

# Chemical composition and palaeobotanical origin of Miocene resins from Kerala–Konkan Coast, western India

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The terpenoid composition of resins from the Miocene lignite horizons from the Kerala–Konkan Coast, western India was analyzed by Curie-point pyrolysis–gas chromatography–mass spectrometry (Cupy–GC–MS). The major pyrolysates were cadalene-based bicyclic sesquiterpenoids including some C<sub>30</sub>–C<sub>31</sub> bicadinenes and bicadinanes typical of dammar resin from angiosperm plants of Dipterocarpaceae family. These plants are typically supported by tropical climates which the western Indian region was known to have experienced during early Tertiary period. The present study suggests that these palaeoclimatic conditions persisted until at least the Miocene epoch. These sesquiterpenoids which are commonly detected in many SE Asian crude oils may be utilised as useful biomarkers for petroleum exploration in the western Indian region.

## 1. Introduction

Fossilised resins have attracted considerable interest in the past few decades since the important contribution they can make to crude oils became known (see Stout 1995 and references therein). Resins are plant exudates or secretions which harden on atmospheric contact. Natural resins represent a complex organic mixture mostly contains terpenoids and/or phenolic compounds (Langenheim 1995). These biochemicals perform a range of key plant functions including protection from predators, antioxidants and ultraviolet light; provision of structural support (lignin) and pigmentation of flowers and other organs; as well as a signal mechanism to microbial and macro-fauna (Langenheim 1995, 2003).

The terpenoid composition of resins typically include a combination of mono-, sesqui-, di-, and triterpenoid fractions, although no resins are

known to contain both di- and triterpenoid fractions (Langenheim 1995). Terpenoid composition varies with resin type which together with a structural resistance to diagenetic alteration underlines their value as sedimentary biomarker providing a direct link to their resin source. The characterisation of fossil resins can therefore provide important information about palaeovegetation and palaeoclimate. For example, our recent appraisal of the terpenoid composition of Eocene resins from Cambay and Kutch basins, western India (Dutta *et al* 2009; Mallick *et al* 2009) identified these resins as derived from Dipterocarpaceae which must have been supported by a warm, tropical climate during the Eocene epoch.

Here we report the chemical composition of Miocene resins from Kerala–Konkan Coast, western India, to track the affinity of the resin producing plants during aforementioned time and complementing our recent study of Eocene resins

**Keywords.** Fossil resin; Miocene; western India; sesquiterpenoids; geochemistry; geology; biogeosciences.

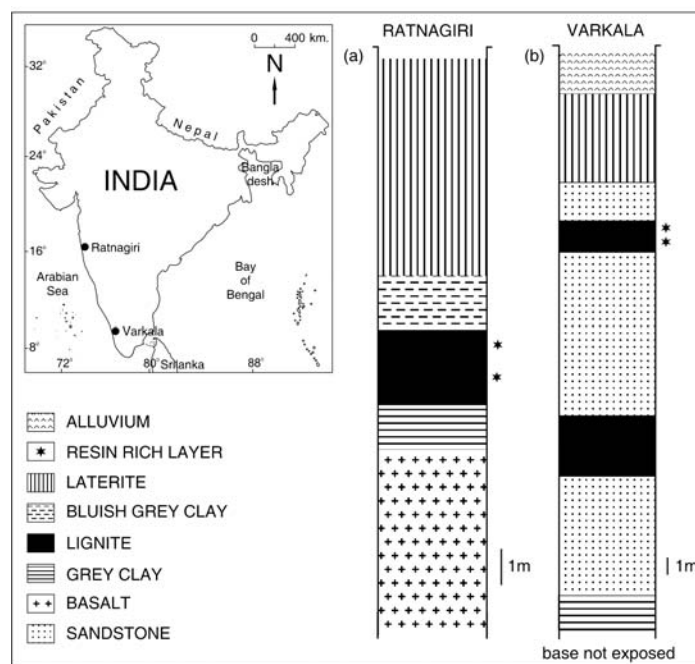


Figure 1. Location map of Ratnagiri and Varkala lignites with lithocolumns showing the positions of fossil resin rich layers.

from Cambay and Kutch basins of west India. This paper also discusses the contribution of fossil resins in hydrocarbon exploration.

