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# ISOLATION AND STRUCTURE OF A MYCOSPORINE FROM THE ZOANTHID PALYTHOA TUBERCULOSA

Shosuke Ito* and Yoshimasa Hirata
Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya 464, Japan

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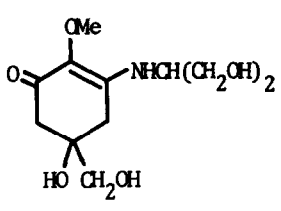
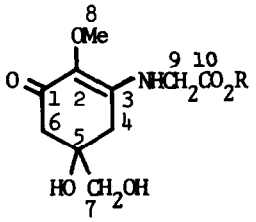
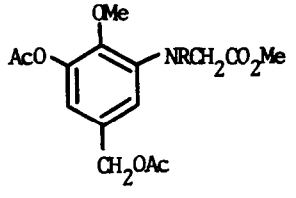
In the course of our studies on the constituents of the zoanthid Palytoa tuberculosa, we have isolated a water-soluble compound with a sharp absorption maximum at 310 nm. It has been known that near-ultraviolet radiation stimulates reproduction in many fungi, which is accompanied by the formation of water-soluble compounds having a sharp absorption maximum at 310 nm.[1] Favre-Bonvin et al. have recently shown that mycosporine 1, one of these compounds, isolated from Stereum hirsutum, has the structure 1.[2] The UV absorbing compound from Palythoa has now been assigned the structure 2 and named mycosporine-Gly.



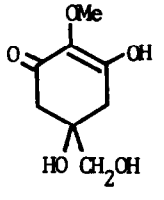
1



2: R=H; 3: R=Me



4: R=H; 5: R=Ac



6

Repeated chromatography of aq. EtOH extracts of P. tuberculosa on Dowex 50W, $H^+$ form (eluent: water) provided compound 2 as a pale yellow, amorphous powder;[3] UV ($H_2O$) $\lambda_{max}$ 310 nm; PMR ($D_2O$) δ 2.50 and 2.73 (2H, AB q, J 17 Hz), 2.72 and 2.83 (2H, AB q, J 17), 3.57 (2H, s), 3.64 (3H, s), and 4.24 (2H, s); CMR (Table 1). As the natural product was rather unstable, it was converted by methylation with diazomethane into the stable methyl ester 3,[3,4] mp 121-122°C (from pyridine-ether); $[\alpha]_D$ -12° (c 0.4 in $H_2O$); MS m/e 259 ($M^+$); UV ($H_2O$) $\lambda_{max}$ 307 nm (ε 28100), $\lambda_{min}$ 240-245 nm (ε 300). Like mycosporine 1 (1), the compound 3 was readily aromatized by dehydration. Treatment with $Ac_2O$-pyridine at 80°C afforded two phenol acetates 4 [δ 6.38 and 6.47 (each 1H, d, J 2 Hz)] and 5 [δ 7.11 and 7.24 (each 1H, d, J 2 Hz)]. Comparison of chemical and spectral properties of 2 with those of 1 led to the structure 2 (mycosporine-Gly) for the UV absorbing compound from Palythoa. This structure is further supported by the following reaction.

Mycosporine-Gly is remarkably susceptible to hydrolysis. When heated in water at 80°C for 3 hr, it gave glycine and the unstable β-diketone 6; MS m/e 188 ($M^+$); UV ($H_2O$-$H^+$) $\lambda_{max}$ 268 nm, ($H_2O$-$OH^-$) $\lambda_{max}$ 294 nm; PMR ($D_2O$) δ 2.60 and 2.90 (4H, AB q, J 17 Hz), 3.57 (2H, s), and 3.64

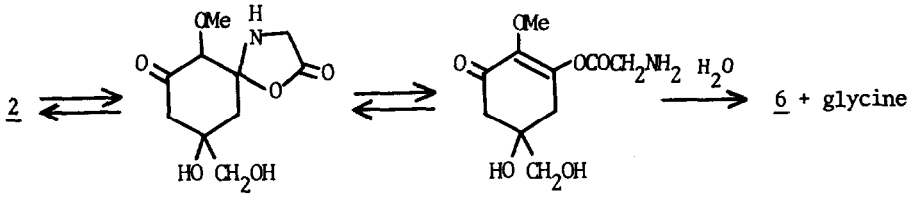
TABLE 1. $^{13}C$ Chemical Shifts (δ in ppm) of 1, 2, and 6.

| Carbon Number | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| 1[2] | 187.9 | 132.5 | 160.5 | 35.9 | 74.5 | 45.4 | 70.0 | 61.5 | | |
| 2[a] | 187.2 | 130.4 | 159.7 | 33.8 | 72.9 | 45.4 | 68.4 | 60.2 | 43.7 | 174.5 |
| 6[a] | 181.0 | 134.7 | 181.0 | 41.4 | 73.1 | 41.4 | 68.5 | 60.9 | | |
| Multiplicity[b] | s | s | s | t | s | t | t | q | t | s |

[a]Internal standard: dioxane (67.4 ppm).

[b]Multiplicities in the off-resonance decoupled spectra of 1, 2, and 6.

(3H, s). Both the PMR and CMR (Table 1) spectra are fully consistent with the symmetrical structure 6. Under similar conditions the methyl ester 3 was relatively stable, although it was gradually converted to a phenolic compound. Therefore, the facile hydrolysis of 2 should result from an intramolecular participation of the carboxylate anion in the glycine moiety. A plausible reaction mechanism is presented below.




The occurrence of a mycosporine in marine animal is unique, as the mycosporines have so far been found only in fungi. In this connection, it should be noted that a compound showing a sharp absorption maximum at 310 nm has been isolated by Price and Forrest from Physalia physalis which belongs to the same Coelenterata as Palythoa.[5] They suggested that a function of the compound might be protection of the organism from ultraviolet light.

## REFERENCES AND NOTES

1. R. E. Hite, Plant Dis. Reptr., 57, 760 (1973), and references cited therein.
2. J. Favre-Bonvin, N. Arpin, and C. Brevard, Can. J. Chem., 54, 1105 (1976). For another example of mycosporine, see N. Arpin, J. Favre-Bonvin, and S. Thivend, Tetrahedron Lett., 1977, 819.
3. These compounds gave satisfactory elemental analyses.
4. IR (KBr) 3300, 1740, 1620$^{sh}$, 1570-1550s cm$^{-1}$; PMR ($D_2O$) δ 2.47 and 2.61 (2H, AB q, J 17 Hz), 2.72 and 2.83 (2H, AB q, J 17), 3.56 (2H, s), 3.63 (3H, s), 3.83 (3H, s), and 4.26 (2H, s). This compound exists in the enamine form as depicted; in the PMR spectrum taken in pyr-$d_5$ the methylene protons in the glycine moiety appeared at δ 4.22 as a doublet (J 6.5 Hz) which became a singlet on the addition of $D_2O$.
5. J. H. Price and H. S. Forrest, Comp. Biochem. Physiol., 30, 879 (1969).