Methyltrimethyltridecylchromans in Mature Oils from Saline Lacustrine Settings in the Dongpu Depression, Bohai Bay Basin, East China
Donglin Zhang, Youjun Tang, Hongbo Li, Tianwu Xu, Yunxian Zhang, Chengfu Zhang, Yahao Huang, and Ting Wang*

ABSTRACT: The measured composition and distribution of methyltrimethyltridecylchroman (MTTC) compounds in the crude oils from Wenliu (salt-rich zone) and Machang (salt-free zone) areas of the Dongpu Depression were correlated with redox conditions and paleosalinity. The oil samples derived from the mesosaline environment were found with all alkylated MTTC series present. In addition, the dimethyl MTTCs developed more favorably in the oils derived from a relatively reducing and hypersaline environment (Wenliu) compared to those from the fresh lacustrine settings (Machang), while the trimethyl MTTCs developed more favorably in the fresh water environment (Machang). Determination of the oil maturity in the "oil window" by a series of aromatic maturity indicators suggests that MTTC compounds are not only present in immature or low-mature oils but also distributed in mature oils. Therefore, the "low-mature" oil found with abundant MTTC compounds, especially derived from the saline lacustrine settings, should be assessed with caution.

1. INTRODUCTION
Methyltrimethyltridecylchromans (MTTCs) are considered a class of compounds produced by vitamin E to remove C-6 hydroxyl with a carbon skeleton of 2-methyl-2-(4,8,12-trimethyl tridecyl)-chromans. According to the number and position of substituents on the benzene ring, MTTCs can be divided into three types of homologues: methyl methylated chromans (δ-MTTC), dimethyl methylated chromans (β-MTTC, γ-MTTC, and ζ-MTTC), and trimethyl methylated chromans (α-MTTC). MTTC compounds were first detected by Sinninghe Damsté et al. (1987) in the gypsum sedimentary region of Italy. Since then, MTTCs have been identified all over the world, including from the source rock extracts and crude oils of saline depositional settings in China, such as Jianghan Basin, Caidamu Basin, and Songliao Basin. Despite their wide occurrence, the origin of MTTCs is still under debate. Sinninghe Damsté and co-workers believed that MTTCs came from the direct biosynthesis of the primary producer. Li (1995) and Tulipani (2013), on the other hand, supported that MTTC may have come from early diagenetic condensation reactions of alkylated phenols with phytol. Recent research shows that the origin of MTTCs is related to terrigenous organic matter input induced by riverine freshwater incursions and MTTCs are formed via condensation reactions.

Although there is a debate on its origin, previous studies have shown a good correlation between MTTC compositional characteristics and paleosalinity, and MTTCs are often used to indicate the salinity of the paleowater column. For instance, δ-MTTC is dominant in the samples of a hypersaline environment, while α-MTTC is the most abundant member in samples of nonhypersaline environments. The relative abundance of α-MTTC is not only important for paleosalinity but is also considered a new indicator for the intrusion of freshwater incursion into a stratified marine environment. In addition, the crossplot of Pr/Ph (pristane/phytane) and MTTCI (MTTCI = α-MTTC/total MTTCs) has been used to distinguish hypersaline, mesosaline, and normal environments from each other.

MTTC compounds are relatively abundant in immature and low-mature source rock extracts and crude oils from hypersaline settings; thus, they are considered indicators of immature
and low-mature oils. Conversely, Wang et al. (2011) suggested that maturity has no effect on the distribution of MTTC in sediments from Songliao Basin. In the present study, the distribution characteristics of MTTC in mature oils of the Wenliu area (salt-rich zone) and Machang area (salt-free zone) of Dongpu Depression, Bohai Bay Basin were investigated in detail, and the influences of sedimentary environment, maturity, and redox conditions on the distribution characteristics of MTTC were scrutinized.

2. GEOLOGICAL SETTINGS

The Bohai Bay Basin is an important petroliferous basin in the eastern part of China (Figure 1), which is 2600 km long and 1200 km wide, with a total area of approximately 200,000 km². It is in the eastern part of the Sino-Korean Plate consisting of Yanshan, Taihang, Luxi, Jiaodong, and Liaodong uplifts. As a Mesozoic and Cenozoic sedimentary basin, the Bohai Bay Basin went through initial rifting between 60 and 24 Ma, with largest rifting and subsidence during the Eocene.

