

Stable Carbon Isotopic Compositions of Methylated-MTTC in Crude Oils from Saline Lacustrine Depositional Environment: Source Implications

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Abstract: Significantly high abundant methyl-MethylTrimethylTridecylChromans (MTTCs) have been detected in aromatic hydrocarbon fractions in crude oils from the Jizhong Depression and Jiangnan Basin. The distribution of these compounds is dominated by methyl-MTTC and dimethyl-MTTC series, which indicate diagenetic products of a hypersaline depositional environment in the early stage and show a low degree of methylation. The occurrence of significantly high abundant methyl-MTTC depends mainly on good preservation conditions with a strongly reductive, hypersaline and water-columned depositional environment and subsequent non-intensive diagenetic transformations. The stable carbon isotopic compositions of the methyl-MTTCs and dimethyl-MTTCs in two samples are far different from the stable carbon isotopic composition of C₃₀ hopane of apparent bacteria biogenesis (up to 4.11‰ and 5.75‰, respectively). This obviously demonstrates that the methyl-MTTC and dimethyl-MTTCs cannot be of bacteria origin, which is different from the previous point of view about non-photosynthetic bacteria products or possible bacteria-reworked products. On the contrary, the stable carbon isotopic compositions of methyl-MTTC and dimethyl-MTTCs in the two samples were similar to that of the same carbon-numbered *n*-alkanes (*n*C₂₇-*n*C₂₈-*n*C₂₉), which indicates that they share the same source origin. Especially in the crude oil from the Zhao61 well, stable carbon isotopic compositions are also similar to that of the same carbon-numbered steranes with $\alpha\alpha\alpha$ -20R isomer (mostly less than 0.4‰). In consideration of the results of previous studies on saline lake ecological sedimentation, the authors hold that the methyl-MTTC and dimethyl-MTTCs in the saline lake sediments should be of algal biogenesis origin.

Key words: chroman, tocopherol, methylated-MTTC, stable carbon isotopic composition, algae biogenesis, saline lacustrine facies

1 Introduction

Tocopherols are abundant in photosynthetic organisms such as phytoplankton, algae and higher plants. As one kind of the oxygenic compounds, it has three homologues, namely α -tocopherols (R1, R2, R3 are methyl), γ -tocopherols (R1 is H) and δ -tocopherols (R1, R2 are H) according to the differences of R1, R2 and R3 in the basic benzene ring skeleton.

Alkyl-chromans can be structurally regarded as the form of elimination of the hydroxyl group (at the C-6 position) of the tocopherols and have three kinds of corresponding homologous products, namely α -alkyl-chroman (2, 5, 7, 8-Tetramethyl-2-Methyl-4, 8, 12-TrimethylTridecyl-Chroman), γ -alkyl-chroman (2, 7, 8-Trimethyl-2-Methyl-4,

8, 12-Trimethyl Tridecyl-Chroman) and δ -alkyl-chroman (2, 8-Dimethyl-2-Methyl-4, 8, 12-TrimethylTridecyl-Chroman). Thus, the above compounds can be abbreviated as methylated α -MTTC, β -MTTC, γ -MTTC and δ -MTTC since the 2-Methyl-4, 8, 12-TrimethylTridecyl-Chroman (abbreviated by MTTC) is the basic structural unit.

Alkyl-chroman was firstly detected in bituminiferous limestones in the Italian gypsum salt area co-injected with authentic standards (Sinninghe Damste, 1985) and it was dominated by α -MTTC and γ -MTTC. Sheng et al. (1987) reported the occurrence of δ -MTTC, γ -MTTC and α -MTTC in crude oil samples from the gypsum sediments in the Jiangnan Basin, while the only two γ -MTTC and δ -MTTC were detected in dark gray gypsum mudstones in the 4th member of the Tertiary Shahejie Formation in the Jizhong Depression. Fan et al. (1988) subsequently reported the occurrence and detection of α -MTTC, β -MTTC and γ -

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MTTC in some Fushun cannel-coal samples. Schwark and Puttmann (1990) only reported the occurrences of trimethyl-MTTC and low concentration of dimethyl-MTTC and absence of methyl-MTTC in sediments from the Permian Kupferschiefer Formation in the Rhine Basin, northwestern Germany. Jiang et al. (1990) discussed diagenetic and geochemical significance of MTTC compounds. Zhu et al. (2005) also detected the distribution of dominated α -MTTC in crude oils from the saline lacustrine facies sediment of the Qaidam Basin in northwestern China.

