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Original Article

Brazilian gorgonians: a source of odoriferous compounds?

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ABSTRACT

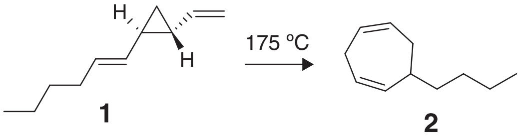
The gorgonian *Phyllogorgia dilatata* Esper is an octocoral known to be source of biologically active terpenes. In this study, odoriferous compounds present in *P. dilatata* tissues were investigated, due to their exotic olfactory notes. The search of volatile compounds was performed in a dichloromethane/methanol extract submitted to a silica gel vacuum chromatography and HPLC, yielding the isomers (*Z*,*E*) and (*E*,*E*)-germacrones, identified by GC/MS, 1 and 2D NMR. The stereochemistry of (*E*,*E*)-germacrone, as well as its preferred conformation, was confirmed by NOESY. Sensory analysis of the two isomers revealed a fragrant, citrus, woody and weak marine odor, similar to the odor of the natural gorgonian, and (*E*,*E*)-germacrone has a three times more intense aroma than the (*Z*,*E*) isomer.

Introduction

A typical marine sea-breeze has interesting nuances to perfumery and awakens a sense of peace, well-being and lightness of the sea, which is a pleasant characteristic for those who appreciate the beauty and cooling sensation caused by marine atmosphere.

Marine trend is considered recent compared to all scents present in traditional perfumery (Kraft et al., 2000), such as amber and musk, perhaps the oldest fragrances used in religious traditions of ancient cultures, culinary and beautification.

The first studies on the description of marine-smelling molecules dated from late 1960s, with brown algae and their pheromones (Moore, 1977). (+)-Dictyopterene A (**1**), which possesses a characteristic odor of seawater, was the first odoriferous hydrocarbon isolated from *Dictyopteris* sp. algae (Moore and Pettus, 1968). Cope rearrangement of **1** gives (−)-dictyotene isomer (**2**), which was also found in marine brown algae (Ohloff and Pickenhagen, 1969). The odor of **2** is fishy, somewhat reminiscent of salmon roe. Other sea-algae odor hydrocarbons, responsible for the chemical communication in algae, are giffordene (**3**), isolated from *Giffordia mitchellae* (Boland et al., 1987) and ectocarpene (**4**) isolated from the brown algae *Ectocarpus siliculosus* (Mueller et al., 1971).



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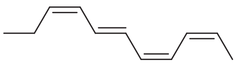

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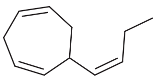

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Chemical substances that smell like marine sea-breeze are mainly associated to four groups of organic compounds from natural or synthetic origin. The first group belongs to the cyclic and alicyclic C_{11} hydrocarbons just shown, that act as pheromones (**1**, **2**, **3** and **4**). The second group is represented by polyunsaturated aldehydes, such as (*E*,*Z*)-2,6-nonadienal (**5**) (Triqui, 2006) from the degradation of fatty acids, as also the synthetic Melonal® (**6**). The third group is constituted by synthetic benzodioxepanes as Calone 1951® (**7**), a very unusual structure in fragrant substances that was patented by Pfizer in 1969

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[1] In memoriam.

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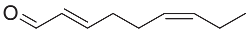
(Beereboom et al., 1969). It is considered the basis of all marine accords and often blended with different ozonic, aldehydic or watermelon-like odorants in order to induce olfactory impression of seashore (Kraft et al., 2000). Since then, many new benzodioxepanones were prepared to study their odor-structure correlation (Kraft and Eichenberger, 2003). Halogenated phenols consist the fourth group and have been considered the main component of the flavor of several seafoods (Chung et al., 2003), specifically bromophenols, exemplified by 2-bromophenol (**8**) (Boyle et al., 1992).



