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Occurrence of polycadinene in fossil and recent resins

B. G. K. VAN AARSSEN,[1,*] J. W. DE LEEUW,[1,†] M. COLLINSON,[2] J. J. BOON,[3] and K. GOTH[4]

[1]Delft University of Technology, Faculty of Chemical Technology and Materials' Science, Organic Geochemistry Unit,
De Vries van Heystplantsoen 2, 2628 RZ Delft, The Netherlands
[2]Royal Holloway and Bedford New College, Department of Geology, University of London, Egham Hill, Egham,
Surrey TW20 0EX, England
[3]Unit for Mass Spectrometry of Macromolecular Systems, FOM Institute for Atomic and Molecular Physics,
Kruislaan 407, 1098 SJ Amsterdam, The Netherlands
[4]Sächsisches Landesamt für Umwelt und Geologie, Halsbrückerstrasse 31a, D-9200 Freiberg, Germany

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Abstract—Dammars produced by Dipterocarpaceae growing in Southeast Asia are partly composed of a macromolecule with a polycadinene structure. This polymer is the precursor of many specific compounds encountered in crude oils and sediment extracts from South Asia. Until recently there was no evidence for a more widespread geographical occurrence of this resinous polymer. Using different pyrolysis methods it is shown that the polymers present in a resinite from Utah, USA, and in resins contained in resin canals of Eocene fossil fruits from Germany and England are also polycadinenes. The fossil fruits were undoubtedly produced by ancient representatives of mastixioid Cornaceae, a group of plants which was widespread in the Tertiary of Europe and North America and which is not related to Dipterocarpaceae. These findings extend the known occurrence and origin of the sesquiterpenoid type resin polymer. It is to be expected that catagenetic products of these resin polymers should be present in oils, coals, and sediment extracts from areas outside Southeast Asia.

INTRODUCTION

THE TERM dammar is used for a group of natural resins originating from trees of the Dipterocarpaceae (MILLS and WERNER, 1955). Presently, angiosperm trees belonging to this family grow abundantly in Southeast Asia. They are especially diverse and abundant in the western part of Malaysia (WHITMORE, 1988). Dammar is mainly composed of triterpenoids. In addition, the resin contains a considerable amount of a high-molecular-mass substance (RENÉ DE LA RIE, 1988; VAN AARSSEN et al., 1990). This macromolecular material consists of a polysesquiterpene of which the basic structural unit has a cadinene carbon skeleton (VAN AARSSEN et al., 1990). The structure of this polycadinene is completely different from that of polymers present in resins produced by many gymnosperms. Macromolecules of the latter consist of polymerised diterpenoid acids with a labdane carbon skeleton (LANGENHEIM, 1990).

Simulation experiments at elevated temperatures have shown that polycadinene decomposes into compounds consisting of one or more basic cadinene units (VAN AARSSEN et al., 1991; Fig. 1). These small molecules react intramolecularly yielding thermodynamically stable compounds. Such compounds, e.g. bicadinanes, are present in crude oils and sediment extracts from Southeast Asia (GRANTHAM et al., 1983; VAN AARSSEN et al., 1990, 1992; ALAM and PEARSON, 1990), indicating that polycadinene contributes to components of these oils and sediment extracts.

The fossil record of pollen (MULLER, 1981), woods (BANDE and PRAKASH, 1986), and leaves (LAKHANPAL and GULERIA, 1986) indicates that Dipterocarpaceae have been growing in Southeast Asia since the Oligocene and were abundant in the Neogene. It therefore seems very likely that the polycadinene precursors of the bicadinanes (and other catagenetic compounds) originated from the dammars produced by trees of the Dipterocarpaceae family.

Recently, the occurrence of a polysesquiterpene was reported outside Southeast Asia (CRELLING et al., 1991; MEUZELAAR et al., 1991). Resinites present in Eocene coal seams in Utah, USA, were shown to contain a polymer very similar to the dammar polycadinene. No direct fossil evidence was available for the botanical origin of this resinite, but an affinity with Dipterocarpaceae was suggested on basis of the chemical analyses (CRELLING et al., 1991; MEUZELAAR et al., 1991). However, plant fossils which can be assigned to Dipterocarpaceae are extremely rare outside Southeast Asia (COLLINSON et al., 1993). Only one Dipterocarpaceae macrofossil has been reported in the northern hemisphere, a few leaf specimens from the Eocene of North America identified as *Parashorea* (WOLFE, 1977). The extensive Eocene floras of Europe, which do contain many elements whose closest living relatives grow in South East Asia, do not contain Dipterocarpaceae (COLLINSON, 1983; COLLINSON and HOOKER, 1987; MAI and WALTHER, 1978, 1985; WILDE, 1989).

