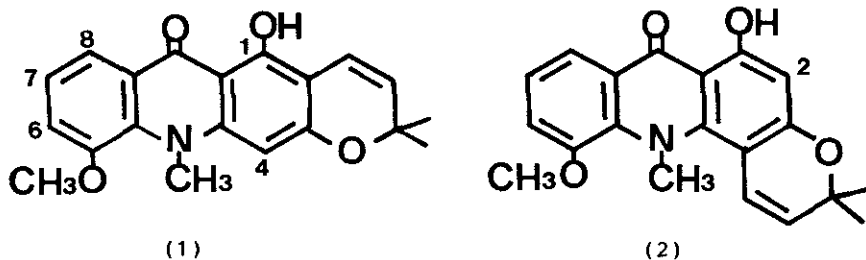
Abstract — From the root bark of Citrus junos Tanaka, a new acridone alkaloid, junosidine (1), was isolated and its structure was elucidated on the basis of spectral data.

In the course of our studies on the constituents of Citrus plants, we recently isolated junosine,² 5-methoxynoracronycine² and junosmarin³ from the barks of Citrus junos Tanaka (Rutaceae) and elucidated the chemical structures of these new compounds. We further investigated the constituents of the root barks of this plant and isolated a new linear pyranoacridone alkaloid named junosidine (1). In this paper, we wish to report the structure elucidation of this new alkaloid. The acetone extract was chromatographed over silica gel and eluted with n-hexane, n-hexane-benzene, benzene and acetone, successively. The benzene eluate was further purified by repeated preparative TLC using solvent systems of iso-propyl ether, and then benzene:ethyl acetate (17:3) to afford junosidine (1).

Junosidine (1), orange needles, mp 188-189°C, C₂₀H₁₉NO₄. The uv spectrum [$\lambda_{\max}^{\text{EtOH}}$ nm (log ϵ): 225 (4.23), 263 (sh, 4.28), 297 (4.73), 307 (4.79), 414 (3.81)] showed typical absorption of 1-hydroxy-9-acridone skeleton.⁴ The ¹H-nmr spectrum showed signals of a hydrogen-bonded hydroxy (δ 15.06), an N-methyl (δ 4.03), and a methoxy (δ 3.98) group. The presence of 1,1-dimethylchromene system was suggested by the signals of δ 1.47 (6H, s), 6.72 (1H, d, J= 9.77 Hz) and 5.69 (1H, d, J= 9.77 Hz). Among ABC type three-proton signals at δ 7.95 (1H, dd, J= 8.30, 1.95 Hz), 7.41 (1H, dd, J= 8.30, 1.95 Hz) and 7.28 (1H, t, J= 8.30 Hz) in the aromatic proton region,

the lower signal at δ 7.95 could be assigned to H-8 which was affected by a deshielding of the carbonyl moiety, and hence the remaining two signals could be assigned to H-6 and H-7. One more aromatic proton singlet at δ 6.38 was supposed to be H-2 or H-4. These signal patterns were closely resembled to those of 5-methoxynoracronycine (2).⁵ The significant difference was the chemical shifts of lone aromatic proton signal at δ 6.38 assignable to H-4 in (1) and δ 6.13 (H-2) in (2), respectively. In the ¹H-nmr spectrum of 1,3-dioxygenated acridone alkaloids, the H-2 usually resonates at higher fields about δ 6.1-6.2, whereas H-4 appears at lower fields about δ 6.3-6.7.⁶ From these spectral data, the structure of junosidine could be represented to 1.

Although a number of pyranoacridone alkaloids have been known,⁷ most of them are angular pyranoacridones as (2). The isolation of linear pyranoacridone is rare and junosidine is the fourth example from natural sources.^{8,9} The occurrence of junosidine (1) and 5-methoxynoracronycine (2)¹⁰ in the same plant material is of our interest from the biogenetic view.¹¹



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