



A distinct oil group in the Dongying Depression, Bohai Bay Basin, China: New insights from norcholestane and triaromatic steroid analyses

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ABSTRACT

The lower third and upper fourth members of the Eocene Shahejie Formation (lower Es3 and upper Es4) are known as two sets of effective source rocks in the Dongying Depression, Bohai Bay Basin. In this study, the saturated and aromatic steroids of 20 crude oil samples from the Dongying Depression were systematically investigated using gas chromatography–mass spectrometry (GC–MS) and GC–MS metastable reaction monitoring. Based on the distribution patterns of the steranes, norcholestanes, and triaromatic steroids, the Group I and II oils were clearly identified and shown to be derived from the lower Es3 and upper Es4 source rocks, respectively. Significantly, it was discovered that three oil samples collected from the Eocene Kongdian Formation and the Ordovician reservoirs exhibit completely different steroid and isotopic compositions from those of the Group I and II oils. These oils, as a distinct oil group (Group III), have the characteristics of abnormally high concentrations of C₂₉ steranes, 24-nordiacholestane, 27-nordiacholestane, C₂₈ triaromatic steroids, C₂₇ 4 α -methyltriaromatic steroids, and C₂₉ 4 α -methyl-24-ethyltriaromatic steroids, and low concentrations of 24-norcholestane, 27-norcholestane and triaromatic dinosteroids, and ¹³C depletion. Although the related source rock of Group III oils needs to be further clarified in the study area, the ¹³C depletion, abundant C₂₉ steranes, and low 24-norcholestane content may suggest greater bacteria/algae inputs (e.g., green algae rather than dinoflagellates) than both the lower Es3 and upper Es4 source rocks. Identification of the Group III oils indicates that the norcholestanes and triaromatic steroids may be more effective molecular fossils for the classification of crude oils in complicated petroleum exploration fields.

1. Introduction

Crude oil classification is of great significance to understanding the distribution of petroleum accumulations (Peters et al., 2005; Hao et al., 2009a, 2009b). Petroleum isotope and biomarker compositions related to biological sources (Bobrovskiy et al., 2018; Brocks et al., 2017; Summons and Erwin, 2018) and depositional environments (Moldowan et al., 1985; Volkman et al., 1986) have been extensively applied in the analysis of oil-source rock correlations and crude oil group classifications (Seifert et al., 1984; Farrimond et al., 2004; Luo et al., 2016; Xiao et al., 2019a). In addition to the most commonly used biomarkers, such as acyclic isoprenoids, hopanes, gammacerane, and steranes, norcholestanes and triaromatic steroids (TAS) can also be used for crude oil classification (Zhang et al., 2002; Wang et al., 2008; Li et al., 2012; Yang

et al., 2015; Xiao et al., 2019b).

Norcholestanes (C₂₆ steranes), including 21-, 24-, and 27-norcholestane isomers, have been identified in petroleum and source rocks using authentic standards (Moldowan et al., 1991; Holba et al., 1998b). 24-norcholestanes are considered to be a diagnostic biomarker for diatoms and dinoflagellates from the Jurassic to the Tertiary (Holba et al., 1998a, 1998b; Volkman, 2003; Rampen et al., 2007; Abogilila et al., 2011). 21-norcholestanes have been identified as major components of the Eocene evaporitic sediments in the Jinxian Sag, the Bohai Bay Basin (Bao and Li, 2001). However, their biological source remains to be further determined, as does that of 27-norcholestane (Bao and Li, 2001; Peters et al., 2005). In addition, it is widely accepted that the C₂₆–C₂₈ TAS detected in geological samples were probably formed by aromatization and loss of a methyl group from C₂₇–C₂₉ regular steranes during

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the process of diagenesis and thermal burial processes (Moldowan and Fago, 1986; Peters et al., 2005). Due to their high thermal stability and resistance to biodegradation compared to regular steranes, C_{26} – C_{28} TAS are usually more effective in biodegraded oils or high-over mature samples (Li et al., 2012; Yang et al., 2015). Furthermore, the triaromatic dinosteroids were recognized as originating from dinoflagellates (e.g., Thomas et al., 1992), so their related parameters can be used to reflect the dinoflagellate contribution (Ando et al., 2017).

In the Dongying Depression, two confirmed oil groups have been identified based on the distribution patterns of the acyclic isoprenoids, hopanes, gammacerane, and steranes in the sediments and crude oils (Zhang et al., 2009; Meng et al., 2011; You et al., 2020). One oil group is characterized by high pristane to phytane ratio (Pr/Ph), low C_{35}/C_{34} 22S hopane and C_{29} steranes to C_{30} hopane ($C_{29}St/C_{30}H$) ratios, and extremely low gammacerane content. This oil group has been confirmed to be sourced from the source rock of the lower third member of the Eocene Shahejie Formation (lower Es3) (Zhu et al., 2004; Li et al., 2010). In contrast, another oil group was determined to be sourced from the source rock of the upper fourth member of the Eocene Shahejie Formation (upper Es4), which has high gammacerane index ($Ga/C_{30}H$), C_{35}/C_{34} 22S hopane and $C_{29}St/C_{30}H$ ratios, and low Pr/Ph ratio (Pang et al., 2003; Li et al., 2010; Meng et al., 2011; You et al., 2020).

In addition to the two confirmed oil groups, another oil group, which was mainly discovered in the Paleogene Kongdian Formation and the Ordovician reservoirs in the Niuzhuang South Slope, has been reported (Li et al., 2005a, 2005b; Meng et al., 2011; Zhan et al., 2019, 2020). Based on gammacerane-rich nature and the predominance of C_{29} sterane, the newly identified oil group was considered to be from mixed sources of the Es4 and the Ek2 source rocks (Li et al., 2005a, 2005b) or the source rock developed in shallow lake-swamp facies (Meng et al., 2011). Recently, Zhan et al. (2019, 2020) proposed that this distinct oil group was not derived from any of the known source rocks or mixed sources based on chemometric analysis of the saturated hydrocarbon parameters. In this study, the norcholestane, triaromatic steroids, and isotopic compositions of 20 crude oils from the Dongying Depression, Bohai Bay Basin, were investigated. The distinct oil group was confirmed to be non-mixed, and the biogenic compositions of its related source rock were further discussed. Another different unrecognized

petroleum system was also identified, and deep exploration is needed in the Dongying Depression.

2. Geological setting

The Bohai Bay Basin is a petroliferous basin in eastern China (Fig. 1a) (Hao et al., 2009a; Ping et al., 2017). It experienced two main tectonic evolution stages, the syn-rifting stage at 66.0–23.0 Ma and the post-rifting stage from 23.0 Ma to the present (Huang and Pearson, 1999). It is separated by several major faults into several fault-bounded sub-basins, including the Jiyang and Liaohe sub-basins (Hao et al., 2007). The Dongying Depression, as one structural unit of the Jiyang sub-basin, is an asymmetric dustpan-shaped lacustrine basin with a total area of 5850 km² (Zhang et al., 2009). Overall, this depression consists of five structural units, which are the northern steep slope zone, the northern sag zone, the central anticline zone, the southern sag zone, and the southern gentle slope zone (Guo et al., 2010). The northern sag zone contains the Minfeng and Lijin sags, and the southern sag zone includes the Niuzhuang and Boxing sags (Fig. 1b) (Zhu et al., 2004; Ping et al., 2017).

Moreover, a set of fluvial-lacustrine sequences from the Paleogene to the Quaternary were deposited in the Dongying Depression above the metamorphic basement, which is composed of the Paleogene Kongdian (Ek), Shahejie (Es), and Dongying formations (Ed) (Fig. 2), and the Neogene Guantao (Ng) and Minghuazhen (Nm) formations, and the Quaternary Pingyuan Formation (Qp) (Li et al., 2003; Yang and Xu, 2004; Guo et al., 2010). The Kongdian Formation mainly comprises coarse clastic red-beds deposited under oxidized depositional conditions, which were unconformably deposited on the Mesozoic metamorphic basement (Li et al., 2003). The Shahejie Formation was developed as a fluvial-lacustrine facies and is the main petroliferous strata in the Dongying Depression, Bohai Bay Basin (Pang et al., 2003; Zhu et al., 2004). Moreover, it can be subdivided into four members, and most of the discovered commercial oils are mainly distributed in the fourth and third members of the Eocene Shahejie Formation (Es4 and Es3). In addition, the mudstones and shales within the Es4 and Es3 are the most effective source rocks in the study area, including the upper Es4 and the lower Es3 (Zhu et al., 2004; Zhang et al., 2009; Li et al., 2010).

