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The occurrence of norlupanes and bisnorlupanes in oils of Tertiary deltaic basins

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Abstract

Lupanoid hydrocarbons are known to occur in several petroleum systems, and lupane (C_{30}) has recently been confirmed to exist in several crude oils. In contrast, norlupanes (C_{29}) and bisnorlupanes (C_{28}) are rarely observed in oil. All of these compounds are considered to derive from natural products of angiosperms, and numerous examples of their functionalized analogs are known. The occurrence of C_{28} and C_{29} lupanoids in biochemical and geochemical systems is reviewed here, and the presence and origin of their hydrocarbon analogs in crude oils are examined in detail. Although direct biochemical precursors for the lupane of crude oil are evident, such precursors for norlupane and bisnorlupane are not obvious. Nor is it clear if the C_{28} and C_{29} analogs are diagenetic descendants from the lupane structure. Adding additional confusion is the occurrence of these analogs in oils which show numerous indications of post-source molecular addition during migration and entrapment, making it unclear if they originate from a conventional source rock or from carrier or seal rock. Despite these uncertainties, there is extensive potential – some of which has already been realized – to use these compounds in oil–oil and oil-source rock correlations, particularly in instances where extensive biodegradation has occurred. Deconvolution of the time(s) of introduction of norlupane and bisnorlupane into the fluid – as well as various other hydrocarbons, including olefins – also provides great potential as a tool for mapping the migration history of an oil.

1. Introduction

High concentrations of lupanoid hydrocarbons are rarely observed in crude oils, despite the relatively common occurrence of the lupanoid skeleton in angiosperms. Norlupanes and bisnorlupanes in particular were first identified in crudes oils fifteen to twenty years ago (Brooks, 1986a,b; Curiale, 1991; Peakman et al., 1991), although they have been sought rarely since then – and even more rarely observed. In this paper, the occurrence of these compounds in crude oils is reviewed, their origin and precursors in land plant biota and terrigenous sediments are discussed, and applications to oil–oil and oil-source rock correlation efforts are presented. In addition, the potential for unconventional (i.e., non-source rock) origins of these compounds in crude oil is discussed in light of the possibility of migration–contamination during and after migration of oil in basins which contain Tertiary deltaic petroleum systems.

Despite the scarcity of these C_{28} and C_{29} lupanoid hydrocarbons in crude oils, the sedimentary basins in which they occur are widely distributed

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geographically. Norlupanes and bisnorlupanes have been reported in subsurface and seep oils of Tertiary basins in Canada, Alaska, Greenland, Egypt, Russia, China and Indonesia. The most extensive documentation is available for oils of the Beaufort–Mackenzie Basin of northwestern Canada (Snowdon et al., 2004, and references therein) and oils and condensates of the Kutei Basin of central Indonesia (Curiale et al., 2005).

The extensive vertical migration that is characteristic of the petroleum systems of Tertiary deltaic sedimentary basins creates the potential for a migrating oil to extract syndepositional organic matter from sediments encountered along its migration pathway or trap. Because of this phenomenon – referred to here as migration–contamination (Curiale, 2002) – the origin of bisnorlupanes and norlupanes in Tertiary oils is unclear: Are these components derived (a) directly from the source rock, (b) from the migration pathway or reservoir, or (c) from both? This uncertainty can lead to inaccuracy in oil–oil and oil-source rock correlations. A secondary objective of this paper is to discuss the consequences of this inaccuracy, and how to use them to our advantage.

A variety of nomenclature for lupanoid hydrocarbons and their precursors is available in the chemical, geochemical and geological literatures, and naming conventions have changed depending upon the time of publication and the chemical rigor of the investigators (Fig. 1). In the present paper, compounds which are structurally consistent with single or double absence of a methyl group from the lupane skeleton are referred to, respectively, as norlupanes and bisnorlupanes [the latter are more rigorously referred to as dinorlupanes by some workers – see ten Haven et al. (1992) for a brief discussion of IUPAC rules and systematic naming, and Wahhab et al. (1991) for synthesis and numbering information]. It is important to emphasize that the phrase "absence of a methyl group" is employed as a structural descriptor only, and does not imply

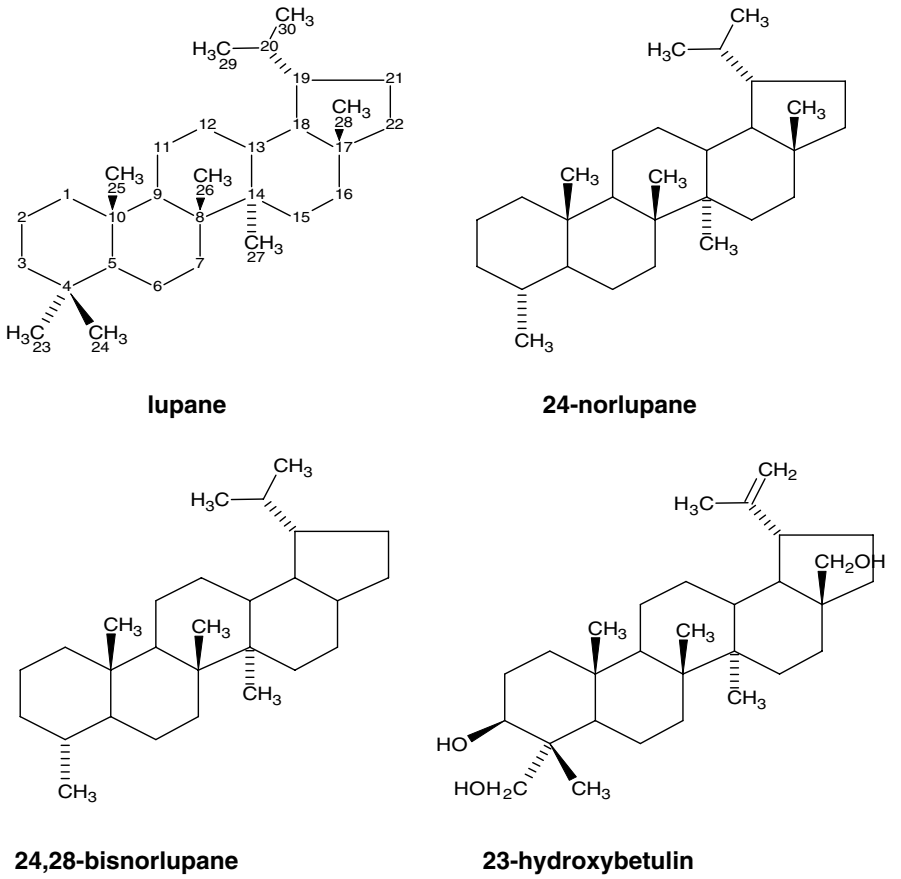

Fig. 1. Selected structures discussed in the text. Conventional numbering is shown for lupane.

that either norlupanes or bisnorlupanes necessarily derive from demethylation of a C_{30} lupanoid (Fig. 1).

