

Plant-derived triterpenoid biomarkers and their applications in paleoenvironmental reconstructions: chemotaxonomy, geological alteration, and vegetation reconstruction

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Abstract

Triterpenoids and their derivatives are ubiquitous in sediment samples. Land plants are major sources of non-hopanoid triterpenoids; these terpenoids comprise a vast number of chemotaxonomically distinct biomolecules. Hence, geologically occurring plant-derived triterpenoids (geoterpenoids) potentially record unique characteristics of paleovegetation and sedimentary environments, and serve as source-specific markers for studying paleoenvironments. This review is aimed at explaining the origin of triterpenoids and their use as biomarkers in elucidating paleoenvironments. Herein, application of plant-derived triterpenoids is discussed in terms of: (i) their biosynthetic pathways. These compounds are primarily synthesized via oxidosqualene cyclase (OSCs) and serve as precursors for a variety of membrane sterols and steroid hormones. Studies on OSCs and resulting compounds have helped elucidate the diversity and origin of the parent terpenoids. (ii) their chemotaxonomic significance. Geochemically important classes of triterpenoid skeletons are useful in gathering and substantiating information on botanical origin of these compounds, evolution and diversification of angiosperms, and organic matter preservation during different periods in geological history. (iii) current knowledge on their transformation into geoterpenoids via diagenetic alterations. This knowledge helped in paleoenvironmental reconstructions from the local depositional environments to paleoclimatic variations. This review focuses on triterpenoids as paleoenvironmental biomarkers, and consolidates relevant literature that can form the basis for developing tools and techniques for improved paleoenvironment reconstruction. Future investigations should focus on detecting as yet unknown classes of triterpenoids and their biosynthetic pathways, inclusion of this information in automated databases, and identification of geoterpenoids as potential biomarkers to further our understanding of paleoenvironments and paleoclimate.

1. Introduction

Triterpenoids with various carbon skeletons have been used in the geochemical exploration and paleoenvironmental studies as source-specific biomarkers that provide insights into the biological sources of organic matter, early diagenesis, and thermal maturity (e.g. Peters et al., 2005 and references therein). Hopanoids are the ubiquitous bacterial triterpenoids, while other pentacyclic triterpenoid skeletons (e.g. oleanane; **1** in appendix I) are primarily derived from land plants (embryophytes). Plant triterpenoids usually possess oxygenated functionality at C-3 carbon; functional groups include either alcohols and acids, or occur in the form of esters or ethers (with alkyl, aryl, and glycosyl groups), resulting in a huge diversity in the molecular structures of bio-triterpenoids (Pant and Rasto-

gi, 1979; Das and Mahato, 1983; Mahato et al., 1988; Mahato and Sen, 1997). Previous reviews pertaining to the phylogenetic distribution of pentacyclic triterpenoids (Das and Mahato, 1983; Jacob, 2003; Vincken et al., 2007) state that because some skeletal structures such as oleanane **1**, lupane **2**, ursane **3**, and friedelane **4** are widespread among angiosperms, triterpenoid alcohols such as lupeol **5**, α -amyrin **6** and β -amyrin **7** are widely employed as angiosperm biomarkers, though these are not taxa- or species-specific (Haven and Rulíkötter, 1988; Woolhouse et al., 1992; Killops et al., 1995; Regnery et al., 2013). Meanwhile, some classes of C-3 substituted triterpenoids serve as taxa-specific biomarkers, and can be useful in decoding the complex spectrum of taxonomic diversity in terrestrial flora. For instance, pentacyclic triterpene methyl ethers (PTMEs) are present particularly in *Poaceae* (e.g. Ohmoto et al., 1970; Jacob et al., 2005) and some of them are domi-

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nant in specific angiosperms (e.g. miliacin **8** in *Panicum miliaceum*) (Jacob et al., 2008a; Jacob et al., 2008b; Zocatelli et al., 2010; Bossard et al., 2013). Some classes of pentacyclic triterpenoids are not primarily related to angiosperm. For example, fernanes **9** are widely distributed among pteridophytes (e.g. Ageta et al., 1963; Bottari et al., 1972), while serratane **10** triterpenoids are found in lycophytes (Boonya-udtayan et al., 2019), gymnosperms (e.g. Tanaka et al., 1999), and bryophytes (Asakawa et al., 2013; Wang et al., 2005).

The major forms of ‘geo (tri) terpenoids’, triterpenoids and their diagenetic derivatives found in the geological samples, are hydrocarbons; especially predominant in thermally mature geological samples such as sedimentary rocks, coal, and petroleum (e.g. Ourisson and Albrecht, 1992). The biologically sourced intact triterpenoid (‘bio (tri) terpenoids’) undergo various diagenetic modifications and degradations in the sediment via photochemical and biological (enzymatic) activities and physicochemical reactions (such as under acidic-basic and oxidizing-reducing conditions); these phenomena occur during the sedimentation and early diagenesis. During subsequent burial, thermal and pressure effects come into play. Diagenetic degradations usually diminish the chemotaxonomic specificity of terpenoid biomarkers owing to the loss of chemical complexity in both carbon skeleton and functionality. Meanwhile, the presence of specific degradation pathways that operates under different conditions also provide important information on diagenesis (e.g. Killops et al., 1995). Thus, plant-derived terpenoids and their geological derivatives serve as molecular biomarkers that can provide independent and complementary clues to infer the past changes in plant community and paleoclimate. Since van Aarssen et al. (2000) highlighted the chemostratigraphic significance of plant terpenoids associated with paleovegetational variations, there has been an increasing numbers of reports on the geological occurrence of plant terpenoids. However, the use of plant terpenoids in the assessment of source organic matter as a general terrestrial biomarker (e.g. terrestrial versus aquatic input; Rullkötter et al., 1982; Freeman et al., 1994; Sabel et al., 2005; Yessalina et al., 2006; Kashirtsev et al., 2008), is as yet limited. Some studies have obtained further evidence on the role of plant terpenoids from an evolutionary perspective, and their applicability in paleovegetation, paleoclimatic, and other geological analysis. Here, the biological and geological occurrence of a variety of plant-derived triterpenoids is reviewed focusing on their significance as taxa-specific and diagenetic markers, and their applications in the paleobotany, and in reconstruction of paleoenvironments and paleoclimate.

2. Triterpenoid biosynthesis in plants

Triterpenoids are isoprenoids consisting of six isoprene units. In plants, cyclic triterpenoid skeletons are synthesized via 30-carbon (C_{30}) intermediate 2,3-oxidosqualene **11** by oxidosqualene cyclases (OSCs), and the cyclization products such as triterpene alcohols retain epoxide oxygen as the hydroxy group at C-3 (Fig. 1). Plant OSCs include cycloartenol synthase (CAS) and lanosterol synthase (LAS) which produce cycloartenol **12** and lanosterol **13**, respectively. These compounds are important precursors to membrane sterols and steroid hormones (Corey and Cheng, 1996; Suzuki et al., 2006). The genes involved in primary metabolism are evolutionarily conserved and exhibit less variation in their number across taxa (Clegg et al., 1997). Other OSCs are known to produce an array of different triterpenoid skeletons, which are notably diverse in angiosperms (Xu et al., 2004; Phillips et al., 2006). Compared to the relatively conserved characteristics in CAS among plant species, OSCs producing angiosperm triterpenoids tend to produce different skeletons even when the gene sequences are closely related (Phillips et al., 2006). Small changes in terpene cyclases can increase product diversity (Segura et al., 2003); apparent lineage-specific diversity in plant OSC sub-families enhances the defense potential of plant triterpenoids which benefits from the chemical diversity of triterpenoid skeletons (Phillips et al., 2006). Extensive skeletal diversity of triterpenoids in angiosperms might have been facilitated by gene duplication, especially whole-genome duplications (WGD) events occurring in the ancestral lineage of extant angiosperms that also resulted in the diversification of genes regulating flower development (Pichersky and Gang, 2000; Jiao et al., 2011; Amborella Genome Project, 2013; Kawai et al., 2014; Edger et al., 2015; Landis et al., 2018).

Hopane **14** triterpenoids (typically found in bacterial membranes), are synthesized from squalene **15** by squalene cyclases (SCs) in bacteria, and probably in ferns bearing bacteria-type hopane synthase that produce C_{30} 3-deoxy-type products (e.g. 22-hydroxyhopane **16** and hop-22 (29)-ene **17**) (Shinozaki et al., 2008; Frickey and Kannenberg, 2009). Meanwhile, other angiosperm-derived compounds with a hopane skeleton (e.g. hydroxyhopanone **18**, moretenol **19**, mollugogenol A **20**) often possess oxygenated functional group at C-3 which still implies cyclization of 2,3-oxidosqualene **11** rather than squalene **15** (Mills and Werner, 1955; Lavie et al., 1968; Chakrabarti, 1969; Inayama et al., 1989; Hamburger et al., 1989; Belin et al., 2018). Fernane **9** triterpenoids are presumed to be synthesized from squalene by putative