In this paper we report the occurrence of polysesquiterpene type resins in resin canals of fossil fruits which do not belong to the Dipterocarpaceae. The fossil fruits were found in the Eocene Messel oil shale (COLLINSON, 1983) and in the Eocene of Dorset, England (CHANDLER, 1962). The structures of

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[*] *Present address*: Centre for Petroleum and Environmental Organic Geochemistry, Curtin University of Technology, GPO Box U1987, Perth 6001, Western Australia.

[†] *Present address*: Division of Marine Biogeochemistry, Netherlands Institute of Sea Research (NIOZ), PO Box 59, 1790 AB Den Burg, Texel, The Netherlands.

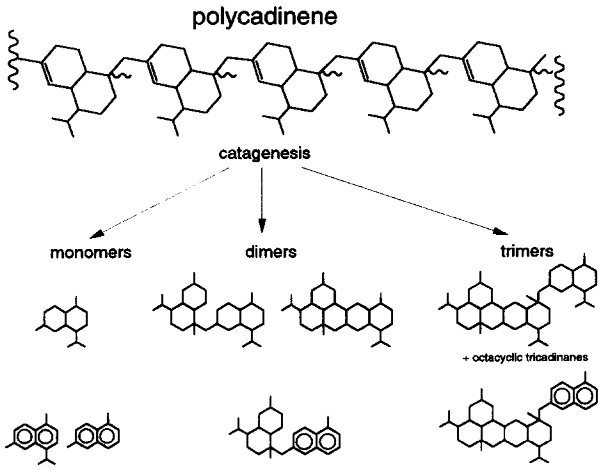

FIG. 1. Polycadinene and its proposed catagenetic products.

these resinous polymers and their botanical relationships are discussed.

EXPERIMENTAL

Samples

Table 1 describes the samples used in this study. The extant dammar is a commercially available resin from Brome and Schimmer, Romsey, England. The fossil resin was handpicked from the Upper Cretaceous Wasatch coal seam in Utah, USA.

The plant material from the Middle Eocene of Messel (near Darmstadt, Germany) is housed in the Palaeobotany Section, Senckenberg Museum, Frankfurt. The collections are stored in glycerol, but specimens for chemical studies were selected from those found in the previous field season which had been stored in water since their collection in the field. Fossil fruits were dissected while being viewed under a low power microscope. Only specimens where resin was seen to be present in internal resin canals were selected for this study. Specimens for chemical analysis were cut in half, enabling the same fruits to be studied by different methods. Samples 3 and 4 were both characterised as *Eomastixia* aff. *rugosa* (Zenker) Chandler (see Fig. 2 for details). Sample 3 contains one seed locule whereas sample 4 contains four.

Material from Dorset, England, is housed in the Palaeontology Department, Natural History Museum, London, where it has been stored dry in glass vials. Sample 5 is a duplicate endocarp from V.41977 of *Eomastixia urceolata* Chandler from the Early Eocene of Lake, Dorset. The species is fully described and figured by CHANDLER (1962, pp. 126–127; Pl. 19, Figs. 8–13).

Sample Preparation for Py–GC and Py–GC–MS Analysis

Dichloromethane (5 mL) were added to 500 mg of the powdered fossil resin. The insoluble residue was removed by centrifugation. The supernatant was pipetted off and concentrated to a viscous solution. Addition of 5 mL methanol yielded a white precipitate, which was separated from the solution by centrifugation.

One gram of the fresh dammar sample was powdered and dissolved in dichloromethane. Apart from plant parts, which were removed by filtration, the resin was completely soluble. The recent dammar was then treated in the same way as the fossil resin.

The split fossil fruits were immersed in dichloromethane for 48 h. The residues were removed by centrifugation. The samples were then treated in the same way as the fossil resin.

Sample Preparation for Py–MS Analysis

Resin in fossil fruits was identified under the microscope by its relatively light brown color and translucency. Samples were taken directly with a fine needle from the resin ducts by micromanipulation under a Nikon SMZ-U binocular microscope. The resin fragment samples were transferred to a glass micromortar, ground, and dissolved in dichloromethane.

Curie-Point Pyrolysis–Gas Chromatography

Curie-point pyrolysis–gas chromatography (Py–GC) analyses were performed on a Hewlett-Packard 5890 gas chromatograph using a FOM-3LX unit for pyrolysis. The samples were applied to ferromagnetic wires with a Curie temperature of 610°C. The gas chromatograph, equipped with a cryogenic unit, was programmed from 0°C (5 min) to 320°C (20 min) at a rate of 3°C/min. Separation was achieved using a fused-silica capillary column (25m × 0.32 mm) coated with CP Sil-5 (film thickness 0.4 μm). Helium was used as the carrier gas.

