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RESEARCH ARTICLE

Qualitative Detection of Some Secondary Metabolites from Turkish Marine Sponges Collected in Kemer

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Qualitative Detection of Some Secondary Metabolites from Turkish Marine Sponges Collected in Kemer

Summary

During our search for bioactive compounds from Turkish marine sponges, we have detected secondary metabolites from five different marine sponges which have been collected from Kemer (Antalya), Turkey. The compounds were detected by DAAD- HPLC from the methanolic extracts of five sponge species Axinella polypoides, Ircinia oros, Sarcotragus spinulosa, Ircinia variabilis, Agelas oroides. Our sponge samples contain bromopyrrole type of alkaloids, furanosesterterpens, and terpens which show similarity with the studies carried out by previous researchers.

Key Words: *Secondary metabolites, alkaloids, sponge, furanosesterterpens, terpens.*

Kemer'den Toplanan Türkiye Denizlerindeki Süngerlerde Bazı İkincil Metabolitlerin Teşhisi

Özet

Türkiye denizlerindeki süngerlerden biyoaktif maddelerin araştırılması konusunda devam eden çalışmalarımızın bir bölümünde, Kemer'den (Antalya) toplanmış beş farklı deniz süngerinde ikincil metabolitler tespit edilmiştir. Tüm tespit analizleri Axinella polypoides, Ircinia oros, Sarcotragus spinulosa, Ircinia variabilis, Agelas oroides süngerleri metanollü ekstreleri DAAD- HPLC yardımı ile tamamlanmıştır. Süngerlerde tespit edilmiş bromopirol alkaloitler, furanosesterterpenler ve terpenler önceki araştırmacılar tarafından yürütülen çalışmalar ile benzerlik göstermektedir.

Anahtar Kelimeler: *İkincil metabolitler, sünger, alkaloitler, furanosesterterpenler, terpenler.*

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INTRODUCTION

The role of natural products from all sources in drug discovery was reviewed and more comprehensive coverage has been given to plants over the last 18 years (1-3). It has been reported at least 119 compounds derived from 90 plant species, can be considered as important drugs. Further evidence of the importance of the natural products is proved by the fact that close to half of the best selling pharmaceuticals were either natural products or their derivatives (4, 5).

Marine natural products chemistry has experienced explosive growth over the last sixty years beginning with Werner Bergmann's pioneering work in 1950's, isolation of three nucleosides: spongouridine, spongothymidine and spongosine from the Caribbean sponge *Cryptotethia crpta* Laubenfels. These compounds have been models for developing the synthesized virustatic Ara-A. From the beginning of last century, ocean biodiversity estimates the number of species to range from 1.5 to 4.5 million.

Sponges have been living on the earth as organisms for several hundred million years. They are sessile, soft- bodied organisms that lack physical defense and, therefore evolved chemical defense mechanisms that produce bioactive secondary metabolites.

Under different groups of marine invertebrates and algae, the sponges are found to be the most productive and interesting sources of natural substances in the last 38 years regarding their contents (6, 7).

Since Bergmann's work, many biologically active and structurally original compounds have been discovered from sponges and many of these compounds have potential application as anticancer agents (8).

During our search for bioactive compounds from Turkish marine sponges, we have analyzed the methanolic extracts of 5 different sponge species (*Ircinia variabilis*, *Ircinia oros*, *Axinella polypoides*, *Sarcotragus spinulosa*, *Agelas oroides*, respectively) collected by scuba divers in Kemer, Antalya, Turkey.

MATERIALS AND METHODS

Materials

The sponges *Axinella polypoides, Ircinia oros, Agelas oroides, Sarcotragus spinulosa, Ircinia variabilis* were collected by scuba divers in Kemer, on the south coast of Turkey, in March 2012, and were identified by Dr. Bülent Gözcelioğlu (one of us) and the sponge samples were deposited at Ankara University, Faculty of Pharmacy, Ankara, Turkey.