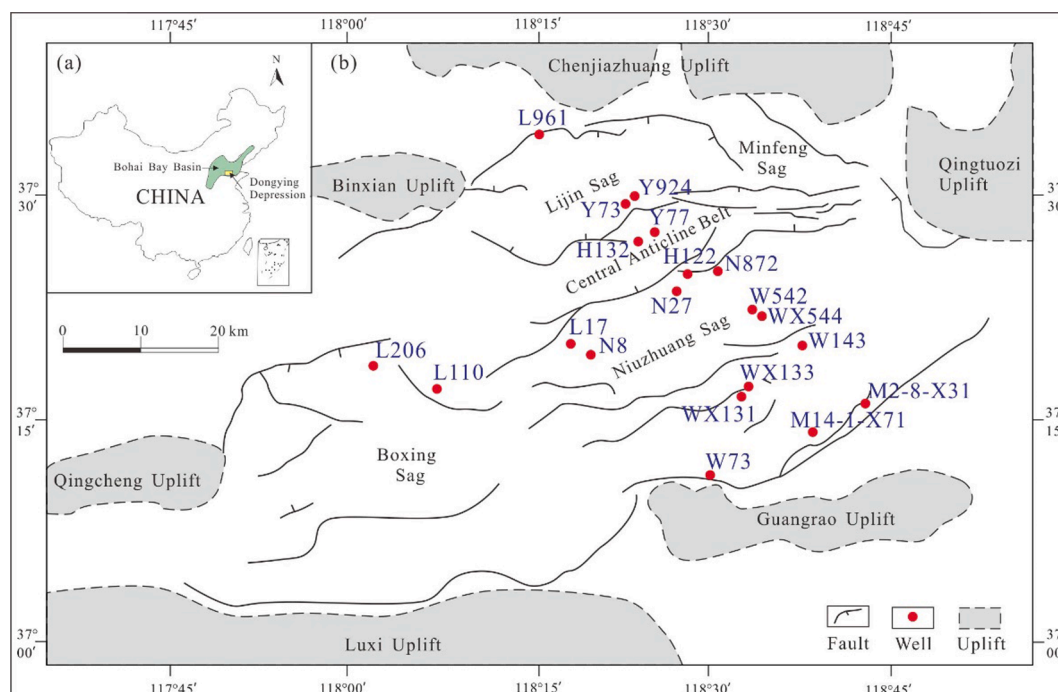


Fig. 1. (a) Location of the Bohai Bay Basin, and (b) the major tectonic units and locations of the sampling wells in the Dongying Depression.

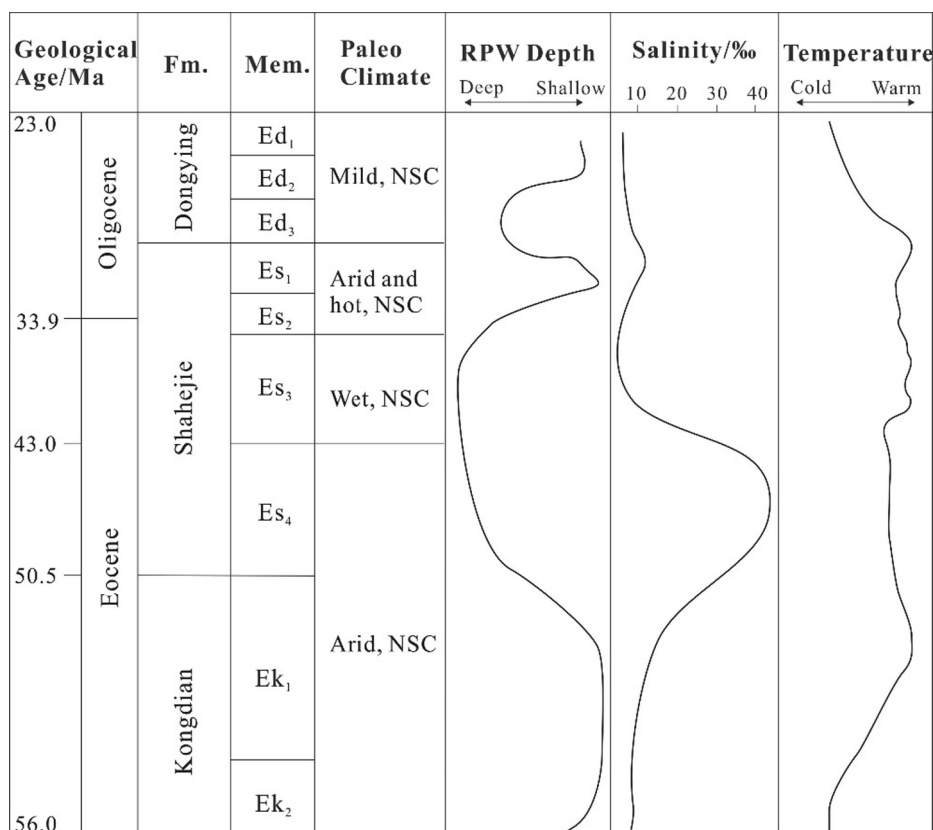


Fig. 2. Paleogene stratigraphy, paleoclimate, relative paleo-water depth, salinity, and temperature in the Dongying Depression (modified after Li et al., 2003; Wang et al., 2008; Hao et al., 2009b). Notes: Fm. = Formation; Mem. = Member; RPW Depth = relative paleo-water depth; and NSC = northern subtropical climate.

The upper Es4 was deposited in an arid climate under high salinity depositional condition, whereas the lower Es3 was deposited in a wet climate under low salinity depositional condition (Fig. 2) (Wang et al., 2008; Hao et al., 2009b). In addition to the Paleogene oil reservoirs, significant oil reserves have also been discovered in the Ordovician buried hill reservoirs within the basement in the Niuzhuang South Slope (Li et al., 2005a, 2005b).

3. Samples and experiments

3.1. Samples

Twenty crude oil samples were collected and analyzed for oil-oil correlations and classification of the crude oils, among them 11 crude oil samples were collected from the Es3 reservoirs, six crude oil samples were collected from the Es4 reservoirs, two crude oil samples were collected from the Ek1 reservoir, and one crude oil sample was collected from the Ordovician reservoir (Table 1). These crude oil samples were

Table 1
Molecular marker parameters of saturate hydrocarbons for the analyzed crude oils.

No.	Well	Depth (m)	Stratum	C ₂₇ /C ₂₉ ααR St	C ₂₇ Diα/C ₂₇ St	4-Me/C ₂₉ St	C ₂₉ St 20S/(20S + 20R)	C ₂₉ St ββ/(ββ + αα)	C ₂₉ St/%
1	W542	3147.4–3162.2	Es3	0.80	0.35	0.46	0.37	0.53	47.0
2	WX544	2826.0–2829.4	Es3	1.04	0.31	0.48	0.35	0.38	45.4
3	L17	2903.2–2921.4	Es3	0.95	0.31	0.49	0.41	0.44	46.9
4	N872	3040.8–3049.2	Es3	0.90	0.25	0.46	0.35	0.45	47.9
5	N27	3271.2–3277.0	Es3	0.86	0.31	0.41	0.39	0.45	49.8
6	H122	3023.4–3026.8	Es3	0.95	0.27	0.36	0.40	0.48	47.6
7	H132	2826.0–2828.0	Es3	1.05	0.33	0.40	0.39	0.50	45.2
8	Y73	2850.0–2894.0	Es3	1.04	0.29	0.41	0.42	0.45	45.7
9	Y77	3096.7–3107.6	Es3	1.01	0.32	0.49	0.39	0.46	45.3
10	Y924	2711.0–2714.0	Es3	1.04	0.30	0.51	0.42	0.39	43.8
11	L961	2419.6–2425.0	Es3	0.95	0.39	0.38	0.39	0.37	49.7
12	L110	2996.8–3032.0	Es4	0.87	0.34	0.48	0.40	0.47	47.4
13	L206	2803.6–2818.0	Es4	0.81	0.23	0.52	0.39	0.43	44.3
14	N8	3081.4–3089.4	Es4	0.81	0.26	0.52	0.42	0.40	48.7
15	W143	2795.4–2801.0	Es4	1.07	0.18	0.17	0.33	0.32	46.3
16	W73	1285.0–1296.0	Es4	1.15	0.11	0.15	0.27	0.28	45.2
17	M2-8-X31	1541.6–1554.6	Es4	1.29	0.14	0.14	0.29	0.28	43.3
18	M14-1-X71	1544.0–1611.0	O	0.57	0.32	0.17	0.38	0.39	55.8
19	WX131	2467.3–2495.8	Ek1	0.40	0.33	0.16	0.46	0.43	57.6
20	WX133	3179.4–3185.8	Ek1	0.44	0.40	0.17	0.47	0.50	53.6

No. = Sample number; C₂₉St/% = C₂₉/(C₂₇ + C₂₈ + C₂₉)Steranes × 100%.

collected from different wells, and their detailed locations are shown in Fig. 1b.