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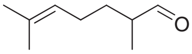

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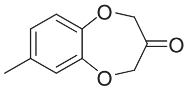

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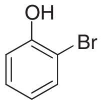

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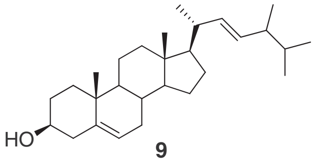
Brazil is blessed with an extensive coast (more than 7500 km) and great biodiversity, but assessments of their natural products have been largely underexplored (Berlinck et al., 2004). The birth of marine natural product chemistry started in 1950 with Werner Bergmann studies (Beedessee et al., 2015). Since then, marine organisms have been recognized to be a rich source of sophisticated chemical structures and biologically active compounds (Beedessee et al., 2015), especially with pharmaceutical properties (Rocha et al., 2007; Stein et al., 2011; Caccamese and Toscano, 1982) and ecological activities (Paul and Ritson-Williams, 2008; Paul et al., 2011). *Gorgonian octocorals* (Gorgonacea, Octocorallia) are a unique group of marine cnidarians, which thrive in tropical to warm temperate oceans, being most abundant and diverse in shallow waters. Notably, the family Gorgoniidae is one of the most abundant in Brazil and a rich source of steroids, sesquiterpenes and diterpenes (Almeida et al., 2014).

Roussis et al. (2000) observed that gorgonians have peculiar aromas, and in their work they tried to identify volatile secondary metabolites to evaluate their potential as taxonomic marker. The *Pseudopterogorgia* species were also described by McEnroe and Fenical (1978) to possess significant differences in their odor; *P. americana*, for example, has a strong smell of lemon, not observed in other *Pseudopterogorgia* species. These authors attributed the odors to the presence of volatile sesquiterpenes.

Up to now, there are no data in literature that address the application of olfatometry techniques to study tropical gorgonians and their extracts, in order to assess the contribution of odorants in these organisms.

Phyllogorgia dilatata Esper (Gorgonacea, Gorgoniidae) is a Brazilian endemic gorgonian, distributed along the southwest Atlantic from Ceará State to Rio de Janeiro, Brazil (Castro, 1990). Chemical composition of *P. dilatata* was first described by Kelecom and collaborators in 1980, who isolated the sterol 23,24-dimethylcholesta-5,22-dien-3β-ol (**9**) (Kelecom et al., 1980). Later, the occurrence of nardosinane sesquiterpenes (**10** and **11**) (Kelecom et al., 1990; Fernandes and Kelecom, 1995), the germacranes (*Z*,*E*)-germacra-1(10),4,7(11)-trien-8-one (**12**), 4,5-epoxygermacra-1(10),7(11)-dien-8-one (**13**) (Maia, 1991), (*E*)-germacra-1(10),4(15),7(11)-trien-5-ol-8-one (**14**) (Martins and Epifanio, 1998), the diterpene 11β,12β-epoxypukalide (**15**) (Martins and Epifanio, 1998), besides the carotenoids peridinin (**16**) (Epifanio et al., 1999; Martins and Epifanio, 1998; Maia et al., 2012), diadinoxanthin (**17**) (Maia et al., 2013), the polyenal (**18**) (Maia et al., 2012) and a 5 kDa peptide **19** (de Lima et al., 2013) was reported.



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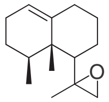

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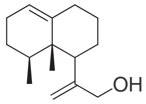

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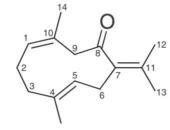

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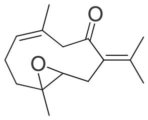

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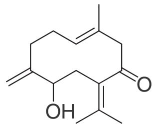

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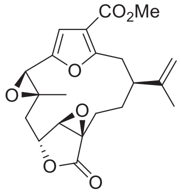

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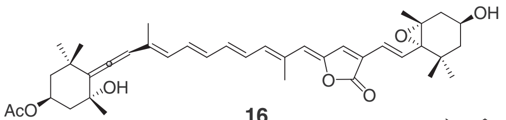

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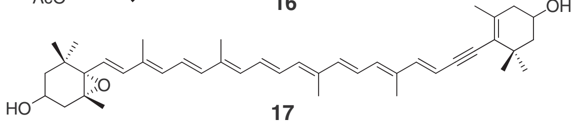

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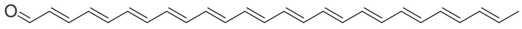

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AKIPGIDQPGCNRQCDVDNDNCCSGYTCQ

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In this work, we report the structure elucidation of the isomers (*Z*,*E*) and (*E*,*E*)-germacrones (**12**) and (**24**), respectively, as well as its contribution to the characteristic citrus, fragrant, slightly woody and marine odor exhaled from *P. dilatata* tissues, performed by a combination of NMR, GC/MS, HPLC and olfactory sensory evaluation.