Methods

Extraction of the crude extracts was carried out as described by Ebel (9). The extracts were evaporated by vacuum and lyophilized by a dry freezer. The extract yields of each sponge are as shown below:

Axinella polypoides: 1,76 g
Ircinia oros: 1,85 g
Agelas oroides: 2,99 g
Sarcotragus spinulosa: 1,73 g
Ircinia variabilis: 1,93 g

The sponge extracts were investigated for their contents of compounds by High Pressure Liquid Chromatography- Diode Array Detector (HPLC-DAD) method, given in table 1. Routine detections were at 235, 254, 280 and 340 nm. Comparison of the online-UV spectra with a spectra library facilitated the compounds detection. Samples were solved in 100 % HPLC methanol, and centrifuged prior to analysis in order to avoid particles that occlude the HPLC column. Analytical HPLC system specifications are as described below:

Table 1. Solvent system and standard gradient employed for analytical HPLC. Flow rate: 1 ml/min.

Time (min)	0.02% phosphoric acid, pH 2 (%) H_2O	Methanol (%)
0	90	10
5	90	10
35	0	100
45	0	100
50	90	10
60	90	10

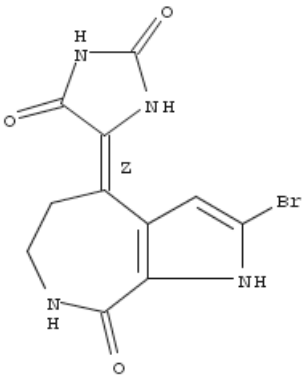
RESULTS AND DISCUSSION

Results

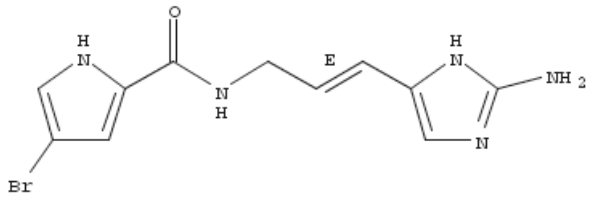
After analysis of the crude extracts of five sponge samples, some bromopyrole alkaloids, pyrol imidazole alkaloids, bromotyrozine alkaloids, indole alkaloids, furanosesterpenes, phytotoxin, and depsipeptide were detected. Detections were carried out by comparing HPLC chromatogram of crude extracts with Heinrich Heine University local library database. The detection of secondary metabolites was summarized in Table 2, chemical structures were shown in Figure 1 and HPLC profile of *Agelas oroides* was given in Figure 2.

Table 2. HPLC results of secondary metabolites from five Turkish marine sponges.

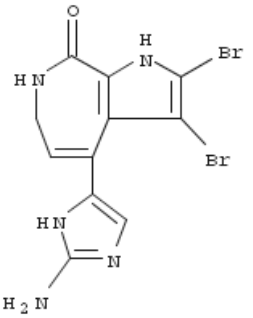
Detected Compound	Classification of Compound	Retention Time (minutes)	Sponge Species
Purealidin R	bromotyrosine alkaloid	15.14 min	*Agelas oroides*
Agelanesin A	terpene	15.74 min	*Agelas oroides*
Oroidin	bromopyrrole alkaloid	18.17 min *Agelas oroides*, 18.20min *Axinella polypoides*	*Agelas oroides*, *Axinella polypoides*
Paxilline	indole alkaloid	20.12 min	*Agelas oroides*
PC 3.3.6.8.4 F	new paraherquonin type meroterpenes	19.26 min	*Agelas oroides*
Mukanadin C	bromopyrrole alkaloid	21.87 min	*Agelas oroides*
Midpacamide	pyrrole imidazole alkaloid	23.61 min	*Agelas oroides*
Manzacidin A	bromopyrrole alkaloid	24.26 min	*Agelas oroides*
Kahalide F	Depsipeptide	8.06 min	*Sarcotragus spinulosa*
Communesin B	indoline alkaloid	35.51 min S*arcotragus spinulosa*, 35.23min *Ircinia variabilis*	*Sarcotragus spinulosa*, *Ircinia variabilis*
Cerebroside C	glycosphingolipid	39.40 min	*Sarcotragus spinulosa*
6-cyclo-S-Pro-R-Leu	proline containing dioxopiperazine	41.16 min	*Sarcotragus spinulosa*
Cyclopenol	amino acid	31.73 min	*Ircinia variabilis*
Spongiacidin D	bromopyrrole alkaloid	12.73 min	*Axinella polypoides*
Hymenialdisin	brominated alkaloid	13.37 min	*Axinella polypoides*
Hymenidin	bromopyrrole alkaloid	14.11 min	*Axinella polypoides*
Stevensin	bromopyrrole alkaloid	15.97 min	*Axinella polypoides*
Aeroplysinin-1	brominated alkaloid	35.35 min	*Axinella polypoides*
Fasciculatin	furanosesterterpene	31.98 min	*Ircinia oros*
Mauritamide	bromopyrrole alkaloid	35.35 min	*Ircinia oros*