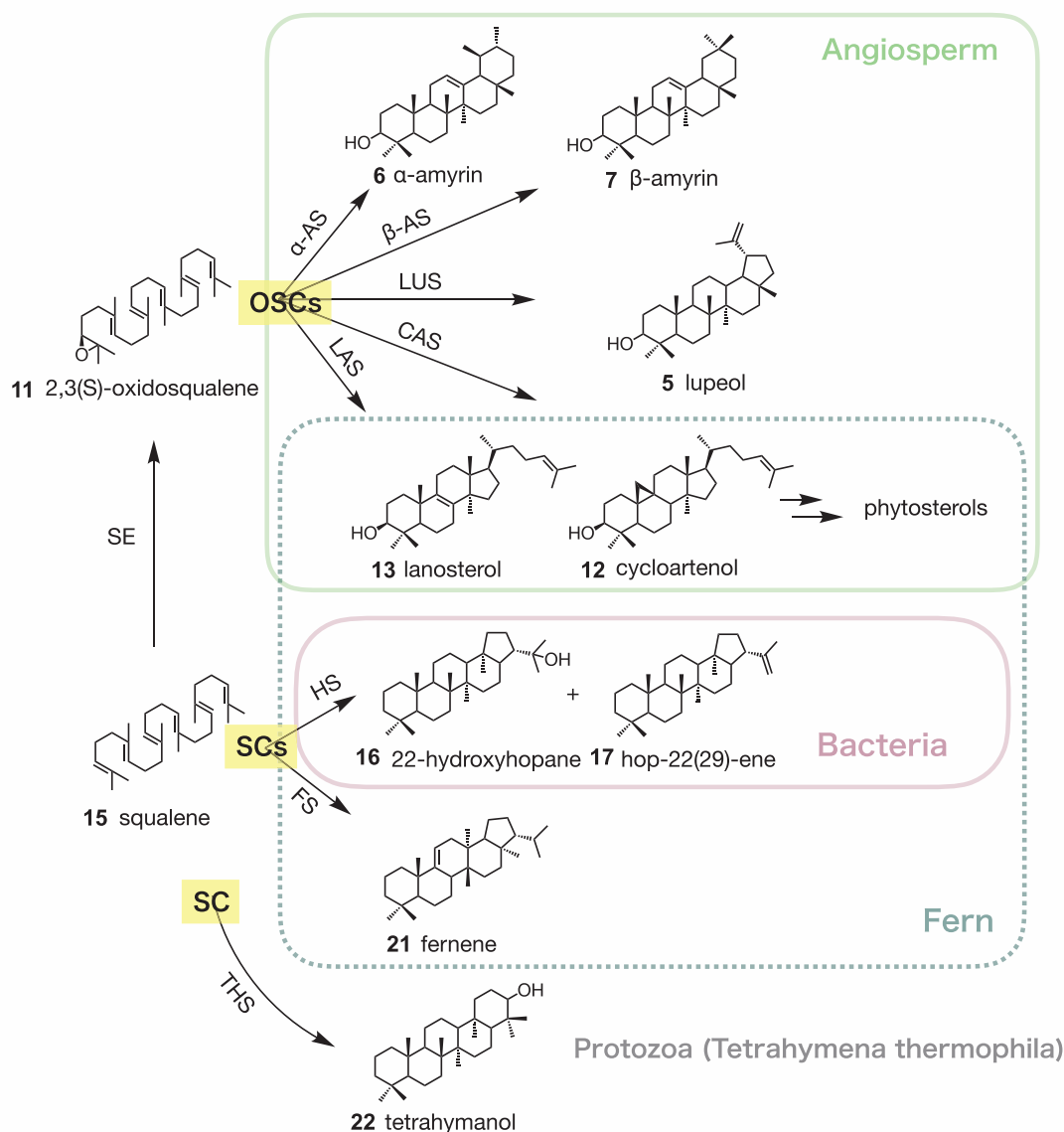


Fig. 1. Simplified triterpenoid biosynthetic pathways. SE, squalene epoxidase; OSCs (oxidosqualene cyclases: LAS, lanosterol synthase; CAS, cycloartenol synthase; LUS, lupeol synthase; β -AS, β -amyrin synthase; α -AS, α -amyrin synthase); SCs (squalene cyclases: HS, putative hopane/hydroxyhopane synthase; FS, putative fernene synthase; THS, tetrahymanol synthase). Adopted from Shinozaki et al. (2008a; 2008b).

fernane **21** synthase, a SC, although this has not been established as yet. Tetrahymanol **22**, ciliate lipid with gammacerane **23** skeleton is also synthesized by tetrahymanol **22** synthase (a SC), in *Tetrahymena thermophila*.

3. Diagenetic transformation of plant-derived triterpenoids

Plant-derived triterpenoids undergo alterations during diagenesis, transport, and burial. Reductive altera-

tion generally leads to the formation of parent triterpenoid skeletons with epimerization of key chiral centers (Poinso et al., 1995; Simoneit, 2007), while rearrangement to different skeletal isomers can also occur (Murray et al., 1997; Nytoft et al., 2010; Nytoft et al., 2014). Oxidative transformation of plant-derived pentacyclic triterpenoids is considered to involve multiple reactions such as oxidation, dehydration, hydrolysis, decarboxylation, and subsequent aromatization by dehydrogenation. A postulated pathways is sequential aromatization that initiates ring A, triggered by the elimination of C-3 oxygenated functional group forming

Δ^2 -triterpenoids (i.e. **24**), and proceeds to ring D (i.e. **25–28**) (pathway 1 in Fig. 2: progressive aromatization) (Streibl and Herout, 1969; Laflamme and Hites, 1979; Wakeham et al., 1980; Tan and Heit, 1981; Chaffee et al., 1984; Hazai et al., 1986; ten Haven et al., 1992; Tuo and Philp, 2005). Another pathway starts with the loss of ring-A, probably involving ring

cleavage step forming **30**, followed by aromatization reactions (e.g. **31–33**) (pathway 2 in Fig. 2: loss of A-ring followed by aromatization) (Spyckerelle et al., 1977; Laflamme and Hites, 1979; Trendel et al., 1989; He et al., 2018). These aromatization reactions occur during the earlier stages of diagenesis and are suggested to be mediated by microbial and, potentially, also

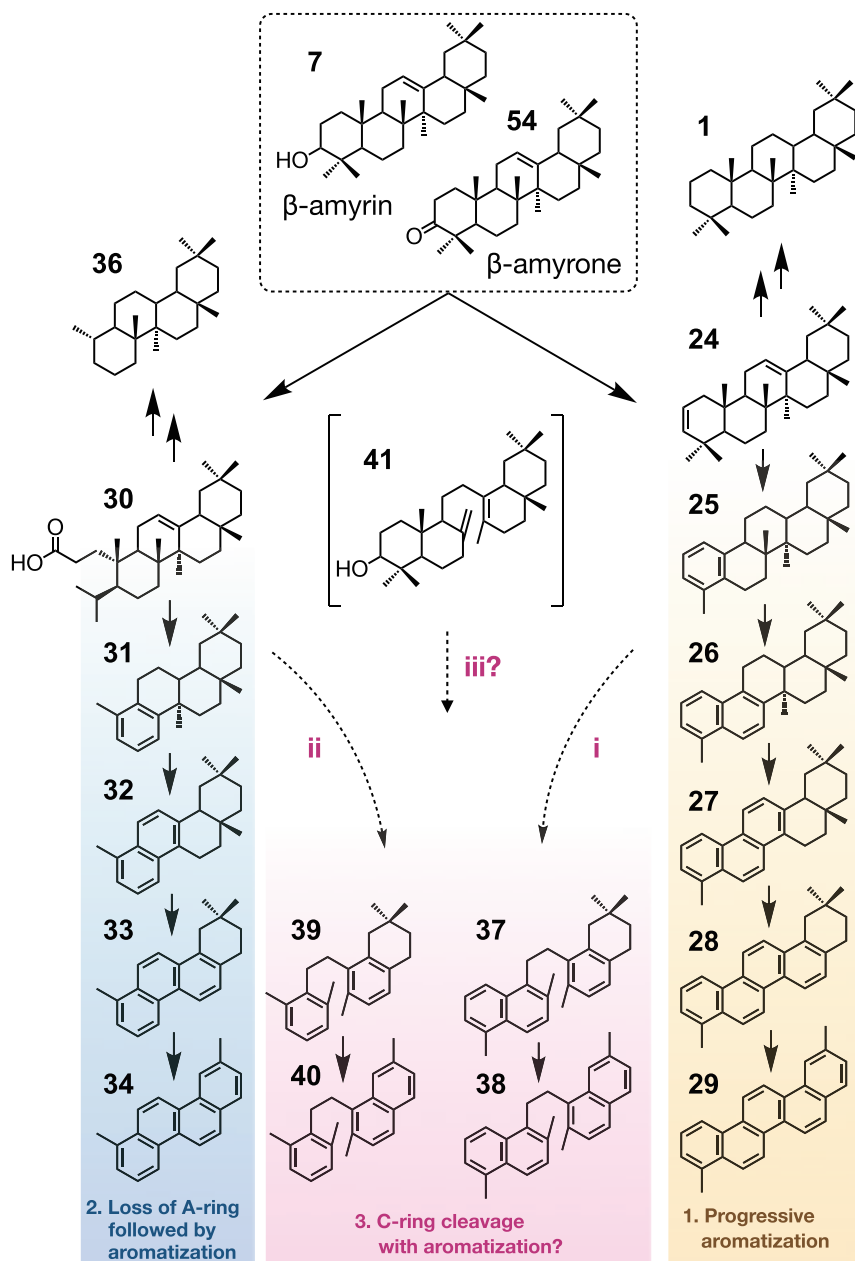


Fig. 2. Diagenetic pathways for plant-derived triterpenoids as represented by oleanane type bioterpenoids (β -amyrin **7** and β -amyrone **54**). Representative aromatic derivatives are shown along with aromatization pathways 1–3 with downward arrows. Typical aliphatic geoterpenoids, des-A-oleanane **36**, and oleanane **1**, are also shown. Arrows (i) and (ii) denote putative C-ring cleavage reactions, whereas an arrow (iii) represents potential input of 8,14-*seco*-biotriterpenoids.

by photochemical processes (Corbet et al., 1980; Trendel et al., 1989; Wolff et al., 1989; Lohmann et al., 1990; Simoneit et al., 2009; He et al., 2018). It is considered that the presence of C-3 oxygenated functional groups makes plant-derived triterpenoids more susceptible to aromatization including ring-A degradation (Corbet et al., 1980; Simoneit, 2007) that results in the general predominance of the aromatic derivatives over saturated hydrocarbons in most sedimentary records (Murray et al., 1997; Kalkreuth et al., 1998; Nakamura et al., 2010). The possible end-products of oxidative triterpenoid transformation, i.e. dimethyl 2,9-dimethylpicene **29** and 1,9-dimethylchrysene **34**, are rarely identified in recent sediments (e.g. Wakeham et al., 1980; Garrigues et al., 1986; Bouloubassi and Salot, 1993). However, they are more often found in thermally mature sediments along with higher proportions of tetraaromatic derivatives (Killops et al., 1995; Murray et al., 1997; Suzuki et al., 2010; Inoue et al., 2012; Baeten et al., 2014) which suggests that complete aromatization requires increased temperatures.