Unless otherwise noted, data presented here were generated using techniques described by Curiale et al. (2005) for molecular analysis of aliphatic hydrocarbon elution fractions of crude oils and condensates (aromatic hydrocarbons with the lupanoid skeleton, although known to occur in sediments and oils, will not be examined in detail here). Unless otherwise noted in figure captions, data were generated by Baseline/DGSI (The Woodlands, Texas) under contract to Unocal Corporation, using methods described in Curiale et al. (2005). Data analysis and statistical approaches were accomplished using Infologic's *PeakView*, StatSoft's *Statistica* and IGI's *pIGI* software packages.

2. Natural products and sediments

The ultimate precursors of norlupanes and bisnorlupanes in crude oils are likely to be found within a wide range of functionalized lupanoids or structurally similar angiosperm-derived compounds occurring in living organisms. Deposition and subsequent diagenesis and catagenesis of sediments containing appropriate terrigenous organic debris can lead to the formation of several oxygenated lupanoids and olefinic lupanoid hydrocarbons. These components and their diagenetic descendants, when present in an organic-rich rock subjected to elevated temperatures over geologic time, can be expelled into a migration pathway and ultimately occur as norlupanes and bisnorlupanes in reservoired crude oil, although the details of this process are largely unknown.

Olefinic hydrocarbons and oxygenated compounds in living organisms which are likely to act as structural precursors for the bisnorlupane, norlupane and lupane of crude oils occur in cuticular and vascular components of several angiosperms, and are documented extensively in the natural products literature. For example, O'Connell et al. (1987, 1988) have isolated lupeols from the bark of various species of birch, and Lee (1998) has isolated norlupene from leaves of other angiosperms. Although ostensible precursors for sedimentary lupane are widespread (Kulshreshtha et al., 1972; Mahato et al., 1992; Mahato and Sen, 1997), 24- and 28-norlupanoid natural products are relatively rare. For example, Kulshreshtha et al. (1972) cite only a single norlupanoid (from Euphorbiaceae) in their extensive catalog of triterpenoid natural products. Lischewski et al. (1985), in another rare identification of these compounds, have identified 24-norlupanoic acids in southeast Asian leaves, and suggest biosynthetic demethylation of lupane as a formation mechanism for these 24-nor acids. A limited number of 28-norlupanoids have also been identified in resin (Marner et al., 1991) and various plant structures (Koul et al., 2000).

Of even greater rarity are 24,28-bisnorlupanoid natural products. No reports of these compounds are available in the natural products literature, although lupene-23,28-dioic acids have been reported in the leaves of a Vietnamese plant (Adam et al., 1982; Lischewski et al., 1984). In addition, White et al. (1998) and Rouquette et al. (2005) have speculated that 23-hydroxybetulin may serve as a precursor for the 24,28-bisnorlupanes. Alternatively, it is possible – even likely – that they are produced through sedimentary diagenesis (ten Haven et al., 1992).

The early identification of norlupanes and bisnorlupanes in sediments (Rullkötter et al., 1982) spawned efforts to synthesize them and confirm their stereochemical configurations (Peakman et al., 1991). Rullkötter et al. (1982) identified bisnorlupanes in sediments of Greenland. Later, ten Haven and Rullkötter (1989) and ten Haven et al. (1992) identified 24-norlupane, an A-ring aromatized bisnorlupanoid hydrocarbon [24,25-dinorlupa-1,3,5(10)-triene], and several alcohols and ketones possessing the lupanoid structure in Miocene sediments of a Baffin Bay ODP core west of Greenland. The same aromatic compound, accompanied by an aromatized des-A-lupanoid, had been identified previously by Saptorahardjo (1985) and Wolff et al. (1989) in sediments of the Mahakam Delta in central Indonesia, and was very recently spotted in Eocene rocks of Germany (Sabel et al., 2005). Much earlier, and of particular interest in the present study, Corbet et al. (1980) had described des-A-lupane and des-A-lupene hydrocarbons, along with ketones and carboxylic acids of the same structural configuration, in Mahakam Delta sediments which ranged from 2% to 30% total organic carbon.

Developments through the early 1990s were summarized by Rullkötter et al. (1994), who also established the co-elution of lupane with 18α-oleanane on conventional non-polar chromatographic columns (cf. Nytoft et al., 2002) as a potential reason for the dearth of lupane sitings in terrigenous Tertiary

sediments – i.e., lupane may have been extensively misidentified as the 18α-oleanane. Diagenetically-induced structural rearrangement of lupenes – e.g., into oleanenes (ten Haven and Rullkötter, 1988; Rullkötter et al., 1994; Perkins et al., 1995) or taraxastanes (Smith, 1995, p 137) – may be another reason that C_{30} lupanoid hydrocarbons are rarely reported in sediments. Although undocumented to this point, such acid-catalyzed rearrangements may also occur in the case of norlupane and bisnorlupane precursors (i.e., rearrangement of norlupenes and bisnorlupenes to noroleanenes and bisnoroleanenes, respectively).

Several workers have identified lupanoid hydrocarbons in coals and lignites. Wang and Simoneit (1990) reported lupane in Chinese coals, and Stefanova et al. (1995) reported lupane, 28-norlupane and a demethylated des-A-lupane in a Bulgarian lignite. Phenolic 24,25-bisnorlupanoids, lupeol, aromatized lupanoids, des-A-lupenes and lupenes have also been recorded in fine-grained sediments as well as coal-derived resinites and fossil laticifers (Mahlberg et al., 1984; Mahlberg and Haubold, 1989) of German lignites (Otto et al., 2001; Simoneit et al., 2003), and several of these components have been identified in claystones of Germany (Otto and Simoneit, 2001). In addition, 28-norlup-17-ene, lupane, and various other lupanoids have been identified in moderate concentrations in lignites of Western Australia (Sandison et al., 2002, 2003).

Sedimentary rocks other than coal also host these unusual compounds. Lupane has been confirmed in an Oligocene evaporite from France, where it co-occurs with a novel 20,29,30-trisnorlupane (Poinsot et al., 1995), and 28-norlupanes have been identified in extracts of the Green River Shale (Kim and Yang, 1998). More commonly, bisnorlupanes and norlupanes have also been identified in marine shales rich in angiosperm debris. 24,28-Bisnorlupanes occur in Paleogene shales of the Beaufort–Mackenzie Basin (Brooks, 1986a; Snowdon et al., 2004), Greenland (Rullkötter et al., 1982; Christiansen et al., 1996; Bojesen-Koefoed et al., 1999) and Oregon (Kvenvolden et al., 1991). Interestingly, in all of these instances the shales are organically lean.

