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Volatile and semi-volatile components of jetsam ambergris

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Abstract

Volatile and semi-volatile compounds account for the odours, long valued in the perfumery industry, of the natural product, ambergris. Here we demonstrate application of solid phase micro extraction (SPME) and gas chromatography-mass spectrometry (GC-MS) to headspace analysis of the volatiles and semi-volatiles of jetsam ambergris. The samples collected in 2017/2018, ranged from a black, sticky material from New Zealand, likely recently ejected from a sperm whale, to a white solid found on a beach in Chile and radiocarbon-dated previously to be about 1000 years old. The traces of volatile/semi-volatile compounds extracted included, odorous γ-dihydroionone and odor-free pristane (2,6,10,14-tetramethylpentadecane), as the major constituents. The ratios of these to one another and to many other minor constituents, varied, depending on sample colour and age.

Keywords: Ambergris, volatiles, SPME, Sperm whale, jetsam, ambrein.

Experimental

Materials

A sample of blacky sticky, ambergris, verified by GC-MS (Rowland et al., 2018 b) was collected by R. Craig in June 2017 at Cochrane's Gap, Awhitu Peninsula, North Island, New Zealand.

A sample (30g) of whitish ambergris was collected by P. Lillis on a beach at Plouhinec, Brittany, France on 1st September 2017.

A grey sample of ambergris with a brown interior (52g) was collected by S. J. Rowland at Widemouth, Cornwall, UK on 4th March 2018.

Jetsam ambergris samples (300g total) from Grand Somalia, Somalia were collected by a person who wishes to remain anonymous, on 5th May 2017.

A boulder and numerous pieces of ambergris, weighing ~6.3 kg was collected from the beach at Mar Brava, Chiloé Island, Los Lagos, Chile on 12th April 2017, by Tomás Helle Pessot, Salvador Mansilla Bastías and Nathan Wolff Reinarz of Universidad Austral de Chile.

Methods

Headspace SPME-GC-MS was carried out using an Agilent GC-MSD (Agilent Technologies, Wilmington, DE, USA). This comprised a 7890A gas chromatograph and a 5975A quadrupole mass selective detector operated at 70eV ionisation voltage. The column was a HP-5MS fused silica capillary column (30 m x 0.25 mm i.d x 0.25 µm film thickness). The carrier gas was helium, kept at a constant flow of 1.0 mL min^{-1}. The optimal SPME fibre was found to be a 75 µm PDMS/DVB (Supelco). The ambergris samples were placed in 20 mL headspace vials and the fibre exposed for 70 minutes at room temperature before being desorbed in the GC inlet at 250 °C for 10 minutes. The oven temperature was programmed from 40 to 300 °C at 10 °C min^{-1} and held for 10 min and the transfer line and source temperatures maintained at 280°C and 230°C, respectively. The data were collected and analysed in MassHunter.

Figure S1 GC-MS total ion current chromatograms of solid phase microextracts (headspace) of a blank vial (*= components also observed in microextracts of some ambergris samples (denoted with an asterisk in Figures 1 and S2)).

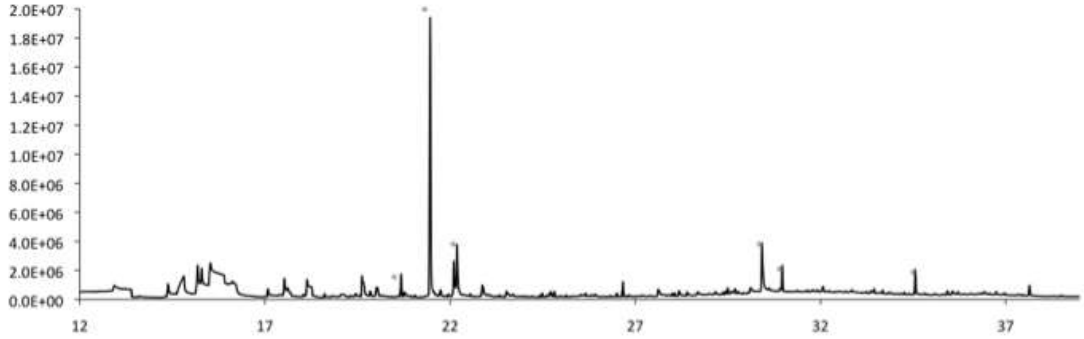

Figure S2. GC-MS total ion current chromatograms of solid phase microextracts (headspace) of jetsam ambergris samples from France, Ireland, France, Ireland and Somalia. **II**= γ-dihydroionone (**IIb** = isomer); **III**=pristane (2,6,10,14-tetramethylpentadecane).

