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RESEARCH ARTICLE

Endogenic loliolide, phenylethylamine and exogenic compounds in marine algae

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Abstract

Endogenic compound loliolide in marine algae *Laurencia obtusa* var. *pyramidata*, *Chondria capillaris*, *Ceramium rubrum*, *Cystaseira barbata*, *Ulva rigida*, and *Ulva intestinalis* and phenylethylamine in *Chondria capillaris* were found. Exogenic compounds were mainly petroleum components and phthalate derivatives. These findings are reported for the first time for the examined algae. These algae are eaten in some eastern Asian countries but its human consumption is not recommended because they potentially absorb many pollutants from the aquatic environment.

Keywords: algae, loliolide, phenylethylamine, exogenic, GC-MS

Introduction

(-)-Loliolide, (6*S*-*cis*)-5,6,7,7*a*-tetrahydro-6-hydroxy-4,4,7*a*,trimethyl-2-(4*H*)-benzofuranone, (Figure 1) is a monocyclic terpenoid. It is a biodegradation product of caretonoids (Klock *et al*. 1984). It was first isolated from alga *Undaria pinnatifida* (Takemoto and Takeshita 1970; Kimura and Maki 2002) and later from various marine algae such as *Centroceras clavulatum* (Rocha *et al*. 2011), *Chaetomorpha basiretorsa* (Shi *et al*. 2005), *Cladostephus spongiosus f. verticillatus* (El Hattab *et al*. 2008), *Corallina pilulifera* (Yuan *et al*. 2006), *Cystophora moniliformis* (Ravi *et al*. 1982), *Dictyota dichotoma* (Ali *et al*. 2003), *Galaxaura filamentosa* (Rasher *et al*. 2011), *Gracilaria lemaneiformis*

(Lu *et al*. 2011), *Jolyna laminarioides* (Khan *et al*. 2011), *Padina tetrastromatica* (Rao and Pullaiah 1980; Parameswaran *et al*. 1996), *Pterocarpus indicus* (Ragasa *et al*. 2005), *Sargassum crassifolium* (Kuniyoshi 1985), *Sargassum thunbergii* (Park *et al*. 2004; Qin *et al*. 2007), *Stockeyia indica* (Shah 1990; Shaikh 1993; Attaurrahman *et al*. 1991). In our earlier work, loliolide was determined in red algae,: *Gelidium crinale*, *Corallina granifera*, *Phyllophora crispa*, *Polysiphonia morrowii, Halymenia floresii*, *Hypnea musciformis*, *Boergeseniella fruticulosa*, brown algae: *Dictyota dichotoma, Cutleria multifida*, *Sporochnus pedunculatus*, *Cystoseira mediterranea*, *Taonia atomaria*, and green algae: *Enteromorpha compressa* (Percot *et al*. 2009a).

In the last years, loliolide has attracted attention of many researchers because of its origin and biological activities such as cytotoxic (Xian *et al*. 2006), ant-repellant (Okunade and Wiemer 1985; Liu *et al*. 1988), germination inhibitor (Hiraga *et al*. 1997; Kato *et al*. 2003; Ragasa *et al*. 2005), immunosuppressive (Okada *et al*. 1994; Duan *et al*. 2002), antioxidative (Yang *et al*. 2011), and melanine formation inhibitor (Ishiwatari and Ono 2008).

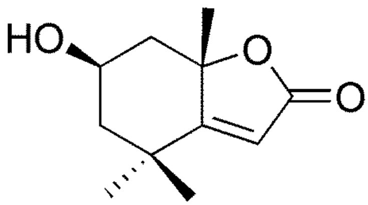

Figure 1. The structures of loliolide

Phenylethylamine (PEA) contains benzene ring attached ethylamine side chain. It is derived from tyrosine and is precursor of many alkaloids. It was found in terrestrial plants (Smith 1977) and in algae *Desmerestia aculeata* (Steiner and Hartman 1968). In our earlier work PEA was found in two green, five brown and ten red algae (Percot *et al*. 2009b). PEA derivative was known to have psychoactive effects (Sabelli *et al*. 1996).

The main exogenic compounds in algae are petroleum derivatives, industrial chemicals, phthalates, minerals.

In this paper, we reported loliolide, phenylethylamine and pollutants as contents of algae collected from the Black Sea, Bosphorus (Istanbul Strait) and Dardanelles (Canakkale Strait).

Materials and Methods

The sites (Figure 2) and dates of the algae collection are: *Laurencia obtusa* (Hudson) J. V. Lamouroux from İğneada (west part of Turkish Black Sea coast, near Bulgarian border) on 20.04.2007; *Ceramium virgatum* Roth (Syn. *C. rubrum*) C. Agardh from Garipçe, Bosphorus on 30.04.2007; *Chondria capillaris* (Hudson) M.J. Wynne from Soğandere, Dardanelles on 04.04.2007; *Cystoseira barbata* (Stackhouse) C. Agardh from Garipçe, Bosphorus on 30.04.2007; *Ulva linza* Linnaeus (*E. linza*) from Garipçe, Bosphorus on 30.04.2007;*Ulva rigida* C. Agardh from Garipçe, Bosphorus on 30.04.2007.

