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THE STRUCTURE OF MUSCAZONE

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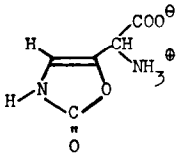
Based on the data given below, structure (1) is postulated for "muscazone", a novel constituent of Amanita muscaria, isolated by Eugster, Müller and Good. [1]

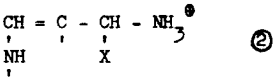


(1)

The NMR spectrum in D_2O displays doublets at τ = 2.98 (1H) and τ = 5.16 (1H) with J-values of 0.7 cps, strongly indicating allylic coupling in $-CH=\overset{|}{C}-\overset{|}{C}H-$.

In conc. H_2SO_4 the $-\overset{|}{C}H$ peak ($\tau \sim 4.4$) is split into a quartet ($J \sim 6$ cps). In addition, a broad 3H-doublet ($J \sim 6$ cps) appears at $\tau \sim 2.75$, proving the existence of $-\overset{|}{C}H-NH_3^{\oplus}$. The doublet splitting ($J \sim 2$ cps) of the olefinic proton signal at $\tau \sim 2.38$ is due to a vicinal $>NH$ whose peak coincides with that of H_2SO_4, but is discernible at

τ = 0.36 in CF_3COOH solution. As expected the 2 cps and 6 cps splittings are not observed in conc. D_2SO_4. These results lead to partial structure ②.

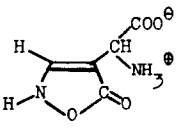


②

According to potentiometric titration, muscazone possesses a basic group B and an acidic group AH with pK^*_{MCS} values [2] of 8.23 and ~ 3.0, respectively. Thus, in neutral solution, the molecule is essentially zwitterionic with $BH^{\oplus}$ corresponding to $-NH_3^{\oplus}$, found by NMR.

The relatively low pK [3] of the acid group together with IR bands at 6.25 μ and 7.25 μ imply an α-amino acid moiety (②, X = $COO^{\ominus}$).

At this point one C and two O-atoms of the molecular formula $C_5H_6N_2O_4$ still have to be accounted for. An IR-band (KBr) at 5.75 μ calls for a C=O group, leaving only ① and ③ as possible structures.



③

The UV-spectrum (pH 2-7: λ_{max} = 212 mμ, ϵ = 8700; pH 12: λ_{max} = 220, ϵ = 7500) lacks significant absorption at about 250 mμ required by ③. We therefore conclude that muscazone has structure ①.

References

1. C.H. Eugster, G.F.R. Müller and R. Good, Tetrahedron Letters 23, 1813 (1965)
2. W. Simon, E. Kováts, L.H.Chopard-dit-Jean and E. Heilbronner, Helv. Chim. Acta 37, 1872 (1954)
3. E.J. Cohn and J.T. Edsall, "Proteins, Amino Acids and Peptides", Reinhold Publ. Corp., New York, 1943.