Materials and methods

Collection of animal material

The gorgonian *Phyllogorgia dilatata* Esper (Octocorallia Gorgonacea) was collected at Tartaruga Beach, Armação dos Búzios, Rio de Janeiro State, Brazil (220 45″ S, 410 53″ W) by snorkel diving, whose depth ranged from 1 to 3 m, in October 2005. Data collection was performed by Dr. Rosângela A. Epifanio and identified as previous work (Martins, 1997; Epifanio et al., 2006). A voucher specimen (PD1295) was deposited at IQ-UFF. The collected material was immediately frozen at −18 °C until processing.

Preparation and fractionation of crude extracts

P. dilatata (699.5 g) was cut into small pieces and extracted four times with a solution of dichloromethane/methanol (Tédia, Brazil) 1:1 for 20 min in ultrasound bath (Bransonic 3210). The solvent was removed under reduced pressure in a rotary evaporator (Buchi R-114) yielding a viscous dark brown colored oil (52 g, 7.7% wet weight). A portion of the crude extract (25.4 g) was fractionated by silica gel (300 mesh) vacuum flash chromatography,

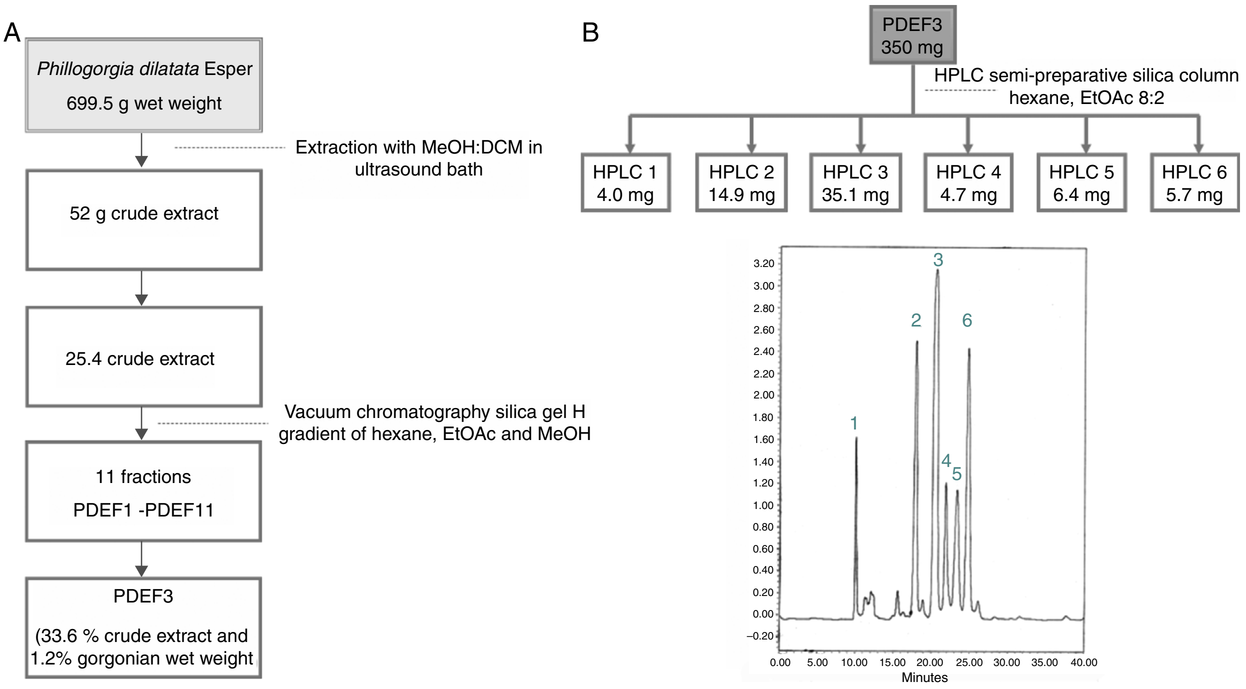


Fig. 1. (A) Fluxogram showing the methodology used for the extraction and fractionation of *Phyllogorgia dilatata*. (B) Chromatogram of PDEF 3 fractionation in HPLC (photodiode detector 220–440 nm).

employing hexane, ethyl acetate (AcOEt) and methanol (MeOH) to yield sixteen fractions (300 ml each). These fractions were analyzed by thin layer chromatography (TLC) on silica gel Plates 60 F254 (Merck), which were observed under ultraviolet light (254/365 nm) and then sprayed with sulfuric acid 50% (v/v) with subsequent heating. After inspection of each fraction by TLC, compounds with similar retention factor (R_f) were combined and the fractions were named as PDEF 1–11. Fraction PDEF 3 (5:95, ethyl acetate:hexane) was submitted to HPLC and GC/MS showing the presence of (*Z*,*E*)-germacra-1(10),4,7(11)-trien-8-one (**24**) and (*E*,*E*)-germacra-1(10),4,7(11)-trien-8-one (**25**).

