Res. Org. Geochem. **20**, 39−47 (2005) 〔有機地球化学会30周年記念事業 地球・環境有機分子検索マニュアルNo.7〕

Occurrences of sesqui-, di-, and triterpenoid hydrocarbons in the Tertiary oils and sediments from the Pacific side of Japan

Svetlana Yessalina* and Noriyuki Suzuki*

(Received April 15, 2005 ; Accepted October 3, 2005)

1. Introduction

Sesqui-, di-, and triterpenoid hydrocarbons are thought to be mainly derived from compounds present in higher plants (Simoneit, 1986 with references therein). Numerous studies have documented occurrence of these compounds in sedimentary organic matter, fossil resins, coals and petroleum (Moldowan *et al.*, 1994). They are essential biomarkers for the assessment of origin of organic matter, depositional environment, maturation, and for correlation studies (Peters *et al.*, 2005). Among these compounds particular attention has been given to the investigation of pentacyclic triterpenoids, especially to those with oleanane type skeleton. Structural affinity of these compounds to the naturally occurring triterpenoid constituents of angiosperms allows to consider them as molecular markers for angiosperms (Moldowan *et al.*, 1994). Indeed, increased abundance of pentacyclic triterpenoids in geological samples does not start until the Tertiary, the time of widespread occurrence of angiosperms (Moldowan *et al.*, 1994). Therefore, these compounds are considered as age-specific biomarkers. In the present study, we document occurrence of higher plant terpenoids in the hydrocarbon fractions of Tertiary sediments, coals, and petroleum, which can be useful for further studies to increase our understanding of terrestrial biomarker distributions.

2. Samples and Experimental

Twenty eight conventional core samples from the MITI Sanriku-oki borehole (JNOC, 2000), 7 oil samples from the Yufutsu oil and gas field and offshore wildcats, and 4 samples from the Sagara oil field were analyzed in this study. The sediment samples analyzed were mainly from depth interval 1820-4250 m, ranging in geologic age from Late Cretaceous to Middle Eocene. The major core lithologies are mudstones, siltstones, sandstones and coals. The total organic carbon contents of the sediments are in the range from 0.5 to 2.0%. Maturity levels based on measurements of vitrinite reflectance values are in the range from 0.3 to 0.6 %, Ro.

The oils from the Yufutsu field and offshore wildcats were obtained at depth intervals between 2,296-4,275 m, which corresponds to the Ishikari Group, Poronai, and Minami Naganuma Formations and fractured granitic rocks of Cretaceous age (JNOC, 2000). The oils from the Sagara oil field were collected from the Tokigaya Formation during Sagara Drilling Program (SDP) (Hirano *et al.*, 2003).

*Division of Earth and Planetary Sciences, Graduate School of Science, Hokkaido University, N10 W8, Kita-ku, Sapporo 060-0810, Japan
Corresponding author : Noriyuki Suzuki
Tel +8-11-706-2730, Fax +81-11-746-0394
Email : suzu@ep.sci.hokudai.ac.jp

Soluble organic matter was extracted from sediment samples (3 g) by ultrasonication for 15 minutes with dichloromethane/methanol (99 : 1). Organic extracts and oil samples were fractionated into aliphatic hydrocarbons and three aromatic fractions by preparative high pressure liquid chromatography (HPLC ; JASCO Gulliver series PU-986/UV-975), using a pressure-resistant glass column (29 cm × 8 mm *i.d.*) with silica gel (WAKOGEL LP-20). A mixture of hexane/dichloromethane (95/5) was used as eluent with constant flow rate at 2.0 ml/min. The cut points of fractionation were detected by ultraviolet light detector at 254 nm using a mixture of standard aromatic hydrocarbons (tetracosane, toluene, dimethylnaphthalene, and phenanthrene). Isolated hydrocarbons were analyzed by Gas Chromatography/Mass Spectrometry (GC/MS ; HP6890/HP5973), equipped with the fused silica capillary column DB-5 (30 m × 0.25 mm *i.d.*). Helium was used as a carrier gas with flow rate at 1.5 ml/min. The temperature of oven was initially programmed to hold at 40°C for 2 minutes, subsequently programmed to 300°C at 4°C/min and then held at 300°C for 20 minutes. The instrument was operated in the electron impact mode at 70 eV. The identification of compounds was accomplished using the mass spectra library data (NIST 98) together with data available from the literatures.

