

Aldehyde and ketone compounds from marine hydrocoral identified by gas chromatography-mass spectrometry

SULTAN S. AL-LIHAIBI

Marine Chemistry Department, Faculty of Marine Science, King Abdulaziz University, P.O. Box 80207, Jeddah 21589, Saudi Arabia, Email: sallihaibi@kau.edu.sa

Abstract:

Five compounds have been identified in fire coral; three of these were aldehydes and the other two were ketones. The identification was based on the sequential elution and they were hexadecan-2-one, hexadecanal, heptadecanal, octadecan-2-one and octadecanal. Their structures were readily determined on the basis of their mass spectra.

Keywords Index: Fire corals, *Millepora sp.*, aldehyde and ketone compounds, Red Sea.

Introduction

The fire coral, *Millepora sp.*, is so-called due to its potential to inflict a painful burning sting from its nematocysts. The sting causes small welts on the skin with red lesions around the raised areas. The severity of the injured area depends on the intensity of the contact and the amount of venom injected was reported (Paradisi *et al.*, 2001; Sagi *et al.*, 1987). Several studies were conducted on fire corals to characterize the proteinous constituent (*e.g.* Shiomu *et al.*, 1989; Radwan and Aboul-Dahab, 2004) and lipid moiety (Al-Lihaibi *et al.*, 2002). The present study is a part of our investigation on fire coral species from the Eastern Red Sea coast.

Results and discussion

Five compounds were identified, namely three aldehydes and two ketones. The characteristic ions and their relative abundance are presented in Table 1. The identified aldehyde compounds were putatively hexadecanal ($C_{16}H_{32}O$) and heptadecanal ($C_{17}H_{34}O$) with respectively M-18 ion peaks at m/z 222 and 236 amu and octadecanal ($C_{18}H_{36}O$) with molecular ion peak at m/z 268 amu. The presence of peaks at M-18 and M-44 indicates that these compounds are belonging to normal saturated alkanals. The relative intensity of the fragment ion at m/z 44, as results of the McLafferty rearrangement, represents 25%. The molecular ions of hexadecanal and heptadecanal were absent. The relative intensity of the octadecanal was the highest followed by hexadecanal and then heptadecanal.

The identification of the ketone compounds revealed the presence of hexadecan-2-one ($C_{16}H_{32}O$) and octadecan-2-one ($C_{18}H_{36}O$) with prominent molecular ion peaks at m/z 240 and m/z 268, respectively.

The presence of the acyl ion ($C_nH_{2n+1}CO^+$), as a results of the C-1 methyl loss, was apparent in both compounds. The base peak at m/z 58 results from a McLafferty rearrangement.

Fig. 1 shows an example of the aldehyde and ketone spectra obtained from this study, whereas the fragmentation schemes of the aldehyde and ketone compounds are presented in Fig. 2. Previous studies have shown that aldehydes were identified in diatoms as short-chain compounds (d' Ippolito *et al.*, 2002), in marine macroalgae (Kajiwara *et al.*, 1992; Rosa *et al.*, 1995). It is worth mentioning that no aldehyde and ketone were reported in the extensive study of the coral specimens from Okinawa-Japan (Yamashiro *et al.*, 1999). Therefore, the saturated alkanals are reported here for the first time in coral and particularly fire coral. The finding of ketone compounds in marine environment is very limited and the only studies available were about the presence of long-chain alkenones ($C_{37}-C_{40}$).

Table 1: Characteristic fragment ions and relative abundance (%) of identified aldehyde and ketone compounds.

Compound	M ⁺	(M-15) ⁺	(M-18) ⁺	Other characteristic ions
C ₁₆ n-alkanones	240 (3.6)	225(2.2)	222(0.9)	197(0.9), 182(2.5), 58 (100), 57(15.7), 43(75.8)
C ₁₆ n-alkanals	240(abs)	----	222(1.8)	196 (3.8), 194(3.8), 82(97), 57(100), 44(28.8), 43(95)
C ₁₇ n-alkanals	254(abs)	----	236(2.0)	210(3.8), 208(4.4), 82(100), 57(87), 44(25), 43(96)
C ₁₈ -n-alkanones	268(4.5)	253(2.5)	250(1.2)	225(0.9), 210(2.1), 58(100), 57(15.8), 43(76.8)
C ₁₈ -n-alkanals	268(0.2)	----	250(2.7)	224(2.5), 222(2.7), 82(100), 57(97), 44(25), 43(95)