High performance liquid chromatography (HPLC)

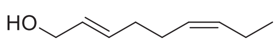
The HPLC analyses were performed on a Waters 510 chromatograph with a photodiode detector (PDA 996, Waters), a semi-preparative silica column Costil LC Si (10 mm × 25 cm × 5 μm), Rheodyne 7725i injector with 200 μl loop. Fractionation of PDEF3 was performed with isocratic elution system with 2% ethyl acetate in hexane (Vetec, Brazil) at a flow rate of 1.5 ml/min. Masses and yields are shown in Fig. 1.

Gas chromatography/mass spectrometry (GC/MS)

GC/MS was performed in a gas chromatograph Agilent 6890 with mass detector 5973 and capillary column DB5 (30 mm × 0.25 mm × 0.25 μm, J&W). Two milligrams of each sample were dissolved in 1 ml of hexane. The initial temperature was set at 80 °C and followed by a heating rate of 4 °C/min to attain a final temperature of 270 °C, which remained constant for 5 min. The temperature of the injector and transfer line were 260 and 280 °C, respectively, and the injection mode is downflow without division by 0.5 min. The carrier gas used was helium (1.0 ml/min) and the delay time was 8 min. The ion source was maintained at 260 °C, operating at 70 eV in scan and 280 °C in transfer line. Mass spectra were obtained in the range of 50–600 Da. Wiley 275 Library (6th ed., version G1034C Hewlett-Packard C0300-1984-1994) and NIST (Version 2.0 – Faircom Corporation 1984–2002) mass database were used.

Sensory analysis

Five experienced panelists were trained on olfactory descriptive terminology, twice a day for two weeks, with six marine odor substances (**5**, **6**, **20**, **21**, **22** and **23**) by the use of paper strips of 6 cm long, 2 cm wide, in different concentrations of ethanolic solutions, in air-conditioned laboratory and without interference of external odors (Delahunty et al., 2006). After that, the volunteers were asked to evaluate six blind standards solutions of **5**, **6**, **20**, **21**, **22** and **23** in different concentrations, in triplicate. The standards were provided by Givaudan, IFF and Vitta Flavour. Nonadienal (**5**) is described as intense, green, cucumber, melon; melonal® (**6**) has an intense odor, green, melon and cucumber; nonadienol (**20**) is intense, with sweetened, green, herbal and melon aspects; cyclemone® has (**21**) marine notes, fruity, woody, herbaceous; ozofleur® (**22**) is green, floral, marine, fruity and floralozone® (**23**) has floral, aldehydic, marine notes.



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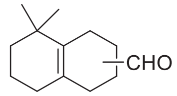

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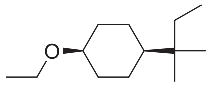

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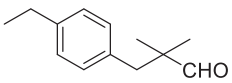

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The order of the standards was changed randomly every session and the analysis of records was evaluated according to the hit rate and individual standard deviation (less than 10%). This group also evaluated the extracts and gorgonian PDEF fractions 1–11, and the HPLC fractions 1–6, for descriptive olfactory sensory analysis as previously (Delahunty et al., 2006).