Geological samples with occurrence of methylated-MTTCs located mainly in the following places: the Rozel point oil seep of the saline lake facies in Utah, United States (Sinninghe Damste, 1987), phosphatic mudstone in the Montana Bay, United States (Sinninghe Damste, 1987), Miocene evaporitic oilseep in Sicily (Sinninghe Damste, 1987) and Miocene marlite in the Perticara Basin, Italy (Sinninghe Damste, 1987), manganese black shale in Germany (Sinninghe Damste, 1987), evaporitic sediment of Permian Kupferschiefer Formation in the Rhine Basin in NW Germany (Schwark and Puttmann, 1990), the DSDP drilling hole deep sea deposition in the Namibian shelf, West Africa (Sinninghe Damste, 1987), crude oils in the Jiangnan oilfield, central China (Sheng et al., 1987), gypsum mudstone in the 4th member of the Shahejie Formation in the Jizhong depression, northern China (Sheng et al., 1987), saline lake facies crude oils in the Qaidam Basin, northwestern China (Zhu et al., 2005) and Eocene cannel-coal in Fushun, northeastern China (Fan et al., 1988). These places are geologically divided into hypersaline and non-hypersaline depositional environments. At present, methylated-MTTCs are mainly used for judging the depositional environment, for example, Sinninghe Damste (1987) suggested that a hypersaline depositional environment is indicated if the ratio of trimethyl-MTTC/methyl-MTTC is less than 2, while a non-hypersaline depositional environment is indicated if the ratio of trimethyl-MTTC/methyl-MTTC > 100. This index is widely accepted and thus methyl-MTTC is regarded as an indicator of the hypersaline depositional environment. However, results obtained from a range of geologic samples from fresh water to the saline environment suggest that this empirical relationship between salinity and MTTC's occurrence and distribution is still not clear (Li and Larter, 1995).

On the basis of the occurrence of methylated-MTTCs mainly in sediment samples with low-maturity and the chemical structural similarity between tocopherols and methylated-MTTCs, Sheng et al. (1987) suggested that the methylated-MTTCs were derived from elimination of the hydroxyl group of tocopherols in the early diagenesis stage.

However, someone considered that the elimination of hydroxyl group cannot happen in the early diagenesis stage while preserving the basic skeleton of tocopherols at the same time. Sinninghe Damste et al. (1987) suggested that methylated-MTTC may be the product of non-photosynthetic bacteria, while the α -MTTC detected in the Fushun cannel-coal may be the bacteria-reworked product.

Tocopherols widely exist in the photosynthetic organisms such as phytoplankton, algae and higher plants (Sheng et al., 1987) together with some bacteria (e.g. cyanobacteria, Li, 1993). There are many contradictions against the view that methylated-MTTCs may be the non-photosynthetic product of bacteria. The concentration of methylated MTTC compounds in the crude oils in this study is so abundant that reliable analyses of stable carbon isotopes of individual hydrocarbon can be done and, finally, used to make discussions and deductions about their sources and origins.

2 Samples and Analysis

Two crude oil samples were collected from the Zhao61 well in the Jinxian Depression (1145–1960 m, Es2+3) and the Zhouxie22 well in the Jiangnan Basin (1522–1528 m, E_{q3}), respectively. The density of the first crude oil (0.9076 kg/m³) and its viscosity (111.7 mPa·S/50°C), together with its polar and asphaltene content (35.6%) indicate that it belongs to heavy oil.

Asphaltenes were removed from the crude oil samples by precipitation with *n*-heptane. Aliquots of the maltene fractions (50 mg) were then fractionated by silica gel chromatography (150°C, overnight) which had been pre-eluted with *n*-hexane. Gradient elution was obtained using solvents of increasing polarity with two column volumes of solvent in all cases. Fractionation of the maltene yielded three fractions: a saturated hydrocarbon fraction (*n*-hexane), an aromatic hydrocarbon fraction (20% dichloromethane in *n*-hexane), and a polar fraction (50% dichloromethane in methanol). The solvent from each fraction was carefully removed in a sand bath (at 80°C). The aliphatic fraction was further separated into straight chains and branched/cyclic hydrocarbon fractions by 5 Å molecular sieve (purchased from Merck).

The saturated and aromatic fractions were analyzed by gas chromatography (GC-FID) and gas chromatography-mass spectrometry (GC-MS). The purified *n*-alkanes and branched/cyclic alkanes were analyzed by gas chromatography-isotope ratio mass spectrometry (GC-IRMS).

GC analyses were performed on a HP 6890 gas chromatograph fitted with a HP-5 fused silica capillary column (30 m×0.25 mm×0.25 µm; from 60°C to 290°C at 3

°C/min; isothermal at 290°C for 20 min) with He as the carrier gas and oven temperature at 300°C.

