Tetrahedron Letters No. 34, pp 3181 - 3182.
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0040-4039/79/0815-3181$02.00/0

OCCURRENCE OF TWO NEW MYCOSPORINE-LIKE AMINOACIDS, MYTILINS A AND B IN THE EDIBLE MUSSEL, MYTILUS GALLOPROVINCIALIS[1]

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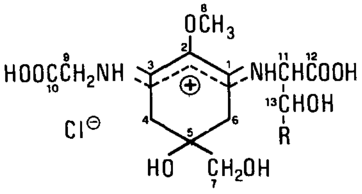
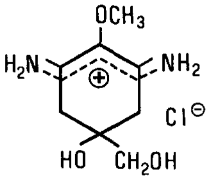
In the course of a survey of biologically active compounds from marine invertebrates, attention was given to the occurrence in mussels, *e.g. Mytilus galloprovincialis*, and other edible mollusks bivalves (oysters, clams, etc.), of some water soluble metabolites whose general properties resembled those of the mycosporins found in fungi[2], algae[3], and in the coelenterate anthozoan, *Palythoa tubercolosa*[4]. The present communication describes the isolation and characterization of the major constituents of *M. galloprovincialis* mytilins A and B, corresponding to two new aminoacid coniugates 1a and 1b[5].



1a R = H
1b R = CH_3



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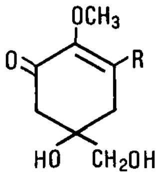

3 R = NH_2
4 R = OH

Fractionation of the aq. EtOH extracts of the mollusks on Dowex 50W-X2 columns (eluents: H_2O and 0.2M HCl) provided mytilins A and B as a 3:1 unseparable mixture characterized by a sharp absorption maximum at 334 nm (H_2O) and ^1H n.m.r. signals at δ (D_2O) 3.63 (2H, *s*, $-CH_2OH$), 3.72 (3H, *s*, $-OCH_3$) and 2.9 (4H, *m*, cyclic $-CH_2-$) typical of the cyclohexenimine mycosporine chromophore; ^{13}C n.m.r. (table 1).

When submitted to acid hydrolysis with 6M HCl (20h, 110°), mytilins afforded glycine, serine and threonine in the molar ratio of 4:3:1 as determined by aminoacids analysis. The same mixture of aminoacids was also obtained by treatment of mytilins with H_2O at 80° or aq. NaOH 1%, indicating lack of peptide bonds. A further characterization of mytilins followed from the reaction with conc. NH_4OH which gave, besides the aminocyclohexenone 3, a degradation product typical of mycosporins[4], the hitherto unknown aminocyclohexenimine 2; MS m/e 168 ($M^+ - H_2O$, $C_8H_{12}N_2O_2$); UV (H_2O, H^+) λ_{max} 307 nm (H_2O, OH^-) λ_{max} 304 nm; ^1H n.m.r. δ (CD_3OD) 3.60 (3H, *s*, $-OCH_3$), 3.46 (2H, *s*, $-CH_2OH$), 2.98 and 2.61 (each 2H, *d*, J = 17Hz, cyclic $-CH_2-$); ^{13}C n.m.r. (table 1).

The combined spectral and chemical evidence allowed the formulation of mytilins A and B as 1a and 1b respectively. Biogenetically mytilins may arise by condensation of the parent aminoacids with the β-diketone 4, derived presumably from shikimic acid. This reaction is reminiscent of the detoxication processes which foreign metabolites, unwanted by the organism, undergo in the body to produce more polar and relatively less active products.

The occurrence of 1 in edible mussels is remarkable in view of the uncertanties about the pharmacological properties of mycosporine aminoacids.

TABLE 1. - ^{13}C Chemical Shifts[a] (δ in ppm, D_2O) of compound 1a, 1b, and 2. (assignments for carbons 1-3 and 4-6 may by exchanged).

Carbon number	1	2	3	4	5	6	7	8	9	10
1a	162.3	127.0	161.0	33.7	71.9	34.1	68.2	60.2	45.8	173.4
		C-11 59.8(*d*)[c]		C-12 173.4(*s*)[c]		C-13 62.6(*t*)[c]				
1b	162.3	127.0	161.0	33.7	71.9	34.1	68.2	60.2	45.8	173.4
		C-11 63.1(*d*)[c]		C-12 173.4(*s*)[c]		C-13 67.4(*d*)[c]		C-14 19.9(*q*)[c]		
2[b]	164.5	126.4	164.5	38.1	72.8	38.1	69.2	59.4		
Multiplicity[c]	*s*	*s*	*s*	*t*	*s*	*t*	*t*	*q*	*t*	*s*

[a] Internal standard: dioxane (67.4 ppm); [b] in CD_3OD; [c] multiplicity in the off-resonance decoupled spectra.

REFERENCES AND NOTES

1. Supported by CNR (Rome) in the frame of the project "Oceonagrafia e Fondi Marini-Risorse Biologiche". We acknowledge Stazione Zoologica (Napoli) for laboratory facilities.
2. J. Favre-Bovin, N. Arpin et C.Brevard, *Can. J. Chem.*, *54*, 1105 (1976).
3. J. Tsujino, K. Yabe, I. Sekikawa, and N. Hamanaka, *Tetrahedron Lett.*, 1978, 1401.
4. a) S. Ito and Y. Hirata, *Tetrahedron Lett.*, 1977, 2429; b) S. Takano, D. Uemura, and Y. Hirata, *ibid.*, 1978, 2299 and 4909.
5. At the Second International Symposium on Marine Natural Products (Sorrento 1978), where a preliminary account of this work was given, Prof. Y. Hirata and his co-workers reported the isolation of a compound identical to 1b from the alga *Porphyra tenera*.