## 2. Samples and methods

### 2.1 Samples and geological background

The resin samples were collected from Ratnagiri and Varkala, western India (figure 1). The resins from Ratnagiri were found for the first time in the lignite horizon from the lignitic beds exposed at Mirjole area, 4 km away from the city collector office (16°59'N:73°17'E) of Ratnagiri in the sub-surface well section. Lignite is an integral part of the Sindhudurg Formation, with clay and carbonaceous matter as the other major lithologies and basalt the basement rock (figure 1a). The Ratnagiri lignite beds are of Miocene age (Kulkarni and Phadtare 1980) and were deposited under estuarine depositional condition (Phadtare and Kulkarni 1980). The resins from Varkala area were found in Warkallai group of rocks exposed at south Varkala cliff (8°43'N:76°42'E), 2.5 km west of Varkala railway station. The lumps of resins were present within lignite beds of Miocene age (Narayanan *et al* 2007). However, palynological assemblages suggest Eocene to Early Miocene age (Rao 1995). The lignites are interbedded with sandstone and clay layers. The studied resin samples were collected from the upper lignite seam (figure 1b). An extant

resin from Dipterocarpaceae family (Genus *Shorea*) obtained from Purulia, West Bengal, eastern India was analyzed for comparative purposes.

### 2.2 Curie-point pyrolysis-gas chromatography-mass spectrometry

Resin samples were pyrolysed at 590°C for 10 s using a Curie-point pyrolyser (Pilodist) coupled directly to an HP 5890 Series II gas chromatograph (GC) coupled with a Finnigan MAT 95SQ mass spectrometer (MS). The GC was operated in the splitless mode and was equipped with a 50 m SGE BPX5 fused silica capillary column with an inner diameter of 0.22 mm and a film thickness of 0.25 µm. An initial oven temperature of 50°C was held for 2 min, and then the oven was heated at a rate of 3°C/min to 310°C maintained isothermally for a final 12 min. The carrier gas was helium. The MS was operated in electron impact mode at an ionization energy of 70 eV and a source temperature of 260°C. Full scan mass spectra were recorded over a mass range of 50–1050 Da at a total scan time of 1.0 s. Peak assignments were based on correlation of GC retention time and mass spectral data to published literature and MS libraries.

## 3. Results and discussion

The total ion chromatograms (TICs) from Curie point Py-GC-MS of the fossil resins are

