



Novel saturated hexacyclic C₃₄ and C₃₅ hopanes in lacustrine oils and source rocks



Hans Peter Nytoft^{a,*}, Henrik Ingermann Petersen^b, Michael Bryld Wessel Fyhn^a, Lars Henrik Nielsen^a, Jussi Hovikoski^a, Ioannis Abatzis^a

^a Geological Survey of Denmark and Greenland (GEUS), Øster Voldgade 10, DK-1350 Copenhagen K, Denmark

^b Maersk Oil, Exploration, Esplanaden 50, DK-1263 Copenhagen, Denmark

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ABSTRACT

Novel C₃₄ and C₃₅ hexacyclic hopanes having side chains with a pentacyclic or hexacyclic ring at C-22 are abundant in lacustrine oils and source rocks but almost absent from marine oils. The corresponding C₃₄ and C₃₅ hexacyclic hop-17(21)-enes were identified in thermally immature mudstones from Vietnam cored in the 500 m deep ENRECA-3 well. All the novel hexacyclic compounds were unambiguously identified by comparison with synthetic standards. Traces of heptacyclic hopanes were detected in a lacustrine oil from Thailand. The C₃₄ and C₃₅ hexacyclic hopanes have much longer gas chromatography (GC) retention times than the corresponding pentacyclic hopanes. They are isomerized faster at C-22 than the pentacyclic hopanes and their 22S/(22S + 22R) ratio values at equilibrium are much higher (0.8 for C₃₄). Precursors could be penta- and hexafunctionalised hopanoids in cyanobacteria and methanotrophs.

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1. Introduction

C₃₁–C₃₅ 17 α (H),21 β (H)-hopanes having a side chain with four to eight carbons and a single methyl branch at C-22 are usually the most abundant extended hopanes in oils and mature source rock extracts and are often the only C₃₁–C₃₅ hopanes that can be reliably quantified from typical *m/z* 191 chromatograms. However, it was discovered recently that C₃₃–C₃₅ hopanes having a side chain with two methyls could be as abundant as the normal C₃₃–C₃₅ hopanes in coal (Nytoft, 2011). These novel hopanes are also relatively abundant in oils having a terrigenous source but low in abundance in marine and lacustrine sourced oils. Novel hexacyclic hopanes were also detected in oil and coal (Nytoft, 2011). The most abundant C₃₅ hexacyclic hopanes in oil were identified as 29-cyclopentylhopanes by comparison with synthetic standards.

Recent work on material from the ENRECA-3 core well drilled in 2012 on the Vietnamese Bach Long Vi Island, Song Hong Basin,

offshore northern Vietnam showed the presence of an excellent lacustrine oil-prone source rock succession (Petersen et al., 2014). Description of the geology of the area and detailed geochemical analysis of >300 core samples was carried out by Petersen et al. (2014). The last gas chromatography–mass spectrometry (GC–MS) analyses of selected core extracts were completed later. Analysis of saturated fractions in full scan mode revealed pairs of late eluting C₃₄ and C₃₅ compounds having typical hopane spectra with *m/z* 191 as base peak and a fragment at *m/z* 369, corresponding to loss of the side chain. M⁺ ions were at *m/z* 466 or 480, as opposed to 468 and 482 for regular C₃₄ and C₃₅ hopanes, and the fragments at *m/z* 247 and 261 were shifted to 245 and 259, respectively. This could suggest hopanes with an extra ring formed by the side chain but not fused to the hopane skeleton as in benzohopanes and hexahydrobenzohopanes (Hussler et al., 1984; Connan and Dessort, 1987). The early eluting C₃₅ hexacyclic hopanes described by Nytoft (2011) were also detected. The ENRECA-3 core extracts (56) were re-analysed using GC–MS–MS with relevant transitions and the novel hopanes were detected in all of them. However, because of coeluting compounds, it was not possible to obtain pure spectra of any hexacyclic hopanes directly from the saturated fractions. Structure

* Corresponding author. Tel.: +45 91333776; fax: +45 38142050.

E-mail address: hpn@geus.dk (H.P. Nytoft).

Table 1
Distribution of C₃₄- and C₃₅ hopanes in lacustrine mudstones from ENRECA-3 core, Vietnam and oils from various sources (H34/5 + H34/6 = 100% and H35/5 + H35/6-22 + H35/6-29 = 100%).