3. Results and Discussion

Investigation of the saturate and aromatic fractions of the organic extracts from the MITI Sanriku-oki borehole and oils from the Yufutsu field and adjacent wildcats, and from the Sagara oil field revealed significant abundance of various biomarkers of higher plant origin. The distribution patterns of these compounds and their corresponding mass spectra are given in the Figs. 1-6, respectively. Detected compounds belong to different groups of biomarkers of both angiosperm and gymnosperm origin : bicyclic sesquiterpenoids, diterpenoids, and triterpenoids.

Presence of bicyclic sesquiterpanes in the sediment and oil samples was revealed after selective ion monitoring (SIM) of m/z 123 (Fig. 1). All prominent peaks in the mass

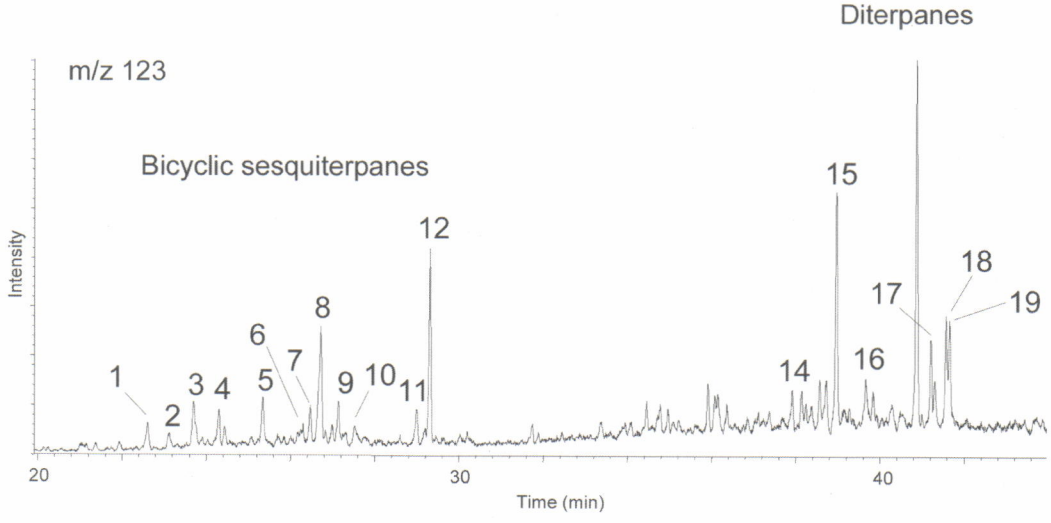


Fig. 1. Representative mass chromatogram at m/z 123, showing the distribution of bicyclic sesquiterpanes and diterpanes in Paleogene oil from the adjacent to the Yufutsu oil and gas field offshore wildcats (sample H-063), Hokkaido. Identification of compounds is shown in Table 1.

chromatogram at m/z 123 eluting in the region between n-C_{13}- and n-C_{16}-alkanes (peaks 1-13) exhibit mass spectra similar to those identified as bicyclic sesquiterpanes by Anders and Robinson (1971), Bendoraitis (1974), and Richardson and Miller (1982) (Fig. 3). Mass spectra with intense peaks at m/z 179 and molecular ion at m/z 194 were reported for C_{14}-bicycloalkanes (Anders and Robinson, 1971 ; Bendoraitis, 1974). C_{15}-bicycloalkanes have been described to show mass spectra with intense peaks at m/z 193 and 123, and molecular ion at m/z 208 (Richardson and Miller, 1982). Base peaks at m/z 179 and 193 have been interpreted to correspond to cleavage of one methyl group.