The Dongpu Depression is in the southern part of the Bohai Bay Basin with an exploration area of 5300 km². It is a Cenozoic continental rift basin, overlying the Neihuang Uplift in the west and bounded by Lanliao Fault and Luxi Uplift in the east, Lankao Uplift in the south, and Xinxiang Depression in the north. The Dongpu Depression shows a north—northeast trend, widening from northeast to southwest. The basement consists of lower Paleozoic Ordovician, Cambrian, and upper Paleozoic Carboniferous—Permian strata. The sedimentary cover has experienced two major stages as the Paleogene rift and Neogene depression. The maximum thickness of the Cenozoic formation is over 9000 m, of which the Paleogene strata are more than 6000 m thick. The Paleogene strata comprise a set of lacustrine salt-bearing facies with sandstone and mudstone deposits, with two obvious transgressive—regressive depositional cycles (Figure 2).

The Paleogene Shahejie Formation (Es), Dongying Formation (Ed), Upper Tertiary Guantao Formation (Ng), Minghuazhen Formation (Nm), and Quaternary Formation (Q) developed in the northern part of the Dongpu Depression. Nearly 94% of oil and 80% of natural gas discoveries are distributed in the Shahejie Formation. It is divided into four parts from bottom to top: the fourth member (Es4), the third member (Es3), the second member (Es2), and the first member (Es1). Rapid subsidence of the depression led to faults that were active during Es4 and Es3-Es2L.
submember of the second member of the Eocene Shahejie Formation) (Figure 2). The Es4U (upper submember of the fourth member of the Eocene Shahejie Formation) and Es3L (lower submember of the third member of the Eocene Shahejie Formation) subunits were formed during the maximum lake expansion period. The humid and warm paleoclimate during this period promoted the prosperity of lacustrine algae. At the same time, the semi-closed saline lake provided ideal anoxic conditions for the preservation of organic matter (OM).

In addition, the Dongpu Depression developed multiple sets of salts in the northern region, but no salts were deposited in the southern region. The northern region is a typical saline lacustrine environment, and the southern region is a fresh water environment. Previous studies have shown that the qualities and quantities of OM in source rocks from the northern Dongpu Depression (salt-rich zone) are greater than those from the southern part (salt-free zone). The difference in sedimentary environmental characteristics between the northern and southern parts provides a good opportunity to study the effects of saline or fresh water depositional environment on MTTC existence and distribution characteristics.

3. RESULTS AND DISCUSSION

3.1. Physical Properties and Regular Geochemical Characteristics. The crude oil studied from the Wenliu area (north of the Yellow River) of the Dongpu Depression shows low density (0.852 g/cm³ in average) and low viscosity (15.18 mPa·s in average) and was reported to have a low sulfur content, high percentage of wax, and high pour point. The main components of the studied Wenliu oils are saturated hydrocarbons. The distribution range of saturates is 38.6–90.9% followed by aromatics (5.8–22.1%). The content of “nonhydrocarbon + asphaltene” also varied greatly, with a distribution range of 2.8–48.6%. The saturate/aromatic ratio of 7.7 is relatively high. There was no significant odd-even predominance (OEP) of n-alkanes in any of the oil samples (Figure 3). The average carbon preference index (CPI) is 0.99 and the average OEP is 1.0, showing the characteristics of mature oil. The average Pr/Ph ratio is 0.462, which reflects the characteristics of a highly reduced environment. From the perspective of regular biomarker compositional characteristics, the regular steranes and terpanes are abundant, while the content of low-molecular-weight steranes (C21–22 pregnane) is relatively low. Moreover, both the rearranged/regular sterane ratio and the sterane isomerization index are relatively low (Table 1). In addition, the Wenliu oils contain abundant gammacerane with an average gammacerane index (gammacerane/C30 hopane) of 0.89. The average C35/C34 homohopane ratio is generally greater than 1.2 (Table 1). The main OM source includes cyanobacteria, dinoflagellata, and coccolithophores. In general, the Wenliu oils have typical biomarker characteristics of saline lacustrine oil.