Des-A-triterpenoids potentially serve as a tracer of environmental changes. Both aliphatic and aromatic *des-A*-triterpenoids have been widely found in various geological samples associated with other terrestrial pentacyclic triterpenoids: peat (Del Rio et al., 1992; Dehmer, 1995; Huang et al., 2008; Zheng et al., 2010), coal/plant fossil (Stefanova et al., 2008; Nakamura et al., 2010; Stefanova et al., 2011; Životić et al., 2013), crude oil (Schmitter et al., 1981; Yessalina et al., 2006), fluviodeltaic and lake sediments (Trendel et al., 1989; Logan and Eglinton, 1994; Jaffe et al., 1996; Prartono and Wolff, 1998; Otto et al., 2005; Bechtel et al., 2007; Jacob et al., 2007; van Bree et al., 2016; van Bree et al., 2018), and marine sediments (Dellwig et al., 1998; van Dongen et al., 2006; Suzuki et al., 2010; Furota et al., 2014). The source contributions of biosynthesized *seco-A*-triterpenes (Baas, 1985), photo-products of common triterpenoids (Simoneit et al., 2009), and other biotically/abiotically transformed compounds to sedimentary aliphatic/aromatic *des-A*-triterpenoids has not been confirmed. However, studies have indicated that the *des-A*-triterpenoid formation and accumulation were related to a more reducing depositional environment, wetter climate, and high water table (Jaffe et al., 1996; Mille et al., 2006; Jacob et al., 2007; Huang et al., 2008; Zheng et al., 2010; Stefanova et al., 2011; Đoković et al., 2018; He et al., 2018). The distribution patterns of *des-A*-triterpenoids and triterpenoid hydrocarbons in a Brazilian freshwater lake were explained by changes in vegetation sources and the development of different diagenetic environments (i.e. the marsh and a rather arid hinterland) over the past 18 ka (Jacob et al., 2007). The elevated amounts of aliphatic *des-A*-triterpenoids

(e.g. *des-A*-lupane **35** and mono- and di-unsaturated derivatives of *des-A*-oleanane **36**) observed during the interval with a higher sedimentation rate in Chinese peat deposits (Huang et al., 2008) were considered to reflect either the prevalence of reducing conditions due to increased organic matter (OM) inputs or inclined preservation of aliphatic *des-A*-triterpenoids induced by suppression of aromatization pathway that occurs during the very early stage of the diagenesis (e.g. Corbet et al., 1980; Lohmann et al., 1990).

Aromatic series of 8,14-*seco*-triterpenoids (C-ring cleaved triterpenoids) occur in various geological materials associated with pentacyclic and *des-A* aromatic terpenoids. These geoterpenoids (i.e. **37** and **38**) are generally considered to be derived from pentacyclic triterpenoids by a process involving C-ring cleavage followed by aromatization (Chaffee et al., 1984); pathway 3 in Fig. 2. However, this diagenetic route is less understood. The absence of potential early intermediates by C-ring cleavage on biomolecules (e.g. aliphatic *seco*-8,14-triterpenoids or monoaromatic *seco*-8,14-triterpenoids) led Stout (1992) to propose pathway (i) diverging from the intermediates of pathways 1 via photochemically mediated or acid-catalyzed C-ring cleavage. The identification of the comparable *des-A* series (i.e. **39** and **40**) suggested the C-ring cleavage after the oxidative loss of ring-A (de las Heras et al., 1991), indicated as pathway (ii) (Fig. 2). Alternatively, the possibility of a rather direct contribution of naturally occurring *seco*-triterpenoids (i.e. **41**) cannot be excluded (pathway iii). Generally, the relative amount of derivatives originating via C-ring cleavage is variable in different samples. Therefore, further elucidation of pathway 3 and determination of related favorable environmental preferences is required. Additionally, the contribution of biosynthetic *seco*-triterpenoids could also be possible: *seco*-C oleanane and ursane triterpenoids (e.g. 8,14-*seco*-oleana-8 (26),13-dien-3 β -ol **41**; Fig. 2) are found in certain species of angiosperm family Asteraceae; *Stevia* spp. (Román et al., 2004) and *Koelpinia linearis* (Shah et al., 2004); OSCs that directly synthesize β -*seco*-amyrin and α -*seco*-amyrin from *Arabidopsis thaliana* (Shibuya et al., 2007) have been identified. Such compounds presumably undergo either aromatization or ring-A loss (pathway iii). Therefore, the relative amount of *seco*-C oleanane and ursane skeletons in the sedimentary records might be partly influenced by the difference in source-input (paleovegetation).

The degree of aromatization (DOA) in the series of cyclic biomarkers, i.e. tricyclic diterpenoids (Alexander et al., 1987) and steroids (Mackenzie et al., 1982), is generally considered to increase during thermal maturation. However, significant variations in DOA could also be attributed to the differences in the depositional

environments (i.e. different facies; Haberer et al., 2006). For example, the occurrence of clay minerals facilitates the acid-catalyzed alteration (Rubinstein et al., 1975; Sieskind et al., 1979). Highly aromatized compounds dominate during the dry and warm period reflecting paleohydrological conditions and temperature (Huang et al., 2013). Đoković et al. (2018) interpreted the variations in DOA of non-hopanoid pentacyclic triterpenoids via progressive aromatization pathway (pathway 1) in relation to changes in the water table.

There are reports on the identification of other unique geoterpenoids demonstrating distinct diagenetic transformation. A-ring aromatized pentacyclic triterpenoids with C-3 methyl substitution (**42**) were considered to be derived from glutinane (**43**) type precursor involving the acid-catalyzed migration of one of the methyl group at C-4 to C-3 (Schaeffer et al., 1995; Regnery et al., 2013). A-ring aromatized phenolic triterpenoids retaining C-3 hydroxy group **44** are also reported from relatively immature sediments (Regnery et al., 2013). In evaporitic sediments, uncommon aromatic and sulfur-containing derivatives of plant triterpenoids have been identified (**45–50**), which suggests the inhibition of reactions responsible in common ring-A-functionality-induced aromatization under saline and highly anoxic environments (Poinot et al., 1995). In addition, characteristic functionalization of the precursors can be related to specific geochemical transformation of geoterpenoids (Poinot et al., 1995); for example, when heated in conjunction with elemental sulfur, olean-12-en-28-oic acid **51** can be converted to **45** and **46** probably via the decarboxylated intermediate 28-norolean-17-ene, whereas 3-hydroxyolean-12-en-24-oic acid **52** leads to the formation of thiophene 24-nor-oleanane skeleton (**47**).

The aromatized derivatives of plant triterpenoids also serve as source-specific markers to trace terrestrial organic matter input, or changes in source vegetation and paleoenvironments, as they inherit the chemotaxonomic properties of the parent triterpenoids skeletons (e.g. Bouloubassi and Saliot, 1993; Belicka et al., 2004; Widodo et al., 2009; van Bree et al., 2016). Progressive aromatization involves the loss of methyl substituents which causes the stereochemical and positional information of the resulting compounds to differ from that of the original skeletons. For example, progressive aromatization of taraxerane **53** skeleton up to diaromatic derivatives (rings A and B) retains the characteristic methyl substitution (C-27) at C-13 instead of C-14 in oleanane skeleton, but subsequent aromatization products are structurally indistinguishable from the oleanane series (He et al., 2018). Additionally, acid-catalyzed conversion of triterpenoid skeletons (i.e. taraxer-14-ene to olean-12-ene) occurs in immature

sediments (Haven and Rullkötter, 1988). Such skeletal interconversion and assimilation into oleanane-type skeletons might be partially responsible for the oleananes being the most abundantly detected class of non-hopanoid triterpenoid biomarkers.

These major pathways proposed for plant-derived triterpenoids are still largely based on the co-occurrence of structurally related compounds in geological samples. Experimental identification of specific reaction mechanisms and evaluation of their conditional constraints will enhance the utility of geoterpenoids as proxies for paleoenvironment and diagenetic alterations of organic matter.

