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A Chemical Research on Three Red Algae *Gracilaria bursa-pastoris*, *Phyllophora crispa* and *Laurencia obtusa* var. *pyramidata*

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In this paper, the exogenic and endogenic compounds in three red algae *Gracilaria bursa-pastoris*, *Phyllophora crispa* and *Laurencia obtusa* var. *pyramidata* were reported. Exogenic compounds detected are oil components and other pollutants such as, saturated and unsaturated aliphatic, cyclic and aromatic hydrocarbons, BHT, nonyl phenol and halogenated compounds as hexachloroethane and 4-chlorophenol. Endogenic compounds were fatty acids and its esters, eicosane, squalene, phytol. The algae can be used for monitoring of the sea pollution.

Keywords: *Gracilaria bursa-pastoris*, *Phyllophora crispa* and *Laurencia obtusa* var. *pyramidata*, Exogenic, Endogenic.

INTRODUCTION

The algae contain many compounds which were biosynthesized (biogenic, autochthonous) or taken from the sea pollutants (exogenic, anthropogenous). Biogenic compounds as halogenated compounds, sulfated and nonsulfated polysaccharides are specific for algae. Marine algae also absorb many sea pollutants such as metals[1-2], radionuclides[3] and numerous organics including hydrocarbons. These exogenic compounds have been monitored in terms of marine pollution. On the other hand, the origin of some hydrocarbons in algae still remains unexplained. The main problem of chemistry of algae is to decide whether these hydrocarbons found in algae are biogenic or exogenic, for example aliphatic petroleum hydrocarbons are also synthesized by algae[4] and also taken from the sea[5-6]. This problem can be solved by showing the difference in contents of the algae collected from various polluted and unpolluted areas[7-9] but it is difficult to decide for an area which is polluted or unpolluted because today the oil contamination was demonstrated for all sea environments. Oil pollution of algae was shown by various authors[4-20]. Recently 69 aliphatic and 55 aromatic petroleum hydrocarbons were identified from the algae collected from Turkish coasts[6].

Biogenic compounds detected in *Laurencia* sp. are: squalene[13] and cytotoxic squalene derivatives in *L. obtusa*[21], phytol in *L. papillosa*[22], *L. tristicha*[23], tetradecanoic acid in *L. papillosa*[24], hexadecanoic acid in *L. nipponica*[25], octadecanoic acid in *L. pinnatifida*[26], fatty acids in *Gracilaria bursa-pastoris*[27], *Gracilaria verrucosa* and *Phyllofora nervosa*[27]. Gallaxolide® pollution was found in *L. pyramidalis*[9].

In this paper, exogenic and endogenic compounds identified in three red algae were reported.

EXPERIMENTAL

The algae collected were *Gracilaria bursa-pastoris* (S.G. Gmelin) from Sogandere (Dardanelles) in June 2007; *Phyllophora crispa* (Hudson) P.S. Dixon (Syn. *P. nervosa* D. C. Grew) from Sile (Black Sea coast) in June 2007; *Laurencia obtusa* var. *pyramidata* Bory ex J. Agardh (Syn. *Laurencia pyramidalis* Bory de Saint-Vincent ex Kützing) from Igneada (west part of Turkish Black Sea coast) in June 2007. The sampling sites are shown in the map (Fig. 1). All solvents and chemicals used were Merck products (Darmstadt, Germany).

Fig. 1. Sampling sites of the algae

Extraction: The algae sample is washed with sea water and then distilled water for elimination of sand and other foreign materials. Excess water drained from the algae and then washed with methanol. After drying the algae sample was milled. Powdered algae (60 g) was mixed 40 g anhydrous sodium sulfate and extracted with dichloromethane in soxhlet apparatus for 8 h. the extract was distilled at 40 °C. The residue was taken with 1 mL hexane and applied to GC-MS.

GC-MS analysis: HP 6890 capillary GC equipped with a split/splitless injector was used (splitless time 1 min, flow rate 1 mL min^{-1}, 29.4 psi) the injector temperature was maintained at 240 °C. The GC temperature programmed as from 50 °C (2 min) to 290 °C (15 min) at 5 °C min^{-1}. The capillary column used is PONO (HP) 60 m × 0.25 mm × 0.25 mm. The GC was coupled to an HP 5972 Mass Selective Detector. The mass spectrometer was operated under the selective ion monitoring mode and the signal was acquired on the molecule ion of the studied components. (Electron impact at 70 eV, 2000 V, 1.4 scans s^{-1}, dwell time 40 ms). The interference temperature was 290 °C.

The compounds in algal extracts were identified by comparing their spectrum on the peaks on GC with HP memory (Wiley database). Quality of identified compounds on GC-MS is varied 90-99 %.