GC-MS analysis was conducted on a Micromass Platform II mass spectrometer coupled to a Hewlett-Packard 6890 gas chromatograph. Chromatographic separations were performed with a 30 m×0.25 mm i.d. fused silica capillary column coated with a 0.25 µm film of the HP-5 phase. The oven temperature program was from 65°C for 1 minute, and then from 65°C to 290°C at 3°C/min, hold for 30 min. Helium was used as carrier gas with a flow rate of 1.0 ml/min. The transfer line temperature was 250°C, and the ion source temperature was 200°C. The ion source was operated in the electron impact (EI) mode at 70 eV.

GC-IRMS was carried out on a Micromass Isoprime mass spectrometer attached to a HP 6890 gas chromatograph. A 60 m×250 µm i.d. capillary column coated with 0.25 µm 5% phenyl-methyl-silicon stationary phased was fitted to the gas chromatograph. Samples were dissolved in hexane and 1 µl of the sample was injected using a HP 6890 auto-sampler. The GC oven was programmed from 50°C to 310°C at 3°C/min with initial and final hold times of 1 and 30 minutes, respectively. The carrier gas used was helium, at a flow rate of 1 ml/min with the injector operating at constant flow.

The $^{13}\text{C}/^{12}\text{C}$ isotopic ratio was calculated by the integration of the masses 45, 45 and 46 ion current counts of the CO_2 peaks produced by the combustion (copper oxide reaction furnace at 850°C) of hydrocarbons separated by gas chromatography. A CO_2 reference gas (calibrated to Vienna Pee Dee belemnite) with a known ^{13}C is pulsed into the mass spectrometer and the isotopic composition of samples is reported in the notation relative to the reference gas. The average values of at least two runs for each sample is reported and only results with a standard of less than 0.5 were used.

3 Results

3.1 GC-MS analysis

3.1.1 Detection and identification of methyl-MTTC compounds

Methylated-MTTCs were detected from the aromatic hydrocarbon fractions. The TIC chromatogram of the aromatic hydrocarbon fractions show a pattern with $\delta\text{-MTTC}=\gamma\text{-MTTC}>\alpha\text{-MTTC}$. The mass spectra features of these compounds are as the following: the major fragment ions of $\delta\text{-MTTC}$ are 121 and 161; molecular ion, 386; carbon number, C_{27} ; the major fragment ions of $\gamma\text{-MTTC}$, 135 and 175; molecular ion, 400; carbon number, C_{28} ; the major fragment ions of $\alpha\text{-MTTC}$, 149 and 189; molecular

ion, 414; and carbon number is C_{29} .

Sinninghe Damste et al. (1987) reported that most of the $\alpha\text{-MTTC}$ occur mainly in a non-hypersaline depositional environment while $\delta\text{-MTTC}$ is scarce.

In this study, the distribution patterns of $\delta\text{-MTTC}=\gamma\text{-MTTC}>\alpha\text{-MTTC}$ and the lower ratios (<2.0) of $\alpha\text{-MTTC}/\delta\text{-MTTC}$ (0.17 and 0.24, respectively) indicate a hypersaline depositional environment.

3.1.2 Main compounds of aromatic hydrocarbon fractions

In the TIC chromatogram of aromatic hydrocarbon fractions, triaromatic steroids are eluted after methylated-MTTCs. For example, a complete series of triaromatic steroids (m/z 231), methyl triaromatic steroids (m/z 245) and dimethyl triaromatic steroids (m/z 259) are presented in crude oils from the Zhao61 well. In the crude oil sample from the Zhouxie 22 well, higher carbon-numbered compounds are dominated by triaromatic steroids (m/z 231) and lower carbon-numbered compounds are dominated by organic sulfides.

In the crude oil from the Zhao61 well, the compounds eluted before methyl-MTTC are dominated by methyl-alkylbenzene (m/z 91), whose carbon number range is $\text{C}_{13}\text{-C}_{23}$ and the dominant peak carbon is at C_{29} and have a front peak distribution without obvious odd/even predominance. Furthermore, some aryl-isoprenoids (m/z 133+134) compounds are co-eluted in the aromatic hydrocarbon fraction.

3.1.3 Biomarkers in saturated hydrocarbons fraction

In the TIC chromatogram of saturated hydrocarbon fractions from the Zhao61 well, n -alkanes range from $n\text{C}_{11}$ to $n\text{C}_{36}$, and there is no obvious odd-even predominance in the range of $n\text{C}_{11}\text{-}n\text{C}_{18}$ while an obvious odd-even predominance appears in the range of $n\text{C}_{19}\text{-}n\text{C}_{36}$, OEP=1.26. Low concentration of β -carotane is eluted after $n\text{C}_{36}$. In the isoprenoid compounds, the ratios of Pr/Ph=0.33, $n\text{C}_{17}/\text{Pr}=1.02$ and $n\text{C}_{18}/\text{Ph}=0.29$ show an obvious phytane predominance.