The physical properties of Machang oils (south of the Yellow River) are similar to those of Wenliu oils. The Machang oils are characterized by low density (0.821 g/cm³ in average; Table 1) and low viscosity (7.00 mPa·s in average; Table 1) and were reported to have a low sulfur content, high percentage of wax, high pour point, and overall light to medium crude. The saturate contents of Machang oils are dominant (72.1% on average), with the average aromatic content accounting for 20.8%. Both the saturate/aromatic ratio and nonhydrocarbon/asphaltene ratio are relatively high. The hydrocarbon distribution of the saturate and aromatic fractions indicates that the oils are mature. There is no significant OEP of n-alkanes in the saturate fraction of the crude oils (Figure 3).
The relatively high Pr/Ph ratio (0.90–1.29) indicates a relatively exo depositional environment. The oils are not as rich in gammacerane as the Wenliu oils. The average gammacerane index is 0.21, and the average C35/C34 homohopane ratio is 0.37. The C35/C34 ratio of the oils from the Machang area is higher than that from the Wenliu area, indicating a possible lower level of thermal maturity for the oils from the Machang area.
homohopane ratio is below 1, and the sterane isomerization index is high (Table 2). The crude oil produced from the Paleogene Shahejie Formation (Es) in the Machang oilfield, like Wenliu, was reported to be mainly derived from the source rock of the third member of Eocene Shahejie Formation (Es3).38,43 The main OM source includes chlorophyta, dinoflagellata, and the detritus of higher plants.28,39−41

3.2. Distribution Characteristics of MTTCs in the Crude Oils. There are significant differences in the sedimentary environment and the OM source of Wenliu area (saline environment) and Machang area (fresh water environment), which could be attributed to the different distribution characteristics of MTTC compounds (Figure 4). The Wenliu oils could be subdivided into two types based on whether all MTTC homologues are present: type-A (Samples 1, 2, 3, 4, 7, 13, and 14), the oils with all alkylated MTTC series, especially γ-MTTC, and type-B, the oils without all alkylated MTTC series present (γ-MTTCs often absent as shown in Figure 5). The relative abundance of methyl (δ-MTTC) and dimethyl (β-, γ-, and ζ-MTTC) MTTCs is greater than that of trimethyl MTTCs (α-MTTC) as shown by the methylated chroman index (MTTCI) shown in Table 3. Half of the Wenliu oil samples in this study are found with all alkylated MTTC series present. In contrast, trimethyl MTTC (α-MTTC) is quite abundant in all the Machang oils, while the percentage of methyl MTTC (δ-MTTC) is low, leading to consistently high MTTCI values (Table 3). Only one oil (Sample 15) from the Machang area is found to have all alkylated MTTCs present. The gammacerane index (GI) of Sample 15 is higher than that of the other Machang oils (Table 2), indicating that the salinity of Sample 15 is higher than that of the other Machang oils. MTTCs were reported to develop more favorably in saline environments as previously reported.44

The oil samples with different MTTC distribution characteristics were also correlated with different maturation levels (Figure 6). Samples with all alkylated MTTC series exhibit the characteristics of “low-mature oil” based on the sterane maturity indicators, while those without all alkylated MTTC series exhibit the characteristics of “mature oil.” The fingerprints composed of aaaa-20R C_{27−C_{29}} steranes, samples with all alkylated MTTC series present, exhibit an asymmetric “V”-type distribution (Figure 7), indicating that the OM is a mixed input dominated by lower aquatic organisms.45 The sterane maturity parameters, including aaaa C_{29} 20S/(20S + 20R) and C_{29} ββ/ (ββ + αα), show low values, which make those samples with all alkylated MTTC series characteristic of “low-mature oil.” This result seems consistent with the finding that MTTC compounds are mostly found in immature and low-mature oils as reported by the previous literature studies, which make all MTTCs an indicator of immature and low-mature oils.5,10,24 However, this study found that MTTC may also be present in mature oils.

3.3. MTTCs Found in the Mature Oils. Although the samples with all alkylated MTTC series present were suggested to be “immature or low-mature” by regular saturate maturity parameters (Figure 8),46,47 there is obviously insufficient
evidence to label these samples as "immature or low-mature oils" solely by using the sterane maturity parameter. First, the crude oils from Wenliu and Machang are characterized by low density, low viscosity, low sulfur content, high percentage of wax, high pour point, and high saturated hydrocarbon contents (Table 1), which are different from the physical properties of most typical low-maturity oils in China.48 Second, the CPI and OEP values are around 1 and the overall peak distribution type of the \(-n\)-alkane series indicates that the crude oil is mature. Moreover, a series of aromatic hydrocarbon maturity parameters has been used to determine the maturity of these samples with all alkylated MTTC series present already in the "oil window" (Table 4).