Curie-Point Pyrolysis–Gas Chromatography–Mass Spectrometry

Curie-point pyrolysis–gas chromatography–mass spectrometry (Py–GC–MS) was carried out using the same gas chromatograph, pyrolysis unit, capillary column, and carrier gas as described above for Py–GC. The gas chromatograph was connected with a VG-70S mass spectrometer operated at 70 eV with a mass range m/z 40–800 and a cycle time of 1.8 s. One-μL samples were injected on column at 50°C in hexane (ca. 3 mg/mL) and the temperature was programmed at 10°C/min to 70°C and then at 4°C/min to 320°C (20 min).

In-Source Pyrolysis–Mass Spectrometry

In-source pyrolysis-mass spectrometry (PY–MS) was performed on a JEOL DX-303 forward geometry double focusing mass spectrometer (E/B mode). Samples (ca. 5 μg) were deposited on a Rhenium filament ($f = 0.1$ mm) on an insertion probe which was directly introduced into the ion source of the mass spectrometer after evaporation of the solvent in vacuo. Chemical ionization using methane or isobutane as a reagent gas was performed with an in-source pressure of 10^{-2} Torr at an ion source temperature of 180°C and electron impact energy of 250 eV. Mass spectra were taken continuously by repeated scanning from 60–1500 amu with a cycle time of 1 s during the filament heating. The heating of the filament was started after a 10 s initial period with a heating rate of 1A/min up to 800°C. Data acquisition and processing were performed on a JEOL DA-5000 data system.

Table 1. Sample description

sample	description	location	age	botanical origin
1	dammar	South East Asia	Present	various Dipterocarpaceae
2	fossil resin	Utah, USA	Upper Cretaceous	unknown
3	fossil fruit	Messel, Germany	Middle Eocene	*Eomastixia* aff. *rugosa* [a]
4	fossil fruit	Messel, Germany	Middle Eocene	*Eomastixia* aff. *rugosa* [a]
5	fossil fruit	Dorset, England	Early Eocene	*Eomastixia urceolata* Chandler [b]

