



# Identification of aryl isoprenoids in oils from Sergipe–Alagoas Basin, northeastern Brazil using Triple Quadrupole GC-MS/MS

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## Introduction

Biomarker hydrocarbons in oils and sediments have considerable potential for assessing the nature of biological processes in the past, but only a few can be uniquely related to particular organisms. In analysis of Sergipe-Alagoas basin, related to the lacustrine and marine evaporitic source rocks, we identified a large range of diagenetic and catagenetic products of the aromatic carotenoid isorenieratene, including C<sub>40</sub>, C<sub>33</sub>, and C<sub>32</sub> diaryl isoprenoids and aryl isoprenoid derivatives (Sousa Júnior *et al.*, 2013).

In this paper we re-evaluate the serie of trimethyl aryl and dimethyl aryl isoprenoids by GC-MS and GC-MS-MS (EI, CI). In addition we identified the co-occurrence of the dimethyl aryl, structurally related trimethyl aryl series may indicate that the former likely derive from the latter by way of a demethylation process.

## Experimental

### Sample preparation:

About 80 mg of oil were subjected to PTLC on silica gel impregnated with 5% AgNO<sub>3</sub> and then the silica was developed using 98:1 (v:v) n-hexane:ethyl acetate. The plates were then selectively scraped and the silica was treated using dichloromethane:methanol 95:5 (v:v) for desorption of the constituents. The fractions thus obtained (P1 – saturated and P2 – aromatic) were concentrated in a rotary evaporator and analyzed by GC-MS and GC-MS-MS.

### Acquisition Method for TSQ Quantum XLS:

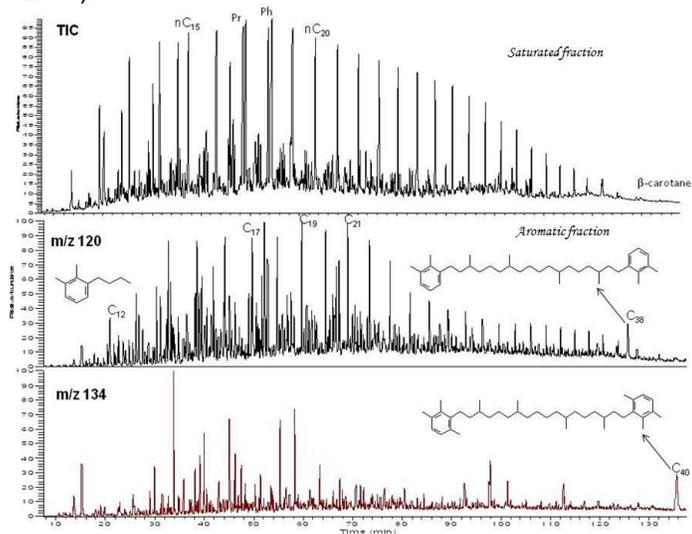
The analyses were performed using a Thermo Scientific TSQ Quantum XLS Ultra Triple Quadrupole GC-MS instrument. Capillary chromatographic column (Equity TM-1, 30 m, 0.25 mm ID). Initial temperature of 70 °C (4 min hold), followed by a ramp of 2 °C/min up to a final temperature of 300 °C (20 min hold). The carrier gas was helium at a constant flow rate of 1.0 ml/min. Transfer line temperature was 310 °C. The quadrupole mass spectrometer was operated in full scan mode over the mass range 50–650 Da (EI mode at 70 eV). Collision Energy 10 eV. Collision Gas Ar. For data acquisition by selected reaction monitoring (SRM) the masses according to Figure 2(a) were used for the two compound groups under investigation. The identification of biomarkers was done by comparison of elution order, retention times and mass spectra with literature data (Summons and Powel, 1987; Peter *et al.*, 2005; Zhang *et al.*, 2011; Santos Júnior *et al.*, 2013).