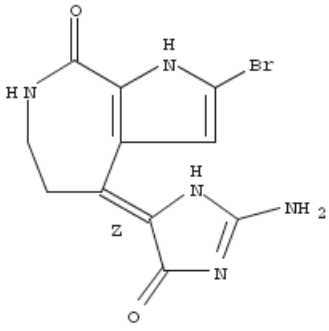
a) Spongiacidin D



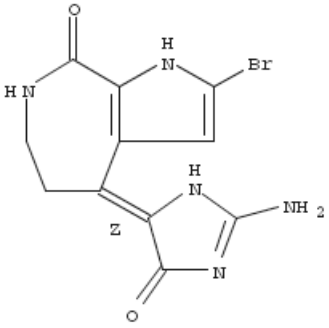
b) Hymenidin



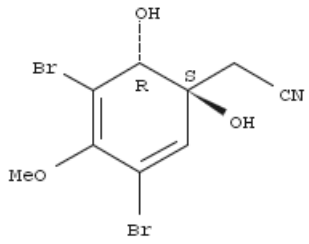
c) Oroidin



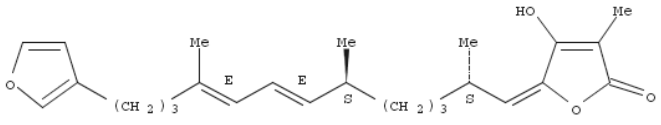
d) Stevensine



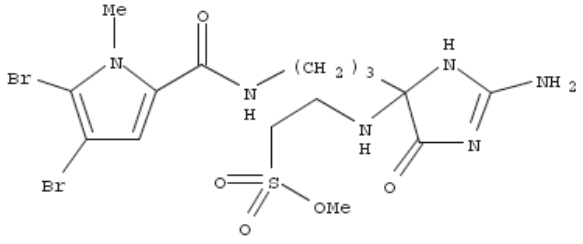
e) Hymenialdisin



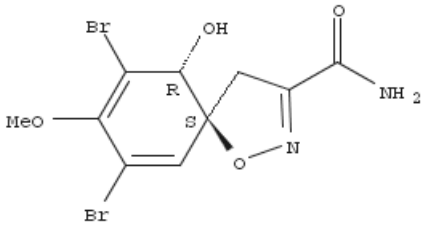
f) Aeroplysinin-1



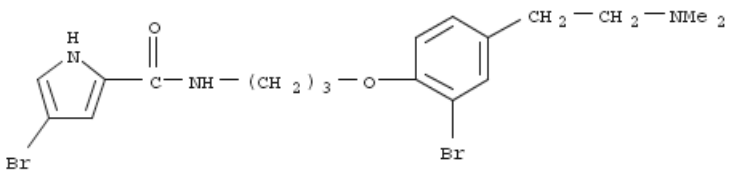
g) Fasciculatin