[a]see Fig. 2 for detail, [b]Chandler, 1962

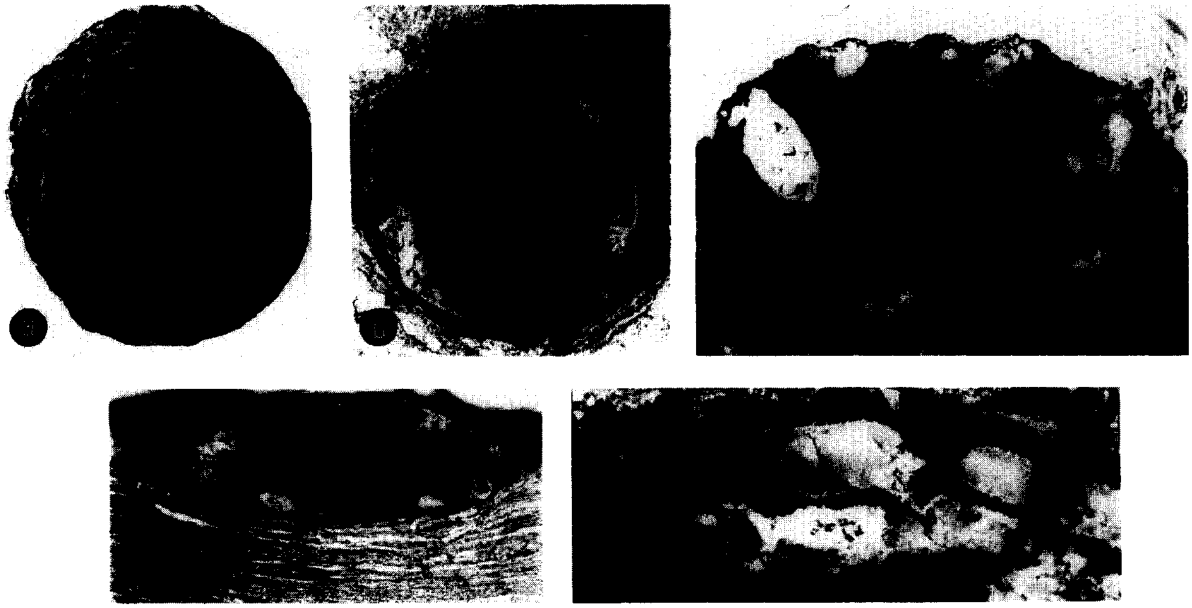

FIG. 2. Fossil fruits of mastixioid Cornaceae from the middle Eocene oil-shales of Messel, Germany. These fruits are determined provisionally as *Eomastixia* aff. *rugosa* (Zenker) Chandler (see CHANDLER, 1962, for details of the species and HOLY, 1975, for later emendation of *Eomastixia* to the concept that is followed here). A detailed description and systematic treatment will be published elsewhere (COLLINSON et al., 1993). The fossil fruits typically contain one to four (rarely five) locules and resin present in resin canals. Specimens housed in the Palaeobotany Section, Senckenberg Museum, Frankfurt, numbers prefixed Me. All photographed under water using reflected light. (a) Complete fruit isolated from the oil-shale, showing apical perianth disc. Me 2241, ×4. (b) Fruit lying on oil-shale; fractured longitudinally, showing elongate internal resin canals just beneath the fruit surface. Me 5175, ×4. (c) Detail from a 5-loculed fruit lying on oil-shale; fractured transversely, showing two U-shaped locules each with a large resin canal between the arms of the U (in the longitudinal infold of the germination valve). Other smaller resin canals can also be seen near the surface of the fruit. Me 5174, ×9.5. (d) Fruit lying on oil-shale; cut transversely with razor; showing internal resin canals of various sizes beneath the surface of the fruit. Multi-loculed specimen but locule number unclear due to compression. Me 7114, ×4. (e) Detail of resin canals from top right of the fruit in Figure 2, ×16.

RESULTS AND DISCUSSION

The GC traces of the pyrolysates are shown in Fig. 3. The structure of the polymer isolated from the dammar has been shown to be polycadinene (VAN AARSSEN et al., 1990), and its pyrolysis compounds are well known. The other chromatograms are all very similar to that of the pyrolysate of polycadinene. Two major groups of pyrolysis products are present in all samples. In the case of polycadinene, the interpretation of mass spectra obtained from the Py–GC–MS analysis showed that the first eluting group of pyrolysis products consists of C_{15}-compounds with molecular weights from 198 to 208 daltons (VAN AARSSEN et al., 1990). These compounds have the cadinane carbon skeleton and possess one to five double bonds. Comparison of mass spectra and mass chromatograms using the molecular weights of the C_{15} compounds shows that the fossil polymers produce the same compounds upon pyrolysis as polycadinene (Fig. 4). The basic structural unit of polycadinene possesses one double bond (Fig. 1). Upon pyrolysis, two carbon-carbon bonds must be broken to form a monomer. The radicals formed in this way react further to yield compounds with different degrees of unsaturation, resulting in the formation of a suite of cadinenes.

The later eluting group of pyrolysis products are compounds composed of two cadinene units. These dimeric cadinenes have molecular weights in the range of 404–410 daltons. Comparison of mass spectra and mass chromatograms showed that the same suite of dimeric compounds is formed upon pyrolysis of polycadinene from recent dammar and the fossil resin polymers (Fig. 4).

Further investigation of the fossil resins by direct sampling from the resin canals of fossil fruits found in the Messel shale was performed by temperature-resolved, in-source Py–MS under isobutane and methane ionization conditions. This method has been successfully used before for the microscale characterization of fossil resin samples (GRIMALDI et al., 1989; BOON et al., 1993) and fossil cuticle (BOON, 1993). The Py–MS data of polycadinene isolated from recent dammar (Fig. 5) show a TIC-profile indicative of high molecular weight material which pyrolyses at higher temperatures. The mass spectrum shows series of oligomers up to the heptamer with a mass increment of 204 daltons starting at m/z 204. The peaks at the higher m/z values show complex isotope patterns which correspond with the expected distributions. The clusters of peaks can be related to suites of unsaturated compounds with the same carbon skeleton which are found in the flash pyrolysates of the resin polymers. Peak series corresponding to oligomeric pyrolysis products are also observed in polysaccharides (LOMAX et al., 1991), β-hydroxy fatty acid polyesters (BOON, 1993), and various synthetic

