

Short Communication

Identification and analysis of trimethylbiphenyls in petroleum

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ABSTRACT

Trimethylbiphenyl isomers (17) have been identified in three Australian crude oils using capillary gas chromatography-mass spectrometry (MRM) techniques. Total concentrations of trimethylbiphenyls in the crude oils ranged from 100 to 600 $\mu\text{g/g}$ and in all cases the most abundant isomers were those with substituents in the *meta* and *para* positions. The elution order of all the isomeric trimethylbiphenyls is reported for four capillary columns with a range of stationary phases.

INTRODUCTION

Alkylbiphenyls are widespread in sedimentary organic matter and have been reported in crude oils [1-3], coal tar [4] and shale oil [5]. More recently, detailed studies on crude oils and sediments [6-8] have led to identification of all the isomers of methylbiphenyl, ethylbiphenyl and dimethylbiphenyl.

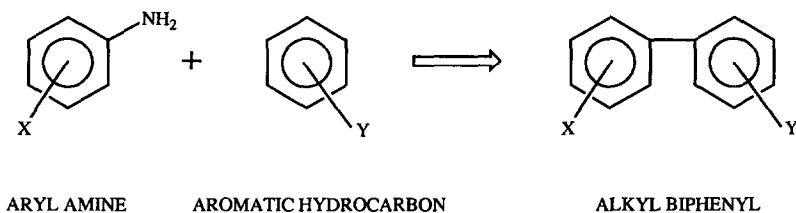
Reports on the distributions of alkylbiphenylisomers in sedimentary sequences have shown that isomers with *ortho* substituents are depleted relative to those without *ortho* substituents as the depth and maturity of sediments increase [8]. In the case of methylbiphenyls, the relative abundance of 2-methylbiphenyl moves further from the equilibrium value [9] with increase in sample maturity. This effect has been attributed to a thermally induced cyclisation reaction in which the *ortho* alkyl group forms an incipient free radical which undergoes further reaction to displace a hydrogen radical from the *ortho* position of the adjacent aromatic ring forming fluorenes [10]. These processes have been suggested to have applications for reconstructing the thermal history of sediments [6,11].

In this note we report on the identification and analysis of isomeric trimethylbiphenyls (TMBPs) in some Australian crude oils.

EXPERIMENTAL

TMBP standards

TMBPs were prepared by the Gomberg reaction as described by Novrocik *et al.* [12] or from the higher-yielding modification of this reaction described by Korzeniowski *et al.* [13]. The compounds were prepared using the coupling reaction between a diazotised aryl amine and an aromatic hydrocarbon:



The trimethylbiphenyls were isolated from the reaction mixture by column chromatography using a mixed bed of activated silica gel (40 g) and alumina (10 g) with light petroleum–dichloromethane (95:5) as eluent. Individual isomers were then isolated by high-performance liquid chromatography (HPLC) on a silica column using hexane as eluent.

Isolation of alkylbiphenyl fractions from crude oil

A dinuclear aromatic fraction was isolated from each of the three crude oils (Table I) using preparative thin-layer chromatographic methods described previously [14].

Gas chromatography (GC) and GC–mass spectrometry (MS)

GC was performed using a Hewlett-Packard 5890 chromatograph equipped with 50 m × 0.22 mm I.D. capillary columns coated with either BP-1, BP-5, BP-10 (SGE, Australia) or CP Wax 57 CB (Chrompack). Hydrogen was used as the carrier gas at a linear flow velocity of 30 cm/s. The oven was programmed from 70 to 190°C at 2°C/min and then at 10°C/min to 300°C or to the upper temperature limit of the column. Peaks in the chromatograms were assigned on the basis of co-chromatography with standard compounds.

GC–MS was carried out using a VG-TS 250 system equipped with a 50 m × 0.2 mm I.D. capillary column with a BP-5 coating and an autosampler facility. The GC

TABLE I
GEOLOGICAL DATA FOR THE CRUDE OILS

Crude oil	Location Australian sedimentary basin	Age of source	Source rock type	Ref.
Barrow No. 1	Carnarvon	Jurassic	Marine shale	16
Blina No. 1	Canning	Devonian	Marine/lacustrine shale	17
Tuna No. 4	Gippsland	Cretaceous	Coal/shale	18

oven was held at 70°C for 1 min and then programmed from 70 to 190°C at 2°C/min and from 190 to 300°C at 15°C/min. The mass spectrometer was operated in the MRM mode with a source temperature of 200°C, an electron voltage of 70 eV and a dwell time of 100 ms.