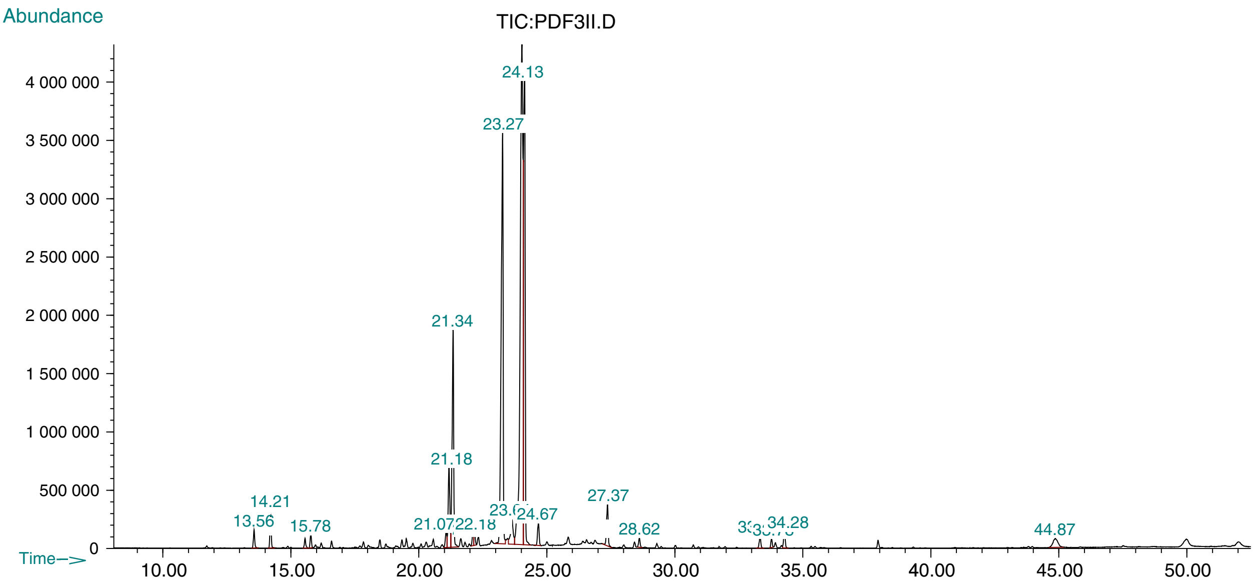


Fig. 2. GC/MS chromatogram of PDEF 3 fraction.

After purification of (*E*,*E*)- and (*Z*,*E*)-germacrones, they were individually evaluated in a 1 mg ml^{-1} ethanolic solution, in paper strips, also for descriptive olfactory sensory analysis.

Nuclear magnetic resonance ^{1}H and ^{13}C

The NMR spectra were recorded on a Bruker AC-300 instrument operating at a frequency of 300–75 MHz for hydrogen and carbon, respectively. Fraction HPLC3 was analyzed by ^{1}H and ^{13}C NMR (fully decoupled and DEPT-135). The 2D NMR spectra (HMQC, HMBC, ^{1}H–^{1}H COSY and NOESY) were recorded. Fraction HPLC2 was submitted to 1D ^{1}H and ^{13}C NMR. Chemical shifts (δ) were taken in ppm with the reference to tetramethylsilane or chloroform as internal standard and coupling constant (*J*) reported in Hertz.

(Z,E)-Germacra-1(10),4,7(11)-trien-8-one
[(12),(Z,E)-germacrone]

15 mg. Colorless viscous material. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.58 (3H, s, H-15); 1.67 (3H, s, H-12); 1.74 (3H, s, H-13); 1.88 (3H, s, H-14); 1.96–2.02 (2H, m, H-2); 3.06 (1H, s, H-9); 2.93 (1H, m, H-6); 5.06 (1H, dd, H-5 *J* = 8.0 and 1.5 Hz, H-5); 5.29 (1H, dd, H-1 *J* = 8.0 and 1.3 Hz, H-1). RMN ^{13}C (75 MHz, $CDCl_3$) δ: 18.1 (C-15); 19.8 (C-13); 22.4 (C-12); 25.6 (C-14); 28.5 (C-2); 28.6 (C-6); 37.5 (C-3); 48.1 (C-9); 121.7 (C-5); 126.2 (C-1); 126.9 (C-10); 132.5 (C-7); 136.4 (C-4); 136.6 (C-11); 211.7 (C-8); MS (EI, 70 eV) *m*/*z* (% rel.): 218 (M^{+}, 10), 203 (8), 175 (20), 136 (82), 135 (84), 121 (26), 107 (100), 91 (29), 79 (17), 67 (43). Odor: lower intensity, fragrant, marine, slightly woody with distinct citrus aspects.