### 3.3.1. Methylphenanthrenes

The ratio of phenanthrene (P), methylphenanthrene (MP), and dimethylphenanthrene (DMP) is usually used to judge the OM maturity. The MPI-1 value increases as the maturity increases. Radke and Welte (1983) proposed the relationship between MPI-1 and the vitrinite reflectance as \(Rc-1 = 0.4 + 0.6 \times MPI-1\). The equivalent vitrinite reflectance (\(Rc-1\)) values of the studied samples are between 0.51 and 0.75, suggesting that the oils are mature. The reason for the several relatively low \(Rc-1\) values
may be attributed to the MPI-1 parameters that are originally derived from the coal-bearing source rocks, while the studied oils are saline oils. Moreover, MPI-1 parameters were reported to be insensitive to the maturity evaluation of Type-II kerogens, while the inferred source rocks for the Wenliu oils contain mainly Type-II kerogens.

3.3.2. Alkyl Dibenzothiophenes. Dibenzothiophene (DBT) is a sulfur-containing aromatic hydrocarbon that is widely distributed in source rock extracts and crude oils. Its composition and distribution are controlled by thermodynamics. Due to its symmetrical molecular structure, it has high thermal stability and antidegradation ability and is often used as a maturity parameter. Luo et al. (2001) found that there is a good linear relationship between the parameters of alkyl DBT and the vitrinite reflectance. The alkyl DBT series were detected in all of the studied oil samples. Rc-2 values (based on DBTs) of all of the oils are greater than 0.64. In addition, the average Rc-2 value of the oils with all alkylated MTTC series present is 0.82, indicating that the oils have been in the “oil window.” The DBT maturity parameters are applicable not only to the low-to-mature stage of OM thermal evolution but also to the high-to-overmature stage, no matter if they are marine or terrestrial oil. Therefore, the DBT maturity parameters are more reliable for assessing the oil maturity in this study.

3.3.3. Alkyl Naphthalenes. Naphthalene series are important components of aromatic hydrocarbons. Previous studies have shown that the relative abundance of naphthalene series increases with maturity, thus forming a variety of maturity indicators such as MNr (methylnaphthalene based), dimethylnaphthalene (DMNr), trimethylnaphthalene (TMNr, TNR-2), and tetracylnaphthalene (TeMNr). In this study, TNR-2 is selected to assess the maturity of oil samples with all alkylated MTTC series present. Based on the conversion relationship between TNR-2 and the vitrinite reflectance, the calculated Rc-3 value is greater than 0.72 (Table 4), indicating that all the oils are mature.
The three commonly used aromatic maturity parameters (MPI-1, DBT, and TNR-2) indicate that the Wenliu oils (north of the Yellow River) are mature. The molecular weights of naphthalene series, phenanthrene series, and benzothiophene series range from light to heavy ends. The mechanisms for scaling OM maturity are identical from the perspective of chemical dynamics. Therefore, it would be no coincidence that all the three parameters suggest that the Wenliu oils have entered the “oil window,” which confirmed the reliability of the maturity assessments from the aromatic maturity parameters. Since the Machang oils are mature oils based on either saturate maturity indicators or aromatic maturity indicators, the Wenliu oils should be mature oils as well.

Based on the physical properties of the oils and a series of aromatic maturity parameters, those “low-mature” oils actually have been mature already. The reason why the sterane isomerization index suggests “low-mature” may be related to the saline depositional settings that suppress sterane isomerization in the study area.\(^{56–68}\) The sediments in the study area are rich in gypsum salt and carbonates. The sediments do not undergo catalysis of clay minerals, resulting in a slow rate of isomerization.