3.2. Molecular markers analysis

All of the crude oil samples were separated into four groups using a standard liquid chromatography column, i.e., the saturated, aromatic, resin, and asphaltene fractions, at the State Key Laboratory of Petroleum Resource and Prospecting, China University of Petroleum, Beijing. The separation was carried out following the method of Xiao et al. (2019c). The saturated and aromatic hydrocarbon fractions were investigated via gas chromatography–mass spectrometry (GC–MS) that consists of an Agilent 6890 gas chromatograph and an Agilent Model 5975i Mass Selective Detector. The GC was equipped with a HP-5 MS fused silica capillary column (30 m × 0.25 mm i.d.) with a film thickness of 0.25 μm. Two temperature programs were used. For the saturated hydrocarbon fraction, the program was as follows: an initial temperature of 50 °C for 1 min, heating to 120 °C at a rate of 20 °C/min, heating to 310 °C at a rate of 3 °C/min, and a hold for 10 mins. For the aromatic hydrocarbon fraction, the program was as follows: an initial temperature of 50 °C for 1 min, heating to 310 °C at a rate of 3 °C/min, and holding at 310 °C for 16 min.

The saturated hydrocarbon fraction was also analyzed by GC–MS–MS, and metastable reaction monitoring (MRM) was used to identify the norcholestanes at the State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing. The GC–MS–MS analyses were performed on an Agilent 6890 series gas chromatograph interfaced with a Quatro II mass spectrometer. A HP-5MS column (60 m × 0.25 mm × 0.25 μm film thickness) was used with split injection (20:1), and the carrier gas was He at a constant flow (1 ml/min). The temperature program was as follows: initial temperature of 50 °C for 1 min, heating to 120 °C at a rate of 20 °C/min, heating to 250 °C at a rate of 4 °C/min, and heating to 310 °C at a rate of 3 °C/min (hold 30 min).

3.3. Hierarchical cluster analysis

Hierarchical cluster analysis (HCA) is widely used to classify oils into different groups (e.g., Peters et al., 1994, 2007; Justwan et al., 2006; Xiao et al., 2019b). The analysis of the molecular marker associations of crude oils and the multivariate analysis of the related molecular marker parameters (hierarchical cluster analysis) were used to classify the crude oils (Hao et al., 2009b). HCA was carried out using the Statistical Package for the Social Sciences (SPSS Inc.). The Euclidean measure interval and the between-groups linkage method were used in the study. The cluster distance was calculated using an n-dimensional space, where n represents the number of parameters.

3.4. Stable carbon isotope analysis

A MAT 253 isotope ratio mass spectrometer (IRMS) was used to measure the stable carbon isotope values ($\delta^{13}\text{C}$) of the crude oil samples and their four fractions. The carbon was converted into CO_2 at 980 °C using a FLASH HT EA reactor containing chromium oxide, copper, and silver-containing cobalt oxide. The carbon isotope values are reported using δ notation in parts per thousand (‰) in reference to the International Atomic Energy Agency-600 caffeine standard.

4. Results and discussion

4.1. Distribution of steranes

4.1.1. Regular steranes

C_{27} – C_{29} regular steranes (C_{27} – C_{29}St), C_{30} 4 α -methylsteranes (4-Me), and C_{27} diasteranes (C_{27}Dia) were identified in the m/z 217 mass chromatograms of the saturated hydrocarbon fraction, which are generally used to determine the organic matter inputs of the source

rocks. In particular, the relative abundances of C_{27} and C_{29} regular steranes reflect the relative contributions of lower aquatic organisms (such as algae) or red algae and terrestrial higher plants or green algae respectively (Volkman et al., 1986; Sepúlveda et al., 2009; Brocks et al., 2017). In this study, 14 of the crude oil samples (samples 1–14 in Table 1) were found to contain similar relative concentrations of C_{27} and C_{29} regular steranes ($\alpha\alpha\text{R}$) (Fig. 3a). Three of the crude oil samples (samples 15–17, Table 1) exhibited dominant C_{27} steranes in the C_{27} – C_{29} steranes (Fig. 3b), whereas three of the crude oil samples (samples 18–20, Table 1) exhibited an abnormal dominance of C_{29} steranes (Fig. 3c). The above three distribution patterns of regular steranes may represent three different types of crude oil, indicating that these crude oil samples may have originated from different source rocks, or some may have mixed sources. The ranges of the $\text{C}_{27}/\text{C}_{29}$ $\alpha\alpha\text{R}$ sterane ratios of these three types of crude oil (samples 1–14, 15–17, and 18–20) are 0.80–1.05, 1.07–1.29, and 0.40–0.57, respectively (Table 1), which directly indicate their distribution differences.

Samples 18–20 exhibited an increased abundance of C_{29} steranes with distinctly low values of $\text{C}_{27}/\text{C}_{29}$ $\alpha\alpha\text{R}$ sterane ratio (0.40–0.57), which probably indicates a great contribution of terrigenous organic matter or green algae (Brocks et al., 2017; Summons and Erwin, 2018) to the related source rock. However, a previous study proposed that there is no set of source rock with such high abundance of C_{29} steranes in the Dongying Depression, so their related source rock remains ambiguous (Li et al., 2005a, 2005b).

4.1.2. 4-Methylsteranes

C_{30} 4 α -methylsteranes are generally divided into 4 α -methyl-24-ethylcholestanes and 4 α ,23,24-trimethylcholestanes (Peters et al., 2005). 4 α -methyl-24-ethylcholestanes in petroleum probably originate from 4 α -methylsterols in living dinoflagellates (Wolff et al., 1986), but they have also been identified in a few species of haptophyte microalgae (Volkman et al., 1990). 4 α ,23,24-Trimethylcholestanes, also known as dinosteranes, are formed by reduction of dinosterol or dinostanol

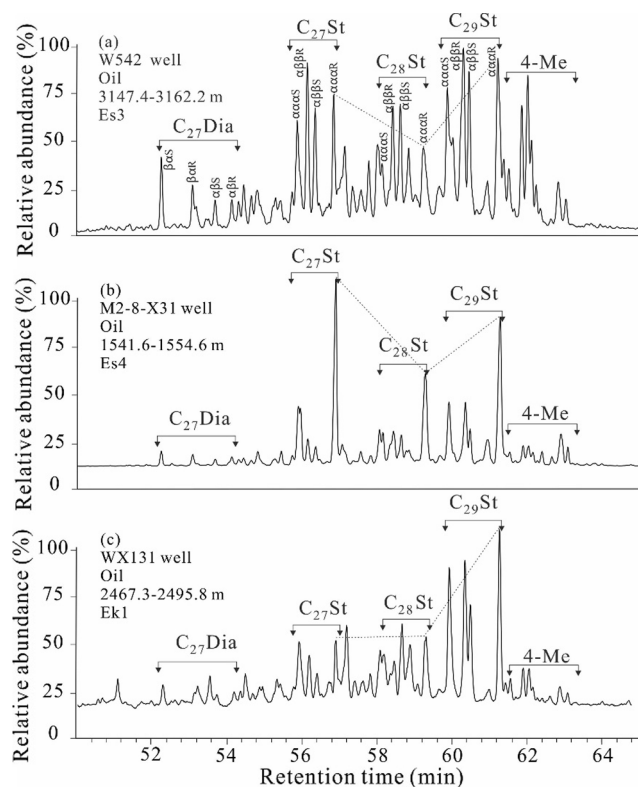


Fig. 3. Representative mass chromatograms (m/z 217) of the sterane series in the crude oils.

produced by dinoflagellates (Withers, 1987). Moldowan et al. (1985) proposed that both 4 α -methyl-24-ethylcholestanes and dinosteranes occur in marine rocks and related oils with marine dinoflagellate input. However, abundant 4 α -methyl-24-ethylcholestanes have also been discovered in non-marine sediments and oils (Summons et al., 1987, 1992; Fu et al., 1990). The differences in the species of dinoflagellates found in freshwater to hypersaline water sedimentary conditions result in different compositions of 4-methylsteranes, and dinoflagellates are usually prone to bloom in freshwater condition (Fu et al., 1990).