(E,E)-Germacra-1(10),4,7(11)-trien-8-one
[(24)(E,E)-germacrone]

35 mg. White solid. Mp 47–48 °C ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.42 (3H, s, H-15); 1.61 (3H, s, H-14); 1.71 (3H, s, H-13); 1.76 (3H, s, H-12); 2.05 (1H, m, H-2a); 2.10 (2H, m, H-3ab); 2.36 (1H, m, H-2b); 2.84 (1H, m, H-6a); 2.93 (1H, m, H-9a); 2.94 (1H, m, H-6b); 3.39 (1H, d, *J* = 10.5 Hz, H-9b); 4.69 (1H, dd, *J* = 11.1 and 2.9 Hz, H-5); 4.97 (1H, d, *J* = 11.0 Hz, H-1). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 15.7 (C-15); 16.8 (C-14); 20.0 (C-12); 22.5 (C-13); 24.2 (C-2); 29.4 (C-6); 38.2 (C-3); 56.0 (C-9); 125.5 (C-5); 126.8 (C-10); 129.6 (C-7); 132.8 (CH-1); 135.1 (C-4); 137.4 (C-11); 208.0 (C-8). EM (EI, 70 eV) *m*/*z* (% rel.): 218 (M^{+}, 12), 203 (8), 185 (7), 175 (25), 161 (6), 147 (12), 136 (62), 135 (83), 121 (31), 107 (100), 91 (31), 79 (18), 67 (42), 53 (15), 41 (17). Odor description: very intense, fragrant, marine, slightly woody with distinct citrus aspects.

Results and discussion

In this work, the use of volatile extraction techniques such as steam distillation of Clevenger type and simultaneous extraction-distillation (SDE), as reported in previous work by Roussis et al. (2000) for marine organisms, showed to be unsuitable. Animal samples submitted to heat showed a darkening of the tissue and an unpleasant odor, resembling a cooked matter, which has a quite distinct aroma from the fresh organism. In contrast, vacuum chromatography on silica gel methodology was used, as shown in Fig. 1A, with the aid of hexane, ethyl acetate and methanol. These eluents gave sixteen fractions that were joined by TLC to give PDEF 1–11 fractions (Fig. 1A), evaluated by descriptive olfactometric analysis. One of them obtained from an ethyl acetate:hexane (5:95) fraction (PDEF 3), revealed an intense citrus, fragrant, woody and marine odor, similar to the observed in the fresh gorgonian. PDEF 3 was evaluated for its chemical composition.

PDEF 3 fraction showed, by GC/MS (Fig. 2), mainly three oxygenated sesquiterpenes with a molecular mass *m*/*z* 218 (t_R 21.34, 23.27 and 24.13 min). The mass spectrum showed similar ions with *m*/*z* 136, 135, 121 and 107, varying in relative abundance. The comparative analysis with database spectral libraries suggested the presence of β-elemenone and major peaks belonging to germacrones.

Thus, PDEF 3 fraction was subjected to semi-preparative HPLC-UV in normal phase, with a gradient of hexane/ethyl acetate, providing six fractions (HPLC 1–6), as shown in Fig. 1B. Descriptive olfactometric evaluation of the fractions showed that HPLC 3 and HPLC 2 had the most intense aroma and so were separated for detailed analyses. GC/MS of HPLC 3 suggested the presence of (*E*,*E*)-germacrone together with β-elemenone. As known, germacrone can undergo Cope rearrangement when subjected to high temperatures, leading to β-elemenone, which could explain its presence in GC due to the heated injector (Takeda et al., 1973). 1D ^{1}H and ^{13}C NMR spectral analysis of fraction HPLC 3 showed only one compound, confirming that β-elemenone is a temperature artifact and so not present in this fraction.

Due to previous descriptions of germacrone isomers in gorgonian species (Roussis et al., 2000), ^{1}H–^{1}H NOESY and ^{1}H–^{13}C

Table 1
^{1}H and ^{13}C NMR from (*E*, *E*)-germacrone (**24**).

C/H	δ ^{13}C (CH_X)[a]	δ ^{1}H (nH, m, *J* Hz)[b,c]	^{1}H–^{1}H COSY	HMBC H $^{2,3}J_{CH}$
1	132.8 (CH)	4.97 (1H, d, *J* = 11.0 Hz)	2a; 2b; 14	9b; 14
2a	24.2 (CH_2)	2.05 (1H, m)	2b; 3	
2b		2.36 (1H, m)	1; 2a; 3	
3	38.2 (CH_2)	2.10 (2H, m)	2a; 2b	15
4	135,1 (C)			6b; 15
5	125.5 (CH)	4.69 (1H, dd, *J* = 11.1 and 2.9 Hz)	6a; 6b; 15	3; 15
6a	29.4 (CH_2)	2.84 (1H, m)	5; 6b; 15	
6b		2.94 (1H, m)	5; 6a;	
7	129.6 (C)			12; 13
8	208.0 (C)			9a; 9b
9a	56.0 (CH_2)	2.93 (1H, m)	9b	14
9b		3.39 (1H, d, *J* = 10.5 Hz)	9a	
10	126.8 (C)			9b; 14
11	137.4 (C)			12; 13
12	20.0 (CH_3)	1.76 (3H,s)		12
13	22.5 (CH_3)	1.71 (3H,s)		13
14	16.8 (CH_3)	1.61 (3H,s)	1	9a; 9b
15	15.7 (CH_3)	1.42 (3H,s)	5; 6a	

