Identification of N-Methyl-α-picolinium and Other Quaternary Ammonium Compounds from the Oyster*1

In the previous studies1-4) we have isolated from marine gastropods and a bivalve a number of quaternary ammonium compounds. Some of these compounds were new as the natural product and the number of the compounds detected in one species was more than expected from the previous literature. Similar complexity of the composition of these compounds in bivalves was also demonstrated by KONOSU et al.,5,6) by the finding of a new betaine, atrinine, and the identification of 10 compounds. These results stimulated us to further the search for new quaternary ammonium bases in marine molluscs.

In this study the specimens of oyster C. gigas collected at Kesennuma Bay, Miyagi Prefecture, in April 1976 were used. They were first freed of lipids with acetone and the residue was then extracted with boiling methanol. The methanol extracts were successively treated on columns of the anion-exchange resin (Amberlite IRA-400) and the cation-exchange resin (Dowex 50W-X8). The compounds retained on the latter resin were eluted with hydrochloric acid by increasing stepwise the concentration, as described in the previous report5). The final purification was carried out by preparative paper chromatography on Toyo Filter Paper No. 514 with the following two solvents: A) 1-butanol-acetic acid-water (4:1:2) and B) 1-propanol-28% ammonium hydroxide-water (7:1:2).

The paper chromatographic examination revealed the presence of 9 compounds reactive to the Dragendorff reagent. Five of them were isolated and identified as choline, glycine betaine, stachydrine, homarine, and trigonelline by comparing their mass spectra with those obtained in the previous study5). Supplementary data were also available from the uv spectra in the case of homarine and trigonelline and from the ir spectra in the case of glycine betaine, choline, and homarine. Comparison by tlc between the isolated and synthesized specimens with the afore-mentioned two solvents on cellulose layers also confirmed their identity. The sixth compound revealed a strong peak at m/e 79 in its mass spectrum indicating the presence of pyridine nucleus. The uv spectrum was in agreement with the presence of pyridine nucleus as indicated by the peak at m/e 79 in the mass spectrum. The pmr spectrum in D2O showed two singlets at δ 2.9 and 4.1 which were assignable respectively to a methyl group attached to the ring and a methyl group attached to a quaternary nitrogen atom. However, the position of the C-methyl group was presumed to be either at C-2 or C-3 from the uv absorption maximum at 262 nm in aqueous solution (ref7) α-picoline 262 nm, β-picoline 263 nm, γ-picoline 255 nm). The uv spectrum of synthetic N-methyl-α-picolinium coincided well with that of the isolated specimen while that of N-methyl-β-picolinium was slightly different in having the maximum at 265 nm. Further evidence was obtained by tlc comparison where the isolated specimen was distinguishable from N-methyl-β-picolinium but was indistinguishable from N-methyl-α-picolinium (Rf 0.56 with both solvents A and B). Attempts to isolate two other compounds were unsuccessful owing to their insufficient sample size and their structures remain unidentified.

Although the present study was not carried out quantitatively it was noticed that glycine betaine was the most abundant. Choline and homarine also were present in considerable amount but the amount of other compounds were quite small.

N-Methylpyridinium has been known to be present in the crab, sea anemone, and mussel8). However, no previous report seems available about the occurrence on N-methyl-α-picolinium in the natural source.

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References


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