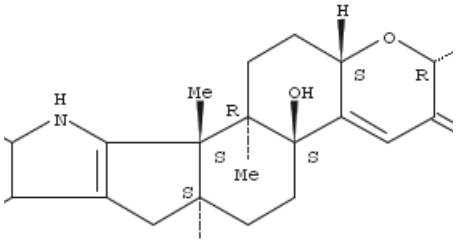
h) Mauritamide A



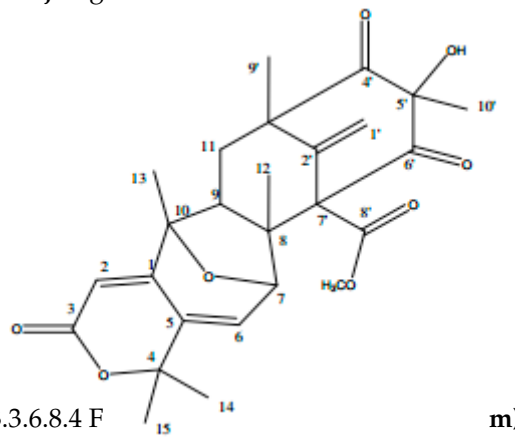
i) Purealidin R



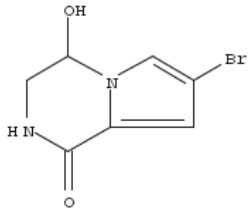
j) Agelanesidin A



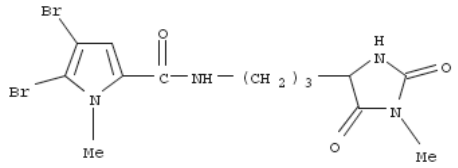
k) Paxilline



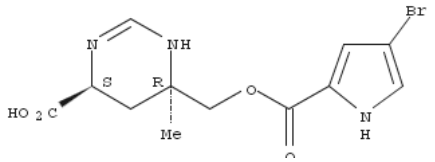
l) PC 3.3.6.8.4 F



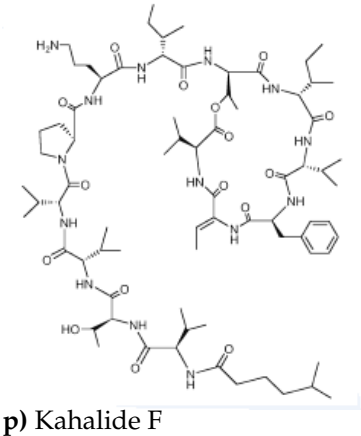
m) Mukanadin C



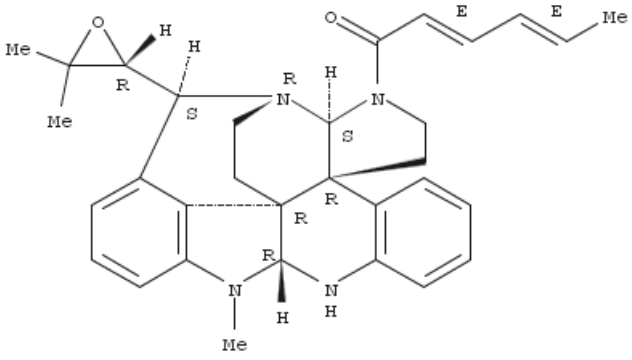
n) Midpacamide