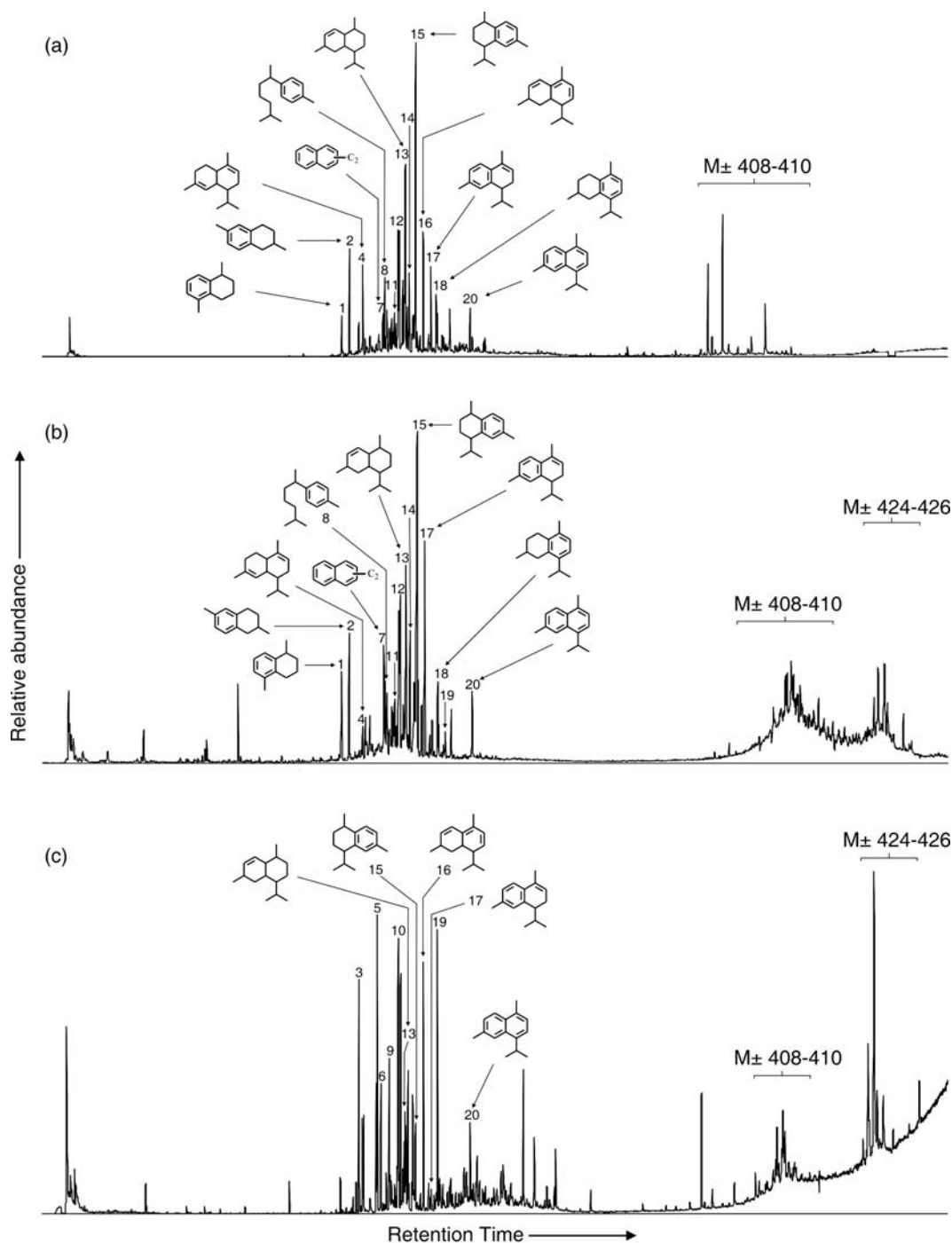


Figure 2. Total ion chromatograms resulting from Curie-point pyrolysis-GC-MS (pyrolysis at 590°C for 10 s) of (a) Miocene fossil resin sample from Sindhudurg Formation, Konkan Coast, western India; (b) Miocene fossil resin sample from Warkallai Group, Kerala Coast, western India; (c) extant resin of genus *Shorea* (family Dipterocarpaceae) from Purulia, West Bengal, eastern India.

presented in figure 2(a–b). The major products were C<sub>15</sub> bicyclic sesquiterpenoids and their dimers (table 1). The sesquiterpenoids ranged in molecular weight from 198 to 206 Da reflecting up to five points of unsaturation. A consistently prominent isopropyl moiety (*m/z* 43) was indicative of a basic cadalene skeleton (van Aarsen *et al* 1991; Stout 1995). Calamanene (1,2,3,4-tetrahydrocadalene;

MW 202) was the most abundant product and 4-isopropyl-1,6-dimethyl-1,2,3,4,4a,5,6,8a-octahydro-naphthalene (MW 206) the next most abundant product. Other products detected in relatively high abundance included 5,6,7,8-tetrahydrocadalene (MW 202),  $\alpha$ -calacorene (1-Isopropyl-4,7-dimethyl-1,2-dihydro-naphthalene; MW 200), cadalene (MW 198)  $\alpha$ -muurolene

Table 1. Major compounds identified from the pyrolysates of Miocene and extant resins from India.

