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ACUTUMININE, A NEW ALKALOID FROM THE LEAVES OF MENISPERMUM DAURICUM DC.

Y. Okamoto, E. Yuge, Y. Nagai, R. Katsuta, A. Kishimoto and Y. Kobayashi

Faculty of Pharmaceutical Sciences, Mukogawa Women's University, Nishinomiya, Japan.

T. Kikuchi

Faculty of Pharmaceutical Sciences, Kyoto University, Kyoto, Japan

M. Tomita

Kyoto College of Pharmacy, Kyoto, Japan.

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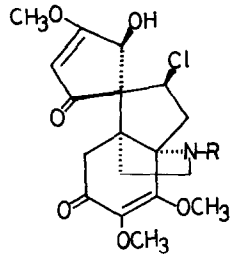
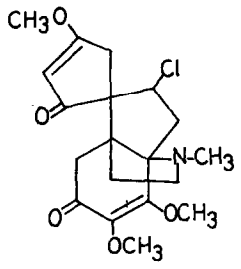
We have previously reported[1] the isolation and structure determinations of two chlorine-containing alkaloids, acutumine(I) and acutumidine(II), from the rhizome of Menispermum dauricum DC. In succession, we examined the components of the leaves of this plant and isolated a small amount of new crystalline alkaloid, for which we proposed the name acutuminine, together with sinomenine, acutumine, disinomenine, stepharine and an unknown crystalline compound.

Acutuminine, m.p. 175-177.5°, $[\alpha]_D$ -110° ($CHCl_3$), shows MS peaks at m/e 283 (M^+, isotope peak), 381 (M^+) and 346 (M-Cl), indicating that the alkaloid has also one chlorine atom in the molecule and its molecular formula is $C_{19}H_{26}O_5NCl$, one oxygen atom less than acutumine(I). Its UV spectrum gives absorption bands at 246 (ε: 21,600) and 272 mμ (ε: 10,460) and the IR spectrum at 1690, 1675 (conjugated C=O) and 1600 cm^{-1}(enol ether). The whole patterns of these UV and IR spectra are quite similar to those of acutumine(I), suggesting the presence of the same conjugated carbonyl systems as in acutumine(I).

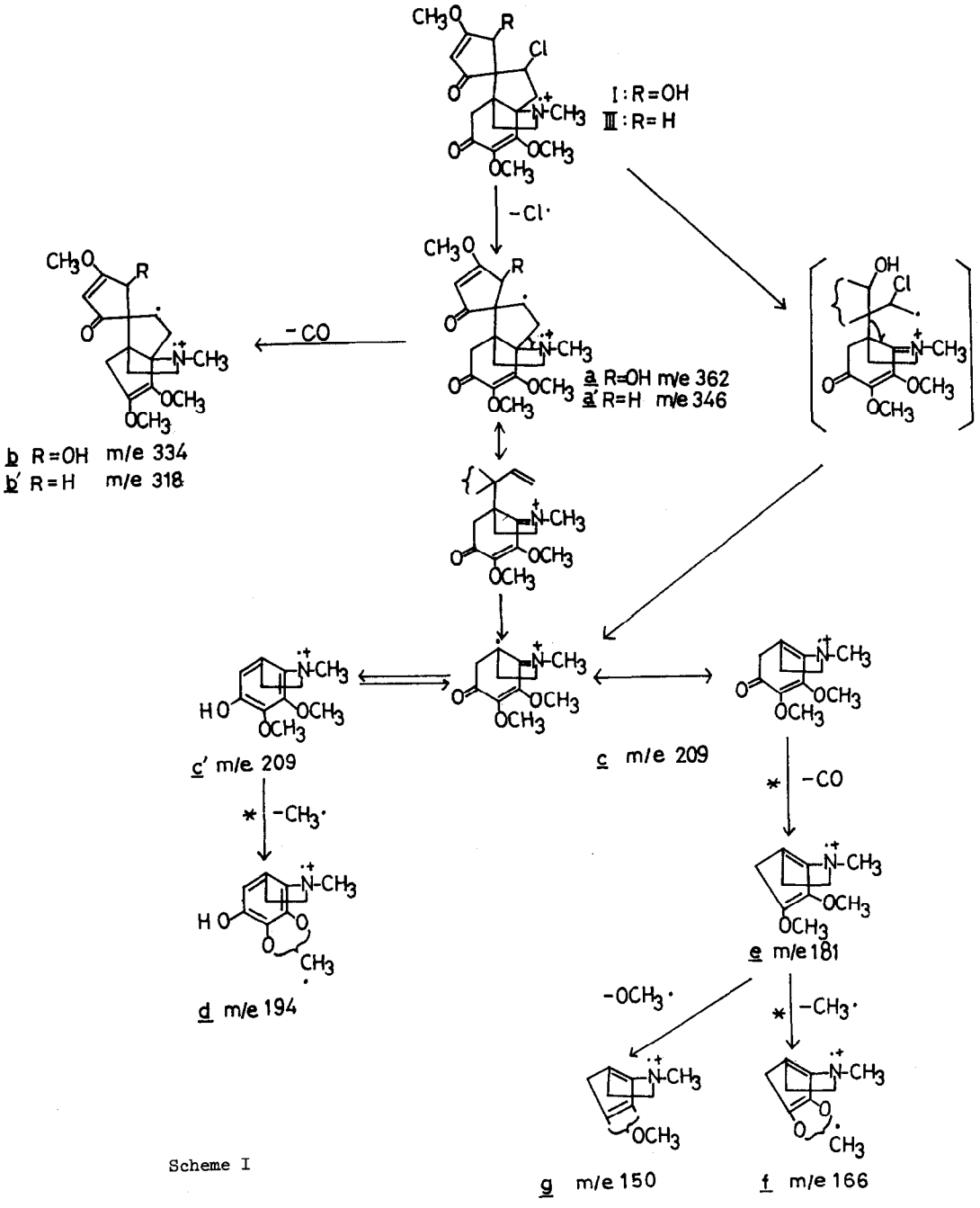
The NMR spectrum of acutuminine gives signals of a hydrogen geminal to the chlorine atom (5.65τ, q., J=7,11 cps), an N-methyl group (7.63τ), three O-methyl groups (5.89, 6.12, 6.29τ) and an olefinic hydrogen (4.73τ, broad s.) and the spectral pattern is also very similar to