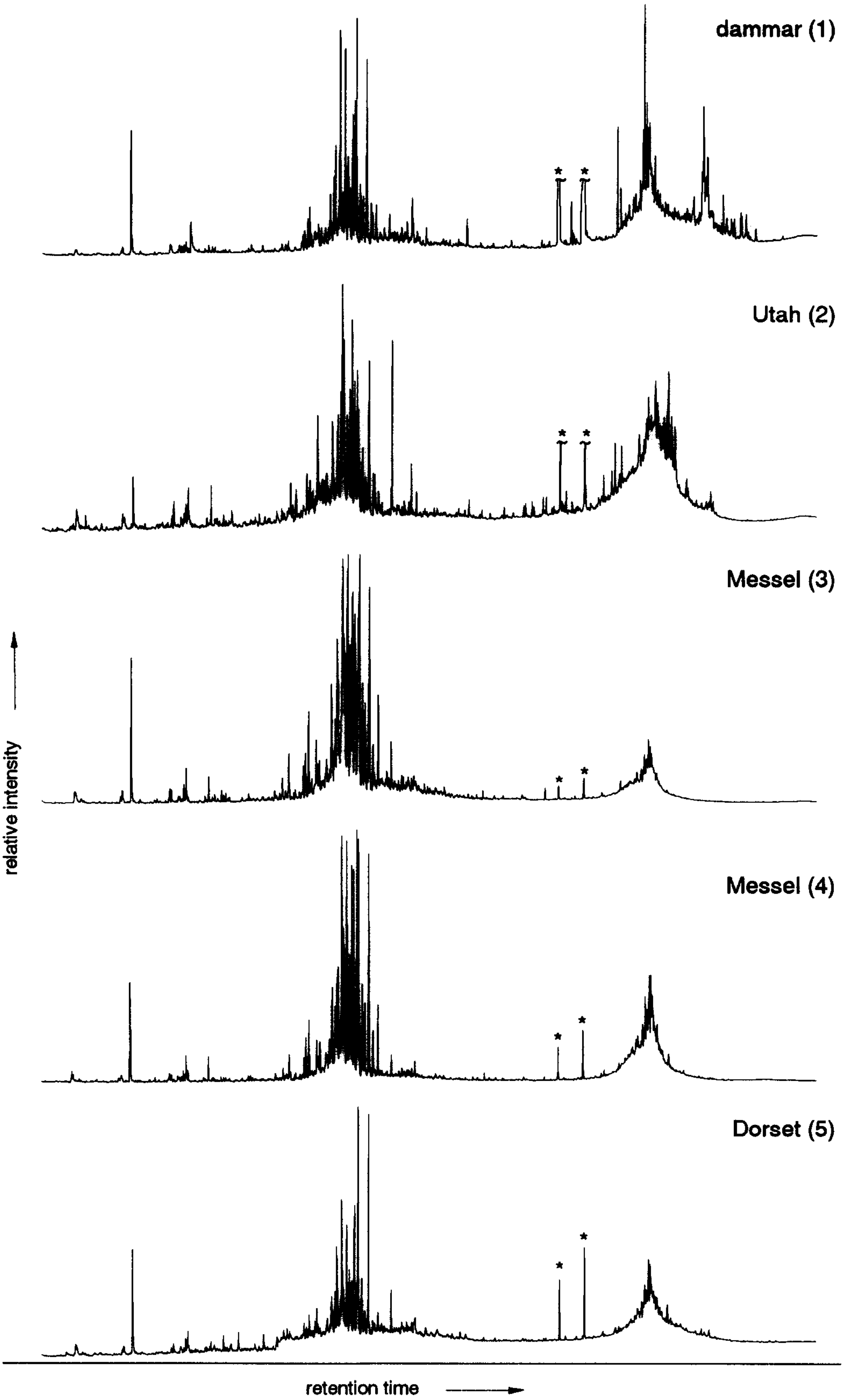

FIG. 3. GC traces of the pyrolysates obtained by Curie-point pyrolysis of the polymers isolated from the resin samples. * = contamination.