Peak	Compound name	Molecular weight	Fragmentation pattern	Reference
1	1,5-Dimethyl-1,2,3,4-tetrahydro-naphthalene	160	145(100), 160(29), 128(23), 115(20), 117(13), 146(12), 105(9), 91(9)	a, b
2	2,6-Dimethyl-1,2,3,4-tetrahydro-naphthalene	160	118(100), 160(97), 145(95), 117(50), 105(43), 115(38), 128(36), 91(24)	a, b
3	Unknown C <sub>15</sub> sesquiterpenoid	204	161(100), 119(89), 105(80), 93(40), 91(40), 81(23), 120(20), 77(17), 55(12), 133(12), 204(12)	a, e
4	1-Isopropyl-4,7-dimethyl-1,2,4a,5,6,8a-hexahydro-naphthalene or $\alpha$ -Muurolene	204	105(100), 161(24), 106(10), 117(8), 204(8), 91(8), 119(7)	b
5	Unknown C <sub>15</sub> sesquiterpenoid	204	93(100), 133(96), 91(87), 79(73), 69(68), 105(62), 120(42), 119(41), 77(39), 67(39), 81(38), 161(32), 55(32), 147(31), 189(19), 204(5)	a, e
6	Unknown C <sub>15</sub> sesquiterpenoid	204	161(100), 105(37), 91(35), 119(21), 93(17), 120(17), 79(15), 81(14), 133(13), 77(12), 55(8), 204(5)	a, e
7	Dimethylnaphthalene	156	156(100), 141(59), 115(15), 128(13)	a
8	1-(1,5-Dimethyl-hexyl)-4-methyl-benzene or Dihydrocurcumene	204	119(100), 105(11), 204(10), 120(10), 91(9)	c
9	Unknown C <sub>15</sub> sesquiterpenoid	204	161(100), 91(47), 105(41), 93(36), 81(33), 79(30), 119(29), 133(21), 77(21), 120(11), 55(11), 204(10)	a, e
10	Unknown C <sub>15</sub> sesquiterpenoid	204	163(100), 121(87), 93(74), 107(60), 119(56), 91(54), 79(43), 105(43), 81(38), 161(32), 77(30), 55(23), 147(14), 189(11), 204(11)	a, e
11	4-Isopropyl-1,6-dimethyl-1,2,3,4,4a,5,6,8a-octahydro-naphthalene isomer	206	163(100), 81(71), 95(69), 107(64), 150(38), 135(36), 69(31), 206(13)	e
12	4-Isopropyl-1,6-dimethyl-1,2,3,4,4a,5,6,8a-octahydro-naphthalene isomer	206	163(100), 95(32), 81(32), 107(26), 79(17), 206(13), 150(11), 135(9)	e
13	4-Isopropyl-1,6-dimethyl-1,2,3,4,4a,5,6,8a-octahydro-naphthalene	206	163(100), 121(22), 81(21), 107(19), 150(11), 164(10), 95(10), 93(8), 79(6), 43(5), 135(4), 206(3)	e
14	4-Isopropyl-1,6-dimethyl-1,2,3,4,4a,5,6,8a-octahydro-naphthalene isomer	206	163(100), 81(39), 95(38), 107(29), 79(18), 121(15), 69(14), 55(13), 206(10), 135(8)	e
15	4-Isopropyl-1,6-dimethyl-1,2,3,4-tetrahydro-naphthalene or Calamanene	202	159(100), 160(12), 128(10), 144(8), 131(7), 202(7), 157(6)	b, c, d
16	8-Isopropyl-2,5-dimethyl-1,2,8,8a-tetrahydro-naphthalene or Cadala-1(10),3,8-triene	202	157(100), 142(50), 159(46), 141(37), 202(19), 200(16), 128(14), 115(13), 131(6)	a
17	1-Isopropyl-4,7-dimethyl-1,2-dihydro-naphthalene or $\alpha$ -Calacorene	200	157(100), 142(46), 141(35), 91(21), 115(19), 128(16), 200(16), 77(11)	a, e
18	8-Isopropyl-2,5-dimethyl-1,2,3,4-tetrahydro-naphthalene or 5,6,7,8-tetrahydro-cadalene	202	187(100), 159(50), 202(36), 128(16), 131(14), 145(13), 115(12)	b, d
19	Calamanene isomer	202	159(100), 202(74), 117(56), 131(53), 91(49), 105(33), 115(30), 187(27), 128(25), 79(20), 77(20),	e
20	Cadalene	198	183(100), 198(48), 168(30), 153(14), 141(6), 128(4), 115(4), 105(3)	b, d

(a) NIST library; (b) Chaler and Grimalt (2005); (c) Czechowski et al (1996); (d) Simoneit and Mazurek (1982); (e) Mass spectral characteristics.

(1-Isopropyl-4,7-dimethyl-1,2,4a,5,6,8a-hexahydro-naphthalene; MW 204) and dihydrocurcumene (1-(1,5-dimethyl-hexyl)-4-methyl-benzene; MW 204). Several polymethylnaphthalenes (e.g., 1,5-dimethyl-1,2,3,4-tetrahydro-naphthalene and 2,6-dimethyl-1,2,3,4-tetrahydro-naphthalene) were also abundantly found in the pyrolysis products of resins.

A separate distribution of peaks at higher retention times mostly comprised  $C_{30}H_{48}$  dimers (MW 408–410) attributed to  $C_{30}$  bicadinenes on the basis of their strong  $m/z$  201–205,  $m/z$  159–163 and  $m/z$  365–367. These are diagnostic biomarkers of dammar resins derived from angiosperm family Dipterocarpaceae (Anderson *et al* 1992; Stout 1995). Several  $C_{31}$  bicadinanes and bicadinenes (MW 424–426; Pearson and Alam 1993) were additionally detected in the pyrolysates of the resin from Varkala.