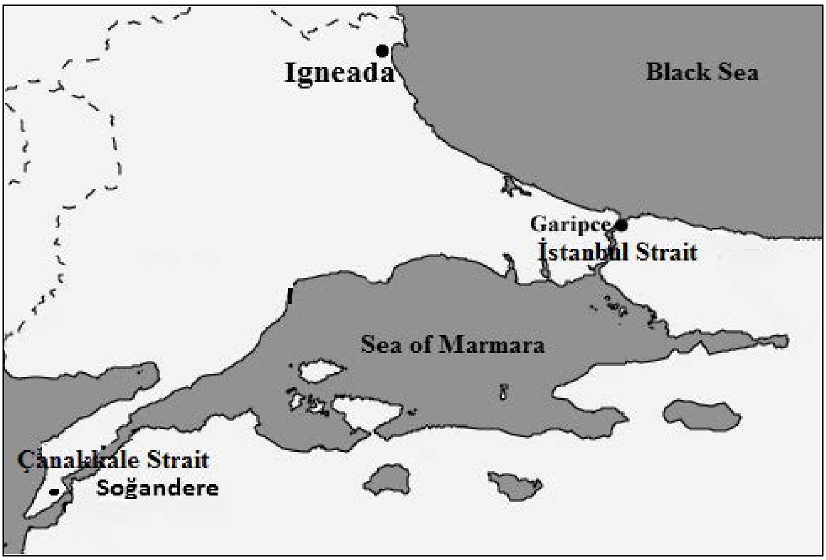

Figure 2. The collection sites of the algae

All solvents and chemicals were supplied from Merck (Darmstadt, Germany). Reference compounds loliolide and phenylethylamine were obtained from Firmenich Inc, USA and Aldrich, Bornem, Belgium, respectively.

The algae sample was washed first with sea water, then with distilled water for elimination of sand and other loose materials. Dried alga sample (60 g) was milled and mixed with 20 g anhydrous sodium sulphate and extracted with dichloromethane in soxhlet apparatus for 8 hours. The extract was distilled at 40°C. The residue was taken with 1 ml hexane and applied to GC-MS apparatus.

The gas chromatography mass spectrometer (HP 6890 Series GC system; Hewlett Packard, Wilmington, DE, USA) was fitted with an electronic pressure control, a mass selective detector (HP 5972A; ionization energy: 70 eV; source temperature 280 ^{o}C) and HP-PONA capillary column (50 m x 0.25 mm i.d., 0.25 µm film thickness). The chromatographic conditions were: sample size 2 µl, injection port temperature 280 ^{o}C, configured for split injection; initial oven temperature 40 ^{o}C rising to 280 ^{o}C at 8 ^{o}C/min, final hold for 20 min. Helium was used as carrier gas (1 ml/min).

Results and Discussion

GC-MS results

Mass spectra of the detected compound from examined algae and the reference compound loliolide is summarized in m/z as: 196 [M^+], 178 [M-H_2O], 163 [M-CH_3], 153, 140, 135 [M-CO], 111 (base peak), 95, 67, 57, 43. Phenylethylamine 121 [M^+], 91, 77, 65, 51. The comparison of the spectrum of examined algae with the MS library and published data (Crotti *et al*. 2004) and retention time of the reference compounds proved the presence of loliolide and phenylethylamine in the examined algae.

Exogenic compounds: Petroleum derivatives as cyclotetradecane, tetracosahexaene, hexatriacontane were found in *L. obtusa*, phenanthrene (2,5-dimethyl), anthracene, anthracene (2-methyl and 9-methyl), norpristan were detected in *Ceramium virgatum*. Various cyclic aliphatics, alkenes, naphthalene were found in *C. barbata*, tribromophenol in *U. rigida* and *U. linza*.

Phthalate derivatives: DIBP, DBP, DEHP, DEP were found in all tested algae. As a result of pollution petroleum derivatives and phthalates are dominant pollutants in examined algae. In addition to these pollutants endogenic compounds loliolide, phenylethylamine and C_6-C_{16} fatty acids were detected.

Conclusions

As indicated in introduction, some exogenic compounds as phthalate derivatives DBT, DIBP, DEHP were found in examined algae. Petroleum derivatives as aliphatic hydrocarbons C_3-C_{17} and poly-aromatic anthracene and phenanthrene derivatives were detected in the algae tested. Petroleum pollution was found in algae for the first time by George (1961). Concentrations of petroleum derivatives were increasingly raised (Guven *et al*. 2009).

The origin of some organic compounds were not found such as 1-4 pyrrole-2,5-dione-3-ethyl-4-methyl4-methoxy in *C. capillaris*, *L. obtusa*, *C. barbata* and *U. linza*.

In this work, loliolide and phenylethylamine content of the sampled algae were reported for the first time. The algae tested were eaten in some eastern Asian countries and we suggest that it is more appropriate to collect algae from non-polluted areas for human consumption because they potentially absorb many pollutants from the surrounding aquatic environment.

Deniz alglerinin endojenik Loliolid, Feniletilamin ve ekzogenik bileşikler içeriği

Özet

Deniz algleri *Laurencia obtusa* var. *pyramidata*, *Chondria capillaris*, *Ceramium rubrum*, *Cystaseira barbata*, *Ulva rigida*, ve *Ulva intestinalis*'te loliolide ve *Chondria capillaris*'te phenylethylamine endojen bileşikler olarak tespit edilmiştir. Bu alglerde tespit edilen eksojen bileşikler ise petrol bileşikleri, fitalatlar ve diğerleridir. Bu bulgular ilk defa bu alglerde tespit edilmiştir. Bu algler potansiyel olarak deniz ortamındaki kirleticileri absorbe ettikleri için bazı doğu Asya ülkelerinde yiyecek olarak tüketmek amacıyla toplanması tavsiye edilmez.

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