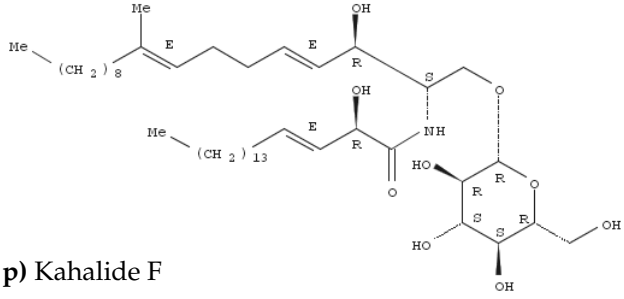
o) Manzacidin A



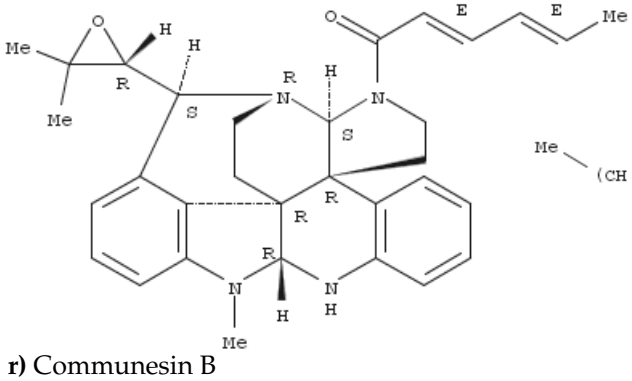
p) Kahalide F



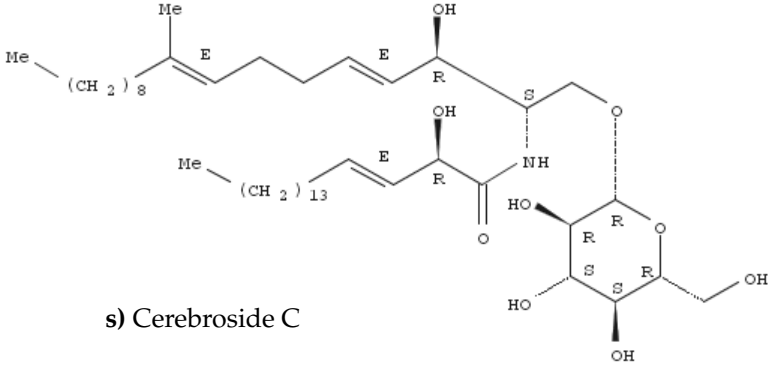
r) Communesin B



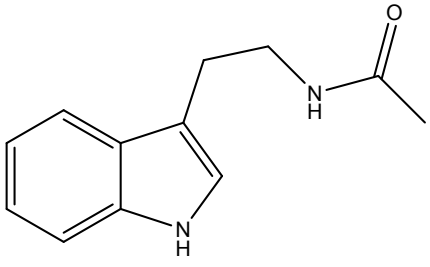
p) Kahalide F



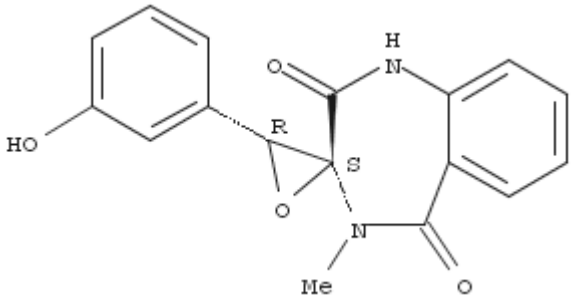
r) Communesin B



s) Cerebroside C



t) 6-cyclo-S-Pro-R-Leu



u) Cyclopenol

Figure 1. The chemical structures of detected compounds **a-u**.