| area        | sample no. | formation | depth/m | C29-αββ/(ααα + αββ) | C29-20S/(20S + 20R) | MPI-1 | Rc-1 | 4,6-DMDBT/1,4-DMDBT | Re-2 | TNR-2 | Re-3 |
|-------------|------------|-----------|---------|---------------------|---------------------|-------|-----|-------------------|------|------|------|
| Wenliu      | 1          | Es1-Es2U  | 1850.0–1907.8 | 0.31               | 0.31               | 0.51  | 0.71 | 0.84              | 0.69 | 0.65 | 0.79 |
|             | 2          | Es2L-Es3U | 2449.1–3054.6 | 0.23               | 0.22               | 0.51  | 0.71 | 1.08              | 0.72 | 0.96 | 0.98 |
|             | 3          | Es3U      | 1967.6–2014.9 | 0.33               | 0.36               | 0.59  | 0.75 | 0.51              | 0.64 | 0.74 | 0.84 |
|             | 4          | Es1L      | 2758.0–2777.3 | 0.03               | 0.18               | 0.19  | 0.51 | 1.02              | 0.71 | 0.54 | 0.72 |
|             | 5          | Es3U-Es3M | 3593.3–3904.6 | 0.40               | 0.43               | 0.21  | 0.52 | 1.26              | 0.75 | 0.50 | 0.70 |
| Machang     | 6          | Es2L      | 3389.8–3647.0 | 0.57               | 0.42               | 0.25  | 0.55 | 1.03              | 0.71 | 0.65 | 0.79 |
|             | 7          | Es2L      | 2856.0–3098.0 | 0.34               | 0.34               | 0.43  | 0.66 | 1.06              | 0.72 | 0.76 | 0.86 |
|             | 8          | Es2L      | 3206.8–3425.0 | 0.48               | 0.48               | 0.39  | 0.63 | 0.98              | 0.71 | 0.75 | 0.85 |
|             | 9          | Es2L-Es3U | 3310.8–3884.9 | 0.50               | 0.50               | 0.47  | 0.68 | 1.70              | 0.81 | 0.80 | 0.88 |
|             | 10         | Es3M      | 3770.6–4081.9 | 0.58               | 0.48               | 0.44  | 0.66 | 1.34              | 0.76 | 0.83 | 0.90 |
|             | 11         | Es3M      | 3622.8–3812.0 | 0.58               | 0.50               | 0.46  | 0.67 | 1.43              | 0.77 | 0.94 | 0.97 |
|             | 12         | Es3M      | 3652.3–3779.5 | 0.52               | 0.44               | 0.45  | 0.67 | 1.24              | 0.74 | 0.75 | 0.85 |
|             | 13         | Es2L      | 2452.6–2491.0 | 0.34               | 0.36               | 0.46  | 0.68 | 0.62              | 0.66 | 0.70 | 0.82 |
|             | 14         | Es2L      | 2294.0–2503.0 | 0.33               | 0.35               | 0.30  | 0.58 | 1.61              | 0.79 | 0.63 | 0.78 |
|             | 15         | Es3U      | 3229.4–3264.5 | 0.29               | 0.32               | 0.51  | 0.70 | 1.82              | 0.83 | 0.79 | 0.88 |
|             | 16         | Es3M-Es3L | 2935.4–3208.9 | 0.46               | 0.46               | 0.48  | 0.69 | 1.91              | 0.84 | 0.84 | 0.90 |
|             | 17         | Es3M-Es3L | 2968.1–3145.3 | 0.47               | 0.47               | 0.62  | 0.77 | 2.80              | 0.96 | 0.89 | 0.93 |
|             | 18         | Es3L      | 3216.3–3316.8 | 0.42               | 0.39               | 0.51  | 0.71 | 1.78              | 0.82 | 0.85 | 0.91 |
|             | 19         | Es3L      | 3125.5–3379.1 | 0.46               | 0.48               | 1.39  | 1.24 | 2.02              | 0.85 | 0.86 | 0.92 |
|             | 20         | Es3M-Es3L | 2451.9–2657.6 | 0.45               | 0.46               | 0.62  | 0.77 | 1.64              | 0.80 | 0.86 | 0.92 |
|             | 21         | Es3M      | 2570.0–2650.9 | 0.45               | 0.47               | 0.70  | 0.82 | 1.97              | 0.85 | 0.92 | 0.95 |
|             | 22         | Es3M      | 2584.8–2740.3 | 0.45               | 0.46               | 0.29  | 0.57 | 0.97              | 0.71 | 0.48 | 0.69 |