3. Crude oils

The widespread occurrence of natural product precursors of lupanoids and the presence of lupanoids in recent sediments, coals, evaporites and shales would imply that lupane, norlupanes and bisnorlupanes should be readily identified in crude oils. Indeed, presumptive degradation products such as des-A-lupane have been noted commonly in Tertiary-sourced crude oils of several basins (e.g., Woolhouse et al., 1992). Yet the pentacyclic hydrocarbons themselves remain relatively rare. In the case of lupane, diagenetic channelling from olefinic precursors to different structural configurations may have masked the prior existence of lupane analogs (Rullkötter et al., 1994; Perkins et al., 1995; Smith, 1995). Furthermore, chromatographic coelution may have resulted in widespread misidentification of lupane as an oleanane (Rullkötter et al., 1994; Nytoft et al., 2002). Detailed studies which overcome these coelution concerns (Nytoft et al., 2002) have shown lupane to be present in crude oils of New Zealand (Taranaki Basin), Papua New Guinea (seep), Vietnam (Hanoi Trough), Canada (Beaufort–Mackenzie Basin) and western Greenland. Although such coelution problems involving lupane do not explain the relatively limited occurrence of the norlupanes and bisnorlupanes in crude oils, it is possible that these C_{28} and C_{29} compounds could be victims of a diagenetic sink analogous to that which may exist for certain lupenes (ten Haven and Rullkötter, 1988; Perkins et al., 1995; Smith, 1995).

Crude oils containing bisnorlupanes were first reported by Brooks (1986a,b), who documented their occurrence in several Tertiary-reservoired oils in the offshore portion of the Beaufort–Mackenzie Basin of northwest Canada. Norlupane was not specifically identified by Brooks (1986a,b), but appears to be present based upon published chromatograms. Curiale (1991) confirmed the presence of 17α(H) and 17β(H) 24,28-bisnorlupanes as well as 24-norlupane in oils of this basin, and the structure of the latter component in an Amauligak Field oil (Beaufort–Mackenzie Basin) was subsequently confirmed by Peakman et al. (1991) through synthesis and co-injection. The bisnorlupanes were also reported by Piggott and Abrams (1996) in oils of another Beaufort–Mackenzie field. In addition, both 24-norlupane and these same bisnorlupanes were shown to occur in an oil in northeastern Alaska, immediately to the west of the Beaufort–Mackenzie Basin (Curiale, 1995). The discovery of the same 24,28-bisnorlupanes in rocks of the Eocene Richards Formation (Canada) was used by Brooks (1986a,b) to suggest a Richards source for at least one of the Beaufort–Mackenzie oil families, and this claim was repeated later by Curiale

(1991). Recent work has identified an additional potential source unit within the Eocene, on the basis of bisnorlupane occurrence (Snowdon et al., 2004).

The only other confirmed high-latitude occurrence of the C_{28} and C_{29} lupanoid hydrocarbons is in western Greenland, based upon work by Christiansen et al. (1994, 1996). 24,28-Bisnorlupanes, identified earlier in mudstones of western Greenland (Rullkötter et al., 1982), were confirmed by Christiansen et al. (1994, 1996), Bojesen-Koefoed et al. (1999) and Nytoft et al. (2002) to be present in the Marraat oil of this region. Co-occurring with these bisnorlupanes in this oil are 24-norlupane and 28-norlupane (Nytoft et al., 2002).

Although the earliest identifications of norlupanes and bisnorlupanes in crude oils were in oils of sedimentary basins which are currently at high latitudes, other reports have confirmed their presence in mid- and low-latitude basins as well. Aref'yev et al. (1996) reported bisnorlupanes in several oils of northern Sakhalin Island, eastern Russia (although the data they reported to support this identification are very limited). Kvenvolden et al. (1989, 1991) established the occurrence of 24,28-bisnorlupanes (and des-A-lupane) in seep and subsurface oils found in western Washington State (USA). Nytoft et al. (2002), based on the spectra published by Kvenvolden et al. (1991), suspects the presence of lupane in these samples as well. Working with samples at even lower latitudes, Trendel et al. (1991b) established the presence of 24-norlupane using NMR techniques in an Egyptian oil from the Sinai, and speculated on a source-rock based diagenetic origin for this hydrocarbon. Most recently, Zhou et al. (2003) have reported 24-norlupane in relatively low concentration in condensates of the South China Sea. Neither Trendel et al. (1991b) nor Zhou et al. (2003) report the occurrence of bisnorlupanes in these Egyptian and Chinese petroleums.

An equatorial occurrence of both norlupanes and bisnorlupanes in crude oils has been reported recently by R. Lin (personal communication, 2002) and Curiale et al. (2005) for oils of the Kutei Basin of central Indonesia. 17α(H)-24,28-bisnorlupane, 17β(H)-24,28-bisnorlupane and 24-norlupane were identified in numerous oils of this basin, with total relative concentrations of these components being up to 40 times greater than hopane in oils recovered from wells drilled on the continental slope. As is the case with several other occurrences of lupanoid hydrocarbons in crude oils, the norlupane and bisnorlupanes in these Indonesian oils co-occur with several other angiosperm-derived components, including oleananes, ursanes, bicadinanes and taraxastanes, and several of their olefinic analogs.

These occurrences of the C_{28} and C_{29} lupanoid hydrocarbons in crude oils are summarized in Table 1.

The internal distribution of the norlupane and bisnorlupanes in crude oils varies significantly among the oils listed in Table 1. Figs. 2 and 3 show selected GC/MS/MS transitions for four lupanoid-containing crude oils from Canada, Alaska, Washington State and Indonesia (see map in Fig. 4). The concentration of 24-norlupane and the identified 24,28-bisnorlupanes in these samples (relative to hopane and the oleananes) varies widely (Fig. 2). The resistance of these lupanoids to biodegradation (relative to hopane) may explain the high relative concentration of norlupane and bisnorlupanes in the Alaskan Hammerhead oil (Curiale,

Table 1
The occurrence of norlupanes and/or bisnorlupanes in crude oils

Location	Components[a]	Reference(s)
Northwest Canada (Beaufort–Mackenzie Basin)	24-NL; 24,28-BNL	Brooks (1986a,b), Curiale (1991) and Piggott and Abrams (1996)
Northeast Alaska (Greater North Slope Basin)	24-NL; 24,28-BNL	Curiale (1995)
Western Greenland	24-NL; 28-NL[b]; 24,28-BNL	Christiansen et al. (1994, 1996); Nytoft et al. (2000, 2002)
Washington State, USA	24,28-BNL	Kvenvolden et al. (1989, 1991)
Sakhalin Island, eastern Russia	24,28-BNL	Aref'yev et al. (1996)
Egypt (Sinai)	24-NL	Trendel et al. (1991b)
South China Sea	24-NL	Zhou et al. (2003)
Central Indonesia (offshore Kutei Basin)	24-NL; 24,28-BNL	Curiale et al. (2005)

[a] 24-NL: 24-*nor*-lupane; 28-NL: 28-*nor*-lupane; 24,28-BNL: 17α(H)- and 17β(H)-24,28-bisnorlupane [designated by Peakman et al. (1991) as 24,28-*dinor*-17α-lupane and 24,28-*dinor*-17β-lupane, respectively].