Abs = absent

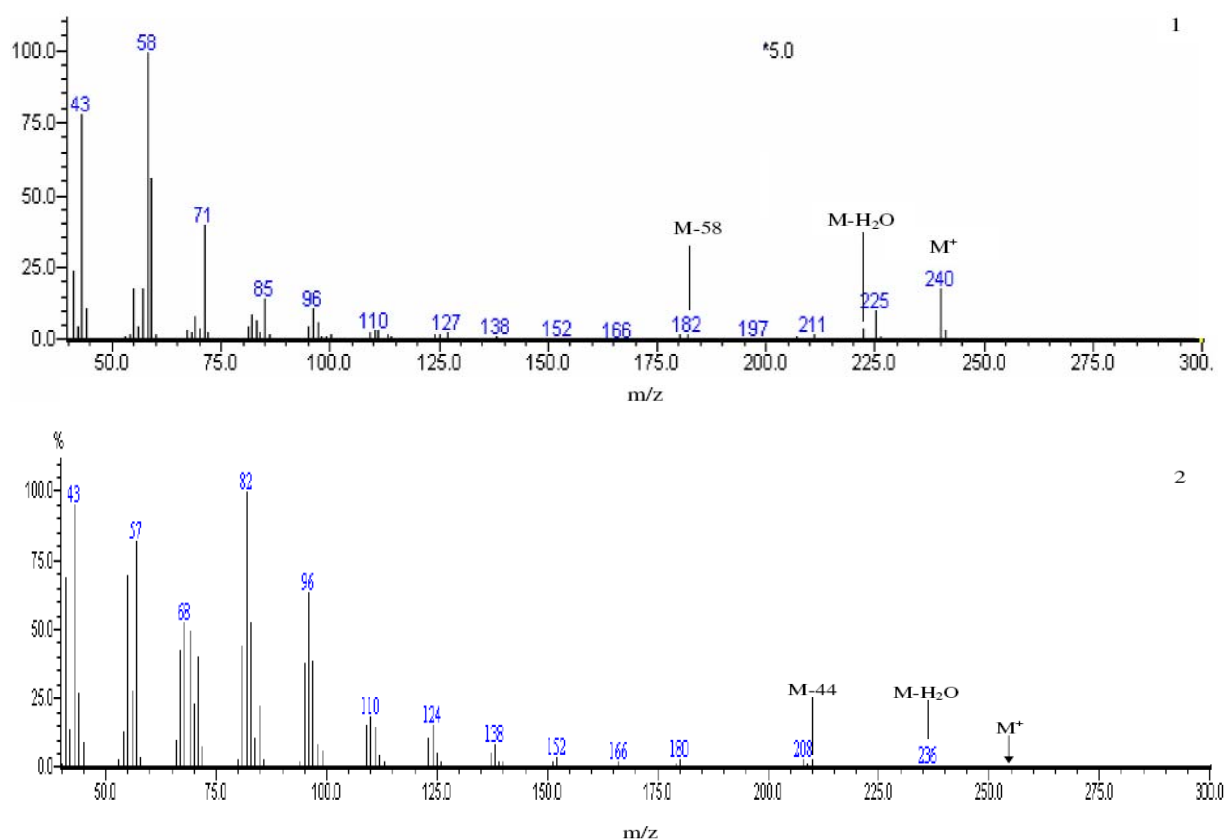


Figure 1: Mass spectra of hexadecan-2-one (1) and heptadecanal (2)