4. Triterpenoids as chemotaxonomic markers for establishing botanical origin

Plant terpenoids are often used as a chemotaxonomic tool in investigations pertaining to the botanical affinities of plant-derived materials such as fossils, resins/ambers, peat, and coal (Ikan and Kashman, 1963; Stout, 1996; Bechtel et al., 2005; Bechtel et al., 2007; Widodo et al., 2009; Bechtel et al., 2016; Đoković et al., 2018). GC-MS analysis of amber extracts or pyrolysates well described the occurrence of plant-derived terpenoids and provided information of botanical origin and organic matter preservation (Grantham and Douglas, 1980; Grimalt et al., 1988; Anderson and Winans, 1991; Anderson and LePage, 1996; Otto et al., 2002; Dutta et al., 2009; Pereira et al., 2009; Pereira et al., 2009; Dutta et al., 2011; Paul and Dutta, 2016). Pentacyclic triterpenoids with oleanane, ursane, and lupane skeletons are mostly produced by angiosperms (e.g. Das and Mahato, 1983) and those contained in natural resins and fossil ambers are indicative of these entities having originated from angiosperms (e.g. Brackman et al., 1984; Yamamoto et al., 2006; Vavra, 2009; Mallick et al., 2013). If preserved, less altered compounds including biotriterpenoids with polar substitutions can provide information regarding the specific source of plant-derived materials. Exceptional preservation of polar triterpenoids such as β -amyrone **54**, hydroxydammarone **55** and its oxidative derivatives in Miocene and Eocene ambers have demonstrated that biotriterpenoid markers can be preserved in thermally immature geological samples for more than tens of millions of years (Yamamoto et al., 2006; Dutta et al., 2014; Shi et al., 2014; Dutta and Mallick, 2017). The presence of biotriterpenoid hydroxydammarone **55** in resins/ambers helps its identification as dammar resin produced by angiosperm trees of Dipterocarpaceae (Dutta et al., 2014). Significant amounts of triterpenoids with oleanane **1**, ursane **3**, lupine **2**, and allobetulane **56** skeletons have been identified from

Oligocene glessite ambers including bioterpenoids (e.g. β -amyrin **7** and allobetulin **57**) (Yamamoto et al., 2006), indicating their angiosperm origin, particularly from birch (*Betula*, Betulaceae) that known to contain allobetulin **57** in its bark and branches (Palo, 1984; Lagemwa et al., 1990). Triterpenoid fingerprint with a predominance of betulin **58** associated with allobetulin **57** and other lupane-type derivatives are often cited as evidence of birch origin of archaeological materials such as birch bark pitch (e.g. Hayek et al., 1990; Koller et al., 2001; Grünberg, 2002; Urem-Kotsou et al., 2002). Although lupane-type precursors are widely distributed among different plant taxa, sedimentary abundance of lupane derivatives has often been attributed to the contribution from Betulaceae that produces significant amounts of lupane-type precursors (e.g. betulin, lupeol, betulinic acids) (Hayek et al., 1989; Regnery et al., 2013; Bechtel et al., 2016).

Taraxerol **59** is a major component of mangrove leaves (e.g. Killops and Frewin, 1994) and mangrove ecosystem (e.g. *Rhizophora mangle*, mangrove surface sediment, mangrove crab excrement) (Koch et al., 2011) and its abundance in marine sediments was demonstrated to co-vary with both the down-core variations of *Rhizophora* pollen and the spatial distribution of coastal mangrove forests (Versteegh et al., 2004). Hence, taraxerol **59** has been used as a molecular tracer of mangrove input in coastal settings (Xu et al., 2006; He et al., 2014). Its potential as a quantitative vegetation marker might be limited to relatively young and immature sediments due to its transformations to other pentacyclic ketones and hydrocarbons during early diagenesis (Haven and Rullkötter, 1988; ten Haven et al., 1992; Boot et al., 2006; He et al., 2018).

Pentacyclic triterpene methyl esters (PTMEs) and triterpenoid acetates are a new class of plant biomarkers in the sense that these have been only recently investigated for their presence and application in geological materials. PTMEs such as miliacin (olean-18-en-3 β -ol methyl ether **8**) are typically contained in graminoids (Poaceae) with fewer reports from the other families of angiosperms and gymnosperms (Ohmoto and Natori, 1969; Ohmoto et al., 1970; Russell et al., 1976; Connor and Purdie, 1981; Conner et al., 1984; García et al., 1995; Connor, 2004; Jacob et al., 2005). Therefore, PTMEs have been used to infer the contribution of Poaceae species including millet and other grasses in geological and archaeological samples. PTMEs have been reported from soils (Le Milbeau et al., 2013; Schwab et al., 2015), surface sediments of the river (Oyo-Ita et al., 2010), lake sediments (Grimalt et al., 1991; Jacob et al., 2005; Xu et al., 2008; Jacob et al., 2008a; Zocatelli et al., 2010), and prehistoric vessels and paleosols (Heron et al., 2016; Motuzaite-Matuzeviciute et al., 2016; Courel et al., 2017).

PTMEs with serratane **10** skeletons have been demonstrated as a specific marker for Pinaceae (Le Milbeau et al., 2013). Although the diagenetic alteration of PTMEs is less known, PTMEs possess a relatively good preservation potential against aerobic degradation as they have been detected in relatively high abundance in the Holocene core sediment affected by strong reworking in aerobic waters (Jacob et al., 2005). Triterpenoid acetates (e.g. taraxasterol acetate **60**) have been shown to be derived from mainly *Asteraceae* and other plants of open habitat (Lavrieux et al., 2011; Zocatelli et al., 2014; Dubois and Jacob, 2016). Pentacyclic triterpenoid acetates are presumed to be more labile than PTMEs due to the natural hydrolysis of the ester bond during the early stage of sedimentation (Oyo-Ita et al., 2010). Nevertheless, their distributions could be useful in recent and young sediments to reconstruct specific plant inputs and to infer related environmental changes including anthropogenic impacts (Dubois and Jacob, 2016).

4.1. Angiosperm Evolution

The geological occurrence of oleanane and related triterpenoid skeletons is mostly limited to materials from Cretaceous and after (Peters et al., 2005). This is probably reflected in the appearance and rapid expansion of source organisms, angiosperms, during the Cretaceous. Indeed, both the frequency of occurrence and the relative amount of oleanane **1** is well related to the diversification of angiosperms (Moldowan et al., 1994). This observation has been applied for age estimation of petroleum source rock; the occurrence of oleanane almost certainly indicates a Cretaceous or younger origin, and the higher ratio of oleanane **1** to hopane **14** (i.e. oleanane index >0.2) implies Paleogene or younger origin (Moldowan et al., 1994; Bence et al., 1996; Holba et al., 1998; Dzou et al., 1999; Alberdi and López, 2000). Although, quantitative assessment based solely on oleanane amount is questioned because the abundance of oleananes in petroleum is not simply controlled by the degree of terrestrial input but is also dependent on sedimentary environments and maturity (Ekweozor and Telnaes, 1990; Murray et al., 1997; Waseda and Nishita, 1998). Other intriguing findings of Moldowan et al. (1994) include rare but reliable occurrences of oleanane **1** apparently predating the earliest angiosperm fossils; a Middle Jurassic marine siltstone and a Carboniferous coal ball. This could be attributed to three scenarios: (i) occurrence of early angiosperms, (ii) occurrence of stem lineages of angiosperms that produce oleanane-related metabolites as a shared feature before the evolution of morphological features of angiosperms, (iii) convergent evolution of oleanane biosynthesis in a different (probably extinct) lineage. Taylor et al. (2006) analyzed the occurrence

of oleanane in Paleozoic and Mesozoic non-angiosperm fossils and discussed the phylogenetic relationships of fossil taxa putatively assigned to the stem group of angiosperms. Oleanane **1** has been detected from Cretaceous (Aptian) Bennetitales and Upper Permian Gigantopterids, indicating that these taxa are stem lineage relatives with distinct morphology; this corresponds to the scenario (ii). Gigantopteris is currently the only source that has been paleochemotaxonomically documented to have oleanoids and might have contributed to a late report of the presence of oleanane derivatives in Permian samples (e.g. monoaromatic *des-A* oleanane **31** from Tasmanian tasmanite: Azevedo et al., 1992). The gap between fossil evidence and molecular dating on the timing of the origin of the angiosperms has been debated (e.g. Doyle, 2012; Magallón et al., 2015). Recently, Coiro et al. (2019) re-evaluated the timing of angiosperm origin from paleobotanical evidence based on the spatiotemporal distribution and diversification patterns of monosulcates and tricolpate eudicots and compared it to molecular phylogenetic inferences on the course of pollen evolution. They found that both results strongly conflict with Triassic and early Jurassic molecular ages, which is difficult to explain by geographic or taphonomic biases. However, the Late Jurassic ages are rather consistent regarding the existence of low-diversity and ecologically restricted nature of early angiosperms (Feild et al., 2004). Therefore, Jurassic occurrence of oleanane could also be attributed to early angiosperms even in scenario (i). However, it is important to further clarify the occurrence of oleanane in bennetitales, especially by analyzing Triassic specimens to rule out the potential contribution of co-occurring angiosperms in the Cretaceous samples analyzed in Taylor et al. (2006). Bennetitales flourished through Mesozoic and potentially interfere with the use of oleanane as a definitive marker for tracing early angiosperms in Mesozoic.

Concerning the evolution of triterpenoid biosynthesis in angiosperm lineage, a bioinformatic approach on the timing of diversification of angiosperm OSCs might provide a complementary view on the origin of oleanane-precursors in the lineage. For example, genome-wide screening of genes associated with terpenoid biosynthesis found the lowest number of genes for triterpene synthesis in basal angiosperm *Amborella* (Goremykin et al., 2003); 3 genes annotated as lanosterol synthases and were unlikely to engage in oleanane synthesis. Moreover, the occurrence of metabolites with typical angiosperm-triterpenoid skeletons is scarce and less diverse among basal angiosperms (e.g. Henry, 2005), though an apparent sampling bias exists in that fewer studies have been conducted on basal angiosperms. Therefore, diversity

in triterpenoid skeletons in angiosperms might not have originated from the earliest angiosperm but occurred later, during their diversification to major groups of extant angiosperms (e.g. eudicots and monocots). Such an evolutionary trend towards higher diversity and production of plant triterpenoids in angiosperms could also be evidenced in the geological occurrence of triterpenoids observed in Moldovan et al. (1994) and Killops et al. (1995).