[b] The western Greenland Marraat oil is reported to contain both 17α(H)- and 17β(H)-28-*nor*-lupane (Nytoft et al. (2000)).

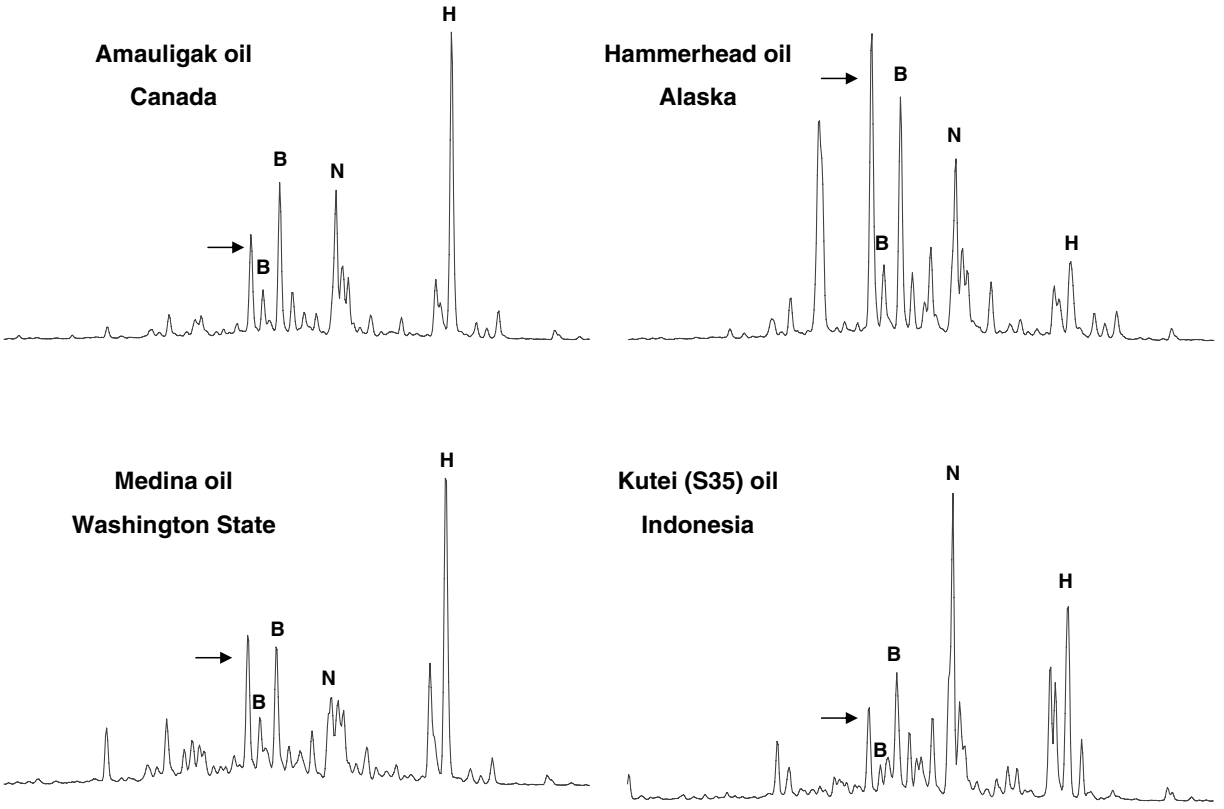

Fig. 2. Norlupane and bisnorlupane distributions for selected oils. Summed GC/MS/MS traces are shown ($384 \rightarrow 177 + 398 \rightarrow 177 + 412 \rightarrow 191$); retention time increases from left to right [experimental conditions as described in Curiale et al. (2005); increasing retention time is to the right]. Labeled peaks are: B = 24,28-bisnorlupanes [17α(H) elutes prior to 17β(H)]; N = 24-norlupane; H = hopane. The peak labeled with an arrow is 24,28-bisnor-18α-oleanane [Nytoft, H.P. (personal communication); Trendel et al., 1991a,b; Curiale et al., 2005]. The oleananes (and possibly lupane) are included in the partially-resolved doublet eluting just prior to hopane. The enhancement of the lupanoids relative to hopane in the Hammerhead oil results from extensive biodegradation of this oil (Curiale, 1995).

1995). Nevertheless, wide variability is also observed in the other three oils of Fig. 2, none of which has been subjected to extensive biodegradation.

Several other identified and unidentified C_{28} and C_{29} non-hopane triterpenoid hydrocarbons elute in the range of the 24,28-bisnorlupanes and 24-norlupane (Fig. 2). Despite the varying concentration of these triterpenoids in the four oils shown in Fig. 2, it is noteworthy that the same unidentified C_{28} and C_{29} components appear to be present in all four samples (and in other samples from the Canadian Beaufort–Mackenzie Basin, from northeastern Alaska, and from the Kutei Basin of Indonesia – J.A. Curiale, unpublished data). Although only one of these other components has been identified – 24,28-bisnor-18α-oleanane [Nytoft, H.P. (personal communication); Trendel et al., 1991a,b; Curiale et al., 2005] – spectral data indicate that the unidentified compounds are also C_{28} and C_{29} oleananes, ursanes or lupanes (J.A. Curiale, unpublished results). These compound distributions provide a rich and largely untapped source of information for use in oil–oil and oil-source rock correlation efforts in Tertiary deltaic sedimentary basins.

Focusing only on the 24,28-bisnorlupanes – as revealed in the $384 \rightarrow 177$ GC/MS/MS transition (Fig. 3) – suggests that much of the variability within the non-hopane triterpenoids in these samples resides in the C_{28} compound group. Indeed, the general invariance of the 17α/17β-24,28-bisnorlupane ratio, despite this wide C_{28} compound variability, may imply that a thermal equilibrium exists for this ratio. The "setting" of this equilibrium value may ultimately be useful in distinguishing source-rock lupanoid contributions from migration-path lupanoid contributions, a distinction discussed in the following section.