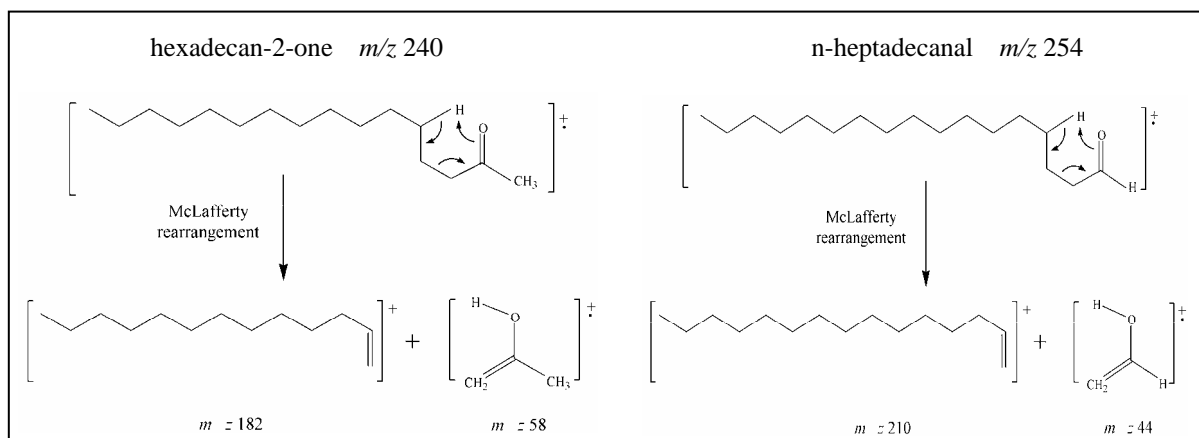


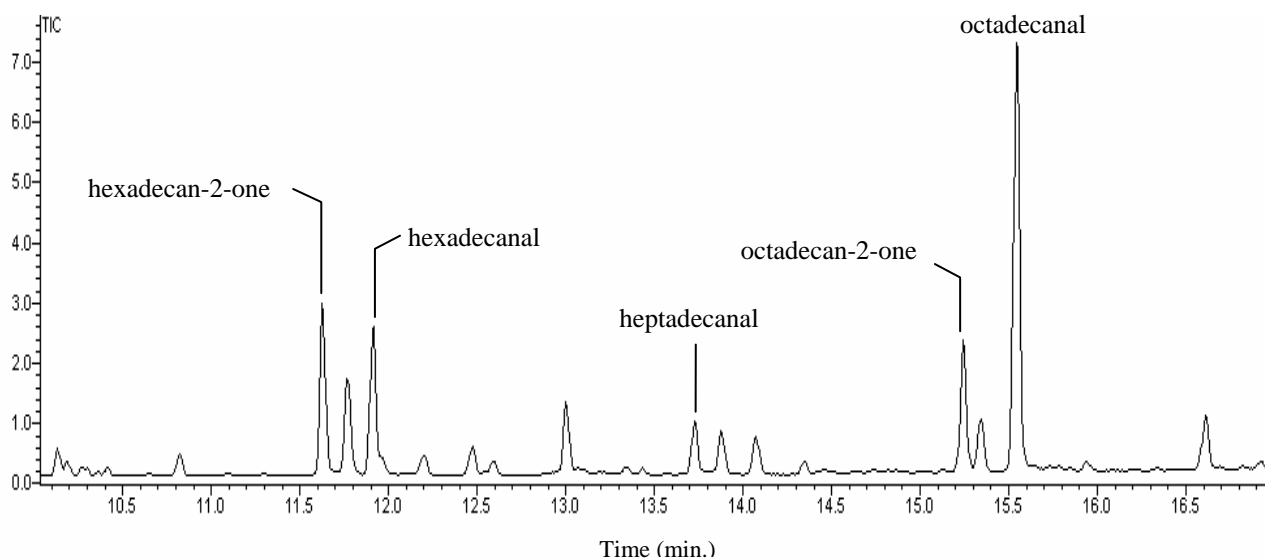
Figure 2: Fragmentation scheme of the ketone and aldehyde compounds

These were found in hypersaline and coastal microbial mats (Lopez *et al.*, 2005), in water column and sediments (Harvey, 2000). Thus, the ketones reported in this study are novel marine natural products. The occurrence and generation are still not clear and also their exact physiological role is still obscure. The author suggests that the compounds very likely originate from endosymbiotic bacteria and it is interesting to note that such symbiosis is the common for sponges and corals.