4.2. Serratane and onocerane triterpenoids

Serratane **9** triterpenoids are characterized by a pentacyclic triterpene skeleton with an unusual seven-membered ring (ring C) and oxygenated functions at both C-3 and C-21. Serratane-type triterpenoids are well-distributed among Lycopodiaceae (Tsuda et al., 1975; Zhou et al., 2003; Boonya-udtayan et al., 2019) and Pinaceae families (Tanaka et al., 1994; Tanaka et al., 1998; Otto and Wilde, 2001). Onocerane **61** triterpenoids, 8,14-*seco*-triterpenoids with a symmetrical tetracyclic skeleton are biochemically related to serratanes and the occurrence of α -onocerin **62** in only reported in lycophyte genus *Lycopodium* (Lycopodiaceae), pteridophyte genus *Lemmaphyllum* (Polypodiaceae), and evolutionally distant angiosperm genus *Ononis* (Fabaceae) (Ageta et al., 1962; Rowan and Dean, 1972; Ageta et al., 1982). Recent studies identified that sequential enzymes cyclize distinctive 2,3,22,23-dioxidosqualene **63** into serratane **10** and onocerane **61** skeletons (e.g. serratane-diol **65** and tohogenol **64**, respectively) through the same intermediate pre- α -onocerin **66** in *L. clavatum* (Fig. 3) (Araki et al., 2016). Additionally, Almeida et al. (2018) identified a single α -onocerin synthase that directly produces α -onocerin **62** in *O. spinosa* and revealed the convergent evolution of α -onocerin pathways in lycophyte and angiosperms.

Compared to the other non-hopanoid pentacyclic triterpenoids, the geological occurrence of serratane and onocerane skeleton is rare and is less explored. Wang et al. (1988) reported aliphatic serratane and onocerane hydrocarbons in the lacustrine crude oils and rocks ranging from Carboniferous to Neogene age. Hitherto, onoceranes have been observed in association with terrestrial input, such as from Miocene fossil *Pseudofagus* leaf from the Miocene lake sediment (Giannasi and Niklas, 1981), and sediments with significant terrestrial input that include Cretaceous lake sediments (Wang et al., 1988), Oligocene fluvial and lacustrine shales (Curiale, 1988), Paleogene lacustrine source rocks (Fu et al., 1988), Late Cretaceous siltstones (Pearson and Obaje, 1999), and Holocene lake sediment (Jacob et al., 2004).

As an aromatic hydrocarbon derivative of serratane skeleton, 4,4'-dimethyldinaphtho[a,d]cycloheptane **67**, i.e. tetraaromatic serratane, was identified from the Oli-

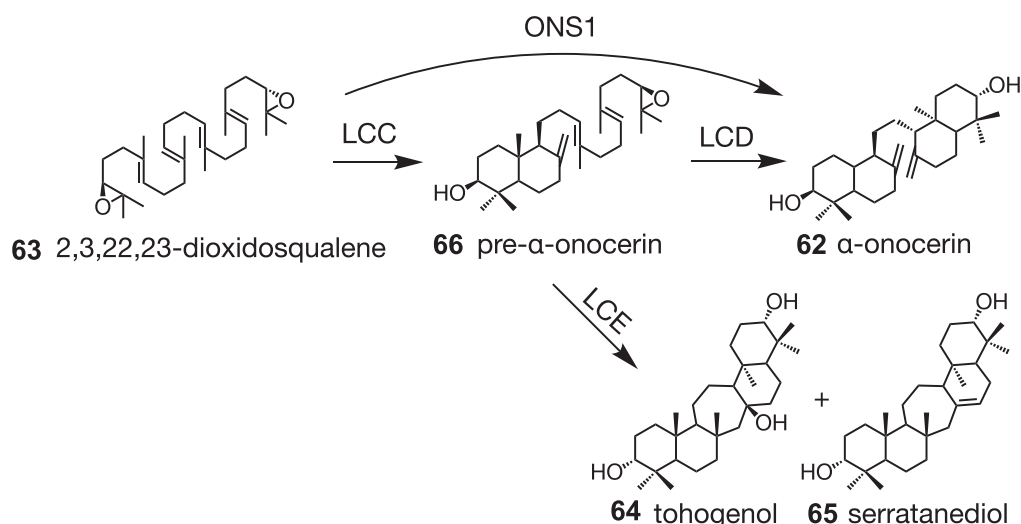


Fig. 3. Cyclization of dioxidosqualene **63** into α -onocerin **62**, tohogenol **64**, and serratanediol **65** catalyzed by unusual sequential OCSs (LCC, dioxidosqualene cyclase; LCD, onocerin synthase; LCE, onoceroid synthase) in *Lycopodium clavatum*. α -onocerin synthase ONS1 directly cyclize dioxidosqualene **63** in *Ononis spinosa*. Adopted from Araki et al. (2016); Saga et al. (2017); Almeida et al. (2018).

gocene fluviodeltaic deposits and related to serratane triterpenoids based on its seven-membered ring-C (Le Métayer et al., 2005; Le Métayer et al., 2008). The serratane derivative **67** were suggested to be derived from specific but yet-undefined plant precursor other than angiosperms based on its contrasting occurrence against other angiosperm biomarkers (Le Métayer et al., 2005). Lycophytes have thrived since >400 Ma and are a major component of terrestrial flora; however, they currently lack specific biomarker that could enable the determination of their botanical origin. Distributions of serratane and onocerane triterpenoids among lycophytes, as well as their geological occurrence since the Carboniferous, gives an idea that this class of triterpenoids could be used as a potential tracer for lycophyte vegetation. Structural similarity with other 3-oxo-triterpenoids implicates that the diagenetic nature of these cyclic terpenoids also favors the aromatization pathway. Therefore, compound **67** and related aromatized derivatives would be targeted in future studies.

4.3. Fernane and arborane triterpenoids

Analysis of morphologically well-preserved fossils can provide key datasets for relating certain geoterpenoids with fossil taxa which attest to the paleochemotaxonomic potential of the compounds as a marker of extinct lineages. For instance, aromatized fernane/arborane hydrocarbons (MATH **68**, MAPH **69**, DAPH1 **70**, DAPH2 **71**) in the Carboniferous sediments were targeted as potential plant biomarkers based on their stratigraphically concomitant occurrence with palynomorphs related to *Gymnospermopsida* (Pteridospermales, Cordaitales, and Coniferales) (Vliex et al.,

1994). Vliex et al. (1994) attributed the origin of aromatic fernane/arborane derivatives in Upper Carboniferous and Early Permian coals to higher plants and related their increase from Westphalian to Stephanian to the increase of *Gymnospermopsida* (Coniferales) in the vegetation possibly reflecting a transition to a drier climate. To further narrow down the source of aromatic fernane/arborane hydrocarbons, Auras (2004) and Auras et al. (2006) analyzed 57 fossil plant remains, identifying those compounds solely from the cordaitan fossils; they were absent in fossils of marattialean tree ferns (*Pecopteris*), giant horsetails (*Calamites*), and arborescent lycophytes. However, the biological origin of geologically occurring arborane **72** triterpenoids, especially those from non-terrestrial settings is relatively unknown. Among extant plants, arborane **72** triterpenoids are found in several plant taxa including some angiosperm families, pteridophytes, and lichens (Jacob, 2003). However, widespread occurrence and abundance of arborane **72** triterpenoids among lake sediments often conflicts with their distribution and is considered to reflect other sources, especially those related to aquatic production (e.g. Ourisson et al., 1982; Hauke et al., 1992; Jaffé and Hausmann, 1995; Volkman, 2005). Hanisch et al. (2003) analyzed Holocene lake sediments and concluded that the terrestrial origin of arborane **72** triterpenoids are unlikely in the studied setting because they do not correlate with other plant terpenoids but with authigenic production markers such as tetrahymanol **22**. van Bree (2018) further suggested an algal or aerobic bacterial origin for arborane derivatives in lake sediments from their relatively depleted $\delta^{13}\text{C}$ values. Therefore, aromatic derivatives