Identification of diterpanes in the oils from the Yufutsu field and ajacent wilcats, and in the sediment samples from the MITI Sanriku-oki by use of SIM at m/z 123 (peaks 14-19, Fig 1) was confirmed by comparison with mass spectra published in Barrick and Hedges (1981), Noble *et al.* (1985), Philp (1985), and Noble *et al.* (1986) (Fig. 3). Detected compounds include tri- and tetracyclic diterpanes, such as norpimarane, norisopimarane, norabietane (fichtelite), phyllocladanes and abietane. Norpimarane, norisopimarane, norabietane, and abietane are tricyclics in structure, while phyllocladanes are tetracyclics. Both tri- and tetracyclic diterpanes generally exhibit a major fragment at m/z 123, which forms as a result of cleavage of the B-ring. Tetracyclic diterpanes are distinct from their tricyclic counterparts by diagnostic ions at m/z 231, 245 and 274 (Noble *et al.*, 1985). The difference between mass spectra characteristics of phyllocladanes and the other common tetracyclic diterpanes, such as kauranes, can be seen in a greater intensity of m/z 231 comparatively to m/z 259, especially for 16β(H)-phyllocladane (Noble *et al.*, 1985).

Dicyclic and tricyclic terpenoids of higher plant origin were also detected in the aromatic fraction of analyzed sediment samples and oils

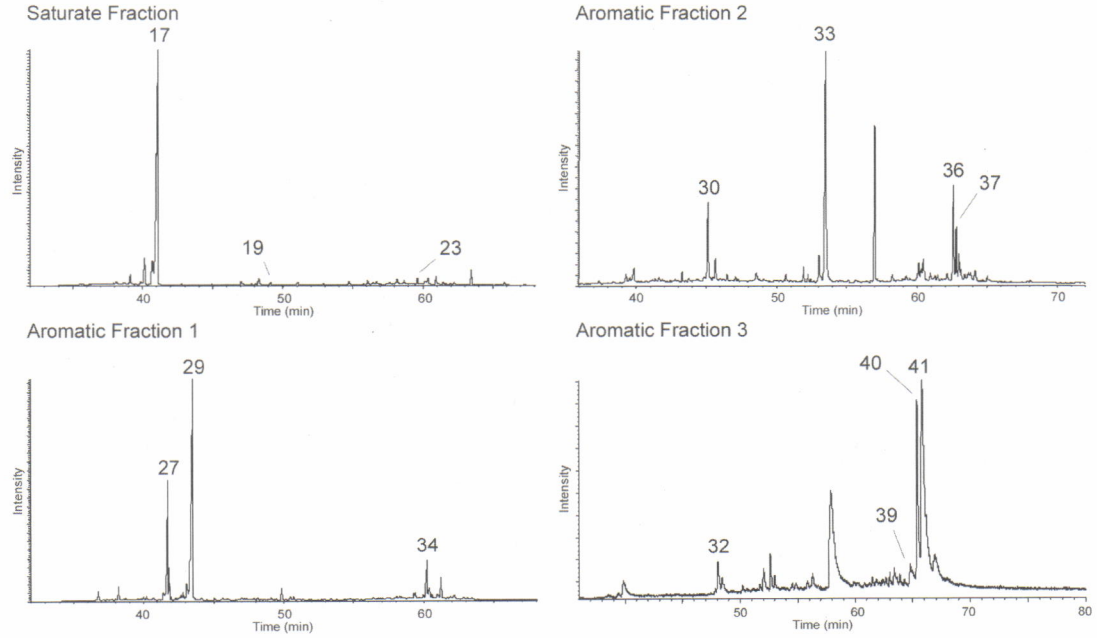


Fig. 2. Representative total ion chromatograms of saturate and aromatic fractions of organic matter isolated from the Middle Eocene sediment (1840m) from the MITI Sanriku-oki borehole. Identification of compounds is shown in Tables 1, and 2.

Table 1. Identification of saturate higher plant biomarkers detected in sediments from the MITI Sanriku-oki borehole and in the oils from the Yufutsu field and adjacent wildcats. and from the Sagara field.