Experimental

The fire coral powder was treated with HCL (2N) and the solution stirred at room temperature for 30 minutes. The solution was neutralized with NaOH (2N) then partitioned with ether (3 x 200 mL) and the ether extract was dried. The extract was subjected to preparative TLC using benzene: ethyl acetate (9:11, v/v). All spots were distinctly visible under ultraviolet lamp. The top spot (R_f 0.8) was further chromatographed on TLC using hexane: chloroform (75:25, v/v). The scraped top spot was extracted with chloroform and analyzed using GCMS. The GCMS analyses were made on a Shimadzu QP-2010 gas chromatograph–mass spectrometer (Fig. 3). The column chromatography was a fused-silica capillary column of cross-linked DB-1 (J & W, USA: 30 m × 0.25 mm i.d., 0.25 μm

film thickness). The GC conditions were as follows: injector temperatures 230 °C; column temperature was held at 120 °C for 1 min and increased to 230 °C by 5°C min⁻¹, then raised by 25 °C min⁻¹ to 300 °C which was held for 3 min. Helium was used as carrier gas at flow rate 1.5 mL min⁻¹ maintained by an electronic pressure controller in split mode (ratio 10:1). The electron ionization mass spectrometry (EI-MS) conditions were as follows: ion-source temperature, 230 °C; ionizing voltage, 70 eV. The full scan mass spectra were ranged from 40–400 amu. Structural identification of these compounds was made by comparing their mass spectra with NIST (27 and 147) library mass spectra database.



Conclusion

The aldehydes and ketones were identified. To the best of our knowledge, the generated compounds identified in the fire coral have not been reported from any coral species. It is believed that these fatty acid derivatives presumably originate from endosymbiotic bacteria or algae.

Acknowledgments

Scientific Research Deanship (SRD) at King Abdulaziz University is acknowledged for the financial support (grant No. 256/422). The author is grateful to Prof. G. Wolff and Prof. G. Niaz for revising the manuscript.

References

- Al-Lihaibi S. S., Al-Sofyani A. M., Niaz G. R., Ahmad V.U., Noorwala M., Mohammed F.V., Long chain wax esters and diphenylamine in fire corals *M. dichotoma* and *M. platyphylla* from Saudi Red Sea Coast. *Scientia Marina* (2002), **66**(2), 95-102.
- d' Ippolito G., Iadicicco O., Romano G., Fontana A., Detection of short-chain aldehydes in marine organisms: the diatom *Thalassiosira rotula*. *Tetrahedron Letts.* (2002), **43**(53), 6137-6140.
- Harvey H. R., Alteration processes of alkenones and related lipids in water columns and sediments, *Geochem. Geophys. Geosyst.* (2000), **1**(8), doi:10.1029/2000GC000054
- Kajiwara T., Hatanaka A., Matsui K., Tomoi T., Fujimura T., Kawai T., Distribution of long chain aldehyde-forming activity from fatty acids and changes in its activity with growth in marine algae. *Phytochemistry* (1992), **31**(8), 2635-2639.
- Lopez J. F., de Oteyza T. G., Teixidor P., Grimalt J. O., Long chain alkenones in hypersaline and marine coastal microbial mats. *Organic Geochemistry* (2005), **36**, 861-872.
- Paradisi M., Grassi A., Conti G., Passarelli F., Cacciaguerra M. G., Fire coral persistent cutaneous reaction. *Acta Dermatoven APA* (2001), **10**, 1.
- Radwan F. F. Y. and Aboul-Dahab H.M., Milleporin-1, a new phospholipase A2 active protein from the fire coral *Millepora platyphylla* nematocysts, *Comparative Biochemistry and Physiology Part C: Toxicology & Pharmacology* 2004, **139**(4), 267-272
- Rosa S. D., De Giulio A., Iodice C., Alcaraz M. J., Paya M., Long-chain aldehydes from red algae *Corallina mediterranea*. *Phytochemistry* (1995), **40**(4), 995-996.
- Sagi A., Rosenberg L., Ben-Meir P. and Hauben D. J., The fire coral (*Millepora dichotoma*) as a cause of burns: A case report, *Burns* (1987), **13**(4), 325-326
- Shiomi K., Hosaka M., Yanaike N., Yamanaka H. and Kikuchi T., Partial characterization of venoms from two species of fire corals *Millepora platyphylla* and *Millepora dichotoma*, *Nippon Suisan Gakkaishi* (1989), **55**, 357-362.
- Yamashiro H., Oku H., Higa H., Chinen I., Sakai K., Composition of lipids, fatty acids and sterols in Okinawa corals. *Comp. Biochem. Physiol. B: Biochem. & Mol. Biol.*, (1999), **122**(4), 397-407.