In the TIC chromatogram of saturated hydrocarbon fractions from the Zhouxie22 well, n -alkanes range between $n\text{C}_{12}$ and $n\text{C}_{28}$. There is no obvious odd-even predominance in the range of $n\text{C}_{12}\text{-}n\text{C}_{28}$ and no carotene was detected. In the isoprenoid compounds, the ratios of Pr/Ph=0.18, $n\text{C}_{17}/\text{Pr}=0.70$ and $n\text{C}_{18}/\text{Ph}=0.10$ show an obvious phytane predominance.

Branched/cyclic fractions by the 5A molecular sieve method can provide us with a more clear distribution of biomarkers since an obvious phytane predominance occurs in saturated hydrocarbon fractions. In Fig. 1, the branched alkanes fractions in crude oils from the Zhao61 well are

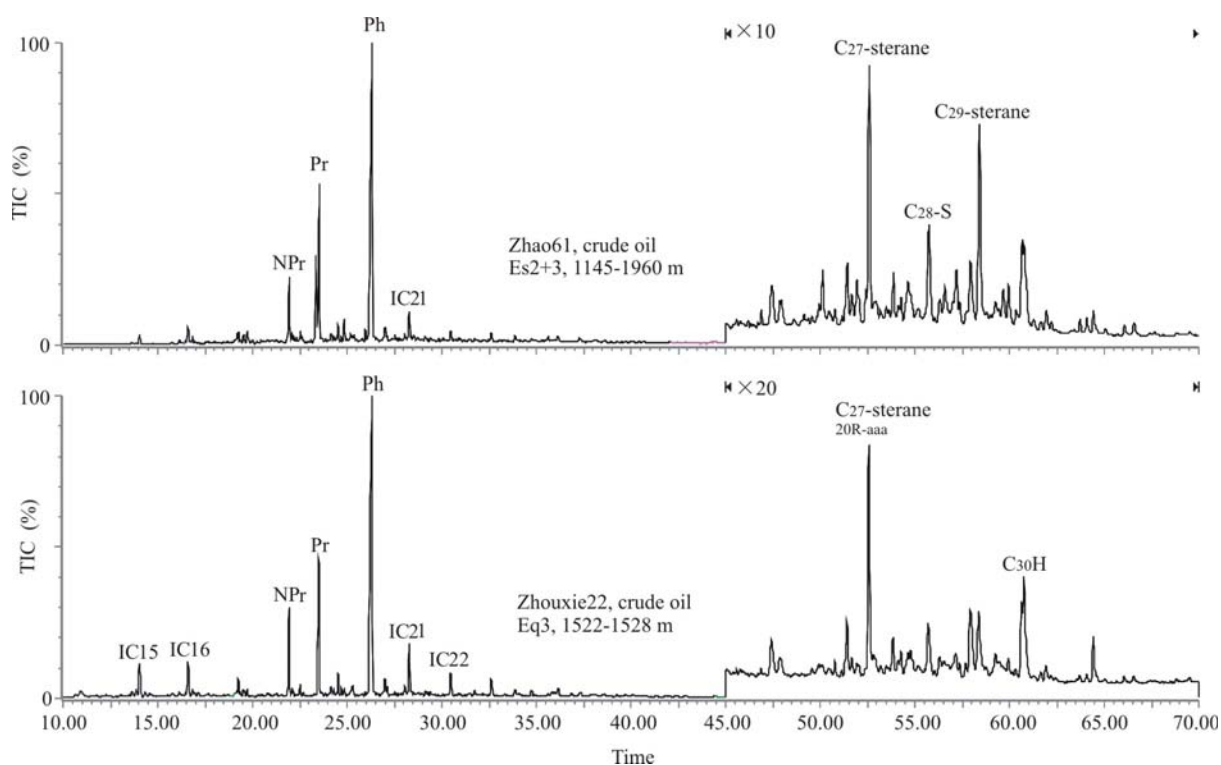


Fig. 1. Distribution of *iso*-alkanes in the branched/cyclic hydrocarbon fractions in crude oils from the Zhao611 and Zhouxie22 wells.