Peak	Compound name	Formula	MW	Base peak	Samples	Reference	LI*	LI**
1,2	bicyclic sesquiterpanes	$C_{14}H_{26}$	194	179	YO,SO,MS(1,2)	Anders and Robinson(1971) ; Bendoraitis(1974)	2(2)	1
3-7	bicyclic sesquiterpanes	$C_{15}H_{28}$	208	193	YO,SO,MS(1,2)	Richardson and Miller(1982)	2(2)	1
8-13	bicyclic sesquitepanes	$C_{16}H_{30}$	222	123	YO,SO,MS(1,2)	Richardson and Miller(1982)	2(2)	1
14	norpimarane	$C_{19}H_{34}$	262	233	YO	Philp(1985)	2(2)	2(2)
15	4β(H)-19-norisopimarane	$C_{19}H_{34}$	262	233	YO,MS(1,2,4,5)	Noble *et al.*(1986)	2(2)	4
16	fichtelite	$C_{19}H_{34}$	262	109	YO	Barrick and Hedges(1981)	2(2)	4
17	16β(H)-phyllocladane	$C_{20}H_{34}$	274	123	YO,MS(1,2)	Noble *et al.*(1985)	2(2)	3
18	abietane	$C_{20}H_{36}$	276	163	YO	Philp(1985)	2(2)	2(2)
19	16α(H)-phyllocladane	$C_{20}H_{34}$	274	123	YO,MS(1-5)	Noble *et al.*(1985)	2(2)	3
20	des-A-triterpane	$C_{24}H_{42}$	330	191	YO,SO,MS(1,2)	Woolhouse *at al.*(1992)	1(2)	1
21	des-A-lupane	$C_{24}H_{42}$	330	123	SO,MS(1,2,4,5)	Schmitter *et al.*(1981)	2(2)	3
22	olean-13(18)-ene	$C_{30}H_{50}$	410	205	SO,MS(1,2,4,5)	Philp(1985)/library(84255)	2(1/2)	2(2)
23	olean-12-ene	$C_{30}H_{50}$	410	218	SO,MS(1-5)	Philp(1985)/library(126853)	2(1/2)	2(2)
24	olean-18-ene	$C_{30}H_{50}$	410	204	SO,MS(2,4)	Philp(1985)/library(84088)	2(1/2)	2(2)
25	18α(H)-olean-12-ene	$C_{30}H_{50}$	410	218	MS(2)	Rullkötter *et al.*(1994)/library(87272)	2(1)*	2(2)

MW, molecular weight ; LI*, level of identification in the present paper, LI**, level of identification in the reference paper ; YO, oils from the Yufutsu field and adjacent wildcats ; SO, oils from the Sagara field ; MS, sediments from the MITI Sanriku-oki borehole : 1, early Late Paleocene-early Middle Eocene (3320m ; 0.4%, Ro) ; 2, early Late Paleocene-early Middle Eocene (3120m ; 0.35%, Ro) ; 3, Middle Eocene (2300m ; 0.35%, Ro) ; MS4, Middle Eocene (1900m ; 0.3%, Ro) ; MS5, Middle Eocene (1840m ; 0.3%, Ro). Structural assigment was based on : 1, interpretation of mass spectra data ; 2(1), coincidence in mass spectral data from library (NIST 98) ; 2(2), coincidence in mass spectral data with that in a reference or literature ; 3, coincidence in mass spectrum and GC data retention time with that of reference compound ; 4, coincidence in mass spectrum and GC retention time with that of authentic standard ; 5, confirmation of level 4 identification by other methods. *, assigment of compound was confirmed by matching of its relative retention time data with that reported in the literature (Rullkötter *et al.*, 1994).

Table 2. Identification of aromatic higher plant biomarkers detected in the sediments from the MITI Sanriku-oki borehole and in the oils from the Yufutsu field and adjacent wildcats, and from the Sagara field.