[a] H number with the aid of DEPT 135.
[b] With HMQC.
[c] nH = n° of H; m = multiplicity.

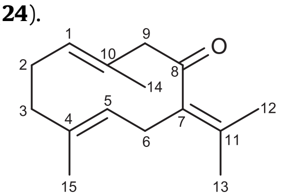
Table 2
^{13}C NMR of (*E*, *E*), (*Z*, *E*) and (*Z*, *Z*)-germacrones (Simova et al., 1984).

No. C	δ ^{13}C RMN		
	(*E*, *E*)	(*Z*, *E*)	(*Z*, *Z*)
1	132.6	126.0	127.2
2	24.2	28.4	25.6
3	38.2	37.5	30.6
4	13.7	136.5	137.2
5	125.5	121.6	122.3
6	29.2	28.8	29.1
7	129.0	132.5	136.4
8	207.0	210.5	207.1
9	55.8	47.9	47.2
10	127.0	126.5	131.7
11	137.5	136.5	137.6
12	22.2	22.1	22.6
13	19.8	19.8	21.1
14	16.7	25.4	24.8
15	15.6	17.9	23.9

Table 3
^{13}C NMR of (*Z*, *E*)- germacrone isolated from *Phyllogorgia dilatata*.

No. C	(*Z*, *E*)
1	126.2
2	28.5
3	37.5
4	136.4
5	121.7
6	28.6
7	132.5
8	211.7
9	48.1
10	126.9
11	136.6
12	22.4
13	19.8
14	25.6
15	18.1

HMBC experiments were performed to allow the complete assignment and characterization of the correct isomer (supporting information in Supplementary Material). Besides, the comparison of NMR spectra with literature data (Takahashi et al., 1983; Yang et al., 2007) indicated that the isomer present in this fraction was (*E*,*E*)-germacrone (**24**).



24

Germacrone isomers (*E*,*E*), (*Z*,*E*) and (*Z*,*Z*) present some typical NMR effects of shielding and deshielding due to double bond geometry (Supplementary material, Tables 1 and 2). The double bond positioned between C-1 and C-10 forces a shielding effect in C-9 in isomers (*Z*,*E*) and (*Z*,*Z*) (δ 47.9 and 47.2, respectively), while in (*E*,*E*) it occurs at δ 55.8. The carbon C-14 is more shielded in (*E*,*E*) isomer (δ 16.7), while in (*Z*,*E*) and (*Z*,*Z*) isomers it occurs at δ 17.9 and 23.9, respectively. The double bond positioned between C-4 and C-5 also affects C-3 and C-15 (supporting information in Supplementary material, Table 3), reinforcing the proposed stereochemistry of (*E*,*E*).

Nuclear Overhauser effect corroborates the observed geometry (*E*,*E*) of the double bonds. The hydrogen H-15 at 1.42 ppm does not correlate with the H-5 at 4.69 ppm, suggesting that they are *trans* to each other. The same occurs with the geometry of the other

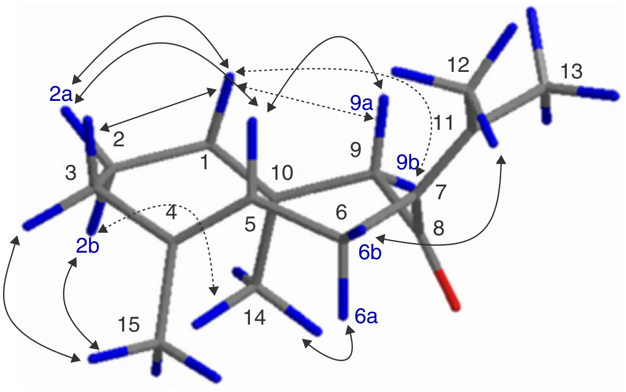


Fig. 3. Nuclear Overhauser effects (↔) observed for **24**.