Previous studies suggest that the C₃₀ 4-methylsteranes/C₂₉ steranes ratio (4-Me/C₂₉St) is one of the most important parameter for oil–source and oil–oil correlations in the Jiyang sub-basin of the Bohai Bay Basin (Chen et al., 1996; Zhang et al., 2005; Hao et al., 2009b). Moreover, abundant C₃₀ 4-methylsteranes generally occur in the lower Es3 source rock (Zhang et al., 2003, 2009), and they were derived from the *Bohaidina* and *Parabohaidina* algae (dinoflagellates) (Chen et al., 1996; Zhang et al., 2005; Hao et al., 2009b). In this study, samples 1–14 were found to contain obvious distribution of C₃₀ 4-methylsteranes (Fig. 3a) with higher 4-Me/C₂₉St ratios (0.36–0.52), which may indicate that the oils originated from the lower Es3 source rock (Zhang et al., 2003, 2009). However, the relative abundances of C₃₀ 4 α -methylsteranes are very low in both samples 15–17 and 18–20 (Fig. 3b–c), and their 4-Me/C₂₉St ratios are in the range of 0.14–0.17 (Table 1). Thus, we can propose that samples 15–20 were derived from the source rock that is completely different from the lower Es3 source rock.

4.1.3. Diasteranes

Diasteranes are commonly considered to be formed by a rearrangement reaction involving the catalysis of clay minerals under oxidizing conditions (Rubinstein et al., 1975). The thermal stability of diasteranes is higher than that of regular steranes, and the ratio of diasteranes to regular steranes gradually increases with increasing maturity (Peters et al., 1990).

Previous studies have revealed that the lower Es3 source rock contains higher abundances of C₂₇ diasteranes than the upper Es4 source rock (Zhang et al., 2003, 2009; Zhu et al., 2004). In this study, samples 1–14 and 18–20 have higher C₂₇ diasteranes contents, and their C₂₇ diasteranes/C₂₇ steranes (C₂₇Dia/C₂₇St) ratios range from 0.23 to 0.40 (Table 1), which is consistent with the lower Es3 source rocks (Zhang et al., 2003; Li et al., 2010). Although both samples 1–14 and 18–20 have distributions of C₂₇ diasteranes similar to those of the lower Es3 source rock, we can rule out the possibility that samples 18–20 were sourced from the lower Es3 source rock because their abundance of C₂₉ steranes over C₂₇ steranes is significantly different from that of the lower Es3 source rock (Fig. 3c). In addition, samples 15–17 have extremely low C₂₇ diasteranes contents compared to those of the samples 1–14 and 18–20 (Table 1), which may indicate the contribution from the upper Es4 source rock (Pang et al., 2003; Li et al., 2010).

Therefore, according to the distribution characteristics of C₂₇–C₂₉St, 4-Me, and C₂₇Dia, 20 crude oil samples were preliminarily classified into three oil groups. Group I, II, and III oils include the samples 1–14, 15–17, and 18–20, respectively.

4.2. Distribution of norcholestanes

In addition to C₂₇–C₂₉ regular steranes, C₃₀ 4-methylsteranes, and C₂₇ diasteranes, C₂₆ norcholestanes were also identified in these oil samples. As an uncommon class of steranes, they have one methyl group less in the side chain than C₂₇ regular steranes, and include 21-, 24-, and 27-norcholestane isomers. Although they have been observed in sediments and crude oils (Moldowan et al., 1991), only 24-norcholestanes have specific sources (e.g., diatoms and dinoflagellates) (Volkman, 2003; Holba et al., 1998a, 1998b; Rampen et al., 2007). Usually, the norcholestanes have low concentrations compared with those of the regular steranes (Moldowan et al., 1991), and thus, GC–MS–MS analysis is needed to accurately detect and identify them and to calculate their

relative contents. Based on the distribution characteristics of the norcholestanes (representative parent–daughter ions of m/z 358 → 217) in the saturated hydrocarbon fraction (Fig. 4), the 20 crude oil samples were divided into three oil groups, and the results are completely consistent with the above classification results.

Group I oils are characterized by very high 24-norcholestanes and 24-nordiacholestanes contents, low 27-norcholestanes and 27-nordiacholestanes contents, and the absence of 21-norcholestanes (Fig. 4a). Group II oils contain abundant 24-norcholestanes and 27-norcholestanes, with an obvious distribution of 21-norcholestanes. Moreover, the relative abundances of 24-norcholestanes and 24-nordiacholestanes in Group II oils are similar to those of 27-norcholestanes and 27-nordiacholestanes (Fig. 4b).

Diatoms and dinoflagellates are two probable sources of the precursors of 24-norcholestanes (Rampen et al., 2007). In the Jiyang sub-basin, dinoflagellates including *Deflandrea* and *Bohaidina-Parabohaidina* are well preserved (Zhang et al., 2009), but no diatom fossils have been observed in the Shahejie Formation (Wang et al., 2008; Wang and Li, 2010). Thus, the 24-norcholestanes in these crude oil samples must have been sourced from dinoflagellates rather than diatoms. Certainly, there are more dinoflagellates to the source rocks of Group I oils than those of Group II oils based on the enrichment of only 24-norcholestanes in Group I oils. In the Jiyang sub-basin, 21-norcholestane and 27-norcholestanes have been detected in the saline and evaporitic source rocks (Bao and Li, 2001; Wang et al., 2006), and they seem to have no direct sterol precursors but may form via bacterial oxidation or thermal cleavage (Peters et al., 2005). Therefore, the high abundances of 21- and 27-norcholestanes in the Group II oils probably indicate that the related source rocks were developed in an evaporative and saline

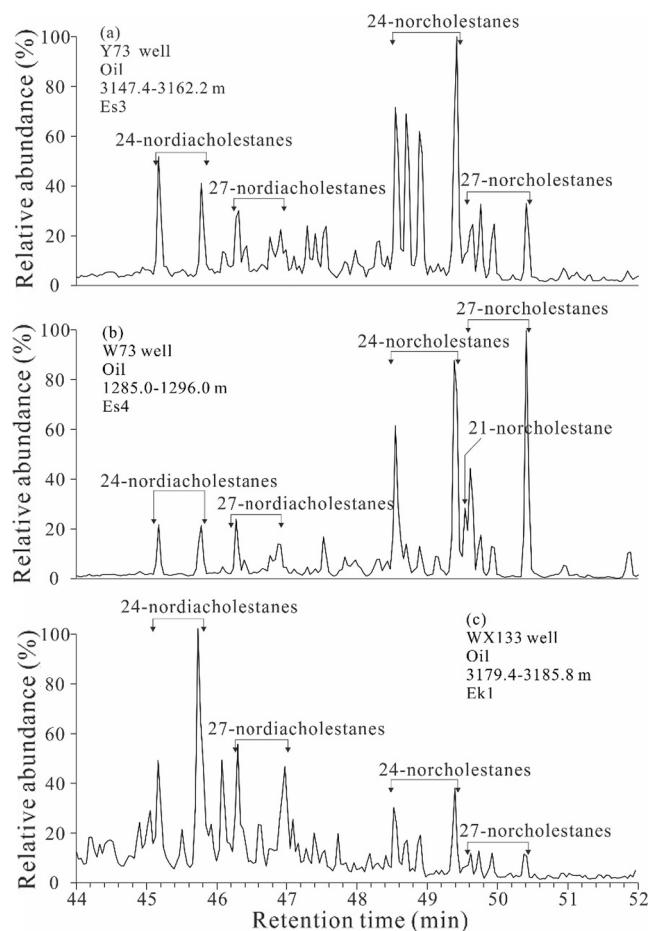


Fig. 4. Representative mass chromatograms (m/z 358,217) of the norcholestanes and nordiacholestanes in the crude oils.