The corresponding pyrolysis data from the extant resin also comprised a dominant distribution of  $C_{15}$  bicyclic sesquiterpenoids (figure 2c) and lesser amounts of  $C_{30}$  bicadinenes (MW 408–410) along with several  $C_{31}$  bicadinanes and bicadinenes (MW 424–426). The extant resin also showed some of the same terpenoid speciation as the fossil resin. For example, calamanene (1,2,3,4-tetrahydrocadalene), 4-Isopropyl-1, 6-dimethyl-1, 2,3,4,4a,5,6,8a-octahydro-naphthalene (MW 206), 5,6,7,8-tetrahydrocadalene (MW 202),  $\alpha$ -calacorene (1-Isopropyl-4,7-dimethyl-1,2-dihydro-naphthalene; MW 200), cadalene (MW 198) were detected in high abundance from all studied samples. Their preservation in the fossil resin reflects minimal diagenetic alteration of these terpenoid biomarkers.

Previous research has distinguished three structurally distinct polymeric fossil resins based on labdanoid (diterpenoid), cadinane (sesquiterpenoid) and styrene polymeric units which derive from different plant sources. Both coniferales and Leguminosae, a family of angiosperm can yield polyditerpenoid resins (Anderson *et al* 1992). Cadinane based resins only derive from Dipterocarpaceae and Mastixioideae of the Cornaceae family of angiosperms (Anderson *et al* 1992; van Aarssen *et al* 1990, 1994). Polystyrene resins have been solely attributed to Hammelidaceae (Genus *Liquidambar*) angiosperms (see Anderson *et al* 1992).

The occurrence of  $C_{15}$  bicyclic sesquiterpenoids with cadalene carbon skeleton and their dimers (bicadinanes) in the present fossil resins identify these as a Dipterocarpaceae-sourced dammar resins. This is consistent with the previous attribution of a fossil wood from the lignite beds of Sindhurg formation (Ratnagiri) to the *Shoreoxylon vayganiensis* sp. nov. of the

Dipterocarpaceae family (Srivastava and Saxena 1998). Dipterocarpaceae angiosperms grow abundantly in warm and humid climate, hence are often prolific in tropical rain forests (Langenheim 1995). Palynological records do suggest that a warm humid climate prevailed in the Kerala–Konkan coast during the Miocene (Phadtare and Kulkarni 1980; Rao 1995). Dipterocarpaceae were abundant on the Indian subcontinent during Neogene times (Lakhanpal 1970) and our recent biomarker studies of Eocene resins from Cambay and Kutch basins, western India suggest that this angiosperm family may be detected in Indian sediments date back to the Early Eocene (Dutta *et al* 2009; Mallick *et al* 2009). Fossil record also confirms that Dipterocarpaceae evolved in India since Palaeogene (Prasad *et al* 2009).

Bicadinanes have been detected in many SE Asian crude oils including Qiongdongnan (South China; van Aarssen *et al* 1992a), Surma (Bangladesh; Alam and Pearson 1990, 1992; Pearson and Alam 1993), Central Myanmar (Myanmar; Curiale *et al* 1994), South Sumatra, West Irian Jaya, Ardjuna, Lumpas, Mahakam Delta (Indonesia; van Aarssen *et al* 1990; Murray *et al* 1994; Sosrowidjojo *et al* 1994; Stout 1995) and Lower Assam (India; Pande *et al* 1994) basins. This prevalence suggests  $C_{15}$  bicyclic sesquiterpenoids and their dimers will be useful biomarkers for source rock–oil and oil–oil correlations vital to petroleum explorations in this region. The  $C_{15}$  bicyclic sesquiterpenoid, especially cadalene and their dimers (bicadinanes) can also reflect thermal maturity of source rocks which has been proved to be useful for oil exploration purposes (Peters *et al* 2005 and references therein). Significantly, polycadinene biomarkers can survive thermal decomposition up to  $\sim 80^\circ\text{C}$  (Tegelaar and Noble 1994) and escape microbial and chemical alteration during early diagenesis.

#### 4. Conclusions

The pyrolysis products of Miocene resins from Kerala–Konkan Coast, western India contain cadalene-based aromatic, saturated, and unsaturated  $C_{15}$  bicyclic sesquiterpenoids and their dienes,  $C_{30}$ – $C_{31}$  bicadinanes and bicadinenes. These are diagnostic biomarkers of dammar resins which are derived from angiosperm family of Dipterocarpaceae. The presence of these terpenoids in both fresh and fossilized resins clearly suggests that dammar resins undergo minimal chemical changes during fossilizations. Our ongoing investigations suggest that detailed studies of these terpenoid biomarkers from Tertiary sediments and oils from western India would be beneficial and

appropriate for understanding the contribution of dammar resins to the generation of hydrocarbon in this region.

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