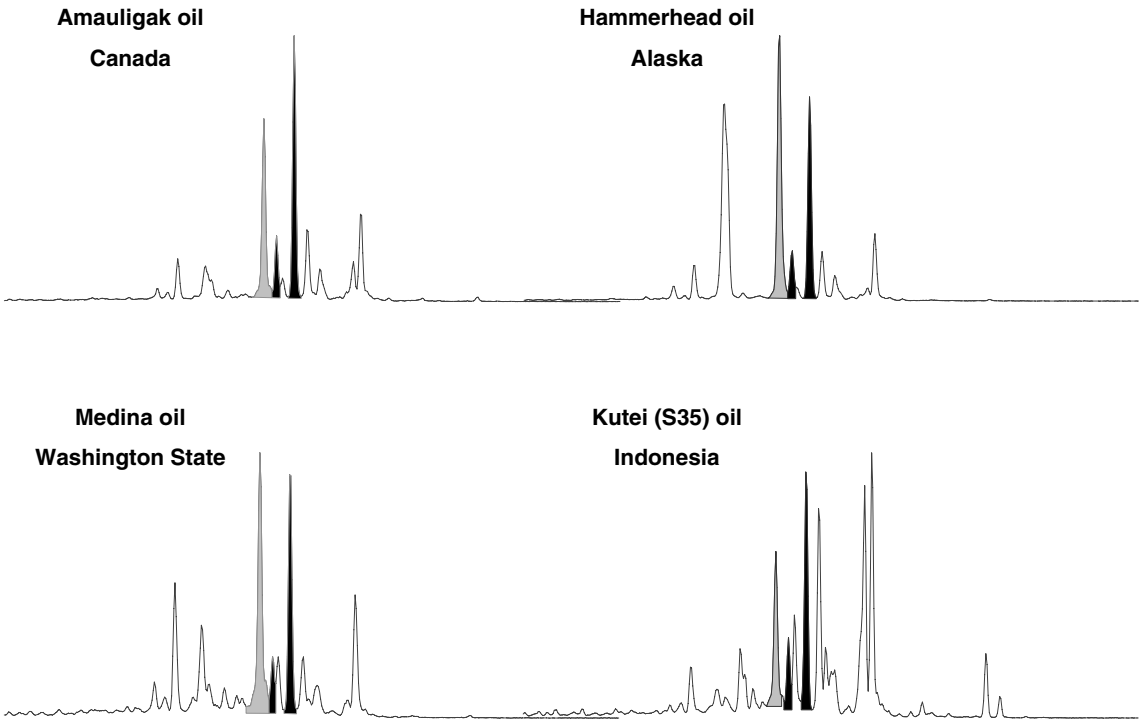

Fig. 3. C_{28} pentacyclic hydrocarbons for selected oils, as depicted by the 384 → 177 GC/MS/MS transition; retention time increases from left to right [experimental conditions as described in Curiale et al. (2005); increasing retention time is to the right]. The two black-shaded peaks are the 24,28-bisnorlupanes [17α(H) elutes prior to 17β(H)]; the grey-shaded peak is 24,28-bisnor-18α-oleanane [Nytoft, H.P. (personal communication); Trendel et al., 1991a,b; Curiale et al., 2005]. Additional bisnorlupanes and bisnoroleananes (and possibly bisnorursanes) are undoubtedly present, but not identified.

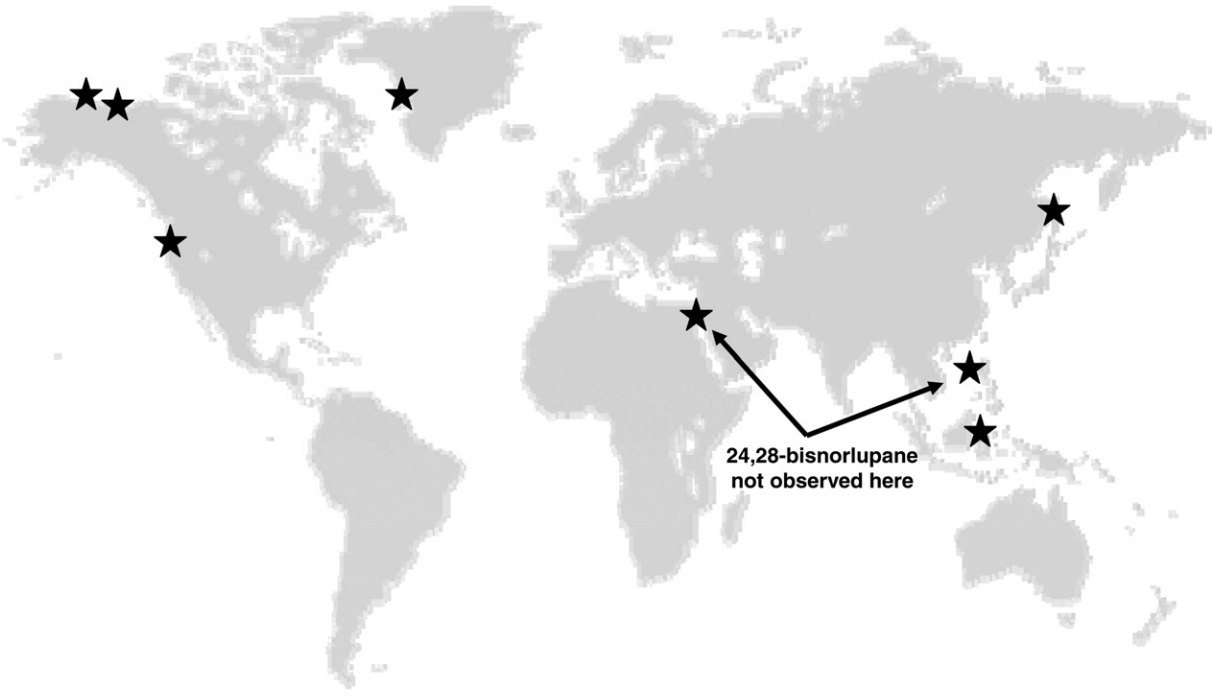

Fig. 4. Map showing the approximate locations of crude oils identified to contain 24-norlupanes and/or 24,28-bisnorlupanes. See Table 1 for details.

4. Source rock and post-source rock origins

The presence of norlupanes and bisnorlupanes in oils and condensates is a presumptive indication of their presence in the source rocks for these petroleums, and in at least two instances (western Greenland and northwestern Canada) these lupanoids have been identified in the syndepositional organic matter of sedimentary rocks from the same basin as the crude oils which contain them. On this basis it is possible, for example, to compare the lupanoid-containing oils of the Canadian Beaufort–Mackenzie Basin to possible Paleogene source rocks in the region (Snowdon et al., 2004). Nevertheless, it is interesting to note that *bona fide* (i.e., comprehensive) oil-source rock correlations (cf. Curiale, 1993) have never been published for any of the oils listed in Table 1.