depositional environment, corresponding to the upper Es4 source rock (Pang et al., 2003; Zhu et al., 2004). Moreover, regular steranes (Fig. 3b) and norcholestanes (Fig. 4b) in Group II oils have a very low degree of isomerization which may be closely related to the oil's origin, i.e., from the upper Es4 source rock with low thermal maturity (Li et al., 2003; Zhang et al., 2003; You et al., 2020). The Es4 source rock was deposited in a saline depositional environment and contains sulfur-rich kerogen, which is conducive to oil generation at relatively low maturity levels (Pang et al., 2003). Therefore, the related oils (e.g., Group II oils) were considered to be typical low-mature oil in the Dongying Depression, which has often been cited as a typical example of an economic low-maturity oil play in the China (Pang et al., 2003; Li et al., 2005a, 2005b).

Group III oils are strikingly different from Group I and II oils. These are characterized by high 24- and 27-nordiacholestanes concentrations, but low 24- and 27-norcholestanes contents, and the absence of 21-norcholestanes (Fig. 4c). The low 24-norcholestanes contents may indicate a minor contribution from dinoflagellates to the related source rock (Rampen et al., 2007; Wang and Li, 2010). The extremely low 21- and 27-norcholestanes contents likely indicate that the source rock was deposited under fresh to brackish depositional conditions (Bao and Li, 2001; Wang et al., 2006). Nordiacholestanes may have a greater thermal stability, e.g., diasteranes (Peters et al., 1990) and rearranged hopanes (Kolaczowska et al., 1990; Xiao et al., 2019c), than norcholestanes. High thermal maturity is conducive to the enrichment of nordiacholestanes.

The $C_{29}St\ 20S/(20S + 20R)$ and $C_{29}St\ \beta\beta/(\beta\beta + \alpha\alpha)$ ratios of Group III oils are 0.38–0.47 and 0.39–0.50, respectively (Table 1). This indicates that the related source rock is still in the early stage of the oil generation window or in the peak oil generation window (Peters et al., 2005), which is consistent with the result of previous research (Zhan et al., 2019). Thus, the thermal maturity is not the key factor controlling the abundant 24- and 27-nordiacholestanes in Group III oils in the Dongying Depression. In addition, a previous study reported that the $Pr/(Pr + Ph)$ and $C_{27}Dia/(C_{27}Dia + C_{27}St)$ ratios exhibit a strong positive correlation, which indicates that oxidizing depositional conditions facilitated the production of the diasterane precursors (Moldowan et al., 1986). Thus, the high of 24- and 27-nordiacholestanes contents in the Group III oils may indicate that its related source rock was probably deposited under oxidizing conditions. Although its specific source rock formation has yet to be further confirmed, it was obviously not derived from the lower Es3 or the upper Es4 source rocks.

4.3. Distribution of triaromatic steroids

4.3.1. Triaromatic steroids

Triaromatic steroids (TAS) were identified in m/z 231 mass chromatograms of aromatic hydrocarbons (Fig. 5). C_{26} – C_{28} TAS are considered to be the aromatization products of C_{27} – C_{29} St (Peters et al., 2005; Li et al., 2012), which can also be effective molecular markers of the organic matter inputs of source rocks (Wang et al., 2008; Yang et al., 2015).

Group I and II oils have similar distribution characteristics of triaromatic steroids (Figs. 5a and b, 6a); that is, they are enriched in C_{26} 20R + C_{27} 20S TAS (Fig. 5a and b) and have high C_{26}/C_{28} 20S TAS (0.30–0.58) and C_{27}/C_{28} 20R TAS (0.70–1.03) ratios (Table 2). Thus, the source rocks of these oils probably have similar organic matter inputs. However, Group III oils exhibit distinct differences from Group I and II oils. These have high C_{28} TAS contents and low C_{27} 20R TAS contents (Fig. 5c), and relatively low C_{26}/C_{28} 20S TAS (0.18–0.28) and C_{27}/C_{28} 20R TAS (0.45–0.58) ratios (Table 2). Interestingly, the relative percentage of C_{28} TAS in the Group III oils is 53.5–59.5% (Table 2), which is consistent with that of $C_{29}St$ ($C_{29}St\%$, 53.6–57.6%) (Table 1), and may further reflect the genetic relationship between the triaromatic steroids and regular steranes. Moreover, by combining the related parameters of the regular steranes and triaromatic steroids, it was found that the 20 crude oils can be classified into three oil groups (Fig. 6b), which are the

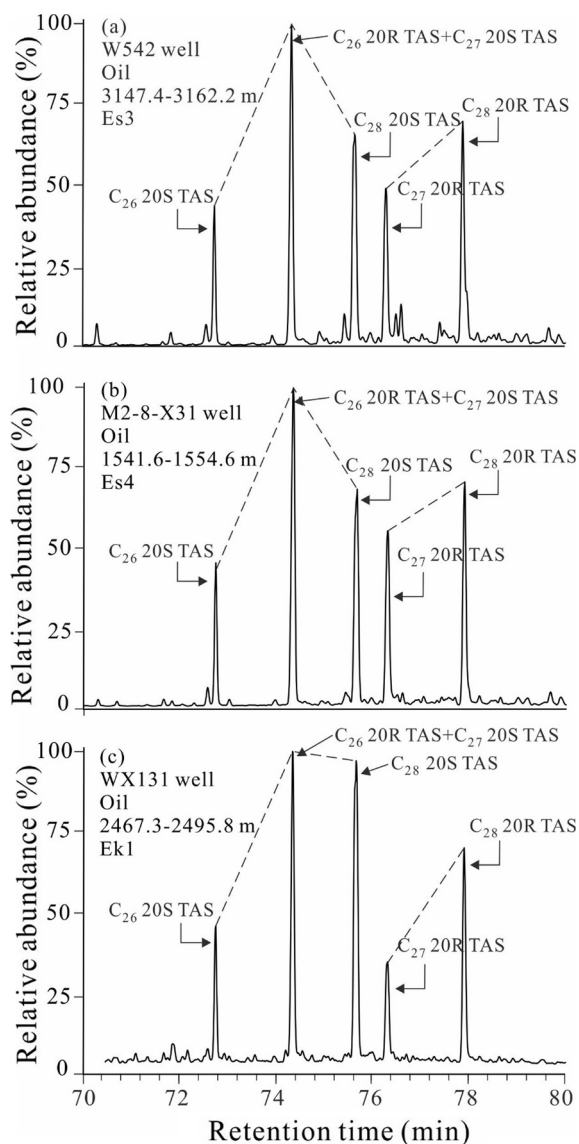


Fig. 5. Representative mass chromatograms (m/z 231) of the triaromatic steroids in the crude oils.

same as the classification results based on the steranes and norcholestanes.

4.3.2. Methyl-triaromatic steroids

Methyl-triaromatic steroids were detected and identified in m/z 245 mass chromatograms of the aromatic hydrocarbons (Fig. 7). Due to the occurrence of deconvolution in the measurements of the dinosteranes, the application of triaromatic dinosteroids (dino-TAS, C_{29} 4 α ,23,24-trimethyltriaromatic steroids) is more suitable (Peters et al., 2005). The triaromatic dinosteroid index is considered to be more effective than the dinosterane index in evaluating the contribution of dinoflagellates (Wang et al., 2008). Therefore, we only systematically analyzed the methyl-triaromatic steroids and applied it to the oil-oil correlation in the study.