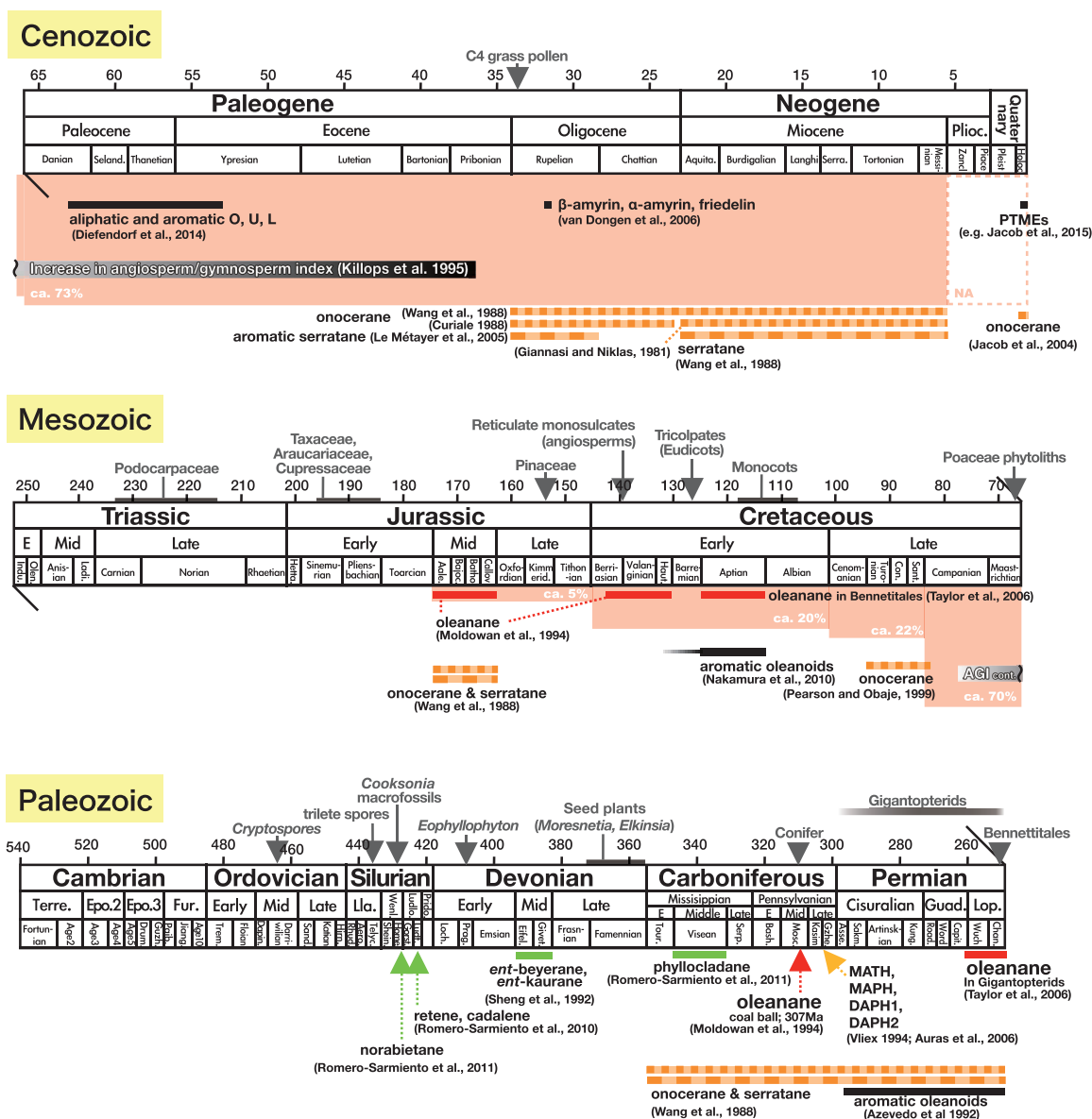


Fig. 4. Geological occurrence of characteristic terpenoid biomarkers discussed in this review. Arrows and bars below the time scale indicate the ages of geoterpenoid detections reported in the references (including age uncertainty). O, U, and L denote triterpenoids with oleanane 1, ursane 3, and lupane 2 skeletons, respectively. The height of the filled area roughly represents the frequency of oleanane detected in Moldowan et al. (1994) for timespans: Jurassic, Early Cretaceous, Cenomanian-Santonian, Campanian-Maastrichtian, and Paleocene-Miocene. Arrows and bars on the time scale shows earliest fossil records of relevant plant taxa; cryptosporites, trilete spores and *Cooksonia* (basal tracheophyte) (Edwards et al., 2000); *Eophyllophyton* (euphyllophyte) (Hao and Xue, 2013); *Moresnetia* and *Elkinsia* (seed plants) (Taylor et al., 2009); Bennettiales (Blumenkemper et al., 2018). Conifer and modern conifer families (Podocarpaceae, Taxaceae, Araucariaceae Cupressaceae, and Pinaceae) (Rothwell et al., 2012); Monocot fossil (Coiffard et al., 2019); C4 grass pollen (Urban et al., 2010); Time scale based on Geologic Time Scale v.5.0 (Walker et al., 2018).

of arborane/fernane triterpenoids might serve as a unique marker for Cordaites and related extinct Paleozoic plants, when identified in plant fossils and terrestrial deposits such as coals. However, source annotation for these compounds occurring in lacustrine and marine sediments are rather equivocal.

5. Development of terpenoid-based paleovegetation proxy

The molecular composition of chemotaxonomic plant terpenoids in marine and lake sediments can

serve as a useful proxy for floral composition. The composition of terrestrial organic matter in lacustrine and marine sediments implies plant community in the larger catchment area, ultimately, attributed to regional vegetation and terrestrial environment (van Aarssen et al., 2000; Hauteville et al., 2006b). Especially, the application of biomarker-based vegetation indices to marine sediments can benefit from its high spatio-temporal distribution and well established biostratigraphic framework (e.g. Pancost and Boot, 2004). The relative abundance of retene **73**, aromatic end-product of tricyclic diterpenoids abundantly produce by conifer species, and cadalene **74**, aromatic sesquiterpenoid as a general marker of land plant, have been successfully applied to trace vegetation change during Jurassic period, and are considered to reflect regional and possibly global climate changes (van Aarssen et al., 2000; Hauteville et al., 2006b). Given the pentacyclic triterpenoids with oleanane **1**, ursane **3** or lupine **2** skeletons are mostly produced by angiosperms, whereas tricyclic diterpenoids (e.g. dehydroabietic acid **75**) are mainly derived from gymnosperms (Simoneit et al., 1986; Otto and Wilde, 2001); the ratio of these di- and triterpenoids can be a useful proxy for the source contributions of gymnosperm/angiosperm or vice versa (Killops et al., 1995; Bechtel et al., 2003; Haberer et al., 2006; Nakamura et al., 2010). Killops et al. (1995) used the ratio of aliphatic triterpenoids to aliphatic dit-

erpenoids as indicative of the relative contribution of angiosperm (Angiosperm Gymnosperm Index; AGI), and found their stratigraphic variation from the Late Cretaceous to Late Eocene were consistent with paleobotanical data that delayed occurrence of invasion and spread of angiosperm vegetation in New Zealand during Cenozoic. As the triterpenoid precursors preferentially undergo aromatization pathways in most sedimentary environments (Fig. 2) (e.g. Murray et al., 1997), the ratio of aromatic derivatives is also useful (Haberer et al., 2006; Widodo et al., 2009), and is highly sensitive to angiosperm input as observed by analysis of plant fossils (ar-AGI; Nakamura et al., 2010) whereas aliphatic ratio can significantly underestimate the triterpenoid input. Bechtel et al. (2007) used di-/ (tri + di) to infer the variations in the contribution from conifers and angiosperms during Holocene environmental changes in a coastal lake.

Understanding the production of terpenoids by taxonomically or ecologically different plants is necessary for the quantitative reconstruction of paleovegetation. Modern exploration of the production of di- and triterpenoids in 44 angiosperms and conifer trees documented the significantly higher concentration and production of terpenoids by evergreen trees than deciduous species (Fig. 5) (Diefendorf et al., 2012); their productions were calculated based on terpene abundances scaled with litter flux data; both evergreen

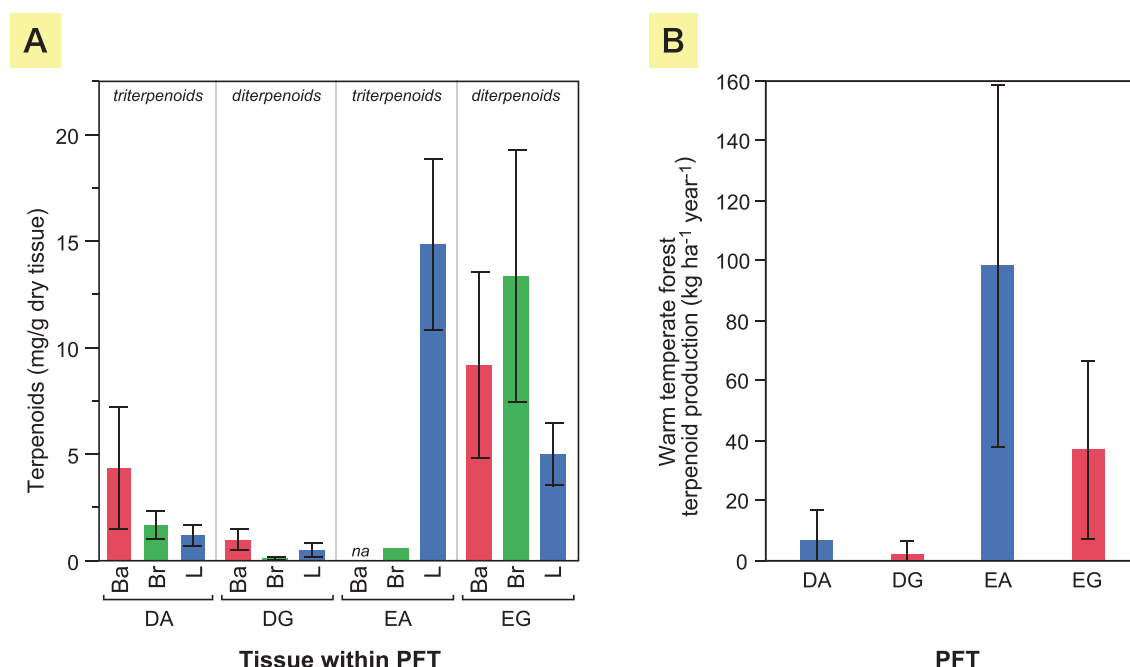


Fig. 5. (A) Terpenoid abundances in different tissues (mg/g dry tissue) and (B) terpene production estimates for warm temperate forests (kg ha⁻¹yr⁻¹) separated by different plant functional types (PFT; phylogeny, leaf habit). Abbreviations: Ba, bark; Br, branch; L, leaf; DA, deciduous angiosperm; DG, deciduous gymnosperm; EA, evergreen angiosperm; EG, evergreen gymnosperm). Adapted from Diefendorf et al. (2012).

angiosperm and gymnosperm were found to produce similar amounts of corresponding terpenoids in proportion to their biomass. The study sheds light on the importance of paleofloral characteristics in terms of leaf lifespan, which is another functional factor in determining the sedimentary terpenoid composition. In the modern fluvial system with small catchment, Giri et al. (2015) observed the substantially lower quantity of angiosperm-derived triterpenoids compared to conifer diterpenoids, although a much larger portion of the catchment area was covered by deciduous angiosperms. This discrepancy was explained and the prediction of the plant community (ratio in conifer/angiosperms) was significantly improved when the differences in plant terpenoid synthesis (significantly lower in deciduous angiosperms) were corrected. This result gives a glimpse of the significance of plant terpenoids for quantitative reconstruction of the surrounding vegetation, at least in modern ecosystems where parameters such as litter production ratio and lipid synthesis of on-site vegetation are also calculable.

