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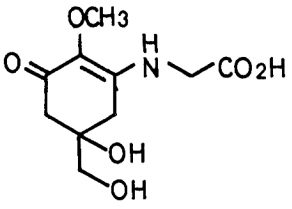
ISOLATION AND STRUCTURE OF A 330 NM UV-ABSORBING SUBSTANCE, ASTERINA-330 FROM THE STARFISH ASTERINA PECTINIFERA

Hideshi NAKAMURA*, Jun-ichi KOBAYASHI, and Yoshimasa HIRATA†
Mitsubishi-Kasei Institute of Life Sciences,
11 Minamiooya, Machida-shi, Tokyo 194
†Faculty of Pharmacy, Meijo University, Tempaku, Nagoya 468

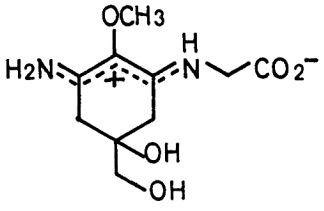
A new mycosporine-like amino acid with a characteristic UV-absorption maximum at 330 nm has been isolated from the starfish Asterina pectinifera, and its structure was determined to be 5.

Mycosporine-like amino acids are characterized by strong UV-absorptions in the range of 310-360 nm and have been isolated from marine plants and animals.[1,2] Our interests concerning to these compounds are focused on their distribution and role in marine organisms. Our survey on their distribution in marine organisms has shown that these compounds are almost ubiquitous among invertebrates and algae, and much attention was given to the occurrence of new related compounds.[3] In this communication, we wish to report the isolation and structure of a new mycosporine-like amino acid characterized by a UV-absorption maximum at 330 nm from the starfish Asterina pectinifera.

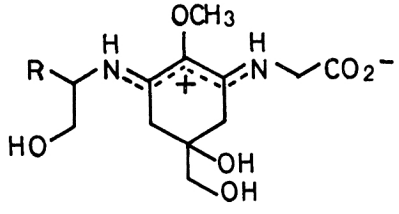
HPLC analysis of partly purified extract of the starfish Asterina pectinifera indicated the presence of a new amino acid with a UV-absorption maximum at 330 nm in addition to compounds 1 - 4. Our procedure for the isolation of the 330 nm UV-absorbing substance (Fig. 1) gave Asterina-330 as colorless syrup in 0.0007% yield; UV(H_2O) λ_{max} 330 nm; EI-MS m/z 270.1205 (M^+-H_2O)(calcd for $C_{12}H_{18}N_2O_5$: 270.1216); ^{1}H-NMR (270 MHz, D_2O) δ2.73, 2.84 (2H, ABq center, J = 17 Hz), 2.92 (2H, s), 3.58 (2H, s), 3.60 (2H, t, J = 5.6 Hz), 3.65 (3H, s), 3.77 (2H, t, J = 5.6 Hz), 4.27 (2H, s). Comparison of these spectral data with those of compounds 3 and 4 led to the structure 5 for Asterina-330 and this structure was supported further by the following result. Treatment of Asterina-330 with diazomethane gave an ester 6 by aromatization, like compound 4[4]; UV(MeOH) λ_{max} 227, 298 nm; EI-MS m/z 284.1391 (M^+) (calcd for $C_{13}H_{20}N_2O_5$: 284.1372); ^{1}H-NMR (270 MHz, $CDCl_3$) δ3.33 (2H, t, J = 5.2 Hz),



1 (λmax 310nm)

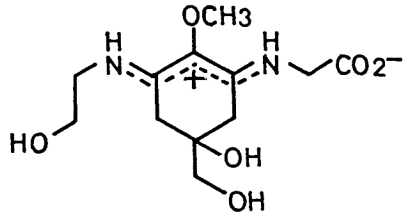


2 (λmax 320nm)



3 R=CO2H (λmax 334nm)
4 R=CH3 (λmax 332nm)

Asterina pectinifera
| 70% EtOH extract
| concentrated
| MeOH
| filtered and concentrated
CHP-20 (porous styrene polymer)
| eluted with H_2O
Carbon column
| eluted with 50% EtOH
HPLC-ODS
| eluted with 0.2% AcOH
Dowex 50W x 8 (H^+ form)
| eluted with 0.5N HCl
Carbon column
| eluted with 50% EtOH
HPLC-ODS
| eluted with 0.1% AcOH
Asterina-330



5 (λmax 330nm)

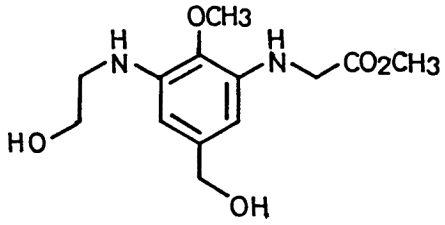


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Fig. 1. Scheme for the isolation of the 330 nm UV-absorbing substance.

3.75 (3H, s), 3.78 (3H, s), 3.83 (2H, t, J = 5.2 Hz), 3.95 (2H, br s), 4.54 (2H, s), 6.02 (1H, d, J = 1.8 Hz), 6.19 (1H, d, J = 1.8 Hz).

Preliminary result of HPLC analysis of the mycosporine-like amino acids indicated the presence of Asterina-330 in other marine organisms (bivalves, red algae etc.) and this compound is supposed to be biogenetically related to the mycosporine-like amino acids 1 - 4. Distribution of these mycosporine-like amino acids in marine organisms will be reported elsewhere.

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