(I) R= CH_3
(II) R= H



(III)


I : R = OH
II : R = H
-Cl·
-CO
a R=OH m/e 362
a' R=H m/e 346
b R=OH m/e 334
b' R=H m/e 318
c m/e 209
c' m/e 209
-CH3·
-CO
-OCH3·
d m/e 194
e m/e 181
f m/e 166
g m/e 150
* : metastable peaks are observed

Scheme I

that of acetylacutumine except that the former shows only a broad singlet (4.73τ) due to an olefinic hydrogen in the lower field than 5.0τ, whereas the latter gives a pair of doublets (4.58 and 4.01τ, J=0.8 cps) arising from the CH=C-CH-OAc grouping.

The above observations suggest the structure III for acutuminine.

A strong support was provided by the mass spectral studies. The mass spectrum of acutumine(I) exhibits significant peaks at m/e values of 362 (M-35), 334, 209 (base peak), 194, 181, 166 and 150 in addition to the molecular ion peak (397) and the characteristic isotope peak(399). These peaks shift to lower mass number by 14 mass units in the case of acutumidine(II) (m/e 383, 348, 332, 195, 180, 167, 152, 136).

Based on the careful examination of mass spectra of various acutumine derivatives[2], we propose a plausible mechanism for the fragmentation of acutumine(I) as shown in Scheme I. The base peak at m/e 209 in the mass spectrum of acutumine(I) is formed most likely by the elimination of A and B rings from molecular ion(I) or (M-Cl) ion a and assigned to ion c or ion c' , which decompose further to ion d (m/e 194), ion e (m/e 181), ion f (m/e 166) and ion g (m/e 150). These peaks are found to be diagnostic for compounds having the dimethoxy-enone system in C-ring.

A quite similar behavior is observed in the mass spectrum of acutuminine(III): i.e. 383, 381(M^+), 346(a'), 318(b'), 209 (base peak, c or c'), 194(d), 181(e), 166(f), 150(g). The fragmentation pattern at lower mass number than m/e 209 appears identical with that of acutumine(I), indicating that acutuminine(III) has the same structural feature in the C and D rings as acutumine(I). On the other hand, the molecular ion peak and the peaks corresponding to ion a and b shift to lower mass number by 16 mass unit (m/e 381, 346, 318). These shifts of mass number are reasonably ascribed to the structural difference in A-ring, i.e. the lack of hydroxyl group, and thus support the structure III for acutuminine.

REFERENCES

1) M. Tomita, Y. Okamoto, T. Kikuchi, K. Osaki, M. Nishikawa, K. Kamiya, Y. Sasaki, K. Matoba, K. Goto, Tetrahedron Letters No. 25, 2421-2430 (1967).

2) Details of the mass spectral investigation of acutumine derivatives will be published elsewhere.