Origin	No. of samples	Type	H34/6 (%)	H34/6 avg. (%)	H34/5 (%)	H35/6-22 (%)	H35/6-29 (%)	H35/5 (%)
Enreca-3 (Vietnam)	56	Lacustrine mudstone	7.9–33.4	19.5	66.6–92.1	5.9–19.5	5.9–13.3	68.5–85.6
E. Greenland	2	Lacustrine shale	10.9–13.5	12.2	69.3–71.7	9.7–20.7	10.0–18.7	69.3–71.7
Song Hong (Vietnam)	2 ^a	Lacustrine oil	4.7–13.3	9.5	86.7–94.3	5.4–6.9	13.1–17.0	76.1–81.5
Cuu Long (Vietnam)	3 ^a	Lacustrine oil	13.2–17.5	14.8	82.5–86.8	6.4–8.5	13.4–18.7	73.5–80.2
Thailand	8 ^a	Lacustrine oil	5.6–21.4	12.6	78.6–94.4	4.6–15.5	9.4–24.8	59.7–86.0
Amaligak (Canada)	1 ^a	Deltaic/terrigenous oil	2.4	2.4	97.6	3.1	11.4	85.5
Marraat (Greenland)	1 ^a	Deltaic/terrigenous oil	2.8	2.8	97.2	3.6	15.6	80.9
Niger Delta	6 ^a	Deltaic/terrigenous oil	3.6–5.8	4.7	94.2–96.4	3.6–5.5	14.2–20.4	75.3–81.9
Assam (India)	4 ^a	Deltaic/terrigenous oil	5.4–7.0	6.0	94.6–93.0	3.6–6.5	18.5–21.2	72.8–76.0
Belize/Guatemala	8 ^b	Marine oil	0.8–1.7	1.3	98.3–99.2	0.9–1.9	1.1–4.3	93.8–97.6
Monterey (USA)	1 ^a	Marine oil	0.8	0.8	99.2	0.6	2.0	97.4
Par-e-Siah (Iran)	1 ^a	Marine oil	1.3	1.3	98.7	1.5	3.7	94.8
Austin chalk (Texas)	2 ^a	Marine oil	0.9–1.3	1.1	98.0–99.2	1.4–2.0	4.5–6.3	91.7–94.0
Hibernia (Canada)	1 ^a	Marine oil	2.0	2.0	98.0	1.7	4.6	93.7
Paris Basin (France)	3 ^a	Marine oil	1.0–1.2	1.1	98.8–99.0	1.10–1.4	6.1–6.4	92.5–92.6
Sirte Basin (Libya)	2	Marine oil	1.5–1.6	1.6	98.4–98.5	2.4–2.7	6.2–6.8	90.8–91.1
Danish North Sea	7 ^a	Marine oil	1.3–2.0	1.6	98.0–98.7	1.2–2.3	6.4–8.5	90.3–91.9
Essungo (Angola)	1 ^a	Marine oil	2.6	2.6	97.4	2.9	7.9	89.2

^a Additional data in Nytoft (2011) and references therein.

^b Petersen et al. (2012).

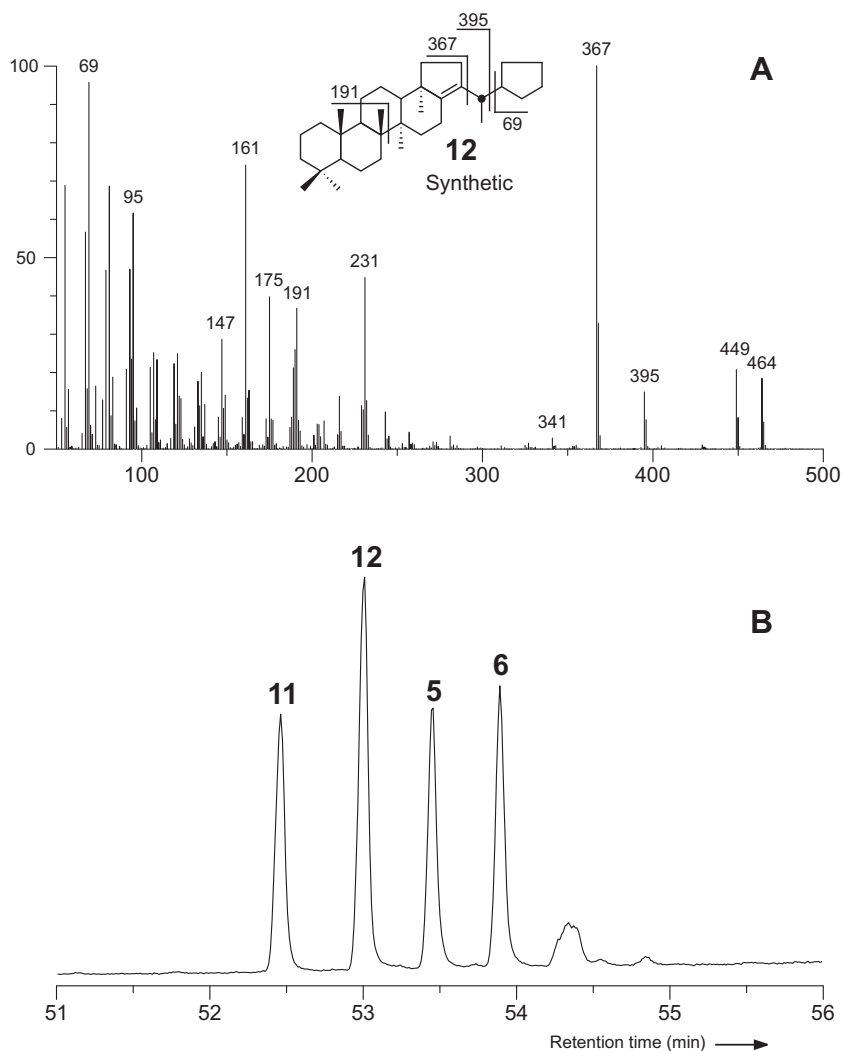


Fig. 1. (A) Mass spectrum of hexacyclic hop-17(21)-ene (**12**). (B) Hydrogenation of hexacyclic hop-17(21)-ene **11** and **12** to hopanes **5** and **6**. Hydrogenation time: 1 h 40 min.

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