Undoubtedly, the relative content of dino-TAS (Peaks 4, 6, 8, 12, 13, 15 and 17 in Fig. 7) in the three oil groups is variable. As can be seen from Fig. 7, Group I and II oils have higher dino-TAS contents (Fig. 7a and b), but Group III oils contain very low concentrations (Fig. 7c). The plentiful dino-TAS in Group I and II oils indicates large contributions from the dinoflagellates to their related source rock (Zhang et al., 2002; Wang et al., 2008; Ando et al., 2017), which is consistent with the results

Table 2

Selected parameters of aromatic hydrocarbons for hierarchical cluster analysis.

No.	Well	Depth (m)	Stratum	R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12	R13
1	W542	3147.4–3162.2	Es3	0.41	0.70	46.6	0.25	0.72	0.18	0.54	0.72	0.67	0.70	0.72	0.52	0.67
2	WX544	2826.0–2829.4	Es3	0.47	0.88	41.8	0.25	0.62	0.16	0.50	0.95	0.57	0.71	0.95	0.50	0.57
3	L17	2903.2–2921.4	Es3	0.58	0.98	38.4	0.16	1.12	0.18	0.35	0.44	1.09	0.65	0.44	0.48	1.09
4	N872	3040.8–3049.2	Es3	0.46	0.89	42.0	0.25	0.68	0.17	0.51	0.81	0.62	0.70	0.81	0.54	0.62
5	N27	3271.2–3277.0	Es3	0.44	0.83	43.6	0.30	0.71	0.21	0.59	0.76	0.60	0.57	0.76	0.63	0.60
6	H122	3023.4–3026.8	Es3	0.47	0.93	41.5	0.32	0.76	0.24	0.73	0.75	0.63	0.52	0.75	0.75	0.63
7	H132	2826.0–2828.0	Es3	0.53	0.93	40.3	0.19	1.03	0.20	0.51	0.48	0.99	0.60	0.48	0.60	0.99
8	Y73	2850.0–2894.0	Es3	0.52	0.91	40.9	0.20	1.06	0.21	0.44	0.47	1.07	0.59	0.47	0.60	1.07
9	Y77	3096.7–3107.6	Es3	0.50	0.94	40.8	0.19	1.02	0.20	0.48	0.47	1.07	0.61	0.47	0.58	1.07
10	Y924	2711.0–2714.0	Es3	0.54	0.90	40.4	0.20	1.07	0.22	0.48	0.44	1.11	0.60	0.44	0.64	1.11
11	L961	2419.6–2425.0	Es3	0.44	0.75	45.4	0.23	0.80	0.19	0.42	0.65	0.77	0.63	0.65	0.56	0.77
12	L110	2996.8–3032.0	Es4	0.36	0.76	46.7	0.22	0.91	0.20	0.41	0.51	0.89	0.57	0.51	0.60	0.89
13	L206	2803.6–2818.0	Es4	0.30	0.71	49.6	0.26	0.88	0.23	0.49	0.54	0.91	0.50	0.54	0.70	0.91
14	N8	3081.4–3089.4	Es4	0.54	1.03	38.7	0.18	0.85	0.15	0.35	0.62	0.74	0.79	0.62	0.46	0.74
15	W143	2795.4–2801.0	Es4	0.41	0.83	44.4	0.44	0.49	0.21	1.03	1.61	0.40	0.52	1.61	0.74	0.40
16	W73	1285.0–1296.0	Es4	0.47	1.01	39.6	0.41	0.55	0.22	1.15	1.64	0.45	0.49	1.64	0.81	0.45
17	M2-8-X31	1541.6–1554.6	Es4	0.41	0.88	43.0	0.50	0.60	0.30	1.10	1.49	0.46	0.38	1.49	1.16	0.46
18	M14-1-X71	1544.0–1611.0	O	0.21	0.58	56.4	0.29	2.01	0.57	0.22	0.26	1.99	0.20	0.26	2.06	1.99
19	WX131	2467.3–2495.8	Ek1	0.28	0.54	53.5	0.26	2.89	0.75	0.25	0.19	2.52	0.14	0.19	2.73	2.52
20	WX133	3179.4–3185.8	Ek1	0.18	0.45	59.5	0.32	2.28	0.74	0.23	0.18	2.36	0.14	0.18	2.90	2.36

No. = Sample number; R1 = C_{26}/C_{28} 20S TAS; R2 = C_{27}/C_{28} 20R TAS; R3 = $C_{28}/(C_{26} + C_{27} + C_{28})TAS \times 100\%$; R4 = C_{29} 3M-24E-TAS/(C_{27} 4M-TAS + C_{29} 4M-24E-TAS); R5 = $(C_{27}$ 4M-TAS C_{29} 4M-24E-TAS)/Dino-TAS; R6 = C_{29} 3M-24E-TAS/Dino-TAS; R7 = Peak 1/Peak 2; R8 = Peak 8/Peak 9; R9 = Peak 16/Peak 17; R10 = Peak 6/Peak 7; R11 = Peak (7 + 14)/Peak (9 + 16); R12 = Peak (9 + 16)/Dino-TAS; R13 = Peak 2/Peak (7 + 14). Peak 1, 2, 6, 7, 8, 9, 14, 16 and 17 are marked in Fig. 7.

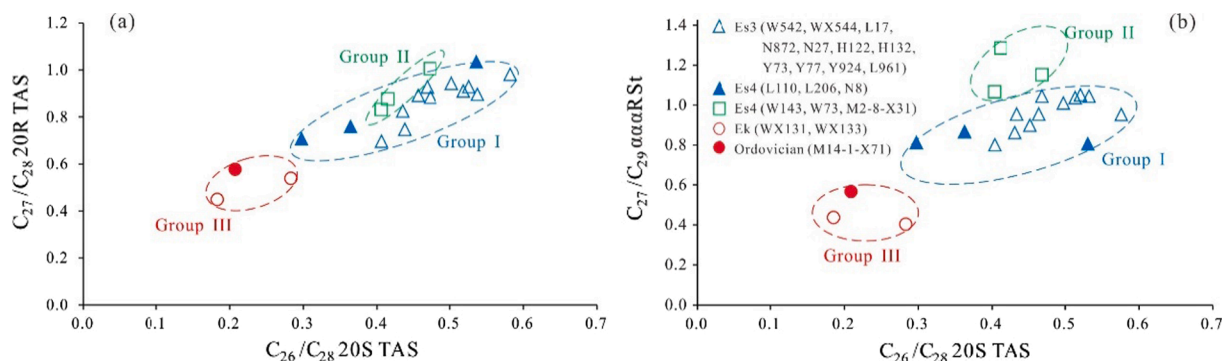


Fig. 6. Plots of: (a) C_{27}/C_{28} 20R TAS vs the C_{26}/C_{28} 20S TAS and (b) C_{27}/C_{29} $\alpha\alpha\alpha$ R St vs the C_{26}/C_{28} 20S TAS for the crude oils from the Es3, Es4, Ek1, and Ordovician reservoirs in the different wells.

based on the norcholestanes (Fig. 4a and b). However, the low abundances of dino-TAS in the Group III oils coincides with their low abundances of 24-norcholestanes (Fig. 4c), which suggests that Group III oils may be originated from a set of source rocks with minor contributions from dinoflagellates.

Although both Group I and II oils have abundant dino-TAS, Group II oils have unique features, including lower abundances of C_{27} 4-methyltri-aromatic steroids (C_{27} 4M-TAS, Peak 2 in Fig. 7b) and C_{29} 4-methyl-24-ethyltri-aromatic steroids (C_{29} 4M-24E-TAS, Peaks 9 and 16 in Fig. 7b) compared to those of Group I oils (Fig. 7a). In contrast, Group III oils have extremely high abundances of C_{27} 4M-TAS and C_{29} 4M-24E-TAS (Fig. 7c). Moreover, based on four cross-plots of the related parameters of the triaromatic steroids, including C_{29} 3M-24E-TAS/Dino-TAS vs C_{29} 3M-24E-TAS/(C_{27} 4M-TAS + C_{29} 4M-24E-TAS) (Fig. 8a), (C_{27} 4M-TAS + C_{29} 4M-24E-TAS)/Dino-TAS vs C_{29} 3M-24E-TAS/(C_{27} 4M-TAS + C_{29} 4M-24E-TAS) (Fig. 8b), Peak 1/Peak 2 vs Peak 8/Peak 9 (Fig. 9a), and Peak 1/Peak 2 vs Peak 16/Peak 17 (Fig. 9b), we easily classified the 20 crude oil samples into three oil groups.