RESULTS AND DISCUSSION

Preparation of authentic TMBPs

For those reactions where two or more TMBPs were produced, each TMBP was separately prepared using the alternative combination of substituted reagents. For example, 3,5,3'-TMBP was prepared from the reaction of 3,5-dimethylaniline and toluene and from *m*-toluidine and *m*-xylene. The TMBP common to both reactions was assigned as 3,5,3'-TMBP. In a similar manner structures were assigned to 2,5,3'-, 3,4,3'-, 2,3,3'-, 2,4,3'-, 2,6,3'-, 3,4,2'-, 2,3,2'-, 2,5,2'-, 2,4,2'-, 3,5,2'-, 2,6,2'-, 2,5,4'-, 2,4,4'-, 3,5,4'-, 2,6,4'-, 3,4,4'- and 2,3,4'- TMBPs.

The remaining six isomers all have the methyl substituents in one ring and were prepared from aniline and the appropriate trimethylbenzene. For reactions that gave multiple products, *e.g.* aniline with 1,2,3-trimethylbenzene (two products: 2,3,4- and 3,4,5-TMBPs) and with 1,2,4-trimethylbenzene (three products: 2,3,6-, 2,3,5-

TABLE II

COMPARISON OF THE GC ELUTION ORDER OF ISOMERIC TRIMETHYLBIPHENYLS USING FOUR STATIONARY PHASES

BP-1	BP-5	BP-10	CP Wax 57 CB
2,6,2'	2,6,2'	2,6,2'	2,6,2'
2,5,2'	2,5,2'	2,5,2'	2,5,2'
2,4,2'	2,4,2'	2,4,2'	2,6,3'
2,6,3'	2,6,3'	2,6,3'	2,4,2'
2,6,4' + 2,4,6	2,4,6	2,4,6	2,6,4'
	2,6,4'	2,6,4'	2,4,6
2,3,2'	2,3,2'	2,3,2'	2,3,2'
2,3,6	2,3,6	2,3,6	2,3,6
3,5,2'	3,5,2'	3,5,2'	3,5,2'
2,5,3'	2,5,3'	2,5,3'	2,5,3'
2,4,3'	2,4,3'	2,4,3'	2,4,3'
2,5,4'	2,5,4'	2,5,4'	2,5,4'
2,4,4'	2,4,4'	2,4,4'	2,4,4'
2,3,3'	2,3,3'	2,3,3' + 2,3,5	2,3,3'
2,3,5	2,3,5		2,3,5
3,4,2'	3,4,2'	3,4,2'	3,4,2'
2,3,4' + 2,4,5	2,4,5	2,4,5	2,3,4'
	2,3,4'	2,3,4'	2,4,5
2,3,4	2,3,4	2,3,4	2,3,4
3,5,3'	3,5,3'	3,5,3'	3,5,3'
3,5,4'	3,5,4'	3,5,4'	3,5,4'
3,4,3'	3,4,3'	3,4,3'	3,4,3'
3,4,4'	3,4,4'	3,4,4'	3,4,4'
3,4,5	3,4,5	3,4,5	3,4,5

2,4,5-TMBPs), each product was separated using HPLC and the structure of each was assigned on the basis of its GC retention behaviour.

Retention behaviour of various chloro-substituted biphenyls has been reported by Mullin and Pochinl [15]. They reported that the position of substitution has a predictable affect on retention behaviour: those compounds with *ortho* substituents have shortest retention times and usually the *para*-substituted isomers have the longest retention times. Similar effects were observed in this study when the trimethylbiphenyls with substituents in both rings were analysed using GC techniques (Table II).

The trimethylbiphenyls with all three methyl groups in one ring which were obtained as mixtures in this study were therefore assigned structures using these principles, e.g. TMBPs with two *ortho* substituents were assumed to elute before compounds with one *ortho* substituent. In cases where compounds differed only in *meta* or *para* substituents the compound with the longest retention time was assigned the *para* structure.