dominated by nor-pristane, pristane and phytane, the concentration of iC_{15} , iC_{16} , iC_{21} and iC_{22} is slightly lower than that of isoprenoids. Common C_{19} – C_{26} tricyclic terpanes and C_{24} tetracyclic terpanes have been detected while sesquiterpanes were not detected. Moreover, pentacyclic triterpanes (C_{27} – C_{35}) are dominated by C_{30} hopane and gammacerane. The general ratios are as follows: $Ts/Tm=0.62$, $C_{29}H/C_{30}H=0.25$, $Ga/C_{30}H=0.44$ and $Ga/C_{31}H=1.53$. Especially the last two ratios indicate a water-columned and hypersaline depositional environment (Fig. 1). Apparently, $C_{31}H$ and $C_{32}H$ are predominated, and $C_{33}H$, $C_{34}H$ and $C_{35}H$ descend abruptly with the increase of the carbon number in the homohopane series compounds, which can be reflected by the ratio of $(C_{31}H+C_{32}H)/(C_{31}H+C_{32}H+C_{33}H+C_{34}H+C_{35}H)=0.74$. The distribution of steranes in this sample (Fig. 1d, e) are dominated by long-chain steranes, which can be showed by the ratio of $(C_{21}+C_{22})/(C_{27}+C_{28}+C_{29})=0.03$. The distribution of C_{27} , C_{28} and C_{29} steranes exhibit a “V”-shaped pattern and the highest abundance in C_{27} , C_{28} and C_{29} steranes is $\alpha\alpha\alpha$ -20R configuration. Moreover, the peak of $\alpha\alpha\alpha$ -20S is relatively lower than that of $\alpha\alpha\alpha$ -20R, and the ratio of C_{29} sterane $20S/(20S+20R)=0.16$ indicates a relatively low maturity.

In the branched/cyclic hydrocarbon fraction of the crude oil sample from the Zhouxie22 well, *iso*-alkane is also dominated by nor-pristane, pristane and phytane. The

content of iC_{15} , iC_{16} , iC_{21} and iC_{22} is slightly higher. Common C_{19} – C_{26} tricyclic terpanes and C_{24} tetracyclic terpane have been detected while sesquiterpanes were not detected. The distribution of the pentacyclic triterpane series (C_{27} – C_{35}) is also dominated by C_{30} hopane and gammacerane. The following ratios, $Ts/Tm=0.58$, $C_{29}H/C_{30}H=0.23$, $Ga/C_{30}H=0.75$ and $Ga/C_{31}H=5.94$, especially the last two indicate a water-columned, hypersaline depositional environment (Zhu et al., 2005) (Fig. 1). In the homohopane series, $C_{31}H$ and $C_{32}H$ are predominated, and $C_{33}H$, $C_{34}H$ and $C_{35}H$ descend abruptly with the increase of the carbon number in the homohopane series compounds and the ratio of $(C_{31}H+C_{32}H)/(C_{31}H+C_{32}H+C_{33}H+C_{34}H+C_{35}H)=0.57$. The distribution of steranes (Fig. 1d, e) is dominated by long-chain steranes and the ratio of $(C_{21}+C_{22})/(C_{27}+C_{28}+C_{29})=0.05$. C_{27} , C_{28} and C_{29} steranes exhibit a “L”-shaped pattern and the highest abundant peak of C_{27} , C_{28} and C_{29} sterane is $\alpha\alpha\alpha$ -20R isomers, which is apparently higher than that of $\alpha\alpha\alpha$ -20S isomers. The ratio of C_{29} sterane $20S/(20S+20R)=0.24$ indicates a relatively low maturity (Chen et al., 2007).

It should be noted that higher abundance of $\alpha\alpha\alpha$ -20R isomer relatively to $\alpha\alpha\alpha$ -20S isomer occurs in C_{27} , C_{28} and C_{29} steranes in the two crude oil samples, which is attributed to good preservation conditions in a relatively reductive brackish lacustrine depositional environment. A