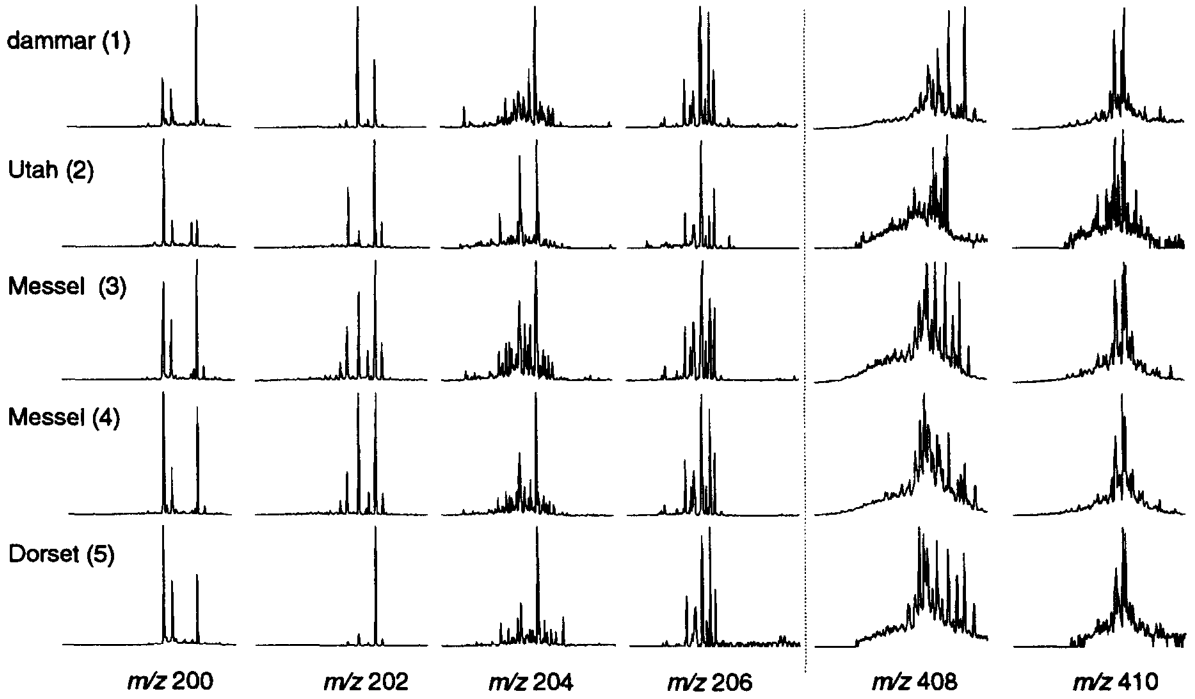

FIG. 4. Partial mass chromatograms obtained from the Py-GC-MS analyses of the isolated polymers, using *m/z* 200, 202, 204, and 206 for the monomeric products and *m/z* 408 and 410 for the dimeric pyrolysis products. Sample numbers are in brackets.

polymers, (e.g., polystyrene; Grimaldi et al., 1989) and are a strong indication for linear domains in the polymer system.

Both methane and isobutane CI data for the fossil resins show relatively complex TIC-profiles indicative of evaporating low molecular weight compounds and a high molecular weight fraction which pyrolyses at higher temperatures. In all samples, the polymeric fraction is reflected by the major second peak in the TIC. Figure 5 shows the averaged mass spectrum of the polymeric fraction of Messel sample 4 taken under isobutane CI conditions. The spectrum shows a high degree of similarity to the polycadinene standard, although there appear to be small differences with respect to the degree of unsaturation of the pyrolysis fragments. The spectrum of the low molecular weight fraction shows the presence of functionalized triterpenoid compounds similar to those found in the low molecular weight fractions of fossil and recent dammars (van Aarssen et al., 1990). The Py-MS data on resins from the other fruits were essentially similar although the oligomeric region of the spectra was less strongly developed in these samples.

The data obtained show that the polymers isolated from the resin samples are polymeric cadinenes. Although the methods that were used cannot establish the exact structures of the polymers, it is clear that they are virtually identical to the polycadinene that was analyzed in recent Dipterocarpaceae resin. The differences that are observed in the distribution patterns of the pyrolysis products can be explained by assuming different degrees of unsaturation in single monomeric units. These differences may have been caused by variations in diagenetic conditions during fossilization.

The present study shows that the occurrence of polycadinene is not restricted to Southeast Asia. Samples from Germany, England, and the USA indicate a widespread geographical distribution of resins containing this sesquiterpenoid polymer.

The botanical origin of the resinite from the Wasatch coal is presently unknown. In contrast, the fossil fruits from Messel and Dorset are characterised members of the Mastixioideae (Cornaceae). Since the resin is contained in the resin canals of these fruits, there is no doubt concerning its origin. Because the *Eomastixia* species are not related to Dipterocarpaceae, it is clear that the latter are not the only producers of polycadinene, whether in the present or in the past.

During catagenesis, polycadinene generates low-molecular-mass compounds. These compounds disproportionate into saturated and aromatic compounds like bicadinanes (van Aarssen et al., 1992). Such compounds have been reported to occur in crude oils and sediment extracts from Southeast Asia (Grantham et al., 1983; van Aarssen et al., 1990, 1992; Alam and Pearson, 1990) and in a hydrothermal oil from Wyoming, USA (Clifton et al., 1990). As the occurrence of polycadinene is obviously not restricted to the Southeast Asian region, its catagenesis products are likely to be encountered in oils, sediments, and coals from different parts of the world, as is shown by Clifton et al. (1990). These compounds can thus be used as markers for higher plant resins of probable angiosperm origin.

The occurrence of any significant amounts of bicadinanes in crude oils seems to be related to vast amounts of resin produced during deposition. The hydrocarbon generation potential of small amounts of polycadinene in the fruits should therefore not be overestimated. However, the presence