Differential transportation and preservation of chemotaxonomically distinct terpenoids can complicate the use of plant terpenoids as quantitative indicators. Angiosperm triterpenoids are leaf wax constituents and diterpenoids are significantly contained in woody tissues in conifers (e.g. Diefendorf et al., 2012). This distribution of terpenoids in plant tissues leads to their differential transportation and deposition; leaf fragments and cuticles tend to accumulate in finer fractions during sedimentation while woody fragments commonly deposit with relatively coarse materials. Such taphonomic characteristics of source materials are often imprinted in the terpenoid compositions of sediments as described in fluvial to estuarine environments and gravitational flow deposits (e.g. Inoue et al., 2012; Furota et al., 2014) and could provide geochemical insights into the sedimentological process as shown by Furota et al. (2014). Quantitative estimates of the differences in the effect of thermal maturation on different classes of terpenoids should also be illuminated. Experimental techniques of artificial maturations are promising, but these focus primarily on precursor-product relationships, and quantitative means are usually difficult to interpret. Diefendorf et al. (2015) showed a relatively rapid loss of biotriterpenoids (acids and alcohols) compared to diterpenoids under relatively lower temperature (-200°C). Taylor et al., (2006) used the pyrolysis method to mimic the diagenetic production of oleanane from the plant material and successfully identified oleanane from species previously reported to contain precursors with oleanane-skeleton such as oleanoic/ursolic acids (*Olea europaea* and *Rosmarinus officinalis*). However, their method did not yield oleanane from *Aesculus californica*

which contains highly functionalized oleanoid saponins. Because many angiosperms produce a significant variety of triterpenoid saponins, such difference in preservation potential between different types of metabolites also needs to be studied. Indeed, the current dataset for terpenoid production among plant functional groups represents terpenoids obtained by extraction and saponification (Diefendorf et al., 2012), which does not recover saponin aglycones.

Few studies have compared molecular and macrofossil/palynological compositions. Otto et al. (2005) found that the triterpenoid/diterpenoid ratio in Miocene sediments of Clarkia Lake was significantly higher than the macrofossil composition of angiosperm/gymnosperm, which was partly attributed to the occurrence of angiosperm leaf detritus and wax in the sediment. Compared to macrofossil records, the advantage of the biomarker approach is obvious in representing original biomass input to the sediment, regardless of morphological preservation potentials. The discrepancy between information from biomarkers and pollen is often explained by the difference in the spatial coverage they represent (Killops et al., 1995; Regnery et al., 2013); the biomarker record is inclined to represent the vegetation growing more closely to the sedimentary basin (in terms of transportation) while pollens represent a rather broader area.

To conclude, terpenoid-based vegetation proxy can provide unique estimates on the contribution of vegetation input at broad (chemo)taxonomic groups, which could be complementarily used with other paleobotanical information. It is important to implement the multiproxy approach because of taphonomic and transport biases in both the molecular and fossil/pollen records.

6. Remarks and Prospects

A better understanding of the (paleo) chemotaxonomic and diagenetic significances of plant terpenoids is essential for the development of geochemical tools for paleobotany, and paleoenvironment reconstruction. Key reactions in the diagenetic alteration pathways, especially where pathways diverge into different types of derivatives, need to be elucidated. Most precursor-product relationships shown in Fig. 2 have not experimentally evaluated as yet, except for the one of possible reaction that is supposed to operate in the earliest step of the formation of *des-A*-triterpenoid in pathway 2 (photochemical degradation of 3-oxo-triterpenoids to A-ring-*seco*-triterpenoids; e.g. Simoneit et al., 2009). Other process, such as microbially-mediated transformation amongst others, are not precisely understood. Thus the contribution of such process to natural environments is yet to be evaluated, which are

also important for the relating geoterpenoids with source input (i.e. vegetation proxies) quantitatively.

Considering the known diversity of triterpenoids, it is presumed that there are still many classes of triterpenoids not yet discovered from geological samples. Some of them might have poor preservation potentials or tend to be converted to commonly detected class of skeletons (e.g., skeletal conversion proposed by Rulkkötter et al. (1994)). Another reason could be the lack of knowledge regarding the identification of potential triterpenoids in the form of geoterpenoids (i.e. hydrocarbons). In this context, experimental approaches such as synthesis of potential biomarkers, or artificial maturation of source materials hold promise. Sutton and Rowland (2016) performed synthetic identification of ambrane **76**, C₃₀ *seco*-C,D-onoceroïd hydrocarbon, by hydrogenation of corresponding unsaturated alcohol extracted from ambergris. They noted similar precedent in the identification of synthetic crocetane (2,6,11,15-tetramethylhexadecane **77**) before the identification of crocetane **77** in geological samples. The hydrocarbon was subsequently developed as a molecular marker for the anaerobic oxidation of methane and photic zone euxinia (e.g. Maslen et al., 2009). Artificial maturation or experimental paleontological approach (e.g. Hautevelle et al., 2006a; Lu et al., 2013; Asahina and Suzuki., 2016) can provide insights into the diagenesis of plant terpenoids, source-product relationship, and candidate biomarker molecules. Artificial maturation generally gives a reasonable distribution of reaction products for plant-derived sesqui- and diterpenoids by the combination of several different conditions (Hautevelle et al., 2006a; Lu et al., 2013). However, to the author's knowledge, the above discussed aromatic triterpenoid derivatives have not been achieved by existing methods of heating experiments using plant-derived materials (plant tissues, clude extracts, and biotriterpenoids with C-3 oxygenated functional group) as starting material. This fact further highlights the importance of elucidation and incorporation of the reaction steps that mimics the postulated early diagenetic reactions which provide essential geological intermediates such as **24** and **30** for the formation of aromatic triterpenoids.

From a technical perspective, the development of an open-access mass spectral database for the identification of plant-derived terpenoids is underway. As shown, partitioning between aromatic and aliphatic derivatives as well as the degree of aromatization and the relative amount of *des*-A and pentacyclic derivatives are sensitive to the sedimentary environment and post-depositional maturation. Hence, comprehensive identification of diagenetically related compounds (i.e. shared origins) is desirable to better represent the source input. This typically applies when applying ge-

neric vegetation indices such as di-/ (tri- + di). However, such exhaustive identification via manual workflow could become increasingly labor-intensive with the increasing number of known diagenetic derivatives; this might discourage researchers from detailed analyses of the plant-derived terpenoids. However, this approach might benefit from the use of analytical software capable of automated identification of compounds, i.e. Automated Mass Spectral Deconvolution and Identification System (AMDIS). The need for geoterpenoid library arises from the fact that even major commercial databases including NIST and the Wiley Registry, do not completely cover the variety of geologically occurring terpenoid derivatives; hence, the automation (as yet) is largely dependent on manual annotation and creation of an in-house library. In addition, a series of aromatic geoterpenoids tend to show similar mass spectral features and the information on the order of elution, i.e. retention index (RI), is critical for their proper annotation. Hence, the open-access mass spectra datasets are prepared using with RI information and preferentially include plant-derived geoterpenoids that have been used to calculate vegetation indices in Nakamura et al. (2010) and other literature for biomarker-based vegetation reconstruction. By using the library, preliminary automatic identification by AMDIS software (Agilent), and subsequent semi-automatic calculation of indices, vegetation indices such as HPP (van Aarssen et al., 2000) and ar-AGI (Nakamura et al., 2010) were obtained for the aromatic fractions of 70 selected Cretaceous marine sediments; the results showed better HPP while systematically lower ar-AGI due to false negatives in minor aromatic triterpenoid isomers (Fig. 6). Lastly, the establishment of automated methods for the determination of indices (e.g. Dillon and Huang, 2015; Fleming and Tierney, 2016) and ‘-omics’ workflow, herein termed the ‘geolipidomics’ approach, involving untargeted analyses and data mining combined with multivariate statistical analysis will be a powerful tool for the development of new biomarkers and vegetation and environmental proxies; the concept is reviewed in Bell and Blais (2019).

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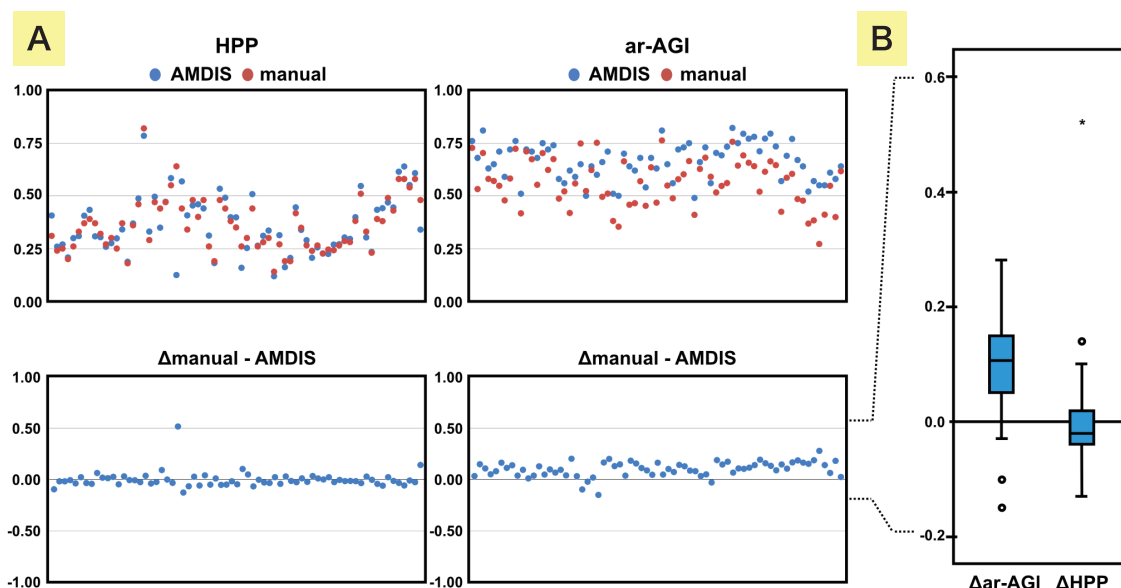


Fig. 6. (A) Preliminary comparison of HPP and ar-AGI values derived from semi-automated identification and integration by AMDIS and manual analysis for the Cretaceous sediments. (B) The box plot summarizing the difference between manual and AMDIS results. The horizontal line within the box indicates the median, boundaries of the box indicate the 25th and 75th percentile, and the whiskers indicate the highest and lowest values of the results whereas data above and below whiskers are considered outliers. Note that mass spectra database is under development and automated identification parameters are not best-optimized yet.

fieldwork and sampling on Cretaceous research. I thank Drs. Yoshihiro Shiraiwa and Hiroya Araie for the collaboration on the study of haptophyte lipids and algal environmental proxies since the postdoctoral project (related topics are reviewed elsewhere). I also thank Dr. Pierre Albrecht for motivating me on the plant terpenoid research through a discussion during his short stay at Hokkaido University in 2008. I want to thank all collaborators and colleagues for every kind of assistance. This work was supported by a JSPS KAKENHI Grant Number 17K18016. Fig. 5 is reprinted from *Geochimica et Cosmochimica Acta* **85**, Diefendorf et al., Distribution and carbon isotope patterns of diterpenoids and triterpenoids in modern temperate C3 trees and their geochemical significance, pp. 342-356. © 2012, with permission from Elsevier.