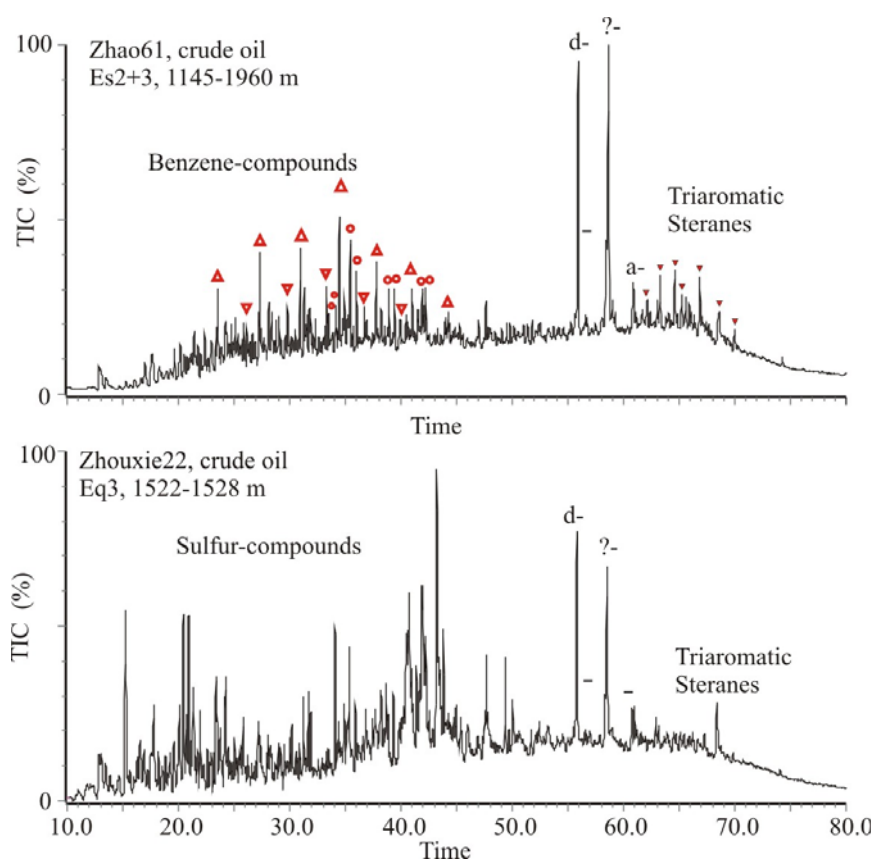


Fig. 2. TIC chromatogram of aromatic hydrocarbon fractions with a large amount of methylated-MTTCs in crude oils from the Zhao61 and Zhouxie22 wells.

similar phenomenon was also observed by ten Haven (1986).

3.2 Stable carbon isotopic composition analysis

The averages and variances of the stable carbon isotopic compositions of *n*-alkanes, *iso*-alkanes and aromatic compounds of the two samples, which were tested with the GC-IRMS, are shown in Fig. 3.

As shown in Fig. 3, in crude oil from the Zhao61 well, the stable carbon isotopic compositions of nC_{12} – nC_{33} range from -27.7‰ to -30.5‰ . However, careful inspection displayed that the stable carbon isotopic composition of nC_{13} – nC_{19} is centralized at -29‰ , and those of nC_{23} – nC_{29} and nC_{30} – nC_{32} are mainly at -30‰ and about -28‰ , respectively, which shows an obvious “three-segment” distribution feature.

In the branched hydrocarbon fractions, stable carbon isotopic compositions of nor-pristane, pristane and phytane are centralized at -30.5‰ , which are about 0.5‰ – 1.5‰ depleted compared with the same carbon-numbered *n*-alkanes. The stable carbon isotopic compositions of C_{27} and C_{29} steranes with $\alpha\alpha\alpha$ -20R isomers are -29.6‰ and -28.9‰ , respectively, and the stable carbon isotopic composition of C_{30} hopane is -24.8‰ .

In the aromatic hydrocarbon fractions, stable carbon isotopic compositions of C_{27} , C_{28} and C_{29} triaromatic steranes with 20R isomers are -27.8‰ , -33.8‰ and -29.2‰ , respectively. The stable carbon isotopic composition of C_{28} triaromatic sterane with 20S isomer is -30.0‰ and those of δ -MTTC, γ -MTTC and α -MTTC are -28.7‰ , -29.9‰ and -29.2‰ , respectively. As shown in Fig. 3, in crude oil from the Zhouxie22 well, the stable carbon isotopic compositions of nC_{12} – nC_{33} range from -26.2‰ to -29.5‰ . However, careful inspection shows that the stable carbon isotopic compositions of nC_{13} – nC_{19} are centralized at -27.0‰ , while those of nC_{21} – nC_{27} and nC_{31} – nC_{33} are about -29.0‰ and -27‰ , respectively. Thus, it is about 2‰ enriched in ^{13}C compared with *n*-alkanes in crude oil from the Zhao61 well on the whole.

In the branched hydrocarbon fractions of crude oil from the Zhouxie22 well, stable carbon

isotopic compositions of nor-pristane, pristane and phytane are centralized at -27.5‰ , which is similar to that of the same carbon-numbered *n*-alkanes. Stable carbon isotopic compositions of C_{27} sterane with $\alpha\alpha\alpha$ -20R isomer and C_{30} hopane are -25.3‰ and -22.5‰ , respectively.

In aromatic hydrocarbon fractions of crude oil from the Zhouxie22 well, abundance of triaromatic steranes is too low to obtain reliable stable carbon isotope values. Stable carbon isotopic compositions of δ -MTTC and γ -MTTC is -27.6‰ and -28.3‰ , respectively.