At least one non-source rock alternative is recognized for the origin of norlupanes and bisnorlupanes in crude oils. This ''post-source origin'' possibility is the result of the introduction of extra-source molecular components during migration of the oil. This phenomenon is referred to as migration–contamination, and occurs during the relatively brief time period while petroleum is moving in a carrier bed and the much larger time period when petroleum resides in a trap. Migration–contamination has been documented extensively in sedimentary basins (Curiale, 2002, and references therein). Evidence for the occurrence of this sort of molecular extraction has been presented previously for the Kutei Basin of Indonesia (Jaffé et al., 1988), and Curiale et al. (2005) have shown that specific angiosperm molecular debris present in Kutei oils is very likely a product of migration–contamination. Most recently, Rouquette et al. (2005) identified a 24-norlupanoic acid in an African oil and suggested the possibility of migration–contamination. The occurrence of norlupanes and bisnorlupanes in some of these same oils raises a significant question about their origin – are they from a primary source, or are they a post-source contribution?

The Kutei Basin shares several characteristics with other basins whose oils also contain lupanoid hydrocarbons. For example, the Kutei region, northeastern Alaska, northwestern Canada and western Greenland (Fig. 4) all contain very thick Tertiary sections, all show evidence for extensive vertical migration, and all contain oil reservoired in thermally immature rocks. This latter point is critical, inasmuch as it is the criterion which provides signature evidence for the occurrence of thermally ''immature'' molecular components in oil. Indeed, the oils from those basins which contain norlupanes and bisnorlupanes also contain oleanenes and/or ursenes (Kutei: Curiale et al., 2005; northeastern Alaska: Curiale, 1991, 1995; northwestern Canada: Curiale, 1991; western Greenland: Nytoft et al., 2002). Because the co-occurrence within individual oils of norlupanes, bisnorlupanes, oleanenes and ursenes can be explained through both source and post-source origins, additional criteria are necessary to make this distinction.

5. Implications for petroleum exploration

The occurrence of the C_{28} and C_{29} lupanoid hydrocarbons in crude oils provides several applications in petroleum and source rock geochemistry, ranging from correlations to assessing biodegradation extent to providing information about migration pathways. Molecularly-based oil–oil and oil-source rock correlations often rely on the presence and distribution of specific tetracyclic and pentacyclic hydrocarbons, and the effectiveness of such correlations increases with increasing novelty of the hydrocarbons that are used. Therefore, the relatively rare occurrence of bisnorlupanes and norlupanes in crude oils provides a useful opportunity for correlating oils to one another and to their source rock(s). This is particularly true in light of evidence that these compound types apparently survive extensive biodegradation (Kvenvolden et al., 1991; Curiale, 1991; Curiale et al., 2005). Oil–oil correlations which utilize the presence or absence of these components have already been presented (or inferred) for oils from Canada, Washington State (USA) and Indonesia (Brooks, 1986a,b; Curiale, 1991; Kvenvolden et al., 1991; Curiale et al., 2005), and evidence for an oil-source rock correlation using the presence of lupanoid hydrocarbons has been provided by Snowdon et al. (2004) for Canadian samples.

As additional oils containing norlupanes and bisnorlupanes are identified, the distribution of these components (rather than just their presence or absence) will become a discerning criteria for correlations. As noted earlier, their distributions are already known to differ from oil to oil in different sedimentary basins (see Figs. 2 and 3, as well as references in Table 1), and evidence for distributional differences within a single sedimentary basin has been pre-

sented (Curiale et al., 2005). In addition to correlation applications, such differences may provide fundamental information about the origin of these components. For example, if the norlupanes and bisnorlupanes in a set of crude oils are derived entirely from a conventional source rock, then one would expect similar distributions of these compounds in those oils and that source rock. In contrast, if their presence is due to a partial or complete post-source rock origin (i.e., migration–contamination), the occurrence of multiple migration pathways and traps in such an instance might yield different distributions among oils of the same basin.

Although the use of lupanoid hydrocarbons as correlation tools is an immediate and obvious application, it is possible that the greatest utility of these compounds will be as a migration indicator – particularly when they are used in conjunction with angiosperm-derived olefinic hydrocarbons which seem to co-occur with the norlupanes and bisnorlupanes in multiple instances (Curiale, 1991, 1995; Nytoft et al., 2002; Curiale et al., 2005). If any or all of these hydrocarbons are imparted to the oil/condensate during migration – either in the carrier or the trap – then deconvolution of their distributions would be possible if multiple oils are available from different locations along the migration pathways. Distinctive isotopic signatures in different portions of the petroleum system (source, carrier, trap) would undoubtedly enhance this possibility. Furthermore, research into the rate at which these components are extracted from the syndepositional organic matter of the carrier or trap rock could ultimately yield information about the residence time of the fluid within its current reservoir. Indeed, because the composition of an oil or condensate represents its full molecular and isotopic history, discrimination into source-contributed and post-source-contributed origins should be possible for each hydrocarbon in the mixture (Wilhelms and Larter, 2004). This ultimately could allow us to use these angiosperm-derived molecular components to deconvolve multiple origins and assess migration timing in sedimentary basins whose organic matter is dominated by terrigenous debris.

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References

Adam, G., Lischewski, M., Phiet, H.V., Preiss, A., Schmidt, J., Sung, T.V., 1982. 3α-Hydroxy-lup-20(29)-ene-23,28-dioic acid from *Schefflera octophylla*. Phytochemistry 21, 1385–1387.

Aref'yev, O.A., Rusinova, G.V., Petrov, A.A., 1996. Biomarkers of crude oils of eastern regions of Russia. Petroleum Chemistry 36, 289–302.

Bojesen-Koefoed, J.A., Christiansen, F.G., Nytoft, H.P., Pedersen, A.K., 1999. Oil seepage onshore West Greenland: evidence of multiple source rocks and oil mixing. In: Fleet, A.J., Boldy, S.A.R. (Eds.), Petroleum Geology of Northwest Europe: Proceedings of the 5th Conference, pp. 305–314.

Brooks, P.W., 1986a. Unusual biological marker geochemistry of oils and possible source rocks, offshore Beaufort–Mackenzie Delta, Canada. Organic Geochemistry 10, 401–406.

Brooks, P.W., 1986b. Biological marker geochemistry of oils from the Beaufort–Mackenzie region, Arctic Canada. Bulletin of Canadian Petroleum Geology 34, 490–505.

Christiansen, F.G., Bojesen-Koefoed, J., Dam, G., Pedersen, A.K., Pulvertaft, T.C.R., 1994. Live oil onshore West Greenland: a new and encouraging discovery. In: Proceedings of the 1994 AAPG Annual Convention, Denver, Colorado, pp. 121.

