CHEMISTRY LETTERS, pp. 419-420, 1979. Published by the Chemical Society of Japan

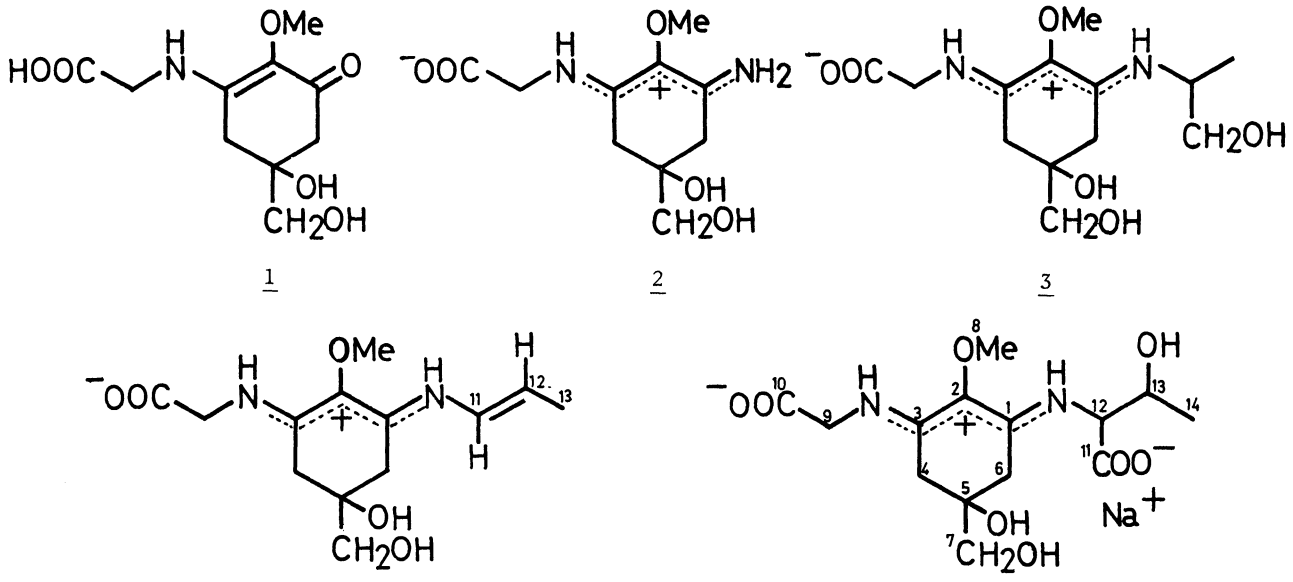
ISOLATION AND STRUCTURE OF A 334 NM UV-ABSORBING SUBSTANCE, PORPHYRA-334 FROM THE RED ALGA PORPHYRA TENERA KJELLMAN

Satoshi TAKANO, Atsushi NAKANISHI, Daisuke UEMURA, and Yoshimasa HIRATA
Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya 464

A new amino acid with a maximum at 334 nm, supposed to be biogenetically related to the characteristic UV-absorbing compounds from the zoanthid Palythoa tuberculosa, has been isolated from Porphyra tenera Kjellman and its structure determined.

During the course of our study of palytoxin, we have isolated several water-soluble compounds with strong absorption maxima in the range of 310-360 nm. Although it is well-known that compounds having UV bands in this range are widely present in marine plants[1] and animals[2], there are only few reports dealing with the structure and their role in vivo. However, we have recently reported the structures of four compounds, mycosporine-Gly[3] 1 (λ_{max} 310 nm), palythine[4] 2 (λ_{max} 320 nm), palythinol[5] 3 (λ_{max} 332 nm) and palythene[5] 4 (λ_{max} 360 nm) from Palythoa tuberculosa. Our attention concerning these compounds was focused on the UV-absorbing substance of the red alga Porphyra tenera Kjellman[6]. Now, we wish to report the isolation and structure of a 334 nm UV-absorbing substance, which has been named porphyra-334, biogenetically related to above compounds.

Our procedure as shown in Fig.1 for the isolation of the new amino acid, porphyra-334, gave compound 5 as a colorless powder; $[\phi]_{221} = -2.19 \times 10^4$ (H_2O); $C_{14}H_{21}N_2O_8Na \cdot CH_3OH$[7]; UV ($H_2O$) λ_{max} 334 nm (ε 4.23×10^4); PMR (D_2O, DSS) 1.25 (3H, d, J= 6.4 Hz), 2.83 (4H, m), 3.58 (2H, s), 3.70 (3H, s), 4.09 (2H, s), 4.11 (1H, d, J= 5.0 Hz), 4.33 (1H, d of q, J= 5.0, 6.4 Hz); CMR Table-1; IR (KBr) 3300, 1600, 1540, 1380, 1080 cm^{-1}.



