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ISOLATION AND STRUCTURE OF A UV-ABSORBING SUBSTANCE 337 FROM THE ASCIDIAN HALOCYNTHIA RORETZI

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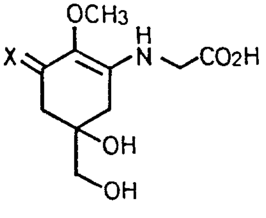
Summary: A new mycosporin-like amino acid with a strong absorption maximum at 337 nm isolated from the ascidian Halocynthia roretzi has the structure 7.

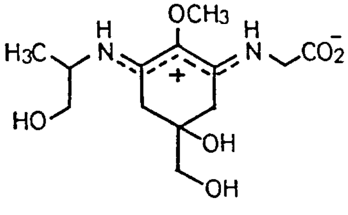
In the course of our studies on the constituents of the ascidian Halocynthia roretzi, much attention was given to the occurrence of several water soluble substances with a strong absorption maximum in the range of 310-340 nm. Recently, mycosporine-like amino acids 1-6 characterized by a UV-absorption maximum in the range of 310-360 nm were isolated from marine plants and animals[1)], however the role of these compounds in vivo is still unkown. Our interests concerning to these compounds are focused on their distribution in marine organisms. Now we wish to report the isolation and structure of a new mycosporine-like amino acid with a UV-absorption maximum at 337 nm, isolated from the ascidian with biogenetically related compounds 2, 4, 5 and 6.

Our procedure (Fig. 1) for the isolation of UV-absorbing substances gave a new mycosporine-like amino acid 7 as colorless amorphous powder (Na^+ form); mp. 153-156°C (decomp.); UV (H_2O) λ_{max} 337 (ε=29200); $[\alpha]_D^{25}$ -50° (c=0.3, H_2O); FDMS m/z 310 (M^+-H_2O, H^+ form). Result of amino acid analysis of hydrolysis product and comparison of 270 MHz PMR and 25.5 MHz CMR spectral data with those of 6 (Na^+ form) (Table-1, 2) led to the structure of 7 for the amino acid

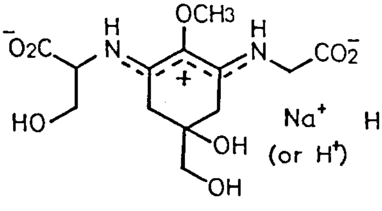


1 X=O (λ max 310nm)

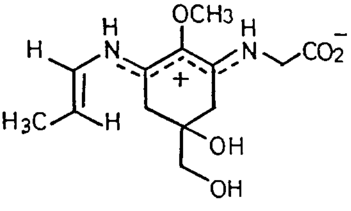
2 X=NH (λ max 320nm)



3 (λ max 332nm)



4 (λ max 334nm)



5 (λmax 360nm)

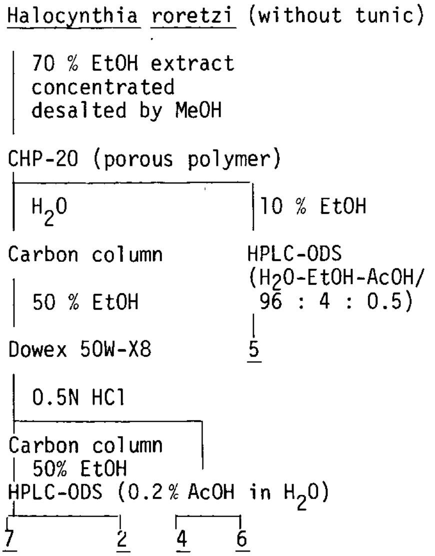
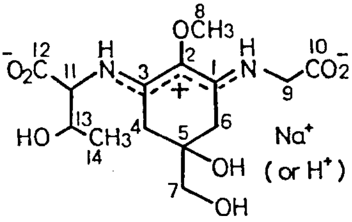
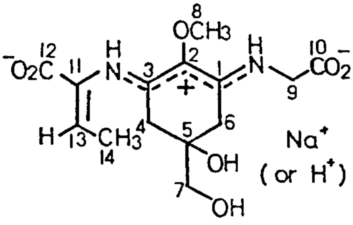


Fig. 1. Scheme for the isolation



6 (λmax 334nm)



7 (λmax 337nm)

Table-1. ^{1}H Chemical Shifts[a] of 6 and 7 in D_2O.

	6	7
H-4	2.74, 2.92 (J=17 Hz)[b]	2.72, 2.85 (J=17 Hz)[c]
H-6	2.73, 2.84 (J=18 Hz)[b]	2.52, 2.69 (J=17 Hz)[c]
H-7	3.56 (s)	3.52 (s)
H-8	3.68 (s)	3.70 (s)
H-9	4.03 (s)	4.05 (s)
H-11	4.06 (d, J=4.7 Hz)	-
H-13	4.29 (dq, J=4.7, 6.3 Hz)	6.82 (q, J=7.2 Hz)
H-14	1.24 (d, J=6.3 Hz)	1.77 (d, J=7.2 Hz)

a) δ in ppm. Internal standard; t-BuOH (1.23).
b,c) ABq center and each assignment may be exchanged.

Table-2. ^{13}C Chemical Shifts[a] of 6 and 7 in D_2O.

	6		7	
C-1	159.9[c]	s[b]	160.2[d]	s[b]
C-2	126.6	s	126.7	s
C-3	161.4[c]	s	162.3[d]	s
C-4	33.6	t	34.1	t
C-5	71.8	s	72.1	s
C-6	34.0	t	34.3	t
C-7	68.2	t	68.4	t
C-8	60.2	q	60.2	q
C-9	47.5	t	47.6	t
C-10	175.6[e]	s	175.5	s
C-11	65.2	d	132.7	s
C-12	176.1[e]	s	171.5	s
C-13	69.0	d	137.0	s
C-14	20.2	q	13.8	q

a) δ in ppm. Internal standard; dioxane (67.4).
b) Multiplicity in the off-resonance decoupled spectrum.
c,d,e) Each assignment may be exchanged.

characterized by the absorption maximum at 337 nm. The configuration of C-14 methyl group was assigned to Z, since chemical shift of methyl proton was higher than that of its isomer[2] (not isolated in pure form; methyl proton at 1.98 ppm, d, J=7.4 Hz, and olefinic proton at 6.00 ppm, q, J=7.4 Hz).

The isolation yields of 2, 4, 5, 6 and 7 were 0.001, 0.0006, 0.001, 0.001 and 0.0006 %, respectively, and compound 7 also occurred in other marine organism[3]. Studies on the role, distribution and composition of mycosporine-like amino acids in marine organisms are continued.

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References and Notes

1) Y.Hirata et al., Pure and Appl. Chem., 51, 1875 (1979) and references are cited in.
2) In a series of 2-acylaminocrotonate derivatives, chemical shift of methyl proton of Z isomer (1.6-1.8 ppm) is higher than that of E isomer (1.9-2.3 ppm), A. Srinivasan et al., Tetrahedron Letters, 891 (1976).
3) At 23rd Symposium on The Chemistry of Natural Products (Nagoya, Japan, 1980), T. Okaichi and T. Tokumura reported the isolation of a compound identical to 7 and its isomer in the ratio of 1:3 from *Noctiluca miliaris*, and proposed name "palythenic acid" for these compounds.

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