For example, the Bamianhe oil from the Bohai Bay Basin was often considered a typical “low-mature oil” based on low sterane isomerization parameters.\(^{70}\) However, as research progressed, Pang (2001) and Li (2002) updated the previous conclusion and confirmed that the Bamianhe oil is a mature oil by oil-source rock correlation based on multiple parameters including thermal maturity indicators and the absolute concentration of characteristic biomarkers.\(^{44,71}\) The content of saturates in Wenliu oils is relatively higher than most of the typical saline oil content from Bamianhe area, Dongying Depression (Bohai Bay Basin); the density and viscosity are also lower in the latter, indicating a higher maturity of the former.\(^{72}\) Moreover, a series of MTTC compounds has also been found in the Bamianhe oil.\(^{71}\) Therefore, the finding of MTTCs in the mature oil in this study is not the sole case. Furthermore, the oil samples with all alkylated MTTC series exhibit lower sterane isomerization parameters than the oils without all alkylated MTTC series as discussed above (Figure 8). Therefore, the “low-mature” oil found with abundant MTTC compounds, especially derived from the saline lacustrine settings, should be assessed with caution.

### 3.4. Discussion on the Controlling Factors of MTTC Distribution Characteristics

**Figure 9 (a,b)** shows that the absolute concentration of total MTTCs in Wenliu oils is higher than that in Machang oils, indicating that in general, the salt-rich zone (Wenliu) is more favorable for the development of MTTCs compared to the salt-free zone (Machang). The data points of the Wenliu oils (salt-rich zone) and the Machang oils (salt-free zone) could be clearly subdivided into two distinct groups (Figure 9), which further confirms the difference in the OM source and the sedimentary environment between the two oils.\(^{56,71}\) **Figure 9 (e,f)** shows that \(\beta + \gamma + \xi\)–MTTC%
(dimethyl MTTC) in the Wenliu oils is higher than that in the Machang oils, which suggest that $\beta + \gamma + \zeta$-MTTC% (dimethyl MTTC) is closely related to the reduced depositional environment and the hypersaline environment. Figure 9 (g,h) shows that $\alpha$-MTTC% (trimethyl MTTC) in the Machang oils is higher than that in the Wenliu oils, which suggest that $\alpha$-MTTC (trimethyl MTTC) is closely related to the less reduced depositional environment and the normal
saline environment. This finding is consistent with what Bao (2009) found in the Jianghan Basin. This finding indicates that the composition and distribution of MTTCs are closely related to the redox conditions and salinity. The reason methyl MTTC do not show a clear relationship with redox conditions or salinity may be attributed to the lack of enough oil samples or the samples are not representative (Figure 9 (c,d)).

According to the relationship between Pr/Ph and MTTCI proposed by Schwark (1998), the data points of oil samples in this study are shown in the Pr/Ph versus MTTCI diagram (Figure 10). The samples with all alkylated MTTC series present (data points with circles shown in Figure 10) mostly fall in the mesosaline section, while only one sample falls in the normal salinity section, indicating that the relatively high salinity is more favorable to the development of all alkylated MTTCs.

4. CONCLUSIONS

(i) A significant difference in the OM source and the sedimentary environment between the salt-rich zone and the salt-free zone of the Dongpu Depression contributed to the different characteristics of the Wenliu oil (from salt-rich zone) and Machang oil (from salt-free zone). The Wenliu oils have typical characteristics of saline lacustrine oil as follows: low Pr/Ph ratio, abundant gammacerane, slight C35 homohopane predominance, and low degree of sterane isomerization. Half of the Wenliu oil samples are found with all alkylated MTTC series present. In contrast, the Machang oils have the characteristics of mature fresh water lacustrine oil as follows: Pr/Ph > 1, not rich in gammacerane, and high level of sterane isomerization. Only one Machang oil was found with all alkylated MTTC series present.

(ii) The saline lacustrine settings in the Wenliu area may inhibit the rearrangement and isomerization of regular steranes, which makes some oil samples to be presented as “low-mature oil.” Actually, the Wenliu oils were mature, which is supported by the oils’ Rc values based on a series of aromatic maturiity parameters. Abundant all alkylated MTTC series are found in the oil samples that look “low mature” but are mature enough in fact. Therefore, the “low-mature” oil found with abundant MTTC compounds, especially derived from the saline lacustrine settings, should be assessed with caution.

(iii) The composition and distribution of MTTCs in the studied oil samples are closely related to redox conditions and paleosalinity. The oil samples with all alkylated MTTC series are dominant in the mesosaline environment compared to normal salinity. The dimethyl MTTCs developed more favorably in the oils derived from a relatively reducing and hypersaline environment (Wenliu) compared to that from the fresh lacustrine settings (Machang), while the trimethyl MTTCs developed more favorably in the fresh water environment (Machang).

