

Article

Some Biogenic-Related Compounds Occluded inside Asphaltene Aggregates

Chupeng Yang, Zewen Liao, Lvhui Zhang, and Patrice Creux

Energy Fuels, **2009**, 23 (2), 820-827 • DOI: 10.1021/ef8007294 • Publication Date (Web): 22 December 2008

Downloaded from <http://pubs.acs.org> on March 3, 2009

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



ACS Publications
High quality. High impact.

Energy & Fuels is published by the American Chemical Society, 1155 Sixteenth Street N.W., Washington, DC 20036

Some Biogenic-Related Compounds Occluded inside Asphaltene Aggregates

Chupeng Yang,[†] Zewen Liao,^{*,†} Lvhui Zhang,[†] and Patrice Creux[‡]

State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, People's Republic of China, and Laboratoire des Fluides Complexes, UMR 5150 TOTAL-CNRS-UPPA, BP 1155, 64013 Pau Cedex, France

Received August 30, 2008. Revised Manuscript Received November 10, 2008

The occluded compounds inside asphaltene aggregates were released from 16 asphaltenes through mild degradation processes oxidized by the H₂O₂/CH₃COOH system. Prior to the oxidation procedure, all of the *n*-C₇ asphaltenes (*n*-heptane-insoluble asphaltenes) were subjected to Soxhlet extraction by acetone continuously for 240 h to rule out interferences from the adsorbed/co-precipitated compounds, which were likely introduced during the asphaltene preparation processes. Among these occluded compounds, a series of even-carbon-numbered *n*-alk-(1)-enes were detected from 13 asphaltenes, 22,29,30-trisnorhop-17(21)-ene and 17 α -hop-20(21)-ene were simultaneously detected from 3 asphaltenes, and C₂₃ tricyclic terp-12(13)-ene and C₂₉ 18 α -30-norneohop-13(18)-ene were found co-existent in another 3 asphaltenes. From all 16 asphaltenes, a series of *n*-alkanoic acid ethyl esters were detected from the occluded compounds, which were generally dominated by the even-carbon-numbered *n*-alkanoic acids in the esters. The above-reported compounds occluded inside asphaltene aggregates are interpreted as hydrocarbon representatives of materials generated from kerogen at an early stage. These unusual compounds were not detected from the crude oil maltenes or from the acetone extracts of asphaltenes, except for some *n*-alkanoic acid ethyl esters that were observed in the acetone extracts of a few asphaltenes. The occurrence of a series of even-carbon-numbered *n*-alk-(1)-enes and some terpenes inside asphaltene aggregates indicated that the macromolecular structures of asphaltenes have protected these compounds from being influenced by the alteration processes in the oil reservoirs and enable them to survive over geological time. In consequence, the geochemical study of these occluded compounds should be very meaningful, especially for heavily altered oils, such as biodegraded oils, from which it is difficult to obtain useful geochemical information directly from the crude oil maltenes because the hydrocarbons have been heavily depleted.

1. Introduction

Asphaltene aggregates have been studied widely during the past few decades. Asphaltene molecules are suggested to contain aromatic cores connected by aliphatic chains and some heteroatoms.^{1–7} These structural features enable asphaltenes to form complex three-dimensional structural configurations.^{8–14} Asphaltenes were reported to exist as aggregates even in solvent, such as toluene, in a very low concentration of a few tens of parts per million (ppm) measured by different methods.^{4,15–20} The asphaltene aggregates were reported as irregular spheres,^{21–23} inside which microscopic cages or caves can be formed.^{24–26}

The structural features of asphaltene aggregates enable them to adsorb and occlude other molecules from the bulk crude oils.^{26–28} Acevedo et al.¹² used the host–guest model to illustrate the trapping of a guest molecule by a folded asphaltene configuration at the molecule level. This kind of trapping of the other molecules into asphaltene aggregates should occur much more extensively at the aggregate level. A thermodynamically favorable interaction between *n*-alkanes and petroleum asphaltenes also indicated that some other fractions can be

* To whom correspondence should be addressed. Fax: +86-20-85290706. E-mail: liaozw@gig.ac.cn or zw_liao@hotmail.com.

[†] Chinese Academy of Sciences.

[‡] UMR 5150 TOTAL-CNRS-UPPA.

(1) Calemme, V.; Rausa, R.; D'Antona, P.; Montanari, L. *Energy Fuels* **1998**, *12*, 422–428.

(2) Strausz, O. P.; Mojelsky, T. W.; Faraji, F.; Lown, E. M.; Peng, P. *Energy Fuels* **1999**, *13*, 207–227.

(3) Strausz, O. P.; Mojelsky, T. W.; Lown, E. M.; Kowalewski, I.; Behar, F. *Energy Fuels* **1999**, *13*, 228–247.

(4) Buenrostro-Gonzalez, E.; Groenzin, H.; Lira-Galeana, C.; Mullins, O. C. *Energy Fuels* **2001**, *15*, 972–978.

(5) Sheremata, J.; Gray, M.; Dettman, H.; McCaffrey, W. *Energy Fuels* **2004**, *18*, 1377–1384.

(6) Stachowiak, C.; Viguie, J. R.; Grolier, J. P.; Rogalski, M. *Langmuir* **2005**, *21*, 4824–4829.

(7) Long, J.; Xu, Z. H.; Masliyah, J. H. *Langmuir* **2007**, *23*, 6182–6190.

(8) Schabron, J. F.; Speight, J. G. *Pet. Sci. Technol.* **1998**, *16*, 361–375.

(9) Murgich, J.; Abanero, J. A.; Strausz, O. P. *Energy Fuels* **1999**, *13*, 278–286.

(10) Rahmani, N. H. G.; Dabros, T.; Masliyah, J. H. *J. Colloid Interface Sci.* **2005**, *285*, 599–608.

(11) Rahmani, N. H. G.; Dabros, T.; Masliyah, J. H. *Ind. Eng. Chem. Res.* **2005**, *44*, 75–84.

(12) Acevedo, S.; Castro, A.; Negrin, J. G.; Fernandez, A.; Escobar, G.; Piscitelli, V.; Delolme, F.; Dessalces, V. *Energy Fuels* **2007**, *21*, 2165–2175.

(13) Sirota, E. B.; Lin, M. Y. *Energy Fuels* **2007**, *21*, 2809–2815.

(14) Barré, L.; Simon, S.; Palermo, T. *Langmuir* **2008**, *24*, 3709–3717.

(15) Roux, J.; Broseta, D.; Deme, B. *Langmuir* **2001**, *17*, 5085–5092.

(16) Savvidis, T.; Fenistein, D.; Barré, L.; Behar, E. *AIChE* **2001**, *47*, 206–211.

(17) Porte, G.; Zhou, H.; Lazzeri, V. *Langmuir* **2003**, *19*, 40–47.

(18) Goncalves, S.; Castillo, J.; Fernandez, A.; Hung, J. *Fuel* **2004**, *83*, 1823–1828.

