Short communication

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

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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. Shiomi 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 (C₁₆H₃₂O) and heptadecanal (C₁₇H₃₄O) with respectively M-18 ion peaks at m/z 222 and 236 amu and octadecanal (C₁₈H₃₆O) 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 presence of the acyl ion (CₙH₂ₙ₋₁CO⁺), 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 (C₃₇-C₄₀).
Table 1: Characteristic fragment ions and relative abundance (%) of identified aldehyde and ketone compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>M⁺</th>
<th>(M-15)⁺</th>
<th>(M-18)⁺</th>
<th>Other characteristic ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₆ n-alkanones</td>
<td>240(3.6)</td>
<td>225(2.2)</td>
<td>222(0.9)</td>
<td>197(0.9), 182(2.5), 58 (100), 57(15.7), 43(75.8)</td>
</tr>
<tr>
<td>C₁₆ n-alkanals</td>
<td>240(abs)</td>
<td>----</td>
<td>222(1.8)</td>
<td>196 (3.8), 194(3.8), 82(97), 57(100), 44(28.8), 43(95)</td>
</tr>
<tr>
<td>C₁₇ n-alkanals</td>
<td>254(abs)</td>
<td>----</td>
<td>236(2.0)</td>
<td>210(3.8), 208(4.4), 82(100), 57(87), 44(25), 43(96)</td>
</tr>
<tr>
<td>C₁₈ -n-alkanones</td>
<td>268(4.5)</td>
<td>253(2.5)</td>
<td>250(1.2)</td>
<td>225(0.9), 210(2.1), 58(100), 57(15.8), 43(76.8)</td>
</tr>
<tr>
<td>C₁₈ -n-alkanals</td>
<td>268(0.2)</td>
<td>----</td>
<td>250(2.7)</td>
<td>224(2.5), 222(2.7), 82(100), 57(97), 44(25), 43(95)</td>
</tr>
</tbody>
</table>

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 (Rf 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.

![Partial total ion chromatogram (TIC) of fire coral extract](image)

**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


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