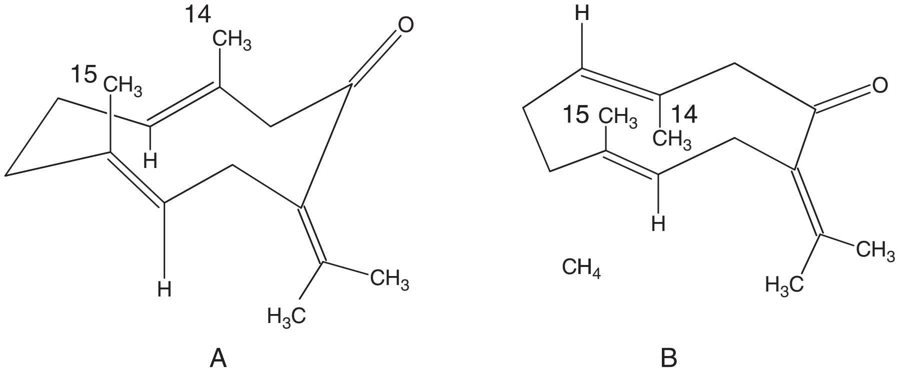


Fig. 4. Molecular conformations of **24**.

double bond, where H-14 at 1.61 ppm does not correlate with H-1 at 4.97 ppm, indicating again a *trans* geometry (Fig. 3).

As previously discussed in the literature, **24** can adopt two conformations involving the methyl groups on C14 and C15, that can be positioned on the same plane or on opposite planes (A and B, Fig. 4), as can also be observed for H-1 related to H-5 (Horibe et al., 1975).

In the NOESY spectrum (Supplementary material), no cross-correlation between H-5 at δ 4.69 and H-1 at δ 4.97 was observed, as expected if CH_3-14 and CH_3-15 were at the same side; thus, H-5 and H-1 have no spatial proximity. The (*E*,*E*)-germacrone (**24**) adopts conformation B, in which the two double bonds have a parallel orientation.

In turn, Fraction HPLC 2 had only one chromatographic peak in GC/MS with the molecular ion at *m*/*z* 218 (10) and base peak at *m*/*z* 107. ^{1}H and ^{13}C NMR showed the presence of (*Z*,*E*)-germacrone (**12**), as previously described by Maia (1991) (in which signals are in accordance with Simova et al. (1984) (^{13}C NMR data in Table 3, Supplementary material).

Both (*E*,*E*) and (*Z*,*E*)-germacrones were submitted to descriptive olfactory evaluation and reported as having a citrus, fragrant, marine and slightly woody odor, with aspects reminiscent of the odor observed in fresh gorgonian. The appraisal also suggests that the intensity of the isomer (*E*,*E*) is three times more intense than the isomer (*Z*,*E*)-germacrone in an ethanolic solution of 1 mg ml^{-1}, but with the same descriptions odor.

By GC/MS, HPLC fractions 1, 4, 5 and 6 proved to be a complex mixture of sesquiterpene composition.

Conclusion

Octocorals are a rich source of volatile terpenes that proved to have potential for perfumery, due to their marine exotic scents evaluated by olfactometry. Through a combination of chromatographic techniques such as silica gel vacuum chromatography and high performance liquid chromatography, associated to descriptive olfactory sensory analysis, this work describes, for the first time, that (*E*,*E*)-germacrone in *P. dilatata*, together with (*Z*,*E*) isomer, are the main compounds responsible for the citrus and woody aroma that impact the scent of this gorgonian. This work comprises the first sensorial analysis of natural products from octocorals. Until the present moment, the main chemical class associated to marine substances has been linear and/or cyclic hydrocarbons from $C_{11}H_{14}$ to $C_{11}H_{18}$.

Authors' contributions

SSO, LFM and RAE contributed in collecting animal sample and identification, confection of herbarium, running the laboratory work, analysis of the data and drafted the paper. LFM and RAE contributed in animal identification and herbarium confection. SSO, YFMF, DT, LFM, RAE and CMR contributed to chromatographic analysis. SSO, LFM and CMR contributed to critical reading of the manuscript. KLM contributed to plant collection. RAE and CMR designed the study, supervised the laboratory work and contributed to critical reading of the manuscript. All the authors have read the final manuscript and approved the submission.

Conflicts of interest

The authors declare no conflicts of interest.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.bjp.2015.08.004.

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