4.4. Hierarchical cluster analysis

In addition to using several source-related or sedimentary environment-related parameters, hierarchical cluster analysis (HCA) is also widely used in oil-source rock correlation and crude oil

classification (Hao et al., 2009a; Xiao et al., 2019b). HCA of thirteen multiple parameters was conducted on the 20 crude oil samples (Table 2), and three oil groups were identified (Fig. 10), which is same as the classification results based on the distributions of the steranes, norcholestanes and triaromatic steroids.

Group I oils consist of samples 1–14, which have relatively high concentrations of 4-methylsteranes, diasteranes, 24-norcholestanes and dino-TAS (Figs. 3a, 4a and 7a). This indicates that they were generated from a source rock with a large amounts of dinoflagellates (*Bohaidina-Parabohaidina*) contribution. The characteristics of Group I oils are consistent with the lower Es3-derived oils (Zhu et al., 2004; Zhang et al., 2009), revealing that the oil originated from the lower Es3 source rock.

Group II oils include samples 15–17, which have low 4-methylsteranes contents, and high 21- and 27-norcholestanes contents (Fig. 3b and 4b). This suggests that the related source rock was formed in an evaporative and saline environment (Bao and Li, 2001; Wang et al., 2008). The Es4 source rock in the study area is known to have been deposited in a saline and reducing environment (Pang et al., 2003; Li et al., 2003, 2010; Zhang et al., 2003, 2009). Therefore, Group II oils are considered to be sourced from the upper Es4 source rock.

Group III oils include samples 18–20, which were collected from the Kongdian (Ek) and Ordovician reservoirs. Moreover, Group III oils have the characteristics of: (1) distinct abundance of C_{29} steranes (Fig. 3c) and C_{28} TAS (Fig. 5c), (2) significantly lower 24- and 27-norcholestanes

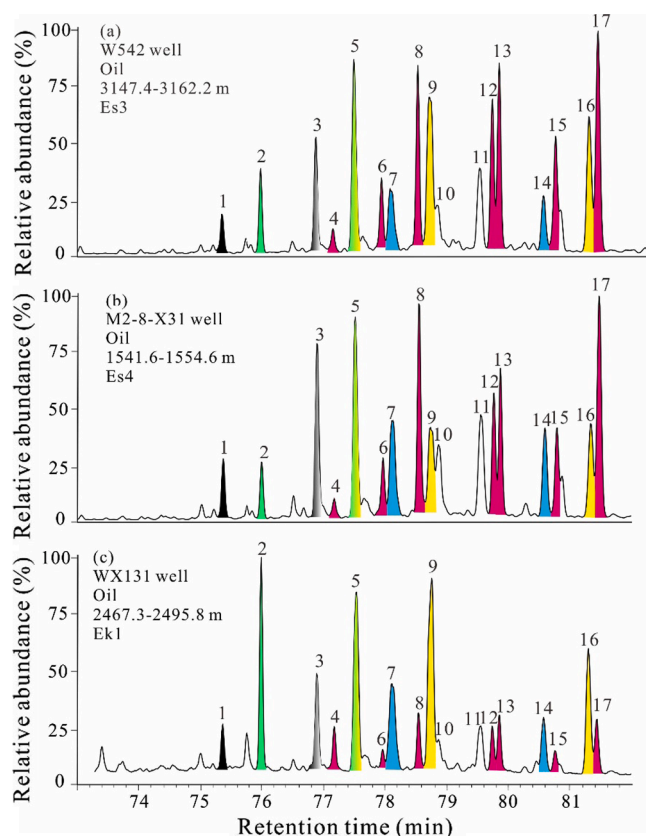


Fig. 7. Representative mass chromatograms (m/z 245) of the methyltri-aromatic steroids and dino-TAS in the crude oils. Notes: 1 = C_{27} 3-methyltri-aromatic steroids; 2 = C_{27} 4-methyltri-aromatic steroids; 3 = C_{27} 3-methyltri-aromatic steroids + C_{28} 3,24-dimethyltri-aromatic steroids; 4 = C_{29} 4,23,24-trimethyltri-aromatic steroids; 5 = C_{27} 4-methyltri-aromatic steroids + C_{29} 4-methyl-24-ethyltri-aromatic steroids; 6 = C_{29} 4,23,24-trimethyltri-aromatic steroids; 7 = C_{29} 3-methyl-24-ethyltri-aromatic steroids; 8 = C_{29} 4,23,24-trimethyltri-aromatic steroids; 9 = C_{29} 4-methyl-24-ethyltri-aromatic steroids; 10 = C_{28} 3,24-dimethyltri-aromatic steroids; 11 = C_{28} 3,24-dimethyltri-aromatic steroids; 12 = C_{29} 4 α ,23,24-trimethyltri-aromatic steroids; 13 = C_{29} 4 α ,23,24-trimethyltri-aromatic steroids; 14 = C_{29} 3-methyl-24-ethyltri-aromatic steroids; 15 = C_{29} 4 α ,23,24-trimethyltri-aromatic steroids; 16 = C_{29} 4 α -methyl-24-ethyltri-aromatic steroids; 17 = C_{29} 4 α ,23,24-trimethyltri-aromatic steroids.

contents than 24- and 27-nordiacholestanes contents (Fig. 4c), and (3) extremely low dino-TAS contents compared to the contents of the other 4M-TAS (Fig. 7c). The above features are completely different from the two established oil groups (Group I and II oils) and the two confirmed

source rocks (the lower Es3 and upper Es4 source rocks) in the study area. Moreover, the values of $C_{29}St\ 20S/(20S + 20R)$ and $C_{29}St\ \beta\beta/(\beta\beta + \alpha\alpha)$ are in the range of 0.38–0.47 and 0.39–0.50 (Table 1), respectively, which are also consistent with the results reported in previous literature (Zhan et al., 2019). The value ranges indicate that these two parameters of the oil samples have not yet reached the equilibrium values (0.52–0.55 and 0.67–0.71, respectively) (Seifert and Moldowan, 1986). Consequently, these parameters can provide reliable information for their source and be used in oil group classification analysis.

4.5. Origin of Group III oils

Several previous studies have reported that some of the discovered oil reservoirs in the Southern Slope in the Dongying Depression have more complicated geochemical characteristics (Li et al., 2005a, 2005b; Meng et al., 2011). Generally, these oils are regarded as mixed oils because some of their characteristics are similar to those of the lower Es3-derived oils and the upper Es4-derived oils (Li et al., 2005a, 2005b; Meng et al., 2011). For example, the high gammacerane index values and low C_{35}/C_{34} 22S hopane values in these oils are representative signatures of the upper Es4-derived oils and the lower Es3-derived oils, respectively.

In this study, Group III oils were collected from the Kongdian and Ordovician reservoirs in the Southern Slope (Fig. 1). These oil samples also have abnormally high C_{29} steranes abundances (Fig. 3c), which may indicate a great contribution of green algae (Kodner et al., 2008; Summons and Erwin, 2018). Moreover, their low 24-norcholestanes contents and limited dino-TAS may suggest minor contributions from diatoms and dinoflagellates (Volkman, 2003; Holba et al., 1998a, 1998b; Rampen et al., 2007). The distributions of the C_{27} – C_{29} regular steranes, norcholestanes and triaromatic steroids are significantly different from those of the two confirmed source rocks, so it is not possible that Group III oils have mixed sources, including the upper Es4 and the lower Es3 source rocks.