(19) Andreatta, G.; Bostrom, N.; Mullins, O. C. *Langmuir* **2005**, *21*, 2728–2736.

(20) Evdokimov, I. N.; Eliseev, N. Y.; Akhmetov, B. R. *Fuel* **2006**, *85*, 1465–1472.

steadily occluded inside asphaltene aggregates.^{6,29} Then, some biomarkers generated at an earlier stage of conversion can be occluded inside asphaltene aggregates and preserved over the geological time scale because of the efficient protection from the macromolecular structures of asphaltenes. Recently, Behar et al.³⁰ reported that the primary cracking of kerogen generated a lot of NSO compounds (molecules with heteroatoms, such as nitrogen, sulfur, oxygen, etc.), and the hydrocarbon generation was mainly from the secondary cracking of those NSO compounds. It seemed that the occlusion phenomenon inside asphaltene aggregates might take place during this primary cracking process before asphaltenes were detached from kerogens.³¹

During the past few years, we studied the occluded compounds inside asphaltenes mainly to probe into the structural features of asphaltenes.^{26,27,31,32} A mild oxidative system of $\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$ has been used to release the occluded compounds from asphaltenes, and the detailed release mechanism has been reported in our previous work.³¹ Prior to the oxidation processes, an acetone Soxhlet extraction of the initial $n\text{-C}_7$ asphaltenes continuously for 240 h has been applied to rule out interferences from the adsorbed/co-precipitated compounds introduced during the asphaltene preparation process.^{27,31} From the oxidation products of asphaltenes, the saturated hydrocarbons obtained generally amounted to around 0.5 wt % based on the initial asphaltenes used in the experiments. Because $\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$ oxidation can release the occluded hydrocarbons from asphaltene structures without interference from the cleaved hydrocarbons covalently bonded to asphaltene molecules, the covalently bonded chains should be cleaved as polar compounds, such as carboxyl acids, under these oxidation conditions. Therefore, the saturated hydrocarbons obtained from the oxidation products of asphaltenes were not generated by bond cracking but from the occluded components inside asphaltene aggregates.

In this work, the occluded compounds from 16 asphaltenes were released by the $\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$ oxidation procedure. Some unusual biomarkers, including some terpenes and a series of esters, were detected as part of the occluded compounds, and their possible geochemical implication was discussed.

2. Experimental Section

2.1. Preparation and Pretreatment of $n\text{-C}_7$ Asphaltenes. All 16 crude oils were collected from the Tarim Basin, northwest China. All of these oils (except for sample Ym321) were derived from marine source rocks, while crude oil Ym321 was a mixed oil

derived from the marine and terrestrial source rocks. The asphaltene contents of these oils were typically 5–10 wt %. The standard reagent, palmitic acid ethyl ester (purity > 99%), was purchased from Sigma-Aldrich, Inc., St. Louis, MO. All solvents used in this work were analytical-purity-grade and redistilled prior to use.

Asphaltenes were prepared from the crude oils by n -heptane precipitation, and the detailed procedure has been reported in our previous work.^{27,31} In short, a certain amount of crude oil was first dispersed with a small amount of dichloromethane, then n -heptane (500 mL) was added, and the mixture was stirred for about 12 h and left overnight in the dark. The asphaltene precipitate was isolated by centrifugation (3500 rpm for 5–8 min). After centrifugation and removal of the supernatant, the asphaltenes were further washed ($\times 2$) in the polytetrafluoroethylene (PTFE) centrifugation tube with n -heptane until the supernatant was almost colorless.

The above-obtained $n\text{-C}_7$ asphaltenes were subjected to Soxhlet extraction with acetone continuously for 240 h to rule out the interferences from the adsorbed/co-precipitated compounds introduced from the asphaltene preparation processes. The acetone extracts were separated into residue and the maltene fraction using n -heptane. The maltenes were further separated into saturates, aromatics, and resins using $\text{SiO}_2/\text{Al}_2\text{O}_3$ column chromatography eluted by n -heptane, toluene, and ethanol, respectively. The acetone-extracted asphaltenes (obtained from the Soxhlet extractor by chloroform extracting for another 72 h) were then subjected to the oxidation procedure as described below.

2.2. Oxidation of the Acetone-Extracted Asphaltenes. Details for the description of the asphaltene oxidation procedure can be found in our previous report.³¹ In summary, around 400–600 mg of acetone-extracted asphaltenes were transferred into a 250 mL flask using 20 mL of benzene and then H_2O_2 (10 mL) and CH_3COOH (20 mL) were mixed in a 50 mL beaker and slowly transferred into the flask containing the asphaltenes, with stirring throughout. The reaction was carried out at ambient temperature (around 25 °C) with vigorous stirring for 48 h.

2.3. Separation of the Oxidation Products of Asphaltenes. The above reaction products were transferred into a 250 mL separating funnel (PTFE material) using 50 mL of chloroform, and another 50 mL of chloroform was added into the separating funnel. The organic layer was collected and dried using anhydrous Na_2SO_4 . The organic phase was reduced to constant weight using a rotary evaporator. This organic phase can be further separated into CH_2Cl_2 -soluble and CH_2Cl_2 -insoluble fractions. The CH_2Cl_2 -soluble fraction was precipitated with n -heptane into residues and maltenes, and the later fraction was then further separated into saturates, aromatics, and resins using $\text{SiO}_2/\text{Al}_2\text{O}_3$ column chromatography, eluted with n -heptane, toluene, and ethanol, respectively.

2.4. Elemental Analysis of $n\text{-C}_7$ Asphaltenes. The oxygen content (wt %) of all of the $n\text{-C}_7$ asphaltenes was performed on a Heraeus CHN-O-RAPID analyzer, and the C, H, N contents (wt %) were performed on an Elementar Vario EL III analyzer. Each asphaltene was run at least twice for a specific element analysis, and the reported results were the average values of the data obtained from the instruments.

2.5. Gas Chromatography–Mass Spectrometry (GC–MS) Analysis. Full-scan GC–MS was performed using a Platform II MS detector combined with an HP6890 GC analyzer. The GC was fitted with a split/splitless injector, and a VF-5 MS column (60 m \times 0.32 mm \times 0.25 μm) was used. Helium was used as the carrier gas (1.2 mL/min). The oven temperature was initially set at 80 °C for 4 min, programmed to 290 °C at 4 °C/min, and then held isothermally for 45 min. The MS was operated with an ionization energy of 70 eV, a source temperature of 155 °C, an electron multiplier voltage of 1765 V, and a mass range of 50–550 amu.

3. Results and Discussion

For all of the $n\text{-C}_7$ asphaltenes used in this work, the elemental results were listed in Table 1, among which Tz12 and Tz122 (O) with a high H/C ratio may imply the low maturity of the oils. However, Ym321 from mixed source rocks of marine and

(21) Tanaka, R.; Hunt, J. E.; Winans, R. E.; Thiagarajan, P.; Sato, S.; Takanoashi, T. *Energy Fuels* **2003**, *17*, 127–134.