RESULTS AND DISCUSSION

Exogenic and endogenic compounds found in examined algae are listed in Table-1. The saturated and unsaturated

TABLE-1
OIL COMPONENTS AND BIOGENIC COMPOUNDS DETECTED IN THREE RED ALGAE

Gracilaria bursa-pastoris	*Phyllophora crispa*	*Laurencia obtusa* var. *pyramidata*
Biogenic		
Dodenoic acid	Butanoic acid	Eicosane
Dodecanoic acid	Tetradecanoic acid	Squalene
Dodenoic acid ethyl ester	Hexadecanoic acid	Phytol
Hexadecanoic acid	Octadecanoic acid	Hexadecanoic acid
Hexadecanoic acid, di octyl ester		Hexadecanoic acid Palmitic acid ester
Hexadecanoic acid ethyl ester		
Octadecanoic acid		
Pentadecanoic acid		
Tetradecanoic acid		
Tetradecanoic acid ethyl ester		
Exogenic saturated		
Heptadecane	Tridecane	Heptadecane
	Tetradecane	Pentadecane
	Heptadecane	Tetradecane
	Eicosane	Heptacosane
	Tetracosane	Tetracosane
	Heneicosane	Hexacosane
	Hexacosane	Pentacosane
	Heptacosane	
Exogenic unsaturated		
	Heptadecene	9,12-Octadecadien-1-ol
		Octadecene
Cyclic		
2-Cyclohexen-1-one-2,4,4-trimethyl (3-oxo-1-butenoyl)	2,6-Di(*tert*-butyl)-4-hydroxy-4-methyl-2,5-cyclohexadiene	Cyclohexadecane
2,6-Di(*tert*-butyl-4-hydroxy-4-methyl-2,5-cyclohexadiene-1-one		
2-Cyclohexene-1-one,2,4,4-trimethyl-3-(3-oxo-1-butenyl)		
Aromatic		
Benzaldehyde	1,2-Benzenedicarboxylic acid dibutyl ester	2,4-Di-*tert*-butylphenol
cis-11*H*-benzo[a]fluoren-11-one 6a,11a-dihydro-9-methoxy-6,6a-dimethyl	3-Nitro-1,2-benzenedicarboxylic acid	2-(4*H*)-Benzofuranone
(+,-)-*cis*-3,4,6,9-Tetrahydro-10-hydroxy-1,3,8-trimethyl-1*H*-naphtha-(2,3c)-pyran-6,9-dione	Benzene acetic acid	
1,3,8-Trimethyl-1*H*-naphtho(2,3c)pyrane-6,9-dione	Benzoic acid	
9,10-Dihydro-9,9-dimethyl-anthracene	Butylated hydroxytoluene (BHT)	
Phenanthrene		
2,5-Dimethylphenanthrene	Butylated hydroxybenzaldehyde	
Dimethyldibenzothiophene	1*H*-pyrrole-2,5-dione-3-ethyl-4-methyl	
Nonyl phenol		
Butylated hydroxyl toluene (BHT)		
Chlorinated		
Hexachloroethane	4-Chlorophenol	

hydrocarbons (alkenes) found in the examined algae are also as a result of sea pollution. Decane series hydrocarbons in *L. papillosa* and *L. coronopus* and cosine series in *L. coronopus* were found[22]. We found these series in *L. obtusa* var. *pyramidata* and *P. crispa* and only heptadecane in *G. bursa-pastoris*.

Three cyclic alkene derivatives were identified in the same algae. Anthracene, phenanthrene and its derivative and dimethyl benzthiophene which are found in the examined algae, are polyaromatic hydrocarbons and they are very toxic to the environment. Nonyl phenol was found in *G. bursa-pastoris* in this study and it was also found in seawater[29], in brown algae *Dilophus fasciola*[30]. It is also very toxic and a degradation product of non-ionic surfactants nonyl phenol-poly-ethoxylates which is widely used world-wide in detergents, cosmetics, water based paints, inks and textiles.

As indicated in the introduction, many chlorinated aliphatic compounds are endogenous for algae[31] but hexachloroethane which is found in this work, also known as perchloroethane is used in military purposes. 4-chlorophenol is used for synthesis of dyes and drugs and refining of mineral oils. The origin of these halogenated compounds found in *G. bursa-pastoris* is unknown.

Butylated hydroxyl toluene is used as a food antioxidant additive for preservative purposes was found in *G. bursa-pastoris* and *P. crispa*.

As can be seen in the Table-1, comparison of contamination in collected algae *G. bursa-pastoris* was found more polluted.

Biogenic compounds phytol, squalene and some fatty acids and their esters were found in examined algae. Of those, phytol is unsaturated alcohol derivated from hydrolysis of chlorophyll. It is precursor of pristane which is used for identification of oil pollution in algae. Phytol was previously found in *L. papillosa* and *L. coronopus*[22]. In addition, squalene which is the precursor of cholesterol is found in algae by Rossi *et al.*[13]. The determined fatty acids were commonly found in algae[22, 24-28, 30].

The algae can be used for monitoring the sea pollution but it is difficult to decide whether some hydrocarbons found in algae are biogenic or exogenic.

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