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ISOLATION AND STRUCTURE OF A NEW AMINO ACID, PALYTHINE, FROM THE ZOANTHID PALYTHOA TUBERCULOSA

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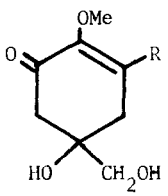
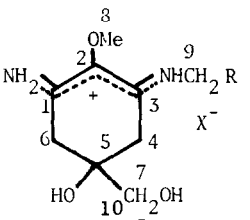
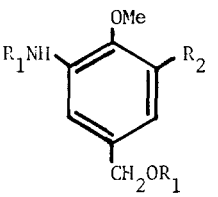
In the course of our studies on the constituents of the zoanthid Palythoa tuberculosa, we have isolated some water soluble compounds with a strong absorption maximum at 310-330 nm. One of these, mycosporine-Gly (λ_{max} 310 nm; structure 1), had been studied and reported.[1] On the other hand, it is well known that a compound with a absorption maximum at 320 nm is present in many marine plants and animals,[2] however the structure and the role in vivo are still unknown. Also, a compoud with the same absorption maximum is found in Palythoa tuberculosa. Now, it has been assigned structure 2 and named palythine.



1. R=NHCH$_2$COOH
5. R=NH$_2$



2. R=COO$^-$
3. R=COOCH$_3$, X=Cl



4. R$_1$=Ac
R$_2$=N(Ac)CH$_2$COOCH$_3$

6. R$_1$=H, R$_2$=NH$_2$
7. R$_1$=H
R$_2$=NHCH$_2$COOH
8. R$_1$=H
R$_2$=NHCH$_2$COOCH$_3$

An oily material containing palythine was obtained by repeated chromatography of aq. EtOH extracts of Palythoa tuberculosa on Dowex 50W (H$^+$form; eluent:0.5N HCl) and TSK G-3000S (polystyrene gel; eluent:H$_2$O). Then, purification of this material by preparative TLC on silica gel gave compound 2 as a white crystal[3,4]; m.p. 142-145 C (dec.); $C_{10}H_{16}N_2O_5 \cdot \frac{1}{2}CH_3OH$[5]; UV (H$_2$O) λ_{max} 320 nm (ε 3.62X10^4); PMR (D$_2$O) 2.69 and 3.00 (2H, AB q, J=17Hz), 2.73 and 2.92 (2H, AB q, J=17Hz), 3.60 (2H, s), 3.67 (3H, s), 4.06 (2H, s); CMR (Table-1); IR (KBr) 3260, 1609, 1540, 1378, 1305, 1273, 1126, 1052 cm^{-1}. As palythine was rather stable under acidic conditions, it was treated with HCl-MeOH at refluxing temperature for 2 hrs. The resulting methyl ester (3)[4] showed the presence of a carboxylate group in palythine; m.p. 186-189 C (dec.); $C_{11}H_{18}N_2O_5 \cdot HCl$; UV (H$_2$O) λ_{max} 318 nm (ε 3.67X10^4); IR (KBr) 1740 cm^{-1}; PMR (D$_2$O) 3.85 (3H, s, -COOCH$_3$). Further, compound 3 was easily aromatized by dehydration, as well as mycosporine-Gly. Treatment with Ac$_2$O-pyridine at room temperature overnight afforded a triacetate (4)[4]; PMR (C$_6$D$_6$) 1.58, 1.66, 1.84, 3.14, 3.33 (3H each, s), 3.63 and 4.89 (2H, AB q, J=17Hz), 4.87 (2H, s), 7.03, 8.76 (1H each, d, J=2Hz); MS m/e 366 (M$^+$, $C_{17}H_{22}N_2O_7$). These spectral and chemical properties suggested that palythine had the same carbon skeleton as mycosporine-Gly.

TABLE-1 ^{13}C Chemical Shifts[a] (δ in ppm) of compounds 1, 2 and 3

Carbon Number	1	2	3	4	5	6	7	8	9	10
1[1]	187.2	130.4	159.7	33.8	72.9	45.4	68.4	60.2	43.7	174.5
2	162.5[b]	125.4	160.9[b]	34.2	72.0	36.6	68.2	59.7	47.5	177.5
3	162.6[c]	126.0	162.8[c]	34.2	72.2	36.8	68.2	60.0	45.3	171.7
Multiplicity[d]	s	s	s	t	s	t	t	q	t	s

[a]Internal standard; dioxane (67.4 ppm)

[b,c]Each assignment may be exchanged.

[d]Multiplicity in the off-resonance decoupled spectra of compounds 1, 2 and 3.

Under basic conditions palythine was remarkably unstable, and easily underwent hydrolysis and dehydration. When palythine was treated with conc. NH_4OH at room temperature overnight, it gave glycine and compounds 5[4,6], 6[4,7] and 7[8]. Formation of these compounds indicates that palythine has the same substituents on a cyclohexene ring as mycosporine-Gly except for the absence of a ketone group in palythine. Based on these results, the stucture of a new amino acid, palythine, is established to be 2, a vinylog of amidine. Further evidence was obtained by the following reactions.

An interesting reaction occurred by the treatment of palythine with diazomethane, that is, it afforded an aromatized methyl ester (8)[4] with only two methoxy groups; PMR ($CDCl_3$) 1.90 (3H, bs, exchangeable with D_2O), 3.77 (6H, s), 3.93 (2H, d, J=5.7Hz; became singlet by the addition of D_2O), 4.72 (1H, bs, exchangeable with D_2O), 6.01, 6.19 (1H each, d, J=2Hz); IR ($CHCl_3$) 1740 cm^{-1}; MS m/e 240 (M^+, $C_{11}H_{16}N_2O_4$). Probably, the methyl ester (8) may be produced by the abstraction of proton with diazomethane followed by dehydration. On treatment of this compound with Ac_2O-pyridine at room temperature overnight, the same triacetate as 4 was obtained.

As shown in structure 2, palythine is considered to be inner salt from ir spectrum, and the actual structure is visualized as a resonance hybrid somewhere between two extreme structures. It is interesting to determine the extent of contribution of each extreme structure from a structural point of view.

REFERENCES AND NOTES

1. S. Ito and Y. Hirata, Tetrahedron Lett., 2429 (1977)
2. I. Tsujino, Bull. Faculty of Fisheries, Hokkaido Univ., 12, 59 (1961); K. Shibata, Plant & Cell Physiol., 11, 427 (1970)
3. Although mycosporine-Gly was optically active, palythine was inactive. Palythine isolated under mild conditions gave the same result.
4. These compounds gave satisfactory elemental analyses.
5. Methanol was determined by gas chromatography.
6. UV (H_2O) λ_{max} 297 nm; PMR (D_2O) 2.42 and 2.73 (2H, AB q, J_{AB}=17Hz, J_{AX}=1.6Hz), 2.60 and 2.96 (2H, AB q, J_{AB}=17Hz, J_{AX}=1.6Hz), 3.56 (2H, s), 3.62 (3H, s); MS m/e 187 (M^+, $C_8H_{13}NO_4$).
7. PMR (CD_3OD) 3.71 (3H, s), 4.36 (2H, s), 6.21 (2H, s); MS m/e 168 (M^+, $C_8H_{12}N_2O_2$).
8. PMR (D_2O) 3.77 (2H, s), 3.81 (3H, s), 4.50 (2H, s), 6.19, 6.37 (1H each, d, J=2Hz). This compound afforded compound 8 by the treatment with HCl-MeOH at refluxing temperature.