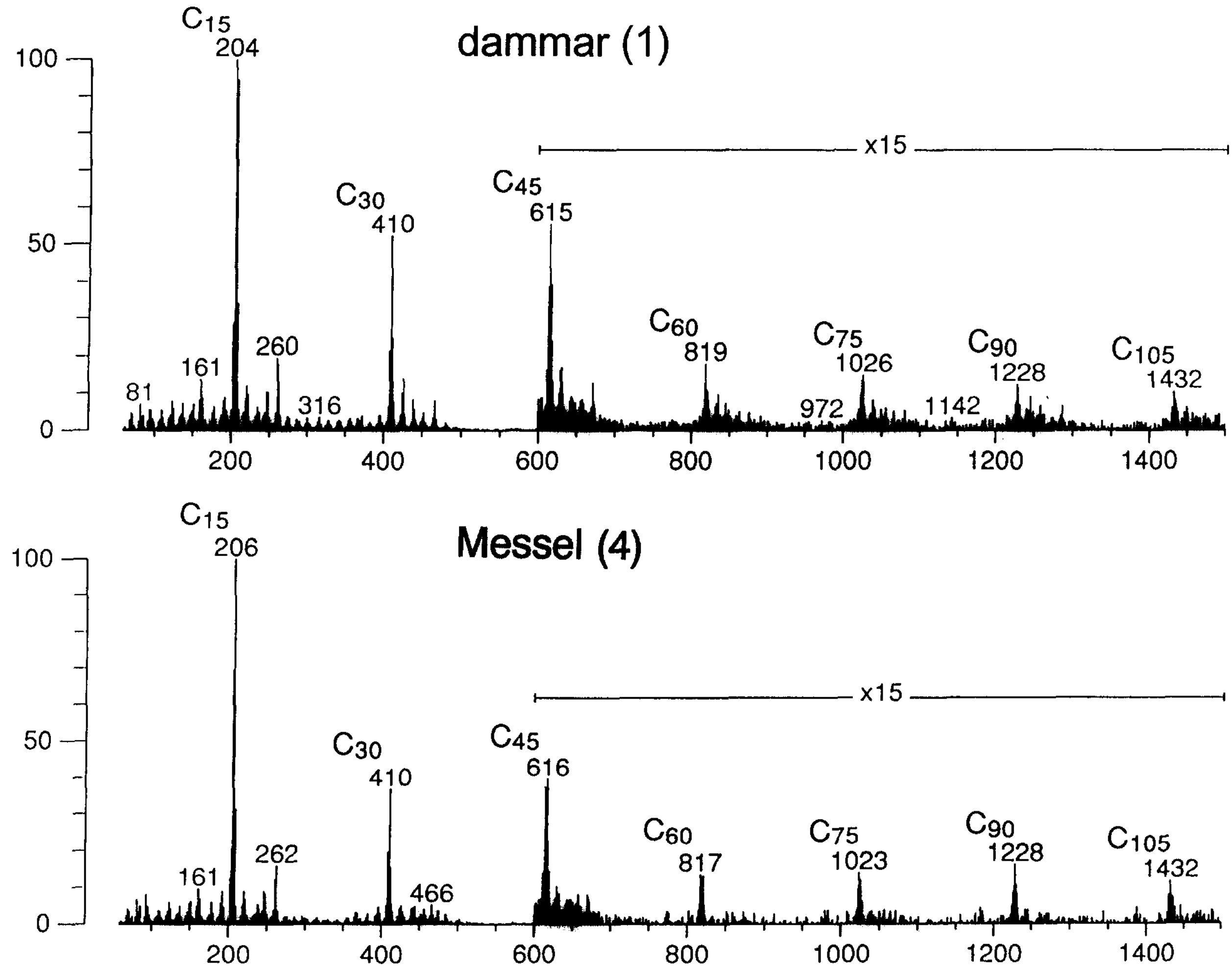

FIG. 5. Mass spectra obtained from Py-MS analysis of (a) polycadinene isolated from recent dammar (averaged over 10 scans) and (b) polymer isolated from the fossil fruit of *Eomastixia* aff. *rugosa* (Messel, sample 4, averaged over 7 scans).

of polycadinene in the preserved fruits does yield a unique opportunity to determine its botanical and geographical origin. Whether the trees that produced the fruits also produced higher quantities of similar resins in other parts of their anatomy is not known.

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REFERENCES

ALAM M. and PEARSON M. J. (1990) Bicadinanes in oils from the Surma Basin, Bangladesh. *Org. Geochem.* **15,** 461–464.

BANDE M. B. and PRAKASH U. (1986) The Tertiary flora of South East Asia with remarks in its palaeoenvironment and phytogeography of the Indo-Malayan region. *Rev. Palaeobot. Palynol.* **49,** 203–233.

BOON J. J. (1993) Analytical pyrolysis mass spectrometry: new vistas opened by temperature resolved in-source PyMS. *Int. J. Mass Spectr. Ion Proc.* **118–119,** 755–787.

BOON J. J., TOM A., and PUREVEEN J. (1993) Microgram scale pyrolysis mass spectrometric and pyrolysis gas chromatographic characterisation of geological and archaeological amber and resin samples. In *Proceedings of the Amber in Archaeology Symposium, Liblice, 1990* (in press).

CHANDLER M. E. J. (1962) *The Lower Tertiary Floras of Southern England. II. Flora of the Pipe-Clay Series of Dorset (Lower Bagshot).* British Museum (Natural History), London.

CLIFTON C. G., WALTERS C. C., and SIMONEIT B. R. T. (1990) Hydrothermal petroleums from Yellowstone National Park, Wyoming, USA. *Appl. Geochem.* **5,** 169–191.

COLLINSON M. E. (1983) Fossil Plants of the London Clay. *Palaeontological Association Field Guides to Fossils No 1.* Palaeontological Association, London.