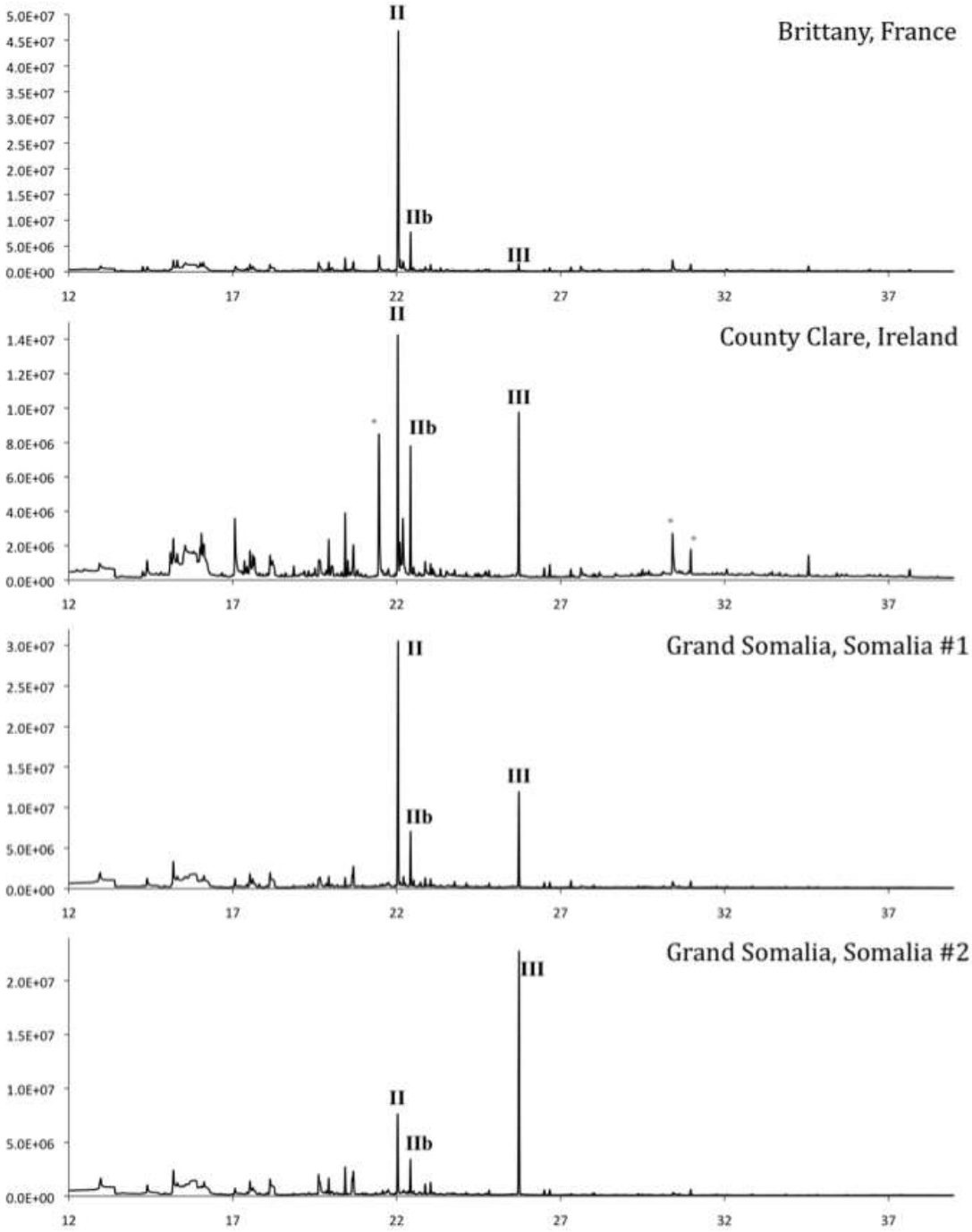

Figure S3. GC-MS total ion current chromatograms of solid phase microextracts (headspace) of jetsam ambergris sample from New Zealand indicating repeatability of analyses for (e.g.) dihydroionone isomer ratios, for duplicates on divinylbenzene SPME phase and duplicates on a Carboxen SPME phase. The chromatographic conditions were changed as indicated, but the ratios (peak identities are shown on Figure S2) remain reproducible.

