

C₄₀ BIS-DITERPENOIDS, NOVEL CHEMOTAXONOMIC BIOMARKERS OF PODOCARPACEAE IN SEDIMENTS?

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In the course of a detailed palaeoenvironmental study based on biomarker distributions in sediments from the Lower Oligocene (Rupelian, Lower Oligocene) of the Rhine rift valley, an outcrop sample rich in higher plant fossil remains was collected in a quarry located near the city of Burnhaupt-le-Haut (South of Alsace, France). In agreement with the macrofossil assemblage, most of the biomarkers were related to terrigenous inputs, as illustrated by the gas chromatogram of the aromatic hydrocarbons shown in Fig. 1a. Indeed, the aromatic hydrocarbons are strongly dominated by diterpenoid- and triterpenoid-related biomarkers attesting of contributions from gymnosperm and angiosperm precursors. However, a rather complex series of unknown high molecular weight compounds eluted at the end of the aromatic hydrocarbon fraction was also present (filled and empty circles in Fig. 1a), showing molecular ions at M^+ 570 and 552. Given the rather poor information obtained from their mass spectra (Figs. 1b), three homologues (**1-3**; Fig. 1a) were isolated by liquid chromatography (LC, HPLC) in order to characterize their structures by NMR. The first isolated compound (**1**) with a molecular mass of 570 Da. was shown to have a dimeric structure made of two phenolic totarol sub-units linked by an ether bond, whereas the two other compounds with a molecular weight of 552 Da. (**2-3**) correspond to dimers made of totarol (**2**) and mixed totarol-sempervirol sub-units (**3**) bearing a central dibenzofuran moiety. Although C₄₀ bis-diterpenoids are not reported yet to occur in the geological record, there are few reports on the occurrence of bis-diterpenoids made of totarol sub-units linked by a carbon-carbon bond in the Plant kingdom. Such is the case of podototarol, a diphenolic diterpenoid which has been shown to be present among the heartwood of various species of Podocarpaceae and which is thought to be formed by the enzymatic oxidative coupling between the two phenolic diterpenoid sub-units. Hence, it can be envisaged that the various bis-diterpenoids present in the sediment sample investigated represent diagenetic transformation products of bis-diterpenoids from Podocarpaceae. However, since “mixed” bis-diterpenoids such as **3** and bis-diterpenoids with a structure related to **1** have never been

characterized among biolipids, an alternative hypothesis regarding the origin and mode of formation of the sedimentary bis-diterpenoids has to be considered. We propose that these novel biomarkers may be formed by purely diagenetic processes, with a first step involving an oxidative coupling between the phenolic sub-units (i.e., totarol and semperviol) following a free radical mechanism and leading to the formation of an ether bond as in the case for **1**, or a carbon-carbon bond (**2-3**), followed by a second, acido-catalysed cyclization forming the central dibenzofuran moiety as in the case for compounds **2** and **3**.

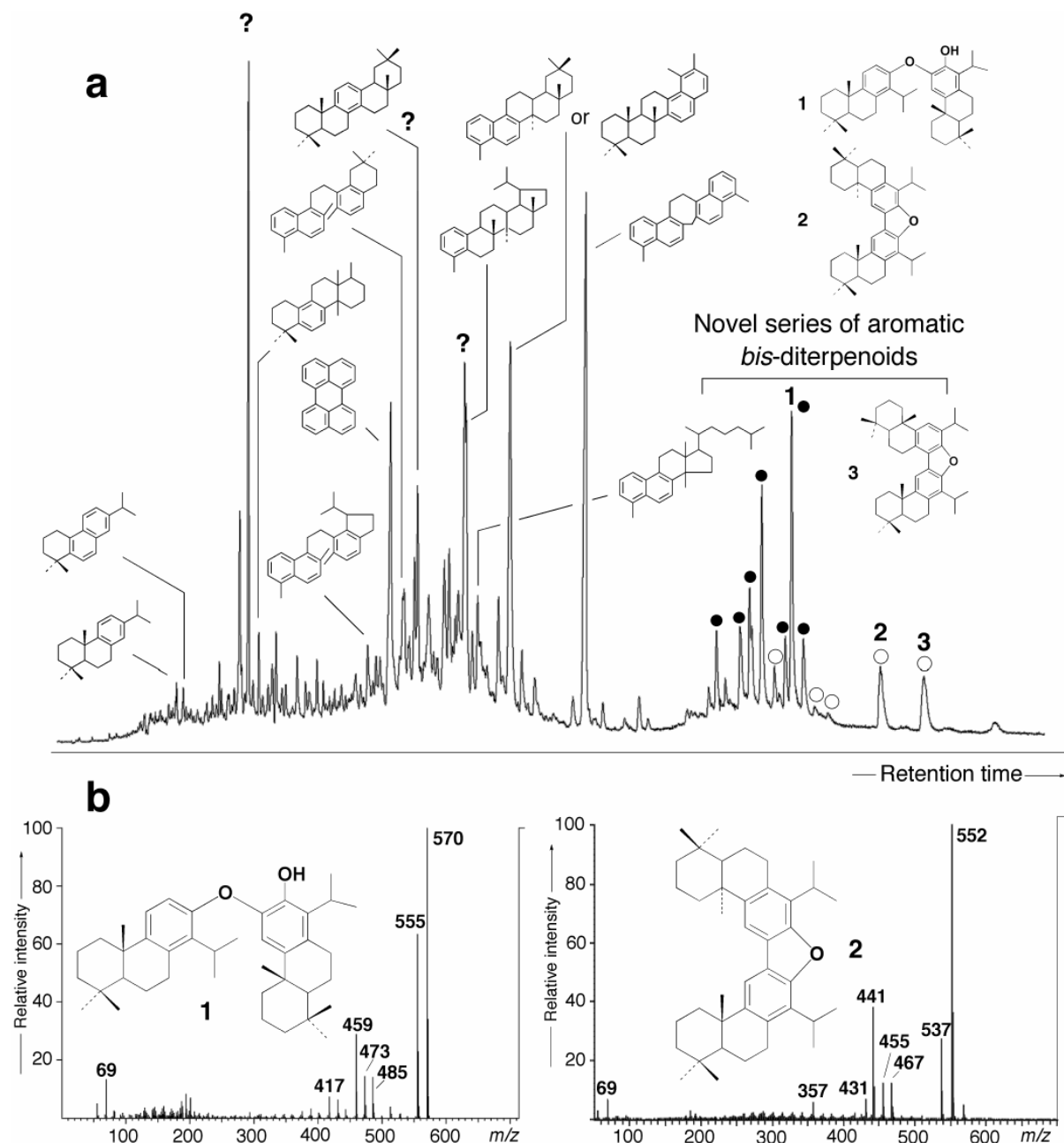


Figure 1: (a) Gas chromatogram (RIC) of the aromatic hydrocarbon fraction from a sample rich in plant fossils collected in an outcrop of the Meletta bed formation (Lower Oligocene) located near Burnhaupt-le-Haut (France). Filled circles: compounds with a M_w of 570 Da.; Empty circles: compounds with a M_w of 552 Da.; (b) Mass spectra of compounds **1-2**.