COLLINSON M. E. (1988) The special significance of the Middle Eocene Fruit and seed flora from Messel, West Germany. *Courier Forschungsinstitut Senckenberg* **107,** 187–197.

COLLINSON M. E. and HOOKER J. J. (1987) Vegetational and mammalian faunal changes in the Early Tertiary of southern England. In *The Origins of Angiosperms and Their Biological Consequences* (ed. E. M. FRIIS et al.), pp. 259–304. Cambridge Univ. Press.

COLLINSON M. E., BOULTER M. C., and HOLMES P. L. (1993) Magnoliophyta. In *The Fossil Record 2* (ed. M. BENTON), pp. Chapman and Hall.

CRELLING J. C., PUGMIRE R. J., MEUZELAAR H. L. C., MCCLENNEN W. H., HUAI H., and KARAS J. (1991) The chemical structure and petrology of resinite from the Hiawatha "B" coal seam. *Energy and Fuels* **5,** 688–694.

GRANTHAM P. J., POSTHUMA J., and BAAK A. (1983) Triterpanes in a number of far-eastern crude oils. In *Advances in Organic Geochemistry 1981* (ed. M. BJORØY et al.), pp. 675–683. Wiley.

GRIMALDI D., BECK C. W., and BOON J. J. (1989) Occurrence, chemical characterisation and paleontology of the fossil resins from New Jersey. *Amer. Mus. Novitates* **2948,** 1–27.

HOLY F. (1975) Representatives of the family Mastixiaceae Celstani 1905 in the Bohemian Tertiary. *Sbornik Narodniho Muzea V Prace B* **31,** 123–147.

LAKHANPAL R. N. and GULERIA J. S. (1986) Fossil leaves of *Dipterocarpus* from the Lower Siwalik beds near Jawalamukhi, Himachal Pradesh. *The Palaeobotanist* **35,** 258–262.

LANGENHEIM J. H. (1990) Plant resins. *Amer. Sci.* **78,** 16–24.

LOMAX J. A., BOON J. J., and HOFFMANN R. A. (1991) Characterisation of polysaccharides by in-source pyrolysis positive- and negative-ion direct chemical ionisation-mass spectrometry. *Carbohydr. Res.* **221,** 219–233.

MAI D. H. and WALTHER, H. (1978) Die Floren der Haselbacher Serie im Weisselster-Becken (Bezirk Lepzig, DDR). *Abhandlungen des Staatlichen Museums fur Mineralogie und Geologie zu Dresden 28.*

MAI D. H. and WALTHER H. (1985) Die Obereozanen Floren des Weisselster-Beckens und seiner Randgebiete. *Abhandlungen des Staatlichen Museums fur Mineralogie und Geologie zu Dresden 33.*

MEUZELAAR H. L. C., HUAI H., LO R., and DWORZANSKI J. P. (1991) Chemical composition and origin of fossil resins from Utah Wasatch Plateau coal. *Fuels Proc. Technol.* **28,** 119–134.

MILLS J. S. and WERNER A. E. A. (1955) The chemistry of dammar resin. *J. Chem. Soc.* 3132–3140.

MULLER J. (1981) Fossil pollen records of extant angiosperms. *The Botanical Review* **47,** 1–146.

RENÉ DE LA RIE E. (1988) Stable varnishes for old master paintings. Ph.D. thesis, Univ. Amsterdam.

VAN AARSSEN B. G. K., COX H. C., HOOGENDOORN P., and DE LEEUW J. W. (1990) A cadinene biopolymer present in fossil and extant dammar resins as a source for cadinanes and bicadinanes in crude oils from Southeast Asia. *Geochim. Cosmochim. Acta* **54,** 3021–3031.

VAN AARSSEN B. G. K., HORSFIELD B., and DE LEEUW J. W. (1991) A comparative study of three different pyrolysis methods used to characterise a biopolymer isolated from fossil and extant dammar resins. *J. Anal. Appl. Pyrol.* **20,** 125–139.

VAN AARSSEN B. G. K., HESSELS J. K. C., ABBINK O. A., and DE LEEUW J. W. (1992) The occurrence of polycyclic sesqui-, tri-, and oligoterpenoids derived from a resinous polymeric cadinene in crude oils from Southeast Asia. *Geochim. Cosmochim. Acta* **56,** 1231–1246.

WHITMORE T. C. (1988) *Tropical Rain Forests of the Far East,* 2nd ed. Oxford Univ. Press.

WILDE V. (1989) Untersuchungen zur Systematik der Blattreste aus dem Mitteleozan der Grube Messel bei Darmstadt (Hessen, Bundesrepublik Deutschland). *Courier Forschungsinstitut Senckenberg* **115,** 1–213.

WOLFE J. A. (1977) Paleogene floras from the Gulf of Alaska region. *Prof. Papers USGS* **997,** 1–108.