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► **To cite this version:**

Eric Lichtfouse, Pierre Albrecht, Françoise Béhar. 3-Methyltriaromatic steroids in sediments. Molecular fossils with unknown precursors. Garrigues P., Lamotte M. Polycyclic Aromatic Compounds, Taylor & Francis Ltd, pp.635-638, 1993. hal-00264409

HAL Id: hal-00264409

<https://hal.science/hal-00264409>

Submitted on 17 Mar 2008

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Revised version.

In Garrigues P., Lamotte M. Polycyclic Aromatic Compounds. Taylor & Francis Ltd. ISBN-10 : 2881245455. Vol. 3. pp. 635-638. 1993.

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3-METHYLTRIAROMATIC STEROIDS IN SEDIMENTS. MOLECULAR FOSSILS WITH UNKNOWN PRECURSORS.

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Abstract. The discovery of novel fossil substances can lead to the discovery of yet unknown modern biological substances such as bacterial hopanols. Here we discuss the origin and formation of some steroids found in petroleum and deep sediments. The occurrence of 3-methyl-triaromatic steroids, 3-methyl-steranes and 3-carboxy-steranes in sediments and petroleum suggest the presence of yet unidentified steroid precursors in biological organisms.

INTRODUCTION

Organic substances in sediments are the molecular fossils of living organisms which were accumulated at the time of deposition. Many molecular fossils bear enough structural information to link them with biotic precursors (1). The identification of new fossil structures might lead to the discovery of new lipids in living organisms. C₃₁-C₃₅ hopanoids, for example, were first found to occur ubiquitously in sediments then later in eubacteria (2).

The wide variety of steroid structures in sediments, such as stanols, sterenes, steranes and aromatic steroids, reflects the geochemical transformations (i.e. dehydration, reduction, aromatization) undergone by their precursors, the eukaryotic sterols, during burial (3). Although most of the steroid structures can be explained in terms of sterol alteration, the recent discovery of triaromatic steroids bearing a methyl group at position 3 (4) is puzzling since 3-methylsterols or other possible precursors have not been reported in living organisms. Furthermore the presence of 3-methyltriaromatic steroids, 3-methylsteranes (5) and 3-carboxysteranes (6) suggests a common origin (7).

ORIGIN OF METHYLTRIAROMATIC STEROIDS

Since triaromatic steroids have not been reported in living organisms, their specific "steroid" structure suggests a derivation from the widespread eukaryotic sterols. Indeed, various steroid classes such as sterenes (8) and monoaromatic steroids (9), which are possible intermediates between sterols and triaromatic steroids, have been identified in sediments. With increasing depth, the predominant steroid classes are successively sterols, sterenes, monoaromatic steroids and triaromatic steroids, this order bringing indirect evidence for their transformations.

In the study of methyltriaromatic steroids, the origin of the methyl group on the aromatic nucleus is of peculiar importance. Three different origins can be drawn: 1) the biological precursors (i.e. sterols) bear a methyl group (or a pro-methyl function) at the same position; 2) there is an intramolecular migration of the methyl group from position 10, during burial; 3) after deposition, steroids are methylated under biogeochemical conditions.

4-Methyl- and 6-methyltriaromatic steroids

Few biological sterols are known to bear one additional methyl group on ring A or B. 4-Methylsterols have been reported so far in substantial amounts in one bacterium (10) and a few algae (11), including the dinoflagellates which are major primary producers in oceans. A ring B monoaromatic sterol bearing a methyl group at position 6 has been recently identified in an amoeba (12). Thus 4-methyl- and 6-methylsterols could possibly be the precursors of 4-methyl- and 6-methyltriaromatic steroids, respectively. This implies the removal of the methyl group at position 10 during burial. 4-Methyl- and 6-methyltriaromatic steroids could also be derived from rearranged ring C monoaromatic steroids (13) after migration of the methyl group from position 5 to 4 or 6 during aromatization. 4-Methyltriaromatic steroids could also arise from the less common 4-methylmonoaromatic steroids (14).

1-Methyltriaromatic steroids

The relative concentration of 1-methyltriaromatic steroids (15) versus triaromatic steroids methylated at position 2, 3, 4 or 6 is usually low in geological samples (16), pointing out its relative instability under geological conditions. Interestingly, a similar behaviour was also observed for 4-methylphenanthrenes, a structurally close substance, in the methylphenanthrenes series (17). The possible precursors for 1-methyltriaromatic steroids are ring A 1-methylmonoaromatic steroids (14). 1-Methyltriaromatic steroids could also be formed by aromatization of ring C monoaromatic steroids (18), although this hypothesis is less favourable due to the increase of steric strain during the migration of the methyl group from position 10 to 1.

2-Methyl- and 3-methyltriaromatic steroids

The origin of 2-methyl- and 3-methyltriaromatic steroids (4) is puzzling since sterols bearing a carbon-containing function at positions 2 or 3 have not been reported in living organisms. The concentration increase of sterically more stable 2-methyl- and 3-methyltriaromatic steroids versus 1-methyl and 4-methyl isomers with burial depth (7) has suggested a possible derivation *via* methyl shifts on the aromatic nucleus (4). Indeed, the structurally related 2-methyl- and 3-methylphenanthrene could be derived

from 1-methylphenan-threne, as suggested by laboratory heating experiments over clay catalysts (16, 19). However no methyl migration was observed after heating of a 4-methyltriaromatic steroid (C_{21}) on montmorillonite clay (16). Furthermore, 3-methyltriaromatic steroids have been detected as sole methyltriaromatic steroids (no 4-methyl homologs) in immature sediments (20), excluding a possible derivation *via* a methyl shift in that case.

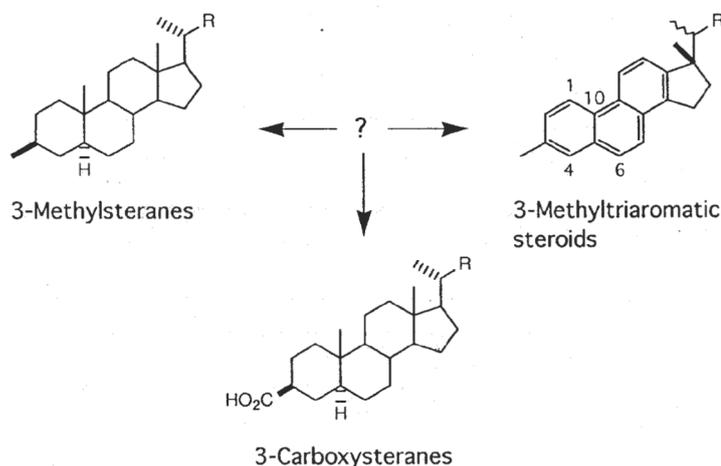


Figure 1. The occurrence of 3-methylsteranes, 3-carboxysteranes and 3-methyltriaromatic steroids in sediments suggests a common origin.

One interesting point is the occurrence of two other steroids classes bearing a carbon-containing function at position 3 in sediments, 3-carboxysteranes (6) and 3-methylsteranes (5,6). It was therefore postulated that 3-methylsteranes, 3-methyltriaromatic steroids and 3-carboxysteranes could be derived from the same precursors (7) (Fig.1). Ster-2-enes, commonly encountered in recent sediments (8), have been recently proposed as possible precursors (6). Similarly, 2-methylsteranes (5) and 2-methyltriaromatic steroids (4) could be derived from the same precursors (7).

We are aware that other pathways of formation are also possible since the knowledge of lipids from aquatic organisms is poor. Moreover, the extreme complexity of sedimentary organic matter is also an obstacle to the recognition of reactant-product relationships.

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