(22) Tanaka, R.; Sato, E.; Hunt, J.; Winans, R.; Sato, S.; Takanoashi, T. *Energy Fuels* **2004**, *18*, 1118–1125.

(23) Espinat, D.; Fenistein, D.; Barré, L.; Frot, D.; Briolant, Y. *Energy Fuels* **2004**, *18*, 1243–1249.

(24) Acevedo, S.; Escobar, G.; Ranaudo, M. N.; Pinate, J.; Amorin, A. *Energy Fuels* **1997**, *11*, 774–778.

(25) Leon, O.; Contreras, E.; Rogel, E.; Dambakli, G.; Acevedo, S.; Carbognani, L.; Espidel, J. *Langmuir* **2002**, *18*, 5106–5112.

(26) Liao, Z.; Zhou, H.; Gracia, A.; Chrostowska, A.; Creux, P.; Geng, A. *Energy Fuels* **2005**, *19*, 180–186.

(27) Liao, Z.; Geng, A.; Gracia, A.; Creux, P.; Chrostowska, A.; Zhang, Y. *Energy Fuels* **2006**, *20*, 1131–1136.

(28) Aguilera-Mercado, B.; Herdes, C.; Murgich, J.; Muller, E. A. *Energy Fuels* **2006**, *20*, 327–338.

(29) Mahmoud, R.; Gierycz, P.; Solimando, R.; Rogalski, M. *Energy Fuels* **2005**, *19*, 2474–2479.

(30) Behar, F.; Lorient, F.; Lewan, M. *Org. Geochem.* **2008**, *39*, 1–22.

(31) Liao, Z.; Gracia, A.; Laporte-Chrostowska, A.; Creux, P.; Geng, A. *Org. Geochem.* **2006b**, *37*, 291–303.

(32) Liao, Z.; Geng, A. *Org. Geochem.* **2002**, *33*, 1477–1486.

Table 1. Elemental Analysis Results of the Initial *n*-C₇ Asphaltenes

sample	wt %				atomic ratio		
	C	H	O	N	H/C	O/C	N/C
Lg7	83.20	8.66	1.15	1.13	1.249	0.0104	0.0115
Td2	80.92	9.16	4.90	0.90	1.358	0.0454	0.0095
Tz122 (S)	86.17	9.23	0.83	0.92	1.285	0.0072	0.0092
Tz122 (O)	85.39	11.07	1.41	0.66	1.556	0.0124	0.0066
Tz104	85.95	8.81	1.41	0.66	1.230	0.0123	0.0066
Tz69	86.75	9.15	1.11	0.72	1.266	0.0096	0.0071
Tz30	87.20	9.06	1.48	0.71	1.247	0.0127	0.0070
Tz35	86.72	8.81	1.03	0.76	1.219	0.0089	0.0075
Tz406	82.48	9.30	1.83	0.57	1.353	0.0166	0.0059
Tz117	84.35	8.64	1.20	0.75	1.229	0.0107	0.0076
Tz4-7-38	84.78	8.34	1.48	0.89	1.180	0.0131	0.0090
Tz12	83.35	11.24	1.99	0.56	1.618	0.0179	0.0058
Ym321	83.14	8.25	2.17	0.78	1.191	0.0196	0.0080
Dh1-6-9	80.12	7.16	1.81	1.18	1.072	0.0169	0.0126
Ym2	78.97	8.70	4.27	0.98	1.322	0.0406	0.0106
Hd4	83.07	8.58	0.99	1.01	1.239	0.0089	0.0104

terrestrial inputs cannot be differentiated from the others by the elemental results. Table 2 showed the mass percentage of different fractions from the experimental processes based on the initial *n*-C₇ asphaltenes. Following the experimental procedures, the acetone extracts of the initial *n*-C₇ asphaltenes generally amounted to around 10–20 wt % and the *n*-hexane solubles from the oxidation products of the acetone extracted asphaltenes can be up to about 10 wt % (DM fraction in Table 2), among which the *n*-hexane and toluene effluents from the DM fraction through the SiO₂/Al₂O₃ column usually were between 0.5 and 3 wt % (DMS and DMA fractions in Table 2).

The relative percentage (wt %) of AMS, AMA, and AMR fractions from the acetone extracts of asphaltenes were showed in Figure 1, and similarly, the ternary diagram in Figure 2 showed the percentage of DMS, DMA, and DMR fractions from the oxidation products of the corresponding acetone-extracted asphaltenes. The highest AMS concentration in Figure 1 was found for samples Tz12, Tz122 (O), and Tz406, which were in agreement with their high H/C ratios in Table 1 and may imply the relatively lower maturity of these samples. Similarly, in Figure 2, the highest DMS concentration was found for samples Tz12 and Tz122 (O), which may be associated with their low maturity level of the oils. From the acetone extracts, the samples distributed toward the AMS fraction, while from the oxidation products of asphaltenes, the samples showed their distribution toward the DMR fraction (Figures 1 and 2). This can be ascribed to the fact that some polar compounds have been introduced into the oxidation products as the DMR fraction during the oxidation process of asphaltenes, and therefore, DMR was the dominated compound from the oxidation products.

From the DMS fractions of most of the samples, even-carbon-numbered *n*-alk-(1)-enes and some terpenes were detected and a series of *n*-alkanoic acid ethyl ester compounds were found from the DMA fractions for all of the 16 asphaltenes.

3.1. Even-Carbon-Numbered *n*-Alk-(1)-enes Occluded inside Asphaltene Aggregates. A series of even-carbon-numbered *n*-alk-(1)-enes have been detected from the oxidation products of acetone-extracted asphaltenes for 13 samples but not found for Tz104, Td2, or Ym321 asphaltenes. Figure 3 showed the chromatogram of the *n*-hexane effluents (DMS fraction) from the oxidation products of Tz406 asphaltene: the distribution features of the even-carbon-numbered *n*-alk-(1)-enes were typically similar for all of the other 12 samples. The mass spectrum in the inset of Figure 3 indicates that the double bond should be positioned at C1/C2 because the fragment ion of “M-28” was clearly present in the mass spectrum. Only even-carbon-

numbered *n*-alk-(1)-enes were found from the DMS fractions, while a complete series of *n*-alkanes were present in Figure 3 with a slight even carbon predominance. These occluded even-carbon-numbered *n*-alk-(1)-enes and alkanes with a slight even-carbon predominance suggest their lower maturity compared to those from oil maltenes, because they have been well-protected by and then preserved inside asphaltene macromolecular structures.