The comparison of spectral properties of this substance with those of palythine, palythinol and palythene led to the structure 5 for porphyra-334 characterized by the absorption maximum at 334 nm. Treatment of 5 with HCl-MeOH afforded a dimethyl ester 6; m/e 356.1592 (M^+-H_2O) (Calcd for $C_{16}H_{24}N_2O_7$: M, 356.1584); PMR (CD_3OD) 1.26 (3H, d, J= 6.4 Hz), 2.83 (4H, m), 3.51 (2H, s), 3.72 (3H, s), 3.81 (3H, s), 3.83 (3H, s), 3.92 (1H, d, J= 5.0 Hz), 4.02 (1H, m), 4.38 (2H, s). This dimethyl ester 6 was easily dehydrated in pyridine at 80° for 6 hours to give an aromatic compound 7: $C_{16}H_{24}N_2O_7$; m/e 356.1602 (M^+)(Calcd: M, 356.1584); PMR ($CDCl_3$) 1.31 (3H, d, J= 6.4 Hz), 3.75 (3H, s), 3.78 (3H, s), 3.80 (3H, s), 3.95 (2H, s), 4.00 (1H, d, J= 5.0 Hz), 4.19 (1H, d of q, J= 5.0, 6.4 Hz), 4.52 (2H, s) 6.06 (1H, d, J= 2.2 Hz), 6.14 (1H, d, J= 2.2 Hz). Furthermore, porphyra-334 gave glycine and threonine by treatment with an aqueous KOH.

Thus, the characteristic UV-absorbing amino acid 5 has been isolated from the red alga and the planar structure of this compound has been determined. In order to clarify the symbiotic relation between coral and algae, our studies are under progress.

Table-1. ^{13}C Chemical shifts[a] (δ in ppm) of palythene 4 and porphyra-334 5

Carbon Number	1	2	3	4	5	6	7	8	9	10
4	161.5[b]	126.4	154.2[b]	33.8	71.8	33.8	68.4	60.3	47.6	175.4
		C-11 124.5 (d)[c]		C-12 117.9 (d)[c]			C-13 15.2 (q)[c]			
5	161.4[b]	126.6	160.0[b]	33.7	71.8	34.1	68.2	60.3	47.3	175.6[d]
		C-11 175.1[d] (s)[c]		C-12 64.9 (d)[c]			C-13 68.9 (d)[c]		C-14 20.1 (q)[c]	
Multiplicity[c]	s	s	s	t	s	t	t	q	t	s

[a]Internal standard; dioxane (67.4 ppm). [b,d]Each assignment may be exchanged. [c]Multiplicity in the off-resonance decoupled spectra of compounds 4 and 5.

Dried Porphyra tenera Kjellman
- 80% MeOH extract, concentrated
- MeOH, filtrated and concentrated

Sephadex G-10
- eluted with H_2O, concentrated

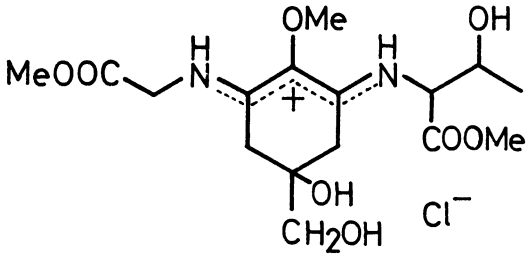
DEAE Sephadex A-25
- eluted with pH 6.9 phosphate buffer, concentrated

Sephadex G-10
- eluted with H_2O

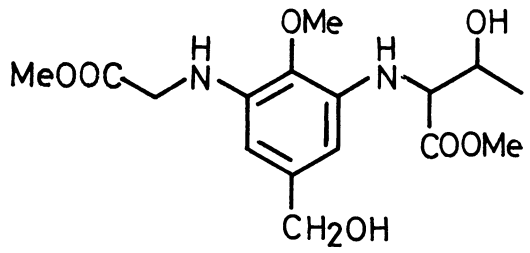
Norit A
- eluted with 50% EtOH, concentrated

CM Sephadex C-25 (Na^+)
- eluted with H_2O, concentrated

Porphyra-334 5



6



7

Fig. 1 Scheme for the isolation of porphyra-334

REFERENCES AND NOTE

1. I. Tsujino, Bull. Faculty of Fisheries, Hokkaido Univ., 12, 59 (1961). 2. J.H. Price and H.S. Forrest, Comp. Biochem. Physiol., 30, 879 (1969). 3. S. Ito and Y. Hirata, Tetrahedron Lett., 2429 (1977). 4. S. Takano, D. Uemura, and Y. Hirata, Tetrahedron Lett., 2299 (1978). 5. S. Takano, D. Uemura, and Y. Hirata, Tetrahedron Lett., 4909 (1978). 6. T. Yoshida and P.M. Sivalingam, Plant & Cell Physiol., 11, 427 (1970). 7. This compound gave satisfactory elemetal analysis. We wish to thank Professor C. Iida (Nagoya Institute of Technology) for Na-analysis by flame spectrophotometry.

(Received February 21, 1979)