EARLY DIAGENESIS OF TRITERPENOIDS DERIVED FROM MANGROVE SPECIES IN A SUBTROPICAL ESTUARY

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Introduction

Pentacyclic triterpenoids (PTs) have been reported as natural products in the environment for years as common chemical constituents of higher plants, especially in plant leaves such as cuticular waxes of mangrove leaves. Due to their stability during sedimentation and diagenesis, they were frequently used to trace terrestrial organic matter in soil cores. A variety of PTs with the oleanane, ursane, lupane, taraxerane, and friedelane skeletons have been identified in higher plants but not in marine organisms, among which the most frequently encountered PTs usually have a 3-oxy functional group, such as taraxerol, lupeol, betulin and amyrin. Taraxerol is of interest to organic geochemists since it has been suggested to be derived exclusively from mangroves and repeatedly detected in marine sediment cores. In addition, various defunctionalized or aromatized compounds in marine sediment cores were suggested to be diagenetic products from triterpenols as their precursors. Various early diagenetic degradation products of triterpenoids have been identified in geological samples, including seco-A-triterpenes, triterpenoid ketones, desmethyl triterpenoids, ring-A degraded compounds with the lupane, oleanane, ursane, and friedelane skeletons. A few mechanisms have been proposed for taraxerol during late diagenesis. However, the fate of PTs, especially taraxerol, during early sedimentation is still unclear, which complicates the interpretation of the PT signal in sediment cores.

With various speculative ideas proposed for the degradation pathways of amyrins and lupeol in geological samples, few studies have examined the early diagenetic products of taraxerol. Therefore, having a better understanding of taraxerol degradation is of major importance for interpretations of its degradation products in estuarine and marine sediments, especially in coastal areas where mangroves grow. Mangroves contain high amounts of PTs, especially taraxerol. Because mangroves usually grow in extreme environments, the species diversity in the mangrove swamp is low. With few potential sources of higher plant lipids (other than mangroves) and typically high organic matter accumulation rates in the mangrove swamp, it is possible to use source specific biomarkers for paleo reconstructions of deposition of mangrove stand soils. As such, PTs have the potential to be applied as indicators of paleovegetation and there is a need to better understand the diagenetic products of these PTs, especially taraxerol, in mangrove swamps. Here we analyzed the PTs from leaves and bark of three dominant mangrove species, surface soils and soil cores along a subtropical estuary dominated by mangroves. We focused on taraxerol and its degradation products in order to: (i) document the degradation/alteration of taraxerol from extant mangrove plants to their sedimentary sink; and (ii) provide insights into the diagenetic pathways for mangrove derived taraxerol.

Results

Several diagenetic degradation products of mangrove derived triterpenoids were identified. The dehydration of pentacyclic triterpenols was observed in mangrove leaves, leading to

pentacyclic triterpadienes with $\Delta^{2,12}$ and $\Delta^{2,14}$ unsaturations. Surprisingly, various mono-triterpenes (with Δ^{12} and Δ^{14}), nor-, dinor- (24,25-dinortaraxer-14-ene) and trisnor-triterpenes (1,2,3-trisnortaraxera-5(10),14-diene and 1,2,3-trisnortaraxer-14-ene) were detected in R. mangle leaves. Most of the unsaturated and nortriterpenes were also detected in mangrove stand soils (*ca.* 200 years old). In addition, a high diversity of aliphatic and aromatic des-A-triterpenes from the oleanane, ursane, lupane, and taraxerane skeletons were found in the surface and deeper soils of mangrove stands.

Conclusions

1. Demethylation and ring A opening of triterpenoids occur prior to mangrove leaf abscission
2. The rapid diagenetic loss of ring-A and further aromatization of triterpenoids occurred mainly after plant decay
3. Early diagenetic degradation scheme for mangrove derived taraxerol is proposed

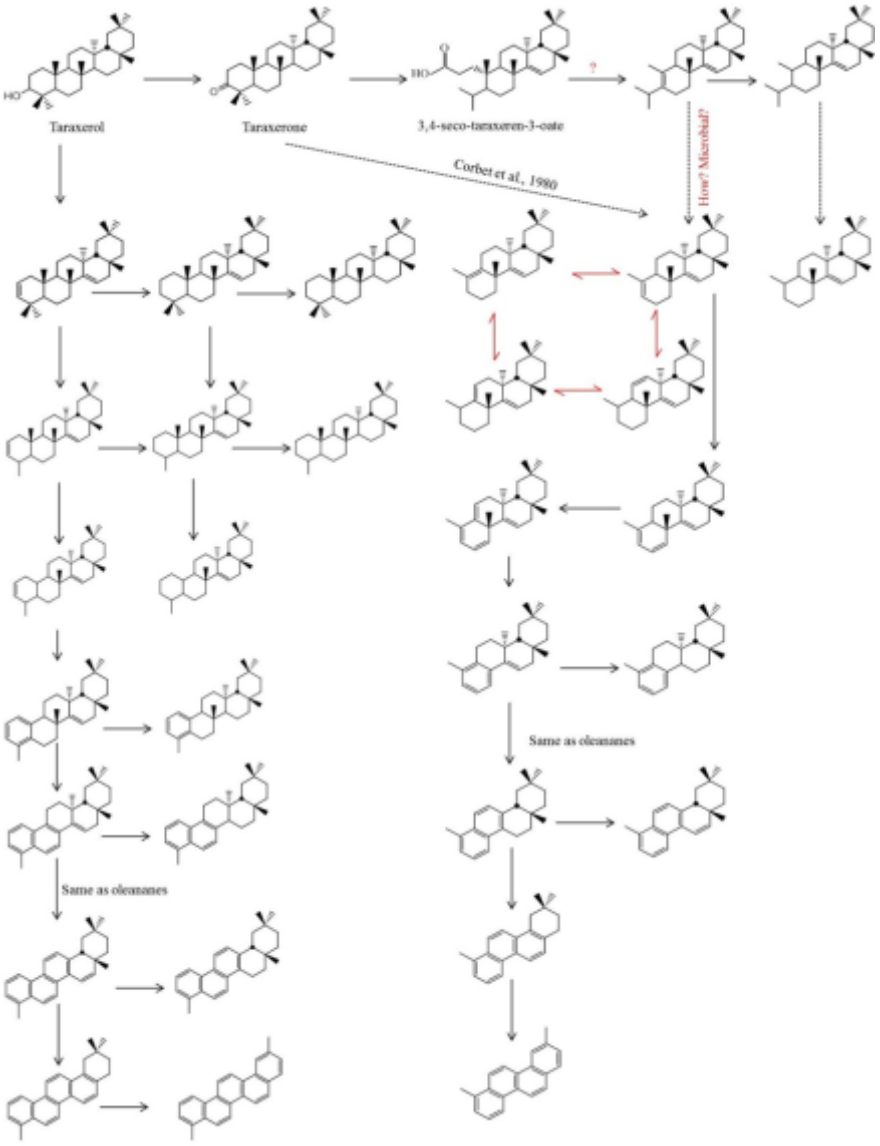

Figure 1 *Proposed scheme summarizing the early diagenesis of taraxerol.*