5. SAMPLES AND METHODS

5.1. Study Area and Sampling. Twenty-two oil samples were obtained from relevant wells in Wenliu and Machang areas of the Dongpu Depression. Gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS) analyses of the oils were conducted in the Key Laboratory of Exploration Technologies for Oil and Gas Resources (Yangtze University, Wuhan, China).

5.2. Pretreatment. All the oil samples were first deasphalted using 60 mL of n-hexane. Then, the samples were fractionated by liquid chromatography on a Pasteur pipette into saturate and aromatic hydrocarbon fractions using silica gel/alumina columns (1:1, w/w; 60–100 mesh). n-Hexane (5 mL) and 6 mL of a mixture of hexane and dichlormethane (7:3, v/v) were used as the eluents, respectively. NSO and some of the polyaromatic compounds were obtained by elution with 5 mL of dichlormethane and methanol (95:5, v/v).

5.3. GC Analysis. The isolated saturate and aromatic fractions were analyzed, respectively, using an Agilent 6890 series GC with a splitless capillary injector and a 30 m × 0.25 mm (i.d.) J&W Scientific DB-5 122-5032 fused silica capillary column coated with a 0.25 μm liquid film. The injector was set up in the splitless injection mode, and the temperature was held at 300 °C. The carrier gas was helium (He) with a flow rate of 1.4 mL/min. The temperature program started with an initial temperature of 40 °C, held for 1.5 min, and increased to 300 °C at a rate of 4 °C per minute followed by an isothermal period of 34 min for a total run time of 100.5 min. The flame ionization detector temperature was set at 310 °C. n-Alkanes and isoprenoids were identified in each chromatogram by comparing their relative retention times with standards.

5.4. GC–MS Analysis. The GC–MS analyses of the saturate and aromatic fractions were separately performed using an Agilent 7890A GC system coupled with an Agilent Technologies 5975C mass selective detector using single-ion monitoring. The GC used a 60 m × 0.25 mm Agilent/J&W Scientific DB-5 122-5562 fused silica capillary column coated with a 0.25 μm liquid film. The injected volume of branched, cyclic, and aromatic fractions was 1 μL per run. The injector temperature was set at 300 °C. The GC temperature program started at 40 °C with a 1.5 min hold time and was later increased to 300 °C at a rate of 4 °C per minute and then held constant for 34 min for a total run time of 100.5 min. Samples were run in the splitless mode, and helium was used as the carrier gas at a flow rate of 1.4 mL/min. Regular biomarker compounds like steranes and terpanes were highlighted using diagnostice ion fragmentograms and identified by comparison of relative retention to published data. δ-MTTCs, β-MTTCs, γ-MTTCs, and α-MTTCs were identified in the oil samples by comparison with fingerprint characteristics, peak sequence, and retention time on m/z 121, 135, and 149 mass chromatograms published by Shen (1987) and Sinninghe (1987).

■ AUTHOR INFORMATION

Corresponding Author

Ting Wang — Hubei Key Laboratory of Petroleum Geochemistry and Environment (Yangtze University), Wuhan 430100, China; State Key Laboratory of Organic Geochemistry, Guangzhou 510640, China; orcid.org/0000-0001-7643-5666; Email: tw@yangtzeu.edu.cn

Authors

Donglin Zhang — Hubei Key Laboratory of Petroleum Geochemistry and Environment (Yangtze University), Wuhan 430100, China
Youjun Tang — Hubei Key Laboratory of Petroleum Geochemistry and Environment (Yangtze University), Wuhan 430100, China
Hongbo Li – Hubei Key Laboratory of Petroleum Geochemistry and Environment (Yangtze University), Wuhan 430100, China
Tianwu Xu – Sinopec Zhongyuan Oilfield, Puyang, Henan 457001, China
Yunxian Zhang – Sinopec Zhongyuan Oilfield, Puyang, Henan 457001, China
Chengfu Zhang – Sinopec Zhongyuan Oilfield, Puyang, Henan 457001, China
Yahao Huang – Hubei Key Laboratory of Petroleum Geochemistry and Environment (Yangtze University), Wuhan 430100, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c01688

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Notes
The authors declare no competing financial interest.

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