The stable carbon isotope composition of crude oil can directly reflect the kerogen types and can indicate the characteristics of the biogenetic organic matter (Galimov, 2006). In this study, the stable carbon isotope compositions of representative samples from three oil groups were analyzed. The $\delta^{13}C$ values of the representative oil samples of Group I oils (from Y73 and N27 wells) and Group II oils (from W73 and M2-8-X31 wells) and their four fractions are -28.8‰ to -26.7‰ and higher than -29‰ (Fig. 11). However, the representative oil samples from Group III oils (from WX131 and WX133 wells) and their four fractions are depleted in ^{13}C and have lower $\delta^{13}C$ values (-28.9‰ to -29.7‰) than Group I and II oils (Fig. 11). Because all of the oil samples have a relatively low thermal maturity (Table 1), the ^{13}C depletion of Group III oils indicates that its source rock may have greater inputs from bacteria and/or algae (e.g., green algae) than the lower Es3 and the

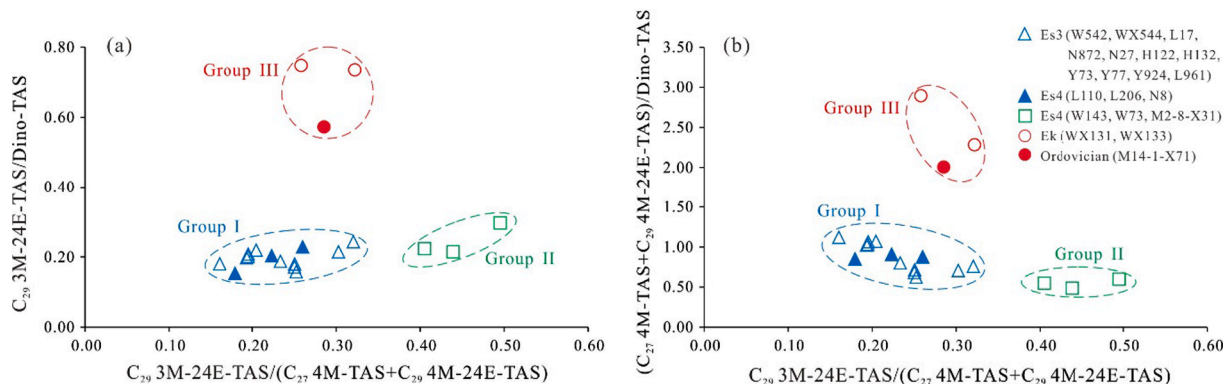


Fig. 8. Plots of (a) $C_{29}\ 3M-24E-TAS/Dino-TAS$ vs $C_{29}\ 3M-24E-TAS/(C_{27}\ 4M-TAS + C_{29}\ 4M-24E-TAS)$ and (b) $(C_{27}\ 4M-TAS + C_{29}\ 4M-24E-TAS)/Dino-TAS$ vs $C_{29}\ 3M-24E-TAS/(C_{27}\ 4M-TAS + C_{29}\ 4M-24E-TAS)$ for the crude oils from the Es3, Es4, Ek1, and Ordovician reservoirs in the different wells.

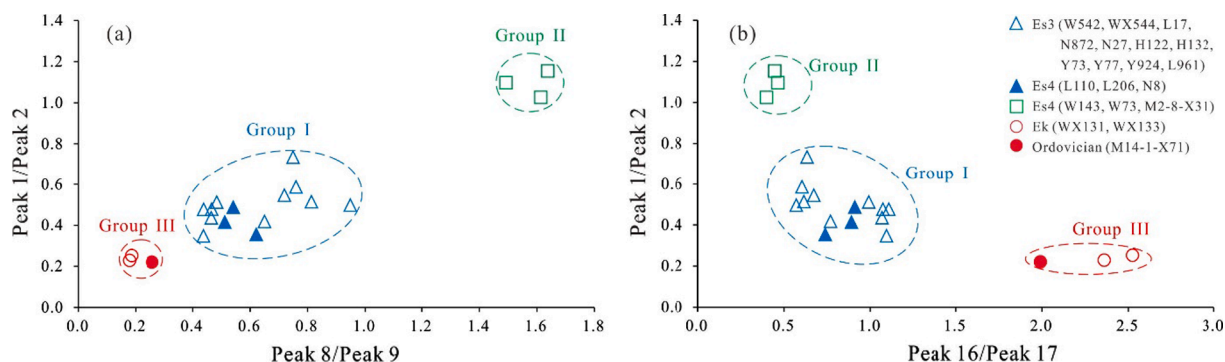


Fig. 9. Plots of (a) Peak 1/Peak 2 vs Peak 8/Peak 9 and (b) Peak 1/Peak 2 vs Peak 16/Peak 17 for the crude oils from the Es3, Es4, Ek1, and Ordovician reservoirs in the different wells. Note: Peaks 1, 2, 8, 9, 16, and 17 are marked in Fig. 7.

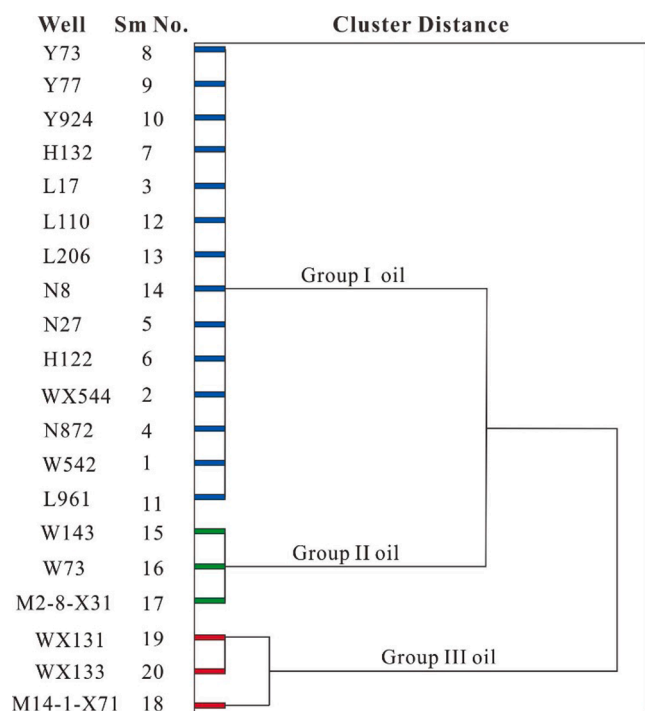


Fig. 10. Hierarchical cluster analysis showing the crude oil groups. Note: Sm No. = sample number in Table 2.

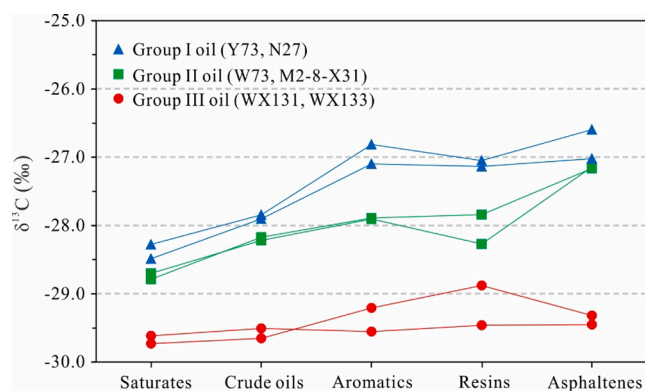


Fig. 11. Carbon isotope distribution patterns of the crude oils and their fractions for the different oil groups.

upper Es4 source rocks.

Overall, Group III is a distinct oil group with unmixed sources, and the related source rock still needs to be clarified. Group III oils have relatively higher maturity than those in the overlying Shahejie Formation (Table 1), and contain a greater contribution of green algae than diatoms and dinoflagellates, we speculate that Group III oils may have been generated from source rocks of the Cretaceous or from older strata.

5. Conclusions

Based on a detailed analysis of the steranes, norcholestanes, triaromatic steroids, methyl-triaromatic steroids, and isotope compositions of 20 oil samples from the Dongying Depression, a distinct oil group composed of three oil samples collected from the Kongdian Formation and Ordovician reservoirs was clearly identified. This oil group is completely different from the two confirmed oil groups derived from the lower Es3 and upper Es4 source rocks. The ^{13}C depletion for the distinct oil group may suggest that its related source rock had greater bacteria/algae inputs than the lower Es3 and the upper Es4 source rocks. Moreover, their abnormally high concentrations of C_{29} steranes and low concentrations of 24- and 27-norcholestane indicate that green algae made a more dominant organic matter contribution to its related source rock than dinoflagellates. The results of this study reveal that the norcholestanes and triaromatic steroid parameters may have broad application prospects in complicated petroleum exploration fields and can at least be well applied in the Dongying Depression.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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