Pergamon

Tetrahedron Letters, Vol. 38, No. 14, pp. 2525-2526, 1997
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0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)00391-2

Two New UV-Absorbing Compounds from *Stylophora pistillata*: Sulfate Esters of Mycosporine-like Amino Acids

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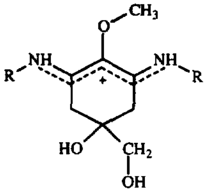
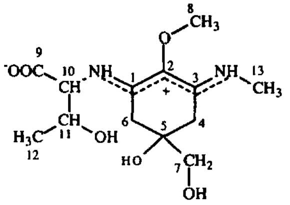
Abstract: Two new water soluble 320 nm UV-absorbing compounds, sulfate esters of two imino mycosporines, were isolated from methanol extracts of a reef-building coral and purified by HPLC. Structural elucidation yielded the molecular formulae $C_{12}H_{19}N_2O_9S$ (**5**) and $C_{11}H_{17}N_2O_9S$ (**6**). These have been given the trivial names Palythine-Thr-sulfate and Palythine-Ser-sulfate respectively.

Mycosporines are amino acids or reduced amino acid derivatives of one of two common ring systems, an aminocyclohexenone and an aminocyclohexenimine[1]. These small water soluble compounds that absorb strongly in the 310-360 nm ultraviolet region[2] are widely distributed among fungi, and marine plants and animals[3]. Quantitative studies in responses to UV radiation have demonstrated increased production of mycosporines in corals[4], and the protective function of mycosporines in sea urchin eggs[5]. Most reported mycosporines are of general structure **1** ($\lambda_{max} \geq 330$ nm). These all contain two amino acid-derived secondary amines in the chromophore. Two recent publications support a wider variety of structural types (e.g. **2**[6], **3**[7]).



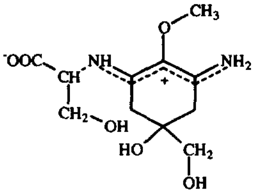
1

λ_{max} 330 nm general structure



2

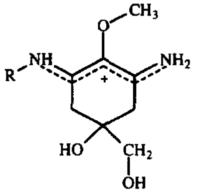
Myc-methylamine:Thr (λ_{max} 330)



3

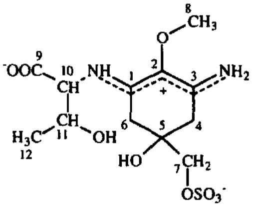
Palythine-Ser (λ_{max} 320)

This is the first report of the isolation and characterisation of mycosporine sulfate esters. HPLC isolations of the mycosporines (Fig. 1) from *S. pistillata* revealed two new, highly polar compounds, **5** and **6** (λ_{max} = 321 nm). This absorption is typical of structure type **4** that possesses a chromophore with an unsubstituted imine functionality.



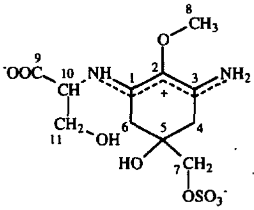
4

λ_{max} 320 nm general structure



5

Palythine-Thr sulfate



6

Palythine-Ser sulfate

Results of ^1H and ^{13}C experiments for the two newly isolated mycosporines are summarised in Table 1.

The chemical shifts are characteristic of the ring and amino acid substituent atoms of mycosporines and are in good agreement with published data[6, 7, 8]. High resolution negative ion ESI suggested formulae of $C_{12}H_{19}N_2O_9S$ (**5**), m/z 367.08201 $[M^-]$ and $C_{11}H_{17}N_2O_9S$ (**6**), m/z 353.06696 $[M^-]$. Correct high resolution ions for the sodium salt of both species were also measured. Stereochemical configurations were not determined. The downfield ^1H and ^{13}C shift of C7, the increased polar nature of the metabolites, and mass spectral data therefore support a mycosporine sulfate ester substituent in place of the hydroxyl group.

Table 1. NMR Data of - **2**, **5** and **6** in D_2O.

C	**2**		**5**		**6**	
No.	$\delta\ ^{13}C$	δ^1H, m, J(Hz)	$\delta\ ^{13}C$	δ^1H, m, J(Hz)	$\delta\ ^{13}C$	δ^1H, m, J(Hz)
[a]1	157.6		160.6		160.4	
2	125.3		125.0		124.9	
[a']3	161.4		160.6		160.6	
[b]4	32.8	2.80, s	34.0	2.81, ABq, 17.0	34.0	2.83, ABq, 17.0
5	71.0		69.8		69.9	
[b']6	33.1	2.75, Abq, 17.5	36.0	2.77, ABq, 17.0	36.0	2.78, ABq, 17.0
7	67.5	3.50, s	72.5	3.90, s	72.7	3.90, s
8	59.3	3.60, s	59.3	3.55,s	59.2	3.55, s
9	175.6		174.9		174.3	
10	64.3	3.95, d, 4.5	64.5	3.98, d, 4.5	60.7	4.25, dd, 6.0, 4.0
11	68.1	4.22, dq, 6.0, 4.5	68.2	4.20, dq, 6.0, 4.5	62.7	[3.80, dd, 11, 7.0
12	19.4	1.19, d, 6.0	19.5	1.12, d, 6.0		3.88, dd, 11, 4.0]
13	29.8	3.00, s				

[x, x'] Shifts may be exchangeable for **5** & **6**.

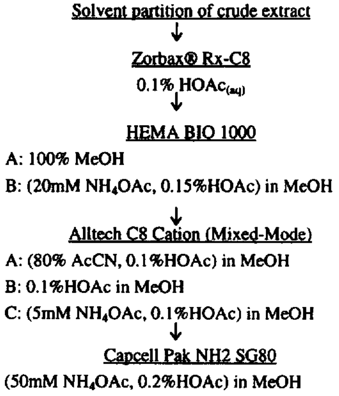


Figure 1. Schematic Isolation of **5** & **6.**

There are a number of sulfated marine natural products with interesting pharmacological properties[9]. Also, given the ubiquitous nature of the mycosporines, and the observations that their response and function may not always be UV related[10, 11, 12]; the presence of sulfate esters enhances interest in the biochemistry of the mycosporines. Metabolic pathways and physiological functions may be broader than previously considered.

Acknowledgements. This research was conducted as part of the Marine Photobiology project at the Australian Institute of Marine Science in collaboration with Central Queensland University. The authors thank Dr.David Bourne (AIMS) for acquiring the mass spectral data, and for his comments on this manuscript. We also thank Anne Lee for assistance with sample collection and the crew of the R.V. Harry Messel for their logistic support.

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(*Received in UK* 20 *November* 1996; *revised* 10 *February* 1997; *accepted* 28 *February* 1997)