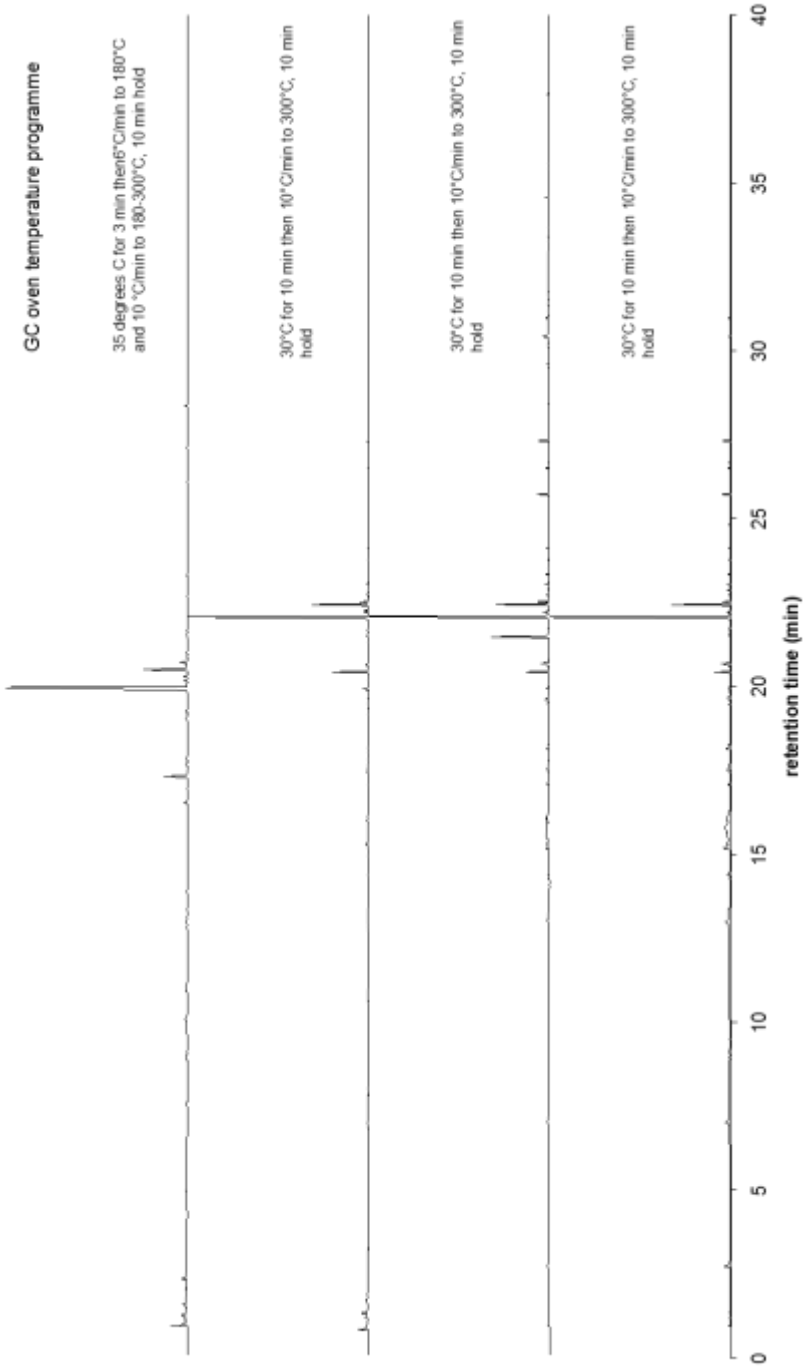

Table S1. List of identified or tentatively identified volatile and semi-volatile constituents of ambergris headspace. Approximate retention time given (minutes). Structure numbers refer to chemical discussed in the text.

IV 20.5 min γ-Homocyclogeranyl chloride
II 22 min γ-Dihydroionone (and isomer IIb 22.5 min)
III 26 min Pristane (2,6,10,14-tetramethylpentadecane
V 26.5 min Ambrox®
VI 27.5 min Ambreinolide
I 37 min Ambrein
Unsaturated ether (Ohloff et al. 1977).
Ambratrienes (36 min artefactual; Governo et al. 1977)

References for Supplemental:

Governo TF. Alessandro RT. Pragger MJ. 1977. Gas-liquid chromatographic-mass spectrometric detection and identification of ambergris. J AOAC Int. 60:160-164.

Ohloff G. Schulte-Elte KH Müller BL. 1977. Formation of ambergris odorants from ambrein under simulated natural conditions. Helv Chim Acta 60:2763-2766