Christiansen, F.G., Bojesen-Koefoed, J., Dam, G., Nytoft, H.P., Larsen, L.M., Pedersen, A.K., Pulvertaft, T.C.R., 1996. The Marraat oil discovery on Nuussuaq, West Greenland: Evidence for a Latest Cretaceous-Earliest Tertiary Oil Prone Source Rock in the Labrador Sea-Melville Bay Region. In: Bulletin of Canadian Petroleum Geology 1996, pp. 39–54.

Corbet, B., Albrecht, P., Ourisson, G., 1980. Photochemical or photomimetic fossil triterpenoids in sediments and petroleum. Journal of the American Chemical Society 102, 1171–1173.

Curiale, J.A., 1991. The petroleum geochemistry of Canadian Beaufort Tertiary "Non-Marine" oils. Chemical Geology 93, 21–45.

Curiale, J.A., 1993. Oil to source rock correlation – concepts and case studies. In: Engel, M., Macko, S. (Eds.), Organic Geochemistry of Topics in Geobiology, vol. 11. Plenum Press, New York, pp. 473–490.

Curiale, J.A., 1995. Saturated and olefinic terrigenous triterpenoid hydrocarbons in a biodegraded Tertiary oil of northeast Alaska. Organic Geochemistry 23, 177–182.

Curiale, J.A., 2002. A review of the occurrences and causes of migration contamination in crude oil. Organic Geochemistry 33, 1389–1400.

Curiale, J.A., Decker, J.D., Lin, R., 2005. Isotopic and molecular characteristics of Miocene-reservoired oils of the Kutei Basin, Indonesia. Organic Geochemistry 36, 405–424.

ten Haven, H.L., Rullkötter, J., 1988. The diagenetic fate of taraxer-14-ene and oleanene isomers. Geochimica et Cosmochimica Acta 52, 2543–2548.

ten Haven, H.L., Rullkötter, J., 1989. Oleanene, ursene, and other terrigenous triterpenoid biological-marker hydrocarbons in Baffin Bay sediments. In: Srivastava, S.P., Arthur, M., Clement, B. et al. (Eds.), Proceedings of the Ocean Drilling Program, Scientific Results, vol 105, pp. 233–239.

ten Haven, H.L., Peakman, T.M., Rullkötter, J., 1992. Early diagenetic transformation of higher-plant triterpenoids in deep-sea sediments from Baffin Bay. Geochimica et Cosmochimica Acta 56, 2001–2024.

Jaffé, R., Albrecht, P., Oudin, J.L., 1988. Carboxylic acids as indicators of oil migration: II. Case of the Mahakam Delta, Indonesia. Geochimica et Cosmochimica Acta 51, 2599–2607.

Kim, K., Yang, J., 1998. Carbon isotope analyses of individual hydrocarbon molecules in bituminous coal, oil shale, and Murchison meteorite. Journal of Astronomy and Space Sciences 15, 163–174.

Koul, S., Razdan, T.K., Andotra, C.S., Kalla, A.K., Koul, S., Taneja, S.C., Dhar, K.L., 2000. Koelpinin-A, B and C – three triterpenoids from *Koelpinia linearis*. Phytochemistry 53, 305–309.

Kulshreshtha, J.J., Kulshreshtha, D.K., Rastogi, R.P., 1972. The triterpenoids. Phytochemistry 11, 2369–2381.

Kvenvolden, K.A., Rapp, J.B., Hostettler, F.D., Snavely Jr., P.D., 1989. Preliminary evaluation of the petroleum potential of the Tertiary accretionary terrane, west side of the Olympic Peninsula, Washington. B. Comparison of molecular markers in oil and rock extracts. USGS Bulletin 1892, 19–35.

Kvenvolden, K.A., Hostettler, F.D., Rapp, J.B., Snavely Jr., P.D., 1991. Biomarkers in Tertiary mélange, Western Olympic Peninsula, Washington, USA. Chemical Geology 93, 101–110.

Lee, C.K., 1998. A new norlupene from the leaves of *Melaleuca leucadendron*. Journal of Natural Products 61, 375–376.

Lischewski, M., Ty, Ph.D., Schmidt, J., Preiss, A., Phiet, H.V., Adam, G., 1984. 3α, 11α-Dihydroxylup-20(29)-ene-23,28-dioic acid from *Schefflera octophylla*. Phytochemistry 23, 1695–1697.

Lischewski, M., Ty, P.D., Kutschabsky, L., Pfeiffer, D., Phiet, H.V., Preiss, A., Sung, T.V., Adam, G., 1985. Two 24-nor-triterpenoid carboxylic acids from *Acanthopanax trifoliatus*. Phytochemistry 24, 2355–2357.

Mahato, S.B., Nandy, A.K., Roy, G., 1992. Review Article Number 67. Triterpenoids Phytochemistry 31, 2199–2249.

Mahato, S.B., Sen, S., 1997. Review Article Number 118. Advances in triterpenoid research, 1990–1994. Phytochemistry 44, 1185–1236.

Mahlberg, P.G., Field, D.W., Frye, J.S., 1984. Fossil laticifers from Eocene brown coal deposits of the Geiseltal. American Journal of Botany 71, 1192–1200.

Mahlberg, P.G., Haubold, H., 1989. Morphology of fossil laticifers from brown coal deposits of the Geiseltal. Hallesches Jahrbuch für Geowissenschaften 14, 27–35.

Marner, F.-J., Freyer, A., Lex, J., 1991. Triterpenoids from gum mastic, the resin of *Pistacia lentiscus*. Phytochemistry 30, 3709–3712.

Nytoft, H.P., Bojesen-Koefoed, J.A., Christiansen, F.G., 2000. C_{26} and C_{28}-C_{34} 28-norhopanes in sediments and petroleum. Organic Geochemistry 31, 25–39.

Nytoft, H.P., Bojesen-Koefoed, J.A., Christiansen, F.G., Fowler, M.G., 2002. Oleanane or lupane? Reappraisal of the presence of oleanane in Cretaceous-Tertiary oils and sediments. Organic Geochemistry 33, 1225–1240.

O'Connell, M.M., Bentley, M.D., Campbell, C.S., Cole, B.J.W., 1987. Betulin variation in four white-barked birches in Maine. American Journal of Botany 74, 703–709.

O'Connell, M.M., Bentley, M.D., Campbell, C.S., Cole, B.J.W., 1988. Betulin and lupeol in bark from four white-barked birches. Phytochemistry 27, 2175–2176.

Otto, A., Simoneit, B.R.T., 2001. Chemosystematics and diagenesis of terpenoids in fossil conifer species and sediment from the Eocene Zeitz formation, Saxony, Germany. Geochimica et Cosmochimica Acta 64, 3505–3527.