Peak	Compound name	Formula	MW	Base peak	Samples	Reference	LI*	LI**
26	cadalene	$C_{15}H_{18}$	198	183	YO,SO,MS(1-5)	Bendoraitis(1974)	2(2)	4
27	dehydroabietane	$C_{20}H_{30}$	270	255	YO,MS(1-5)	Philp(1985)	2(2)	2(2)
28	6-isopropyl-2-methyl-1-(4-methylpentyl) naphthalene	$C_{20}H_{28}$	268	197	YO,MS(1,2,3,5)	Ellis *et al.*(1996)	2(2)	3
29	simonellite	$C_{19}H_{24}$	252	237	YO,SO,MS(1-5)	Simoneit(1977)	2(2)	3
30	retene	$C_{18}H_{18}$	234	219	YO,SO,MS(1-5)	Simoneit(1977)	2(2)	2(1)
31	2-methylretene	$C_{19}H_{20}$	248	233	YO,MS(1,5)	Bastow *et al.*(2001)	2(2)	3
32	des-A-triterpenoid	$C_{23}H_{30}$	306	187	YO,SO,MS(1-5)	Stout(1992)	2(2)	1
33	3,3,7-trimethyl-1,2,3,4-tetrahydrochrysene	$C_{21}H_{22}$	274	218	YO,SO,MS(1-5)	Spyckerelle *et al.*(1977)	2(2)	3
34	24,25-dinor-ursa-1,3,5(10),12-tetraene	$C_{28}H_{40}$	376	145	SO,MS(3-5)	Wolff *et al.*(1989)	2(2)	3
35,37	2,2,4a,9-tetramethly-1,2,3,4,4a,5,6,14b-octahydropicene	$C_{26}H_{30}$	342	257	YO,MS(1-5)	Wakeham *et al.*(1980)	2(2)	2(2)
36	1,2,4a,9-tetramethyl-1,2,3,4,4a,5,6,14b-octahydropicene	$C_{26}H_{30}$	342	342	YO,MS(1-5)	Wakeham *et al.*(1980)	2(2)	2(2)
38	8,14-seco-oleanoid	$C_{27}H_{32}$	356	169	YO,MS(1-4)	Chaffee and Fookes(1988)	2(2)	5
39	1-isopropylpropano-7-methylchrysene	$C_{25}H_{24}$	324	281	YO,MS(1-5)	Chaffee and Fookes(1988)	2(2)	5
40	1,2,9-trimethyl-1,2,3,4-tetrahydropicene	$C_{25}H_{24}$	324	309	YO,MS(1-5)	Chaffee and Fookes(1988)	2(2)	5
41	2,2,9-trimethyl-1,2,3,4-tetrahydropicene	$C_{25}H_{24}$	324	268	YO,MS(1-5)	Chaffee and Fookes(1988)	2(2)	5

MW, molecular weight ; LI*, level of identification in the present paper ; LI**, level of identification in the reference paper ; YO, oils from the Yufutsu field and adjacent wildcats ; SO, oils from the Sagara field ; MS, sediments from the MITI Sanriku-oki borehole : 1, early Late Paleocene-early Middle Eocene (3320m ; 0.4%, Ro) ; 2, early Late Paleocene-early Middle Eocene (3120m ; 0.35%, Ro) ; 3, Middle Eocene (2300m ; 0.35%, Ro) ; MS4, Middle Eocene (1900m ; 0.3%, Ro) ; MS5, Middle Eocene (1840m ; 0.3%, Ro). Structural assigment was based on : 1, interpretation of mass spectra data ; 2(1), coincidence in mass spectral data from library (NIST 98) ; 2(2), coincidence in mass spectral data with that in a reference or literature ; 3, coincidence in mass spectrum and GC data retention time with that of reference compound ; 4, coincidence in mass spectrum and GC retention time with that of authentic standard ; 5, confirmation of level 4 identification by other methods.

(Fig. 2). These are cadalene, dehydroabietane, isohexyl alkylnaphthalene, simonellite, retene, and 2-methylretene. Their presence was revealed by comparison with mass spectra published in Bendoraitis (1974), Simoneit (1977), Philp (1985), Ellis *et al.* (1996) and Bastow *et al.* (2001) (Fig. 5). All of these compounds, except isohexyl alkylnaphthalene, exhibit prominent ion peaks, corresponding to the loss of one methyl group. The prominent peak of isohexyl alkylnaphthalene, which is at m/z 197, is due to loss of C_5-alkyl moiety.

Occurrence of higher plant triterpanes, such as unsaturate oleanenes and des-A-triterpanes (peaks 20-25, Fig. 2) in the sediments and oils was detected by SIM of the m/z 191 and coincidence with mass spectra from the library and literatures (Schmitter *et al.*, 1981; Philp, 1985; Woolhouse *et al.*, 1992) (Fig. 4). Oleanenes have diagnostic ions at m/z 218 and molecular ions at m/z 410. Assigment of 18α(H)-olean-12-ene was based on comparison with mass spectra from the library and retention time described in the literature (Rullkötter *et al.*, 1994). Des-A-triterpanes have mass spectra with molecular ion at m/z 330. The mass spectra of des-A-lupane reported by Schmitter *et al.* (1981) is characterized by diagnostic ion at m/z 287, which corresponds to the loss of an isopropyl sidechain.

Aromatized triterpenoids such as des-A-triterpenoid, trimethyltetrahydrochrysene, dinor-

