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ISOLATION AND STRUCTURE OF A MYCOSPORINE FROM THE RED ALGA CHONDRUS YENDOI

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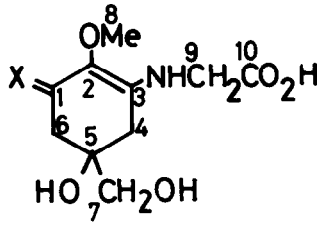
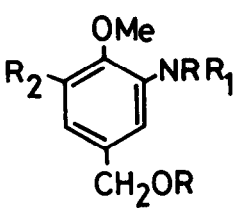
Recently, much attention has been focused on the existence of spectrally characteristic UV-absorbing substance in algae. There are, however, few reports concerning their chemical and physiological properties. Now we have isolated an optically active and water-soluble compound with a sharp absorption maximum at 320 nm from the red alga Chondrus yendoi which was collected at the shore of Zenikamezawa, Hakodate, Japan. More recently, three mycosporines having a absorption maximum at 310 nm have been isolated, from Stereum hirsutum, Botrytis cinera, and Palythoa tuberculosa, and named mycosporine 1, mycosporine 2 [1], and mycosporine-Gly 1 [2], respectively. The present communication describes the isolation and structure of a new mycosporine iminomycosporine-Gly designated as palythine 2**.



1 : X=O

2 : X=NH



3 : R=Ac, R_1=CH_2CO_2H

R_2 = NHAc

6 : R=Ac, R_1 = H, R_2 =OH

7 : R= R_1 = H, R_2 =OH

4 : R = H, X=NH_2

5 : R= Ac, X=NH_2

8 : R = H, X=OH

Repeated chromatography of aq. EtOH extract of C. yendoi on carbon column (eluent:50% aq.MeOH) provided a compound as white crystals, $C_{10}H_{16}N_2O_5$, mp 155-156°C (dec.); $(\alpha)_D$ -7.9 (c=1.5, H_2O); UV (H_2O) λ_{max} 320 nm (log ε=4.55). The pmr spectrum (D_2O) of 2 showed an AB quartet at δ 2.69 and 2.95 (each 1H, J=15.5 Hz), four singlets at 2.78 (-CH_2-), 3.58 (-CH_2O-), 4.02 (>N-CH_2-), and 3.65 (-OCH_3). The cmr spectrum shown in Table 1. Esterification with CH_3OH-HCl gave the methyl ester hydrochloride, $C_{11}H_{18}N_2O_5$.HCl, mp 186-187°C (dec.), ir 1740 cm^{-1}.

Treatment of 2 with Ac_2O-pyridine at room temperature for 6 hr afforded the triacetate 3, $C_{16}H_{20}N_2O_7$, mp 172-174°C (dec.); MS m/e 352 (M^+); ir 3310, 1740, 1725, 1660, 1590 and 1555-1535

cm^{-1}; pmr δ ($CDCl_3$-DMSO-d_6) 1.92, 2.09 and 2.21 (each 3H, s, $-COCH_3$), 3.78 (s, 3H, $-OCH_3$), 3.73 and 4.79 (each 1H, AB_q, J=17 Hz), 5.01 (s, 2H, $-CH_2O-$), 7.17 and 8.15 (each 1H, d, J=3 Hz, aromatic) and 8.98 (bs, 1H, exchanges with D_2O).

Brief hydrolysis of 2 with 1% NaOH at 40°C for 1 hr gave glycine and aminocyclohexenone 4 ***, $C_8H_{13}NO_4$, mp 216-217°C (dec.); MS m/e 187 (M^+); UV (H_2O-H^+) λ_{max} 293 nm (H_2O-OH^-) λ_{max} 297 nm. The pmr spectrum of 4 (D_2O) showed two AB quartets at δ 2.42 and 2.68 (each 1H, J=15.5 Hz), 2.62 and 2.92 (each 1H, J=19.2 Hz), two singlets at 3.52 (2H) and 3.59 (3H). The cmr spectrum (Table 1).

Acetylation of 4 with Ac_2O-pyridine at room temperature for 10 hr afforded two acetates 5 [3], mp 176-177°C (dec.); ir 1730 cm^{-1}; pmr δ (DMSO-d_6) 2.08 (s, 3H, $-COCH_3$), 3.58 (s, 3H, $-OCH_3$), 3.95 (s, 2H, $-CH_2O-$), 4.95 (bs, tert.OH) and 6.18 (bs, 2H, $-NH_2$); δ (Pyridine-d_5) 2.94 (s, 2H, $-CH_2-$), 2.98 and 3.10 (each 1H, AB_q, J=18 Hz), and 6 [3], mp 127-128°C; ir 1720 and 1670 cm^{-1}; pmr δ (DMSO-d_6) 6.60 and 7.38 (each 1H, d, J=3 Hz, aromatic).

Treatment of 4 with 4% NaOH at 80°C for 2 hr followed by careful neutralization yielded the aminophenol 7, $C_8H_{11}NO_3$, mp 113-114°C; UV (H_2O-H^+) λ_{max} 276 nm (H_2O-OH^-) λ_{max} 291 nm; pmr δ (DMSO-d_6) 6.04 and 6.13 (each 1H, d, J=2 Hz, aromatic).

Table 1. ^{13}C Chemical Shifts, ppm (TMS=0), D_2O

Carbon Number	1	2	3	4	5	6	7	8	9	10
1 [2]	187.2	130.4	159.7	33.8	72.9	45.4	68.4	60.2	43.7	174.5
2 [a]	162.0	125.8	160.4	34.6	72.4	37.2	68.5	60.2	48.1	174.7
4 [a]	187.5	130.4	158.8	37.2	73.5	45.0	68.5	60.0		
8 [2]	181.0	134.7	181.0	41.4	73.1	41.4	68.5	60.9		
Multiplicities [b]	s	s	s	t	s	t	t	q	t	s

a) Internal standard; TMS=0, D_2O.

b) Multiplicities in the off-resonance decoupled spectra of 1, 2, 4, and 8.

Furthermore, the chemical shifts (cmr) of 2 are very similar to those of 1 except C_1, C_2 and C_6 carbon atoms. Differences between the chemical shifts of 2 and 1 can be explained by difference of the substituent at C_1.

Studies on the biogenesis and the role of this new compound in the marine plant are now in progress.

Acknowledgement: We are grateful to Professor Y. Hirata, Nagoya University, for helpful discussions

REFERENCES AND NOTE

1) N. Arpin, J. Favre-Bonvin and S. Thivend, Tetrahedron Letters, (1977) 819.

2) S. Ito and Y. Hirata, Tetrahedron Letters, (1977) 2429.

3) These compounds gave satisfactory elemental analyses.

** Professor Hirata and Dr. Uemura also isolated the same compound from Palythoa tuberculosa (private communication). The authors and they proposed name " palythine " for this compound.

*** Hirata et al. have reported that mycosporine-Gly gave glycine and unstable β-diketone 8 when heated in water.