4 Discussions: Source and Origin of Methylated-MTTCs

According to the above discussion, in the two crude oil samples of the Zhao61 and Zhouxie22 wells, stable carbon isotopic compositions of methyl- and dimethyl-MTTCs are distinctly different from that of the C_{30} hopane of bacteria biogenesis (up to 4.11‰ and 5.75‰ , respectively), which demonstrates that methyl- or dimethyl-MTTCs does not derived from bacteria biogenesis. Furthermore, stable carbon isotopic compositions of methyl- and dimethyl-MTTCs are similar to that of the same carbon-numbered *n*-alkanes (nC_{27} – nC_{28} – nC_{29}), indicating that they share the

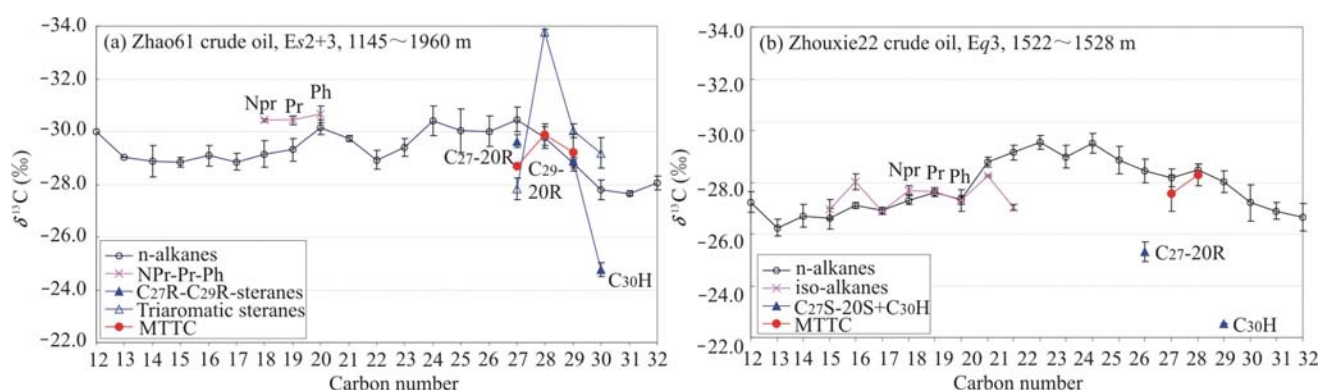


Fig. 3. Stable carbon isotopic composition of *n*-alkanes, isoprenoids, steranes, hopanes and methylated-MTTCs in crude oils from the Zhao61 and Zhouxie22 wells.

identical biogenesis.

Firstly, the contribution of higher plants to the hydrocarbon generation can be excluded since the two samples came from a hypersaline depositional environment. According to the study by Hite et al. (1991), green algae and blue-green algae (cyanobacteria) are the chief contributors to creatures in a low-saline environment ($S=35‰-200‰$), while halophilic bacteria are the chief contributors to the ecological system in a hypersaline environment ($S>200‰$). Based on the studies of ecological systems in the Great Salt Lake, Dead Sea and hypersaline and alkaline lakes in WadiNatrun, Egypt, together with some oceanic salina-field, Larson (1980) considered that bacteria and algae (such as *Halophilic Dunaliella*) are the main creatures. Thus, methyl- and dimethyl-MTTCs might be derived from algae biogenesis since a contribution of bacteria can be excluded in consideration of the great variations of stable carbon isotopic compositions between methylated-MTTCs and hopanes. This can be supported by the following lines of evidence: (1) Typical bimodal distribution of *n*-alkanes of higher plant origin usually do not appear in the saturated hydrocarbon fractions of the two samples. (2) The stable carbon isotopic compositions of all *n*-alkanes in this study are depleted than $-26‰$, which indicates that there is no contribution of higher plant. (3) Generally, the stable carbon isotopic composition of hopane of bacteria biogenesis is greatly depleted compared with *n*-alkanes (about $3‰$). High abundant C_{30} hopane relatively enriched in ^{13}C should be of *halophilic* bacteria biogenesis. (4) In the branched hydrocarbon fractions in the two samples, relatively high carbon-numbered compounds are composed mainly of steranes with $\alpha\alpha\alpha$ -20R isomer. Moreover, the abundance of C_{27} steranes of bacteria origin is higher than that of C_{29} steranes of higher plant origin. The ratios of hopanes to steranes are 0.15 and 0.18, respectively, which also indicate a significant contribution of algae to the hydrocarbon generation. (5) Especially in

crude oil from the Zhao61 well, the stable carbon isotopic compositions of methyl- and dimethyl-MTTCs are very similar to that of the same carbon-numbered steranes with $\alpha\alpha\alpha$ -20R isomers (mostly less than $0.4‰$), indicating that methyl- and dimethyl-MTTCs might be derived from algae.