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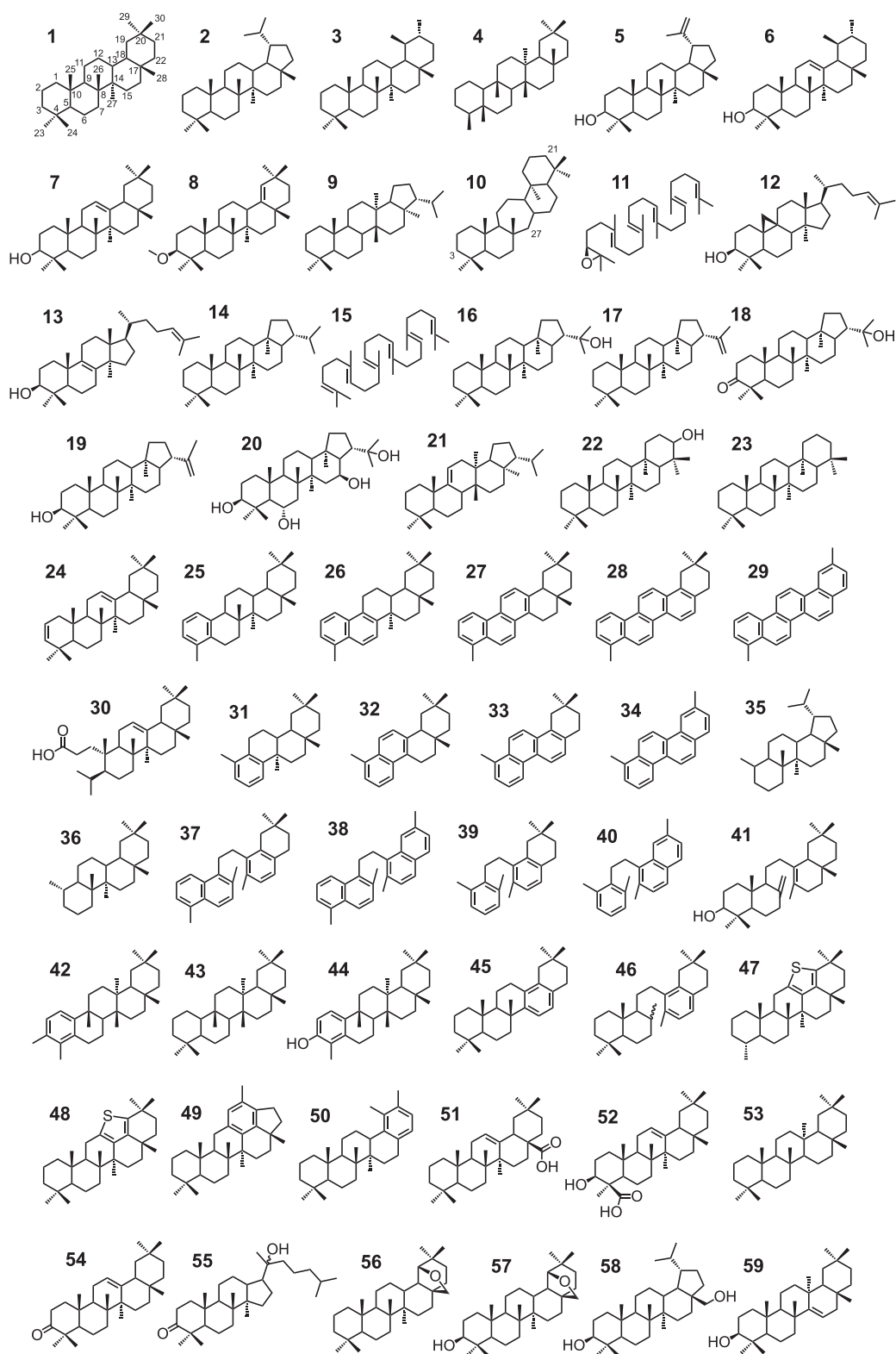
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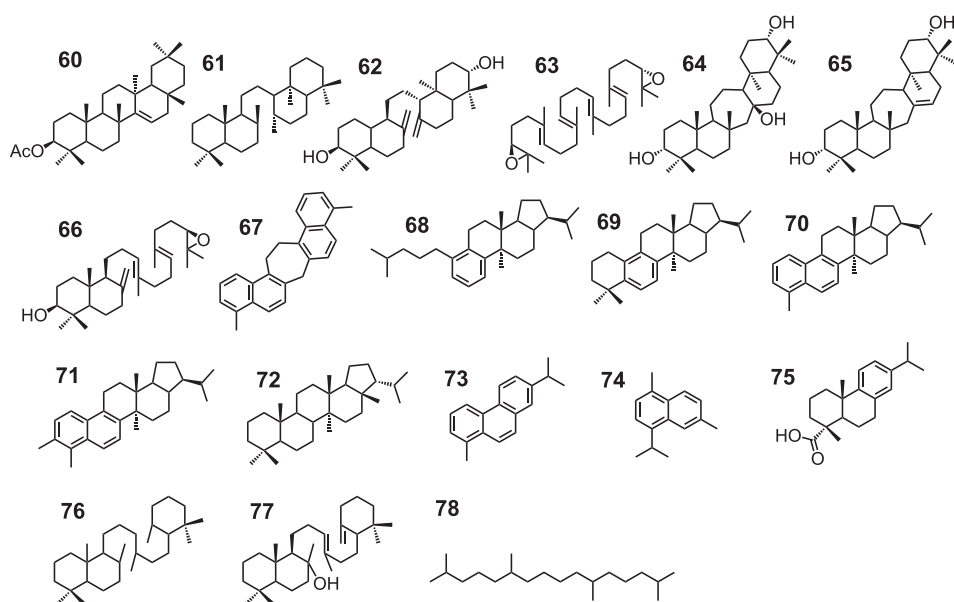
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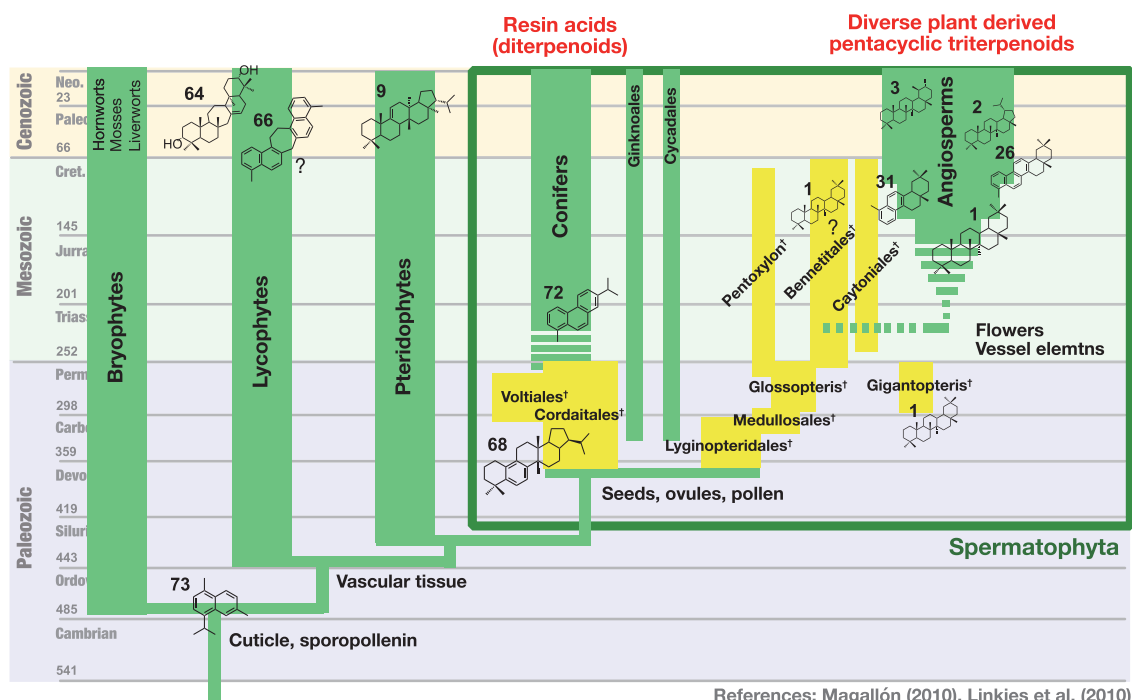


Appendix 1



Appendix 1 (continued)

Generalized illustration of land plant evolution and occurrences of characteristic terpenoids.



References: Magallón (2010), Linkies et al. (2010)

Appendix 2