GC and GC-MS

Table II and Fig. 1 show the GC retention behaviour of all 24 TMBPs. From these results it is apparent that separation of all isomers could be achieved using either a BP-5 or a CP Wax 57 CB column, and further, *ortho*-substituted isomers have lower retention times with all four columns. Fig. 1 shows a partial gas chromatogram of the all-isomer mixture obtained using a BP-5 coated column. Although all isomers can be distinguished on the trace, only partial resolution was achieved between 2,4,6-TMBP and 2,6,4'-TMBP and between 2,4,5-TMBP and 2,3,4'-TMBP.

Fig. 2 shows the results obtained by using MRM GC-MS techniques to analyse an all-isomer mixture of TMBPs and an aromatic fraction of the Blina crude oil. The mass chromatograms show compounds that underwent a 196-to-181 mass transition. Peaks marked in the mass chromatogram from the Blina crude oil represent compounds with similar retention behaviour and mass spectra compared to the standards. The small differences in retention times between the standards and the compounds in the Blina crude oil which are apparent for compounds eluting after 50

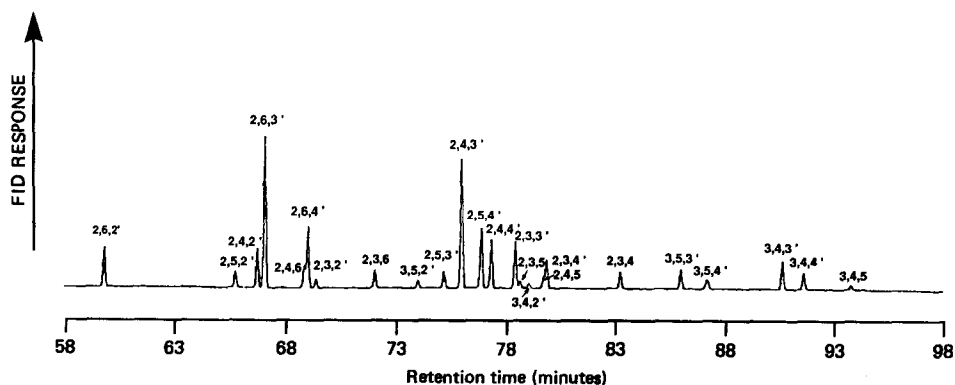


Fig. 1. Partial capillary gas chromatogram showing separation of an all-isomer mixture of TMBPs using a BP-5 capillary column. FID = Flame ionization detection.

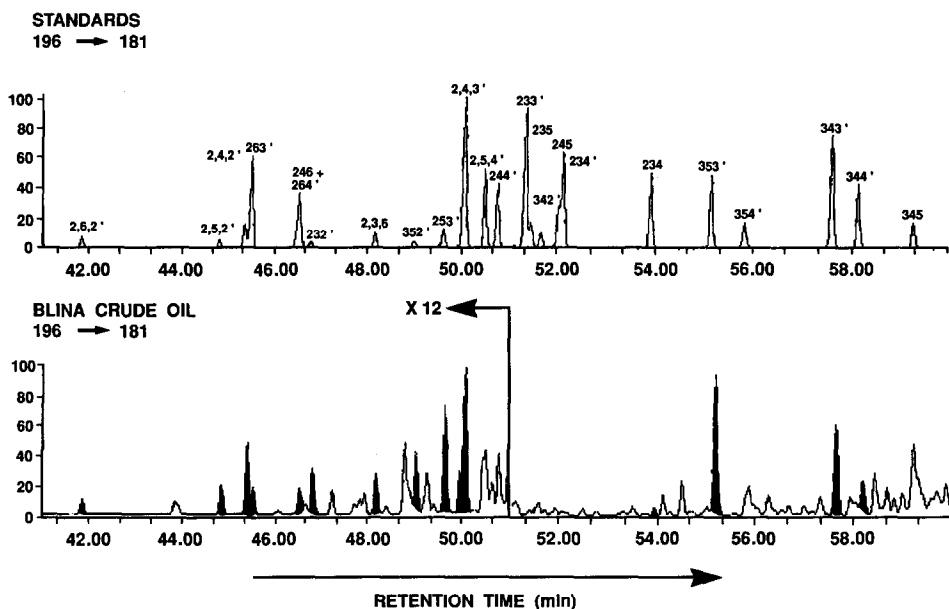


Fig. 2. MRM (196 \rightarrow 181) mass chromatograms obtained from analysis of an all-isomer mixture of TMBPs and an aromatic fraction of the Blina 1 crude oil.