Otto, A., Simoneit, B.R.T., Wilde, V., 2001. Initial results on the biomarker composition of resinites and "Affenhaar" from Middle Eocene lignites of the Geiseltal (Sachsen-Anhalt, Germany). Hallesches Jahrbuch für Geowissenschaften B 13, 57–68.

Peakman, T.M., ten Haven, H.L., Rullkötter, J., Curiale, J.A., 1991. Characterisation of 24-*nor*-triterpenoids occurring in sediments and crude oils by comparison with synthesized standards. Tetrahedron 47, 3779–3786.

Perkins, G.M., Bull, I.D., ten Haven, H.L., Rullkötter, J., Smith, Z.E.F., Peakman, T.M., 1995. First positive identification of triterpenes of the Taraxastane Family in petroleums and oil shales: 19α(H)-Taraxastane and 24-nor-19α(H)-Taraxastane. Evidence for a previously unrecognized diagenetic alteration pathway of Lup-20(29)-ene derivatives. In: Grimalt, J.O., Dorronsoro, C., (Eds.), Organic Geochemistry: Developments and Applications to Energy, Climate, Environment and Human History, Itxaso Estornés, Barcelona, pp. 247–249.

Piggott, N., Abrams, M.A., 1996. Near-surface coring in the Beaufort and Chukchi Seas, Northern Alaska. In: Schumacher, D., Abrams, M.A., (Eds.), Hydrocarbon Migration and its Near-Surface Expression, AAPG Memoir 66, pp. 385–399.

Poinsot, J., Adam, P., Trendel, J.M., Connan, J., Albrecht, P., 1995. Diagenesis of higher plant triterpenes in evaporitic sediments. Geochimica et Cosmochimica Acta 59, 4653–4661.

Rouquette, N., Schaeffer, P., Schweigert, M.-C., Trendel, J.M., Kowalewski, I., Levache, D., Albrecht, P., 2005. A ring-D functionalized nor-triterpenoid of the lupane series as a key

intermediate in the formation of widespread hydrocarbon derivatives of higher plant origin in petroleum. Organic Geochemistry 36, 1227–1233.

Rullkötter, J., Leythaeuser, D., Wendisch, D., 1982. Novel 23,28-bisnorlupanes in Tertiary sediments. Widespread occurrence of nuclear demethylated triterpanes. Geochimica et Cosmochimica Acta 46, 2501–2509.

Rullkötter, J., Peakman, T.M., ten Haven, H.L., 1994. Early diagenesis of terrigenous triterpenoids and its implications for petroleum geochemistry. Organic Geochemistry 21, 215–233.

Sabel, M., Bechtel, A., Püttmann, W., Hoernes, S., 2005. Palaeoenvironment of the Eocene Eckfeld Maar lake (Germany): implications from geochemical analysis of the oil shale sequence. Organic Geochemistry 36, 873–891.

Sandison, C.M., Alexander, R., Kagi, R.I., Boreham, C.J., 2003. Early diagenetic transformation of organic matter in a marine-influenced lignite. Organic Geochemistry 34, 1081–1102.

Sandison, C.M., Alexander, R., Kagi, R.I., Boreham, C.J., 2002. Sulfurisation of lipids in a marine-influenced lignite. Organic Geochemistry 33, 1053–1077.

Saptorahardjo, A., 1985. Diagenese precoce de la matiere organique dans la serie sedimentaire du delta de la Mahakam, Indonesie: aspects moleculaires. Ph.D. Dissertation, Universite Louis Pasteur de Strasbourg, p. 181.

Simoneit, B.R.T., Otto, A., Wilde, V., 2003. Novel phenolic biomarker triterpenoids of fossil laticifers in Eocene brown coal from Geiseltal, Germany. Organic Geochemistry 34, 121–129.

Smith, Z.E.F., 1995. Characterization of A-ring contracted triterpenoids in oils and shales: evidence for an alternative transformation pathway in the diagenesis of higher plant terpenoids. Ph.D. Dissertation, University of Bristol, p. 169.

Snowdon, L.R., Stasiuk, L.D., Robinson, R., Dixon, J., Dietrich, J., McNeil, D.H., 2004. Organic geochemistry and organic petrology of a potential source rock of early Eocene age in the Beaufort–Mackenzie Basin. Organic Geochemistry 35, 1039–1052.

Stefanova, M., Magnier, C., Velinova, D., 1995. Biomarker assemblage of some Miocene-aged Bulgarian lignite lithotypes. Organic Geochemistry 23, 1067–1084.

Trendel, J.M., Albrecht, P., Riva, A., Ghiselli, C., 1991a. Novel demethylated higher plant triterpanes in petroleum. In: Manning, D.A.C. (Ed.), Organic Geochemistry, Advances and Applications in the Natural Environment. Manchester University Press, Manchester, pp. 212–214.

Trendel, J.M., Graff, R., Albrecht, P., Riva, A., 1991b. 24,28-Dinor-18α-oleanane, a novel demethylated higher plant derived triterpene hydrocarbon in petroleum. Tetrahedron Letters 32, 2959–2962.

Wahhab, A., Ottosen, M., Bachelor, F.W., 1991. The synthesis of nor- and bisnorlupanes. Canadian Journal of Chemistry 69, 570–577.

Wang, T-G., Simoneit, B.R.T., 1990. Organic geochemistry and coal petrology of Tertiary brown coal in the Zhoujing mine, Baise Basin, South China. 2. Biomarker assemblage and significance. Fuel 69, 12–20.

White, A., Horsington, E.J., Nedjar, N., Peakman, T.M., Curiale, J., 1998. A novel demethylated oxygenated triterpenoid in crude oils from the Canadian Beaufort Sea and Northeast Alaska. Tetrahedron Letters 39, 3031–3034.

Wilhelms, A., Larter, S., 2004. Shaken but not always stirred. Impact of petroleum charge mixing on reservoir geochemistry. In: Cubitt, J.M., England, W.A., Larter, S. (Eds.), Understanding Petroleum Reservoirs: Towards an Integrated Reservoir Engineering and Geochemical Approach. Geological Society, London, Special Publication 237, pp. 27–35.

Wolff, G.A., Trendel, J.M., Albrecht, P., 1989. Novel monoaromatic triterpenoid hydrocarbons occurring in sediments. Tetrahedron 45, 6721–6728.

Woolhouse, A.D., Oung, J-N., Philp, R.P., Weston, R.J., 1992. Triterpanes and ring-A degraded triterpanes as biomarkers characteristic of Tertiary oils derived from predominantly higher plant sources. Organic Geochemistry 18, 23–31.

Zhou, Y., Sheng, G., Fu, J., Geng, A., Chen, J., Xiong, Y., Zhang, Q., 2003. Triterpane and sterane biomarkers in the YA13-1 condensates from Qiongdongnan Basin, South China Sea. Chemical Geology 199, 343–359.