NEW ACRIDONE ALKALOIDS FROM CITRUS JUNOS TANAKA[1]

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Abstract ——— Two new acridone alkaloids, junosine (1) and 5-methoxynoracronycine (2), were isolated from the bark of Citrus junos (Rutaceae) and their structures were elucidated on the basis of the spectral and chemical studies.

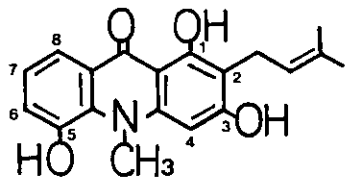
In continuing our investigations on the constituents of Citrus plants,[1] we isolated two new acridone alkaloids named junosine and 5-methoxynoracronycine from the bark of Citrus junos Tanaka. In this paper, we wish to report the structure elucidation of these alkaloids.

Junosine (1), light yellow prisms, mp 210-213°C, $C_{19}H_{19}NO_4$, exhibited λ_{max}^{EtOH} 233, 259 (sh), 268, 279 (sh), 288, 320 (sh), 335, 410 nm: diagnostic absorption of 1-hydroxy-9-acridone skeleton.[2-5] The presence of N-methyl group was clear from the ^{13}C-NMR (CD_3OD) signal at δ 41.29 and ^{1}H-NMR ($CDCl_3$) signal at δ 4.00. The existence of three hydroxyl groups was evident from IR band at 3400 cm^{-1} and ^{1}H-NMR signals at δ 14.92, 6.72 and 6.32. The lowest signal at δ 14.92 is characteristic intramolecular hydrogen-bonded C-1 hydroxyl group in a 9-acridone.[3-5] The ABC type signals at δ 8.07 (1H, dd, J=7.81, 1.96), 7.12 (1H, t, J=7.81) and 7.05 (1H, dd, J=7.81, 1.96) in the ^{1}H-NMR spectrum were assigned to C-8, C-7 and C-6 protons, the lowest signal being deshielded by C-9 carbonyl moiety. The signals at δ 1.79, 1.87 (each 3H, s), 3.51 (2H, d, J=7.32) and 5.34 (1H, m) suggested the presence of prenyl group and one-proton singlet at δ 6.20 was assigned to aromatic proton. Biogenetically,[6] one phenolic hydroxyl group is considered to locate at C-3. The location of another hydroxyl and a prenyl group was established by

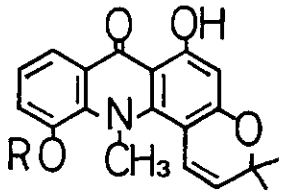
^{13}C-NMR spectrum. In the ^{13}C-NMR spectrum of junosine,[7] N-methyl signal resonates at δ 41.29 indicating that no substituent situates at C-4 position,[8] and hence a prenyl group was assumed to locate at C-2. Furthermore, it is known[8-9] that in the ^{13}C-NMR spectrum of 1,3-dioxygenated acridone alkaloids the methylene carbon signal of prenyl group at C-2 resonates in the region of 21.1-22.5 ppm. On the other hand, the methylene signal of the prenyl group at C-4 in the N-methyl compounds move downfield to 26.0-27.1 ppm. The observation of the signal of prenyl methylene at δ 22.25 in the ^{13}C-NMR spectrum of junosine also supported the location at C-2. On the basis of the foregoing data, the structure (1) was assigned for junosine.

5-Methoxynoracronycine (2) was obtained as light yellow prisms, mp 146-148°C, $C_{20}H_{19}NO_4$. The IR spectrum disclosed the presence of hydroxyl, carbonyl groups and aromatic ring: $\nu_{max}^{CHCl_3}$ cm^{-1} 3400, 1630, 1560. The UV spectrum exhibited λ_{max}^{EtOH} 232, 269, 300, 310, 416 nm and resembled with those of 1-hydroxy-9-acridone.[2-5]

The ^{1}H-NMR spectrum ($CDCl_3$) of 2 showed the signals corresponding to four protons in the aromatic proton region. The ABC protons resonate at δ 7.95 (1H, dd, J=7.81, 1.95), 7.28 (1H, t, J=7.81) and 7.19 (1H, dd, J=7.81, 1.95) were assigned to C-8, C-7 and C-6 protons and one-proton singlet at δ 6.25 was attributed to C-2 proton. The existence of 1,1-dimethylchromene system was suggested by the signals of δ 6.65, 5.54 (each 1H, d, J=9.77), and 1.51 (6H, s). Two three-proton singlets at δ 4.00 and 3.73 suggested the presence of N-methyl and methoxyl groups. From the above results, the structure of this alkaloid was assigned to 2 and was confirmed by comparisons with an authentic sample obtained by methylation of 5-hydroxy-noracronycine (3).[10]



(1)



(2) R=CH_3

(3) R=H

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7. ^{13}C-NMR spectrum of junosine (1): δ 181.62 (s), 164.45 (s), 162.52 (s), 148.48 (s), 147.16 (s), 135.13 (s), 131.63 (s), 124.88 (s), 124.07 (d), 123.02 (d), 120.59 (d), 117.70 (d), 109.73 (s), 105.76 (s), 91.54 (d), 41.29 (q), 25.96 (q), 22.25 (t), 17.96 (q).
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