## Results and Discussion

Figure 1 showed the distribution of aromatic hydrocarbon and aryl isoprenoids, TIC typical of the saturate fraction; RIC of m/z 134 and 120, pointing out the aryl isoprenoids and remaining diagenetic isorenieratane products.

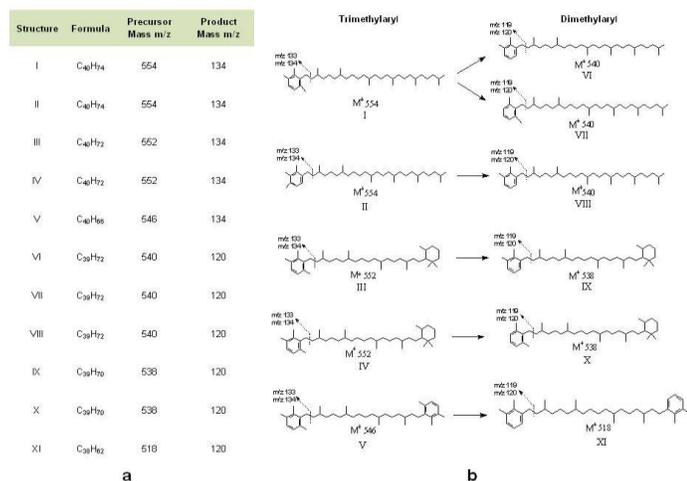
The chromatographic profiles (TIC, Figure 1) and geochemical parameters from the saturated fractions in this study indicate that they are not biodegraded and achieved similar thermal maturity levels (early to middle oil window) and that their source rocks were deposited in a reducing depositional environment, under different levels of salinity.

Figure 1 shows the chromatographic profile of the saturated and aromatic fraction ( $m/z$  120 and 134).  $m/z$  134 mass chromatogram showing distribution of trimethyl aryl isoprenoids, and  $m/z$  120 mass chromatogram showing the novel series of dimethyl aryl isoprenoids. To  $m/z$  120 series can be generated from the  $m/z$  134 counterparts through loss of a methyl from the aromatic ring at C-6 or C-3 or C-4 (Zhang et al., 2011).



**Figure 1.** TIC typical of the saturate fraction; RIC of  $m/z$  134 and 120, showing the aryl isoprenoids and remaining diagenetic isorenieratane products.

The compounds (Figure 2) were identified by their respective molecular ions, base peaks at  $m/z$  134 (McLafferty rearrangement) or  $m/z$  133. In addition,  $m/z$  119, 120, 105, 91 and 77 were used because they are typical of a poly substituted aromatic structure. For data acquisition by selected reaction monitoring (SRM) the masses according to Figure 2 were used for the two compound groups under investigation.



**Figure 2.** SRM Transitions for TSQ Quantum XLS (a) and structures and likely relationships between  $m/z$  134 and 120 series (b).

The presence of diagenetic and/or catagenetic products of isorenieratane in source rocks and crude oils suggests photic zone anoxia during the deposition of organic-rich sediments. Additional confirmation of the origin of aryl isoprenoids from *Chrobiaceae* in this oils can be obtained if these compounds are isotopically heavier than their carotane counterparts of algal origin. However, the presence of these compounds have been often related to anoxic depositional setting, and their structures are strongly correlated to biological precursors derived from *Chlorobiaceae* and *Chromatiaceae*.

## Conclusions

We complemented previous studies (Sousa Júnior et al, 2013) and identified a new series of dimethyl arylisoprenoids in oils of the Sergipe-Alagoas Basin - Northeast of Brazil, saline lacustrine, by GC-MS-MS (EI and CI). The co-occurrence of the dimethyl aryl ( $m/z$  120) and structurally related trimethyl aryl ( $m/z$  134) series may indicate that the former likely derive from the latter by way of a demethylation process, as suggested by (Zhang et al., 2011), but this this specificity needs to be further investigated.

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