min is attributed to minor differences in operating conditions between the two analyses. Similar analyses were also carried out using aromatic fractions from the Barrow crude oil and the Tuna 4 crude oil. Table III shows the TMBPs identified in the oils. The concentrations of total TMBPs in the crude oils varied from 100 $\mu\text{g/g}$ for the Blina crude to 600 $\mu\text{g/g}$ for the Barrow crude. This compares with a typical concentration range of 200–300 $\mu\text{g/g}$ reported for methylbiphenyls in crude oils [1, 7]. It is apparent from these analyses that the most abundant isomers in these crude oils are those with substituents in the *meta* and *para* positions. Compounds with one, two and three substituents in *ortho* positions have been identified but it is apparent from Fig. 2 and Table III that such compounds are in lower abundance than compounds with fewer *ortho* substituents. In the case of dimethylbiphenyls, the lower abundance of *ortho*-substituted isomers in crude oils and mature sediments has been attributed to their higher reactivity, in that they undergo cyclisation to form fluorenes under the thermal conditions required for oil formation in sediments [8]. Similar processes may be responsible for the depletion of *ortho*-substituted TMBPs observed in these crude oils.

Origins of alkylbiphenyls

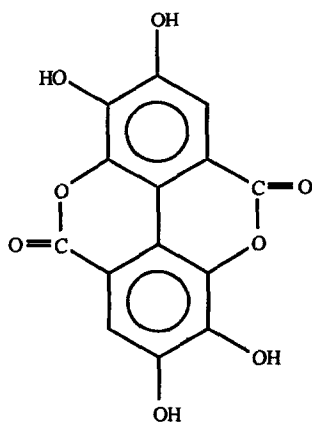
The origins of alkylbiphenyls in crude oils and sediments is uncertain. The most likely sources are natural products with the biphenylcarbon skeleton. Compounds of this type, such as ellagic acid (I), are usually derived from phenolic coupling processes rather than the processes responsible for sterane and terpane biosynthesis. An alternative explanation—that the biphenyls arise from oxidative degradation of the 9–10 bonds of substituted phenanthrenes—is not favoured, as we have been unable to

TABLE III
 TMBP ISOMERS IDENTIFIED IN CRUDE OILS

Double crosses indicate the most abundant isomer(s).

TMBP isomer	Blina No. 1	Barrow No. 1	Tuna No. 4
2,6,2'	+	+	+
2,5,2'	+	+	+
2,4,2'	+		+
2,6,3'	+		+
2,4,6+2,6,4'	+	+	+
2,3,2'	+	+	+
2,3,6	+	+	
3,5,2'	+	+	+
2,5,3'	+	+	+
2,4,3'	+	+	+
2,5,4'			
2,4,4'		+	+
2,3,3'			
2,3,5			
3,4,2'	+	+	+
2,4,5+2,3,4'			
2,3,4	+	+	+
3,5,3'	++	++	++
3,5,4'			
3,4,3'	+	+	++
3,4,4'	+	+	+
3,4,5			

identify significant amounts of the alkylbiphenyls that can be unambiguously related to alkylphenanthrenes by this process in samples containing high concentrations of alkylphenanthrenes.



I

Although the three crude oils analysed in this study were derived from different source materials and differ widely in age and location (Table I), the isomer distributions of their TMBP components is similar. As already noted, maturity no doubt has a significant effect on the abundance of *ortho*-substituted isomers; however, the presence of similar distributions in a crude oil with a major contribution from higher plants (Tuna No. 4), in a crude oil originating from marine organic matter (Barrow No. 1) and in a crude oil (Blina No. 1) whose source predates the widespread distribution of higher plants, suggests a ubiquitous microorganism as their source.

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