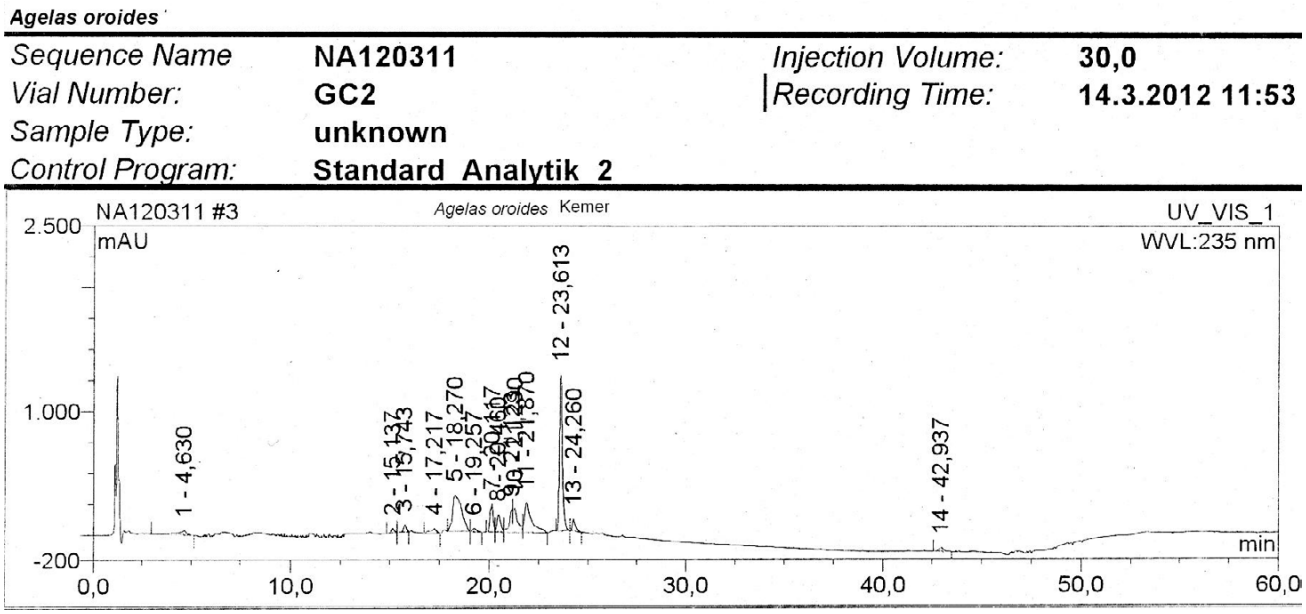


Figure 2: HPLC profile of *Agelas oroides*

DISCUSSIONS

Over the last 25 years, marine secondary products have attracted growing interest due to their unique chemical features and bioactivity of these compounds. Thousands of new marine natural products have been reported proving marine natural organisms to be rich and varied source of new structural classes of secondary metabolites (10).

Until now, there have been many papers on chemistry of the marine sponges of *Agelas*, *Axinella*, *Ircinia*, and *Sarcotragus* genera, which have also been chosen as samples of the current study. It has been reported that bromopyrrol-alkaloids, as major compounds of *Agelas* species, besides the indole alkaloids, and terpenoids have also been isolated (11-13, 27-31). *Axinella* species have been known to contain various terpene derivatives, alkaloids, cyclopeptides (14-17). Over the last 40 years, some compounds mainly furanoterpenes have been obtained from *Ircinia* species. Indole alkaloids and lipids were previously reported in *Sarcotragus* species (23, 24).

The results from this study are in accordance with previous reports on *Agelas*, *Axinella*, *Ircinia*, and *Sarcotragus* genera. Bromopyrrole alkaloids were found in *Axinella*, *Agelas, Ircinia* species. In addition to bromopyrrole alkaloids, while *Agelas oroides* contained bromotyrosine alkaloid, indole alkaloid, pyrrole imidazole alkaloid, terpene, and new paraherquonin type meroterpens, *Ircinia oros* contained furanosesterterpene and *Ircinia variabilis* comprises amino acid and indoline alkaloid. According to our data, depsipeptide, indoline alkaloid, glycosphingolipid and proline containing dioxopiperazine were detected in *Sarcoragus spinulosa*.

As a conclusion, further studies need to be carried out, in order to isolate these detected compounds. Beside the isolation, several investigations have focused on bioactive effects of compounds. In the light of these findings, we are encouraged to isolate and test bioactivity of our detected compounds.

ACKNOWLEDGEMENTS

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