It seems reasonable that bacteria biogenesis of methylated-MTTCs is excluded based on the stable carbon isotopic compositions. From the point of view of precursors, tocopherols exist predominantly in photosynthetic organisms, such as phytoplankton, algae and higher plants, and seldom in bacteria. In the thermal simulation experiment and pyrolysis analysis under the Curie point on α -tocopherols by Goossenes et al. (1984), only prist-1-ene and 2, 3, 5, 6-Tetramethyl-2, 5 cyclohexadiene-1,4 diketone were gained, which provided evidence that pristane may be from the tocopherols. Although no methylated-MTTCs were obtained in the experiment, yet this cannot completely exclude the possibility that tocopherols are the precursors of methylated-MTTCs because no obvious phytane predominance generally featured in the saline lake facies was found, which showed that the conditions in the simulation experiment were different from that in a real saline lake facies. As a matter of fact, it is possible that elimination of hydroxyl in the tocopherols could occur through biochemical and chemical reactions under a high reductive water columned hypersaline depositional environment with no intensive diagenesis and transformation. For example, ten Haven et al. (1986) considered that the occurrence of abundant uncommon steroid and hopanoid isomers with "mature appearance" in an immature stage is related to abnormal diagenesis. In other words, the full isomerization at C-22 of extended 17α (H), 21β (H)-homohopane resulted from direct reduction of the extended hopenes without transformation of $22R$ - 17β (H) and 21β (H)-hopane. Similarly, large amounts of 20R- and 20S- 5α (H), 14β (H), 17β (H)-steranes might be from the

rapid and direct transformation of Δ^7 sterol generally abundant in a hypersaline environment.

Usually, methyl-MTTCs can be detected in source rocks and crude oils in the brackish and saline lake facies. The occurrences of extremely abundant methylated-MTTCs in this study can be attributed to good preservative conditions as the following: (1) High phytane predominance indicates a high reductive environment, which can be partly reflected by obvious even-odd predominance of *n*-alkanes in crude oil from the Zhao61 well. (2) In a water-columned environment indicated by high abundant gammacerane, the oxygen-deficient anoxic condition at the bottom of a lake together with a hypersaline depositional environment is favorable to preservation of biologic organic matter. (3) Occurrence of large amounts of biomarkers with "biological-configuration" in this study, such as 20R-5 α (H), 14 α (H), 17 α (H)-sterane and 22R-C₃₁ and C₃₂ hopane, indicates the early generation of liquid hydrocarbons and non-intensive diagenetic transformation under a hypersaline environment. All of the above-mentioned conditions are very important for effective preservation of methylated-MTTCs since the hydroxybenzene group in their structural skeleton can be easily transferred into quinone.

5 Conclusions

Based on the above discussion, the following conclusions can be reached.

(1) The methylated-MTTCs discussed in this study are dominated by methyl- and dimethyl-MTTCs. The low degree of methylation indicates that they belong to early products in a water-columned hypersaline depositional environment.

(2) Occurrences of high abundant methylated-MTTCs mainly depend on good preservation and weak diagenetic transformation conditions generally occurring in some high reductive water-columned hypersaline depositional environments.

(3) In this study, the stable carbon isotopic compositions of methyl- and dimethyl-MTTCs of both of the two samples are apparently different from that of the C₃₀ hopane (up to 4.11‰ and 5.75‰, respectively), which has been widely accepted as derived from bacteria biogenesis. Thus, it is proved that methyl- and dimethyl-MTTCs were not derived from the bacteria biogenesis, which is distinctly different from the previously published viewpoint stating that they were derived or transformed from non-photosynthetic bacteria.

(4) In the two crude oil samples from the Zhao61 and Zhouxie22 wells, the stable carbon isotopic compositions of methyl- and dimethyl-MTTCs are all similar to that of

the same carbon-numbered *n*-alkanes (*n*C₂₇-*n*C₂₈-*n*C₂₉). This indicates that they share the identical source. Especially in the crude oil from the Zhao61 well, the stable carbon isotopic compositions of methyl- and dimethyl-MTTCs are similar to that of the same carbon-numbered steranes with $\alpha\alpha\alpha$ -20R isomers (mostly less than 0.4‰). The latter is usually regarded as the biologic configuration. Thus, taking into consideration the results of the previous study on saline lacustrine ecological sedimentation we have reasons to deduce that methyl- and dimethyl-MTTCs should be a directly biosynthesized product of algae origin.

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