This series of alkenes cannot be produced from the oxidation procedure through a chemical reaction with H₂O₂/CH₃COOH. Moreover, if these alkenes were produced from some other compounds through a chemical reaction, some odd-carbon-numbered alkenes should have been detected, too. However, no odd-carbon-numbered alkenes have been detected from the DMS fraction (Figure 3). Therefore, it is reasonable to interpret these even-carbon-numbered alkenes as occluded compounds inside asphaltene aggregates.

However, this series of even-carbon-numbered *n*-alk-(1)-enes were not detected either from the crude oil maltenes or from the acetone extracts of the corresponding *n*-C₇ asphaltenes (Figure 4). It appears that occlusion of these alkenes should take place at an early stage of kerogen conversion to hydrocarbons and that these alkenes have survived for geological time inside asphaltene aggregates, owing to the protection from macromolecular structures of asphaltenes. In fact, this kind of protection effect from asphaltene macromolecular structures can also account for the occlusion phenomena for some other compounds inside asphaltene aggregates (see the following sections).

3.2. Terpene Compounds Released from Some Asphaltenes. **3.2.1. C₂₃ Tricyclic Terp-12(13)-ene and C₂₉ 18 α -30-Norneohop-13(18)-ene.** C₂₃ tricyclic terp-12(13)-ene and C₂₉ 18 α -30-norneohop-13(18)-ene were detected in the DMS fractions of Lg7, Tz122(S), and Dh1-6-9 asphaltenes (peaks P and Q in Figure 5). Identification of peaks 1–14 in Figure 5 are listed in Table 3.

Figure 6 shows the mass spectra of peaks P and Q shown in Figure 5. In Figure 6a, the molecular mass ion of *m/z* 316 indicates that peak P is a C₂₃ tricyclic terpene with one double bond eluting just before the C₂₃ tricyclic terpane (peak 1 in Figure 5). Because fragmental ion *m/z* 189 was not clearly detected in Figure 6a, the double bond cannot be in cycle A or B. The detection of fragmental ion *m/z* 259 [M - 57]⁺ suggests that one side chain should be -C₄H₉, indicating that the double bond cannot be in the side chain, either. Thus, it is reasonable to localize the double bond in cycle C, maybe at the C₁₂/C₁₃ position in cycle C because that would be in line with the other fragmental ions in Figure 6a. Peak P is therefore tentatively suggested as C₂₃ tricyclic terp-12(13)-ene. The mass spectrum in Figure 6b suggests that peak Q is C₂₉ 18 α -30-norneohop-13(18)-ene based on a comparison to the mass spectrum results from Philp³³ and Ageta et al.³⁴ Peaks X, Y, and Z in Figure 5 were tentatively assigned as the mono-unsaturated counterparts of peaks 6 and 8 because their molecular masses were 2 mass units less than their assumed counterparts and they nearly co-eluted in the chromatogram. However, the exact positions of their double bond cannot be determined in this work.

C₂₃ tricyclic terp-12(13)-ene, C₂₉ 18 α -30-norneohop-13(18)-ene, and some other unsaturated compounds, such as X, Y, and Z in Figure 5 co-exist in some DMS fractions, but these terpenes were not detected from either the bulk crude oil maltenes or

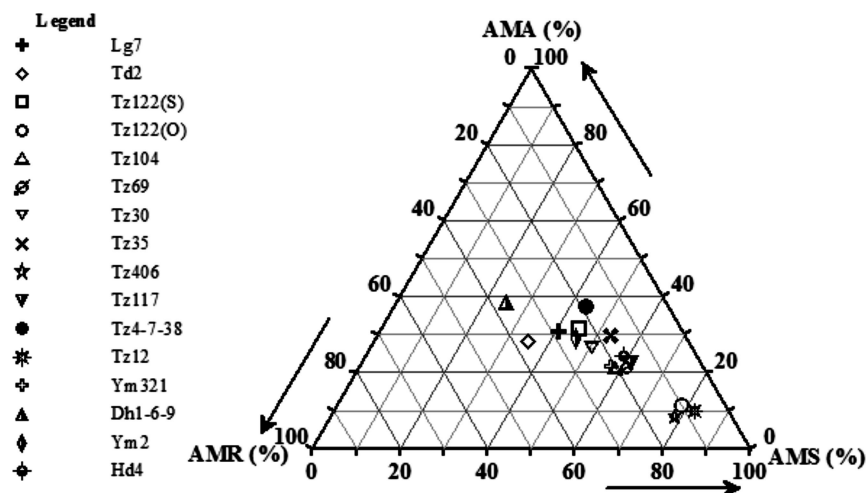
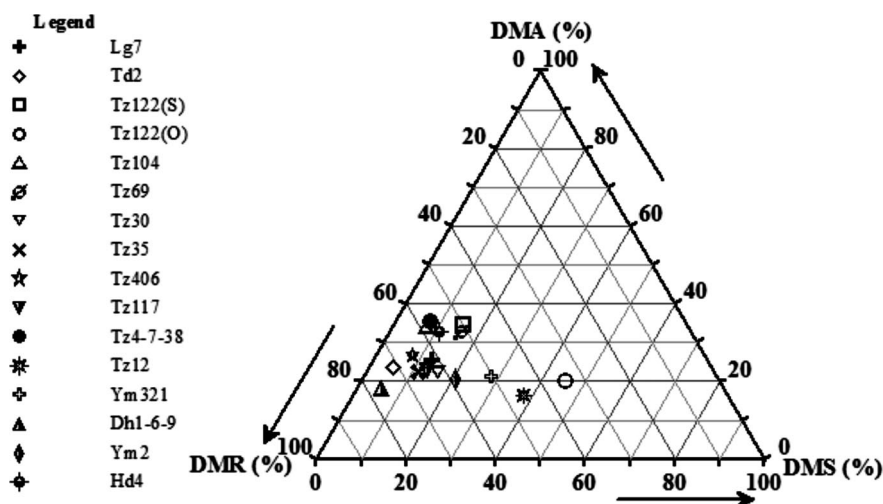
(33) Philp, R. P. *Fossil Fuel Biomarkers: Application and Spectra*; Elsevier Press: Amsterdam, The Netherlands, 1985; p 294.

(34) Ageta, H.; Shiojima, K.; Arai, Y. *Chem. Pharm. Bull.* **1987**, *35*, 2705–2716.

Table 2. Mass Percentage of Different Fractions from the Experimental Procedures^a

sample	mass of the initial <i>n</i> -C ₇ asphaltenes (g)	mass percentage based on the initial <i>n</i> -C ₇ asphaltenes (wt %)								
		A	AM	AMS	AMA	AMR	DM	DMS	DMA	DMR
Lg7	0.5970	12.46	10.12	4.13	3.14	2.85	6.10	0.78	1.56	3.75
Td2	0.5797	23.01	13.47	4.73	3.82	4.93	11.85	0.62	2.81	8.42
Tz122 (S)	0.6089	8.11	6.04	2.72	1.91	1.42	9.34	1.42	3.25	4.67
Tz122 (O)	0.4247	26.96	22.51	17.77	2.54	2.21	2.87	1.30	0.58	0.99
Tz104	0.5315	20.60	18.61	10.90	3.95	3.76	8.35	0.61	2.85	4.89
Tz69	0.6065	21.55	20.25	12.38	4.35	3.51	6.30	0.99	2.07	3.23
Tz30	0.6060	13.23	12.38	6.24	3.31	2.83	5.78	0.92	1.29	3.56
Tz35	0.6849	16.05	14.18	7.57	4.22	2.39	3.78	0.44	0.85	2.49
Tz406	0.6855	13.96	12.02	9.46	1.01	1.55	4.57	0.37	1.22	2.97
Tz117	0.6966	13.24	11.90	7.32	2.67	1.91	4.05	0.54	0.92	2.59
Tz4-7-38	0.8387	15.24	12.02	5.28	4.49	2.25	2.61	0.20	0.93	1.49
Tz12	0.8156	34.00	30.55	25.16	2.99	2.41	3.95	1.50	0.65	1.80
Ym321	1.1001	10.65	2.75	1.57	0.60	0.58	3.27	0.93	0.70	1.64
Dh1-6-9	0.7366	8.34	5.39	1.34	2.09	1.97	4.09	0.22	0.75	3.12
Ym2	1.0590	12.19	8.75	4.01	2.54	2.20	0.68	0.14	0.14	0.40
Hd4	0.8244	8.93	7.85	4.64	1.90	1.31	0.64	0.07	0.21	0.36

^a A, acetone extracts from the *n*-C₇ asphaltenes; AM, *n*-hexane solubles from the fraction A; AMS, AMA, and AMR, the saturates, aromatics, and resins from the AM fraction, respectively; DM, *n*-hexane solubles from the oxidation products of acetone-extracted asphaltenes; DMS, DMA, and DMR, effluents from the DM fractions through the SiO₂/Al₂O₃ column washing by *n*-hexane, toluene, and ethanol, respectively.

**Figure 1.** Ternary diagram showing the relative percentage (wt %) of the AMS, AMA, and AMR fractions from the acetone extracts of asphaltenes.**Figure 2.** Ternary diagram showing the relative percentage (wt %) of the DMS, DMA, and DMR fractions from the oxidation products of the corresponding acetone-extracted asphaltenes.

their corresponding AMS fractions (Figure 7). These findings indicate that the occluded fraction is in a lower maturity compared to those from the AMS or crude oil maltene fractions. It is reasonable to interpret that this series of terpenes may have

been derived from the same or somewhat similar precursors for all three of these samples and then preserved in their early configuration inside asphaltene aggregates over the geological time.

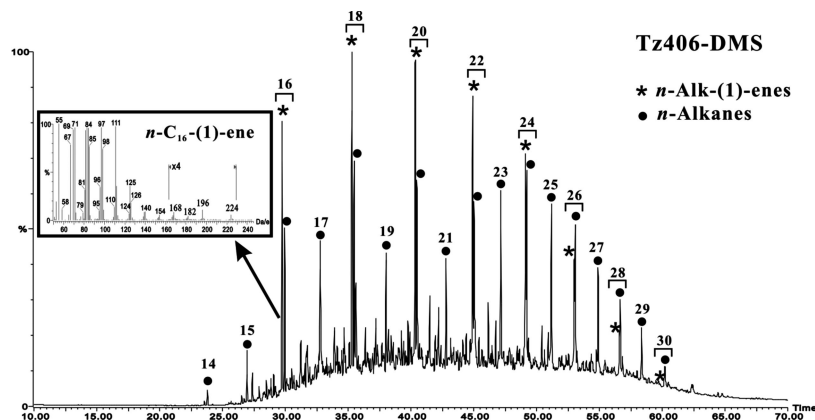


Figure 3. Chromatogram of the *n*-hexane effluents (DMS fraction) from the oxidation products of Tz406 asphaltenes. The inset is a mass spectrum to indicate that the molecule should be *n*-C₁₆-(1)-ene.

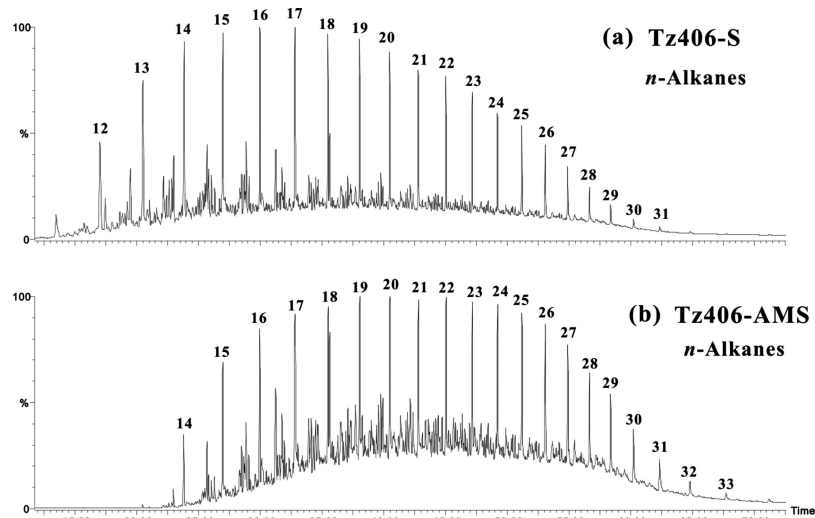


Figure 4. Saturates from (a) the crude oil maltenes of Tz406 and (b) the acetone extracts of the corresponding *n*-C₇ asphaltenes.

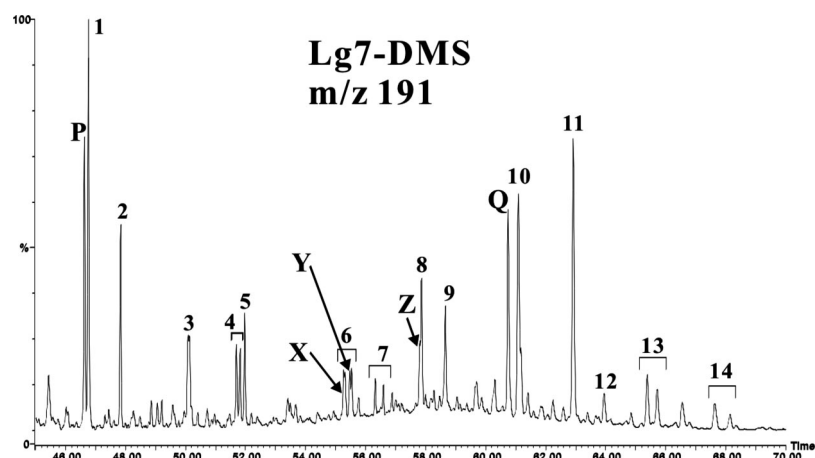


Figure 5. Partial *m/z* 191 mass chromatogram of the DMS fraction from Lg7 asphaltenes. Identification of peaks P and Q is showed in Figure 4, and peaks 1–14 are listed in Table 3.

3.2.2. *C*₂₇ 22,29,30-Trisnorhop-17(21)-ene and *C*₃₀ 17 α (*H*)-Hop-20(21)-ene. *C*₂₇ 22,29,30-trisnorhop-17(21)-ene and *C*₃₀ 17 α (*H*)-hop-20(21)-ene were found in the DMS fractions from Tz104, Tz35, and Td2 asphaltenes (peaks M and N in Figure 8 represented by Tz104). The structural identification of peaks M and N in Figure 8 was performed by comparing their relative retention time and their mass spectra characteristics to the results from Meredith et al.³⁵ These unusual terpenes have been obtained by the authors from the hydropyrolsates generated from severely biodegraded oil seep asphaltenes.³⁵ Besides the

above stated two terpene compounds, they also detected *C*₂₇ 22,29,30-trisnorhop-16(17)-ene and *C*₃₀ 17 β (*H*)-hop-20(21)-ene. However, the last 2 terpenes were not determined in our present work. According to Meredith et al.,³⁵ these unusual terpene compounds may belong to the original constituents of the bound asphaltene structure that were released by catalytic hydropyrolysis (pyrolysis assisted by high H₂ pressure over Mo) or generated from other hopenes during the hydropyrolysis procedure. However, according to our present results, these terpenes [at least for *C*₂₇ 22,29,30-trisnorhop-17(21)-ene and *C*₃₀ 17 α (*H*)-

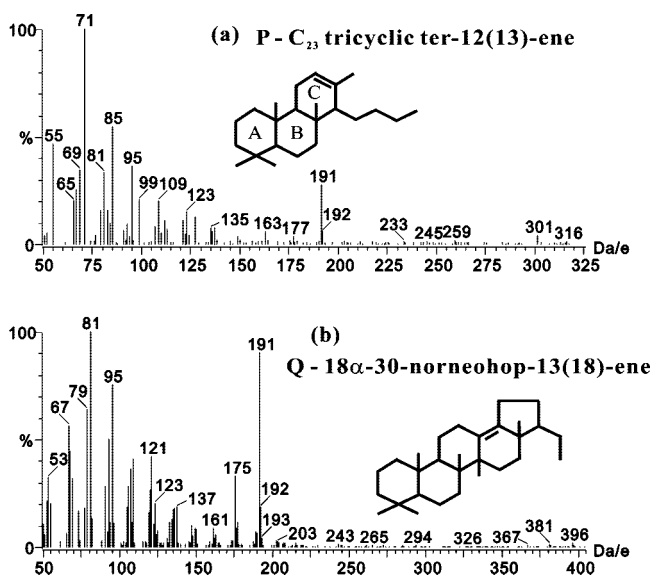
Table 3. Identification of Some Terpane Compounds in Figures 3 and 5–7

peak	identification
1	C ₂₃ tricyclic terpane
2	C ₂₄ tricyclic terpane
3	C ₂₅ tricyclic terpanes
4	C ₂₆ tricyclic terpanes
5	C ₂₄ tetracyclic terpane
6	C ₂₈ tricyclic terpane
7	C ₂₉ tricyclic terpane
8	C ₂₇ 18 α (H)-22,29,30-trisnorneohopane - Ts
9	C ₂₇ 17 α (H)-22,29,30-trisnorneohopane - Tm
10	C ₂₉ 17 α (H),21 β (H)-30-norhopane
11	C ₃₀ 17 α (H),21 β (H)-hopane
12	C ₃₀ 17 β (H),21 α (H)-hopane (C ₃₀ moretane)
13	C ₃₁ 17 α (H),21 β (H)-hopanes
14	C ₃₂ 17 α (H),21 β (H)-hopanes

hop-20(21)-ene] should belong to the occluded compounds inside asphaltene aggregates, which were then released by the experimental procedures.

Similarly, these terpene compounds were not detected from either the crude oil maltenes or the acetone extracts of their corresponding *n*-C₇ asphaltenes (Figure 9 represented by sample Tz104; identification of peaks 1–14 were listed in Table 3). Co-occurrence of the above-reported hopenes inside asphaltene aggregates from three different samples indicates that these hopenes should be derived from similar precursors for all three of these samples, which may be different from those generating C₂₃ tricyclic terp-12(13)-ene and C₂₉ 18 α -30-norneohop-13(18)-ene stated in section 3.2.1.

3.3. Series of *n*-Alkanoic Acid Ethyl Esters Occluded inside Asphaltenes. A series of *n*-alkanoic acid ethyl ester compounds have been detected from the DMA fractions for all 16 asphaltenes used in this work and at the same time from the AMA fractions for 4 asphaltenes (Lg7, Tz4-7-38, Ym321, and Tz117). In Figure 10, all of the series of *n*-alkanoic acid ethyl esters from the DMA fractions of all of the asphaltenes, except for sample Ym321, can be represented by sample Dh1-6-9 (Figure 10b), among which *n*-C₁₆ and *n*-C₁₈ alkanoic acid ethyl esters were overwhelmingly the dominant ones. While the distribution of these ethyl esters from the DMA fraction for Ym321 only showed a slight even-carbon predominance (Figure 10c) and from the AMA fractions for the above-stated 4 asphaltenes, almost only the *n*-C₁₆ alkanoic acid ethyl ester can be determined (Figure 10d).

**Figure 6.** Mass spectra and identification of (a) peak P and (b) peak Q in Figure 3.

Because acetic acid has been used in the experimental procedures, these series of ester compounds detected from the toluene eluates (DMA fractions) were first considered as possible byproducts, e.g., the acetate *n*-alkyl esters, which may have been neoformed during the oxidation process. However, the mass spectra of these compounds were not concordant with this interpretation; therefore, the standard reagent (ethyl palmitate) was used for comparison. Then, ethyl palmitate was subjected to GC–MS analysis under the same instrumental conditions as those for the DMA fraction analyses. Figure 10 shows that the GC retention time was exactly the same for the standard reagent and the corresponding compound from the DMA fractions and their mass spectra (see the inset in Figure 10a) were also the same. This indicates that these compounds from the asphaltene oxidation products should be undoubtedly a series of *n*-alkanoic acid ethyl ester molecules. Because during the oxidation process this series of ethyl esters cannot be formed without ethanol being introduced into the chemical reaction even if some *n*-alkanoic acids have been derived from the oxidation reaction of asphaltenes, therefore, these ester compounds cannot be neoformed during the oxidation process as byproducts. These esters were also determined in some AMA fractions from some samples (Figure 10d), which strongly precludes the possibility that these esters may have been introduced by the oxidation process. All of the above discussion suggests that this series of ethyl ester molecules should be identified as occluded compounds inside asphaltene aggregates and belong to the original fraction derived from kerogens.

Carboxylic esters occur widely in natural products,^{36–38} among which the *n*-alkanoic acid ethyl esters were reported to occur naturally from different sources.^{39–46} These esters can be incorporated into sediments and then as the structural units connected to kerogens, which were reported sufficiently to survive diagenesis and can enter the maturity zone, where thermally induced reactions of organic compounds take place.^{47,48} Under a slight increasing thermal stress, these esters decompose again by a concerted elimination reaction into alkenes and alkanolic acids,^{47,48} and then these esters or alkenes belong to the first compounds released from kerogens. The *n*-alkanoic acid esters might follow the concerted reaction to decompose into *n*-alk-(1)-enes and alkanolic acids. Therefore, those compounds including the above-stated ethyl esters and even-carbon-

(35) Meredith, W.; Snape, C. E.; Carr, A. D.; Hans, P.; Nytoft, H. P.; Love, G. D. *Org. Geochem.* **2008**, doi: 10.1016/j.orggeochem.2008.01.022.

(36) Peters, K. E.; Walters, C. C.; Moldowan, J. M. *The Biomarker Guide*, 2nd ed.; Cambridge University Press: Cambridge, U.K., 2005; Vol. I, Biomarkers and isotopes in the environment and human history, pp 45–71.

(37) Cranwell, P.; Eglinton, G.; Robinson, N. *Org. Geochem.* **1987**, 6, 143–152.

(38) Sturt, H. F.; Summons, R. E.; Smith, K.; Elvert, M.; Hinrichs, K. *Rapid Commun. Mass Spectrom.* **2004**, 18, 617–628.

(39) Duffield, R. M.; Fernandes, A.; McKay, S.; Wheeler, J. W.; Snelling, R. R. *Comp. Biochem. Physiol., Part B: Biochem. Mol. Biol.* **1980**, 67, 159–162.

(40) Matsuo, A.; Nakayama, M.; Hayashi, S.; Nagai, K. *Phytochemistry* **1980**, 19, 1848–1849.

(41) Hollenbeak, K. H.; Kuehne, M. E. *Tetrahedron* **1974**, 30, 2307–2316.

(42) Ming Chu, I.; Wheeler, M. A.; Holmlund, C. E. *Biochim. Biophys. Acta* **1972**, 270, 18–22.

(43) Laseter, J. L.; Weete, J. D. *Science* **1971**, 172, 864–865.

(44) Ikan, R.; Bergmann, E. D.; Yinon, U.; Shulov, A. *Nature* **1969**, 223, 317.

(45) Calam, D. H. *Nature* **1969**, 221, 856–857.

(46) Calam, D. H. *Science* **1971**, 174, 78.

(47) Alexander, R.; Kralert, P.; Kagi, R. *Org. Geochem.* **1992**, 19, 133–140.

(48) Alexander, R.; Kralert, P.; Sosrowidjojo, I.; Kagi, R. *Org. Geochem.* **1997**, 26, 391–398.

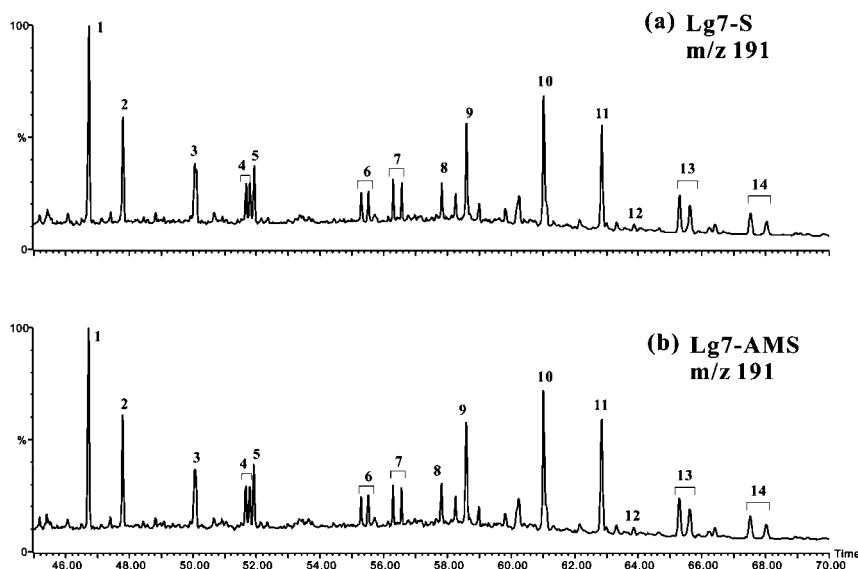


Figure 7. Partial m/z 191 mass chromatograms of (a) the saturates from crude oil maltenes and (b) the AMS fraction from Lg7 asphaltenes. Identification of peaks 1–14 are listed in Table 3.

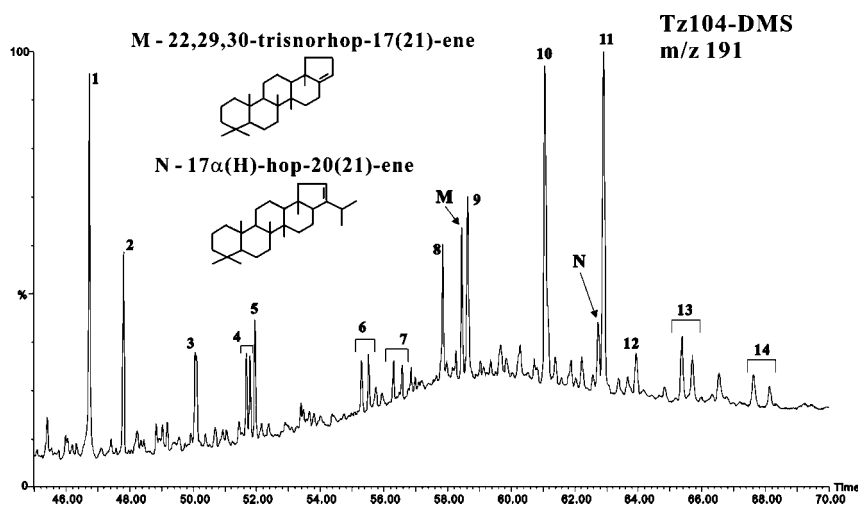


Figure 8. Partial m/z 191 mass chromatogram of the DMS fraction from Tz104 asphaltenes. Identification of peaks 1–14 are listed in Table 3.

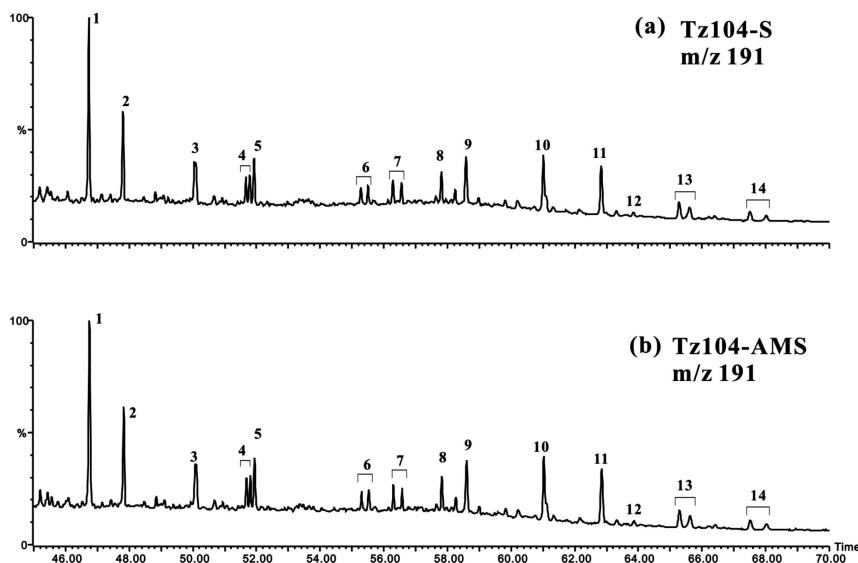


Figure 9. Partial m/z 191 mass chromatograms of the (a) saturates from crude oil maltenes of Tz104 and (b) AMS fraction from Tz104 asphaltenes. Identification of peaks 1–14 are listed in Table 3.

numbered n -alk-(1)-enes can be encapsulated inside asphaltene aggregates and survive the geological time in the oil reservoirs.

In Figure 10b, the dominant compounds of C_{14} , C_{16} , and C_{18} n -alkanoic acids ethyl esters (in fact, all of the samples used in

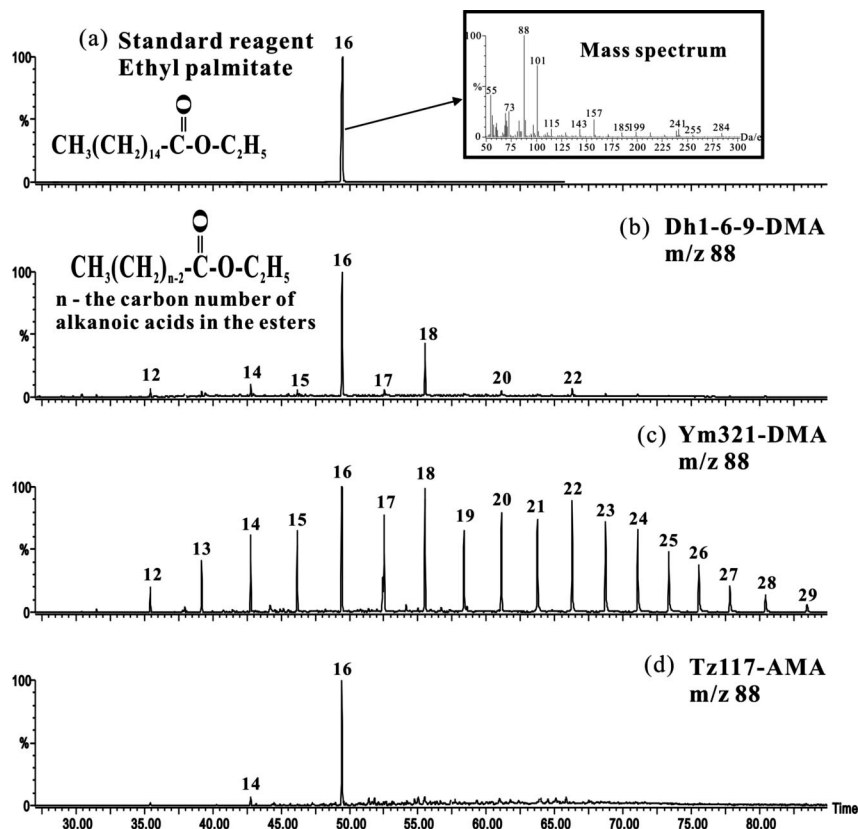


Figure 10. Chromatograms of a series of *n*-alkanoic acid ethyl esters: (a) from the standard reagent of ethyl palmitate with its mass spectrum showed in the inset, (b) from the DMA fraction of Dh1-6-9 asphaltenes, (c) from the DMA fraction of Ym321 asphaltenes, and (d) from the AMA fraction of Tz117 asphaltenes.

this work, except for Ym321, can be represented by this distribution) may indicate that they were derived from the lipids of algae according to the findings of Cranwell et al.,³⁷ while the distribution features of sample Ym321 (Figure 10c) suggested it might be derived from some other precursors. This result is in accordance with the facts that all of the crude oils used in this work were derived from marine source rocks, except for Ym321, which was from terrestrial source rocks. However, this interpretation needs more work to probe the relationship between the distributional features of this series of ethyl esters and the characteristics of their corresponding source rocks. In our laboratory, more efforts are now being bestowed to further probe the geochemical significance of these occluded compounds inside asphaltene aggregates.

4. Conclusion

The $\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$ system was applied to release the occluded compounds from asphaltene aggregates. Among the occluded compounds inside 16 asphaltenes used in this work, a series of even-carbon-numbered *n*-alk-(1)-enes were detected from 13 asphaltenes, 22,29,30-trisnorhop-17(21)-ene and 17 α -hop-20(21)-ene were simultaneously detected from 3 asphaltenes, and C_{23} tricyclic terp-12(13)-ene and C_{29} 18 α -30-norneohop-13(18)-ene were found co-existent in another 3 asphaltenes. A series of *n*-alkanoic acid ethyl esters were detected in the occluded compounds from all 16 asphaltenes, which were generally dominated by the even-carbon-numbered *n*-alkanoic acids in the esters.

These unsaturated alkenes and terpene (hopenes) compounds detected inside asphaltene aggregates indicated that they should belong to the products from kerogens at an early stage of hydrocarbon generation, which have then been occluded inside the asphaltene aggregates and survived geological time because of the efficient protection of the macrostructures of asphaltenes. With respect to the series of ethyl esters occluded inside asphaltene aggregates, the distributional features of Ym321 were markedly different from those of all of the other samples. This may be ascribed to the fact that these ethyl esters from all of the other 15 asphaltenes were mainly derived from the lipids of algae, while those from Ym321 may be derived from some other precursors.

Acknowledgment. This work has been financially supported by the National Science Foundation of China (Grant NSFC 40672091), the National Basic Research Program of China (Grant 2006CB202303), and the Earmarked Fund of the State Key Laboratory of Organic Geochemistry (SKLOG2008A02). We are very grateful to Professors P. Peng, A. Geng, and Y. Sun from SKLOG for helpful discussion. The authors are very grateful to the three anonymous reviewers for their constructive comments to the original manuscript. The authors are especially indebted to one reviewer for supplying a very detailed series of comments and guidance, which significantly improved the manuscript.

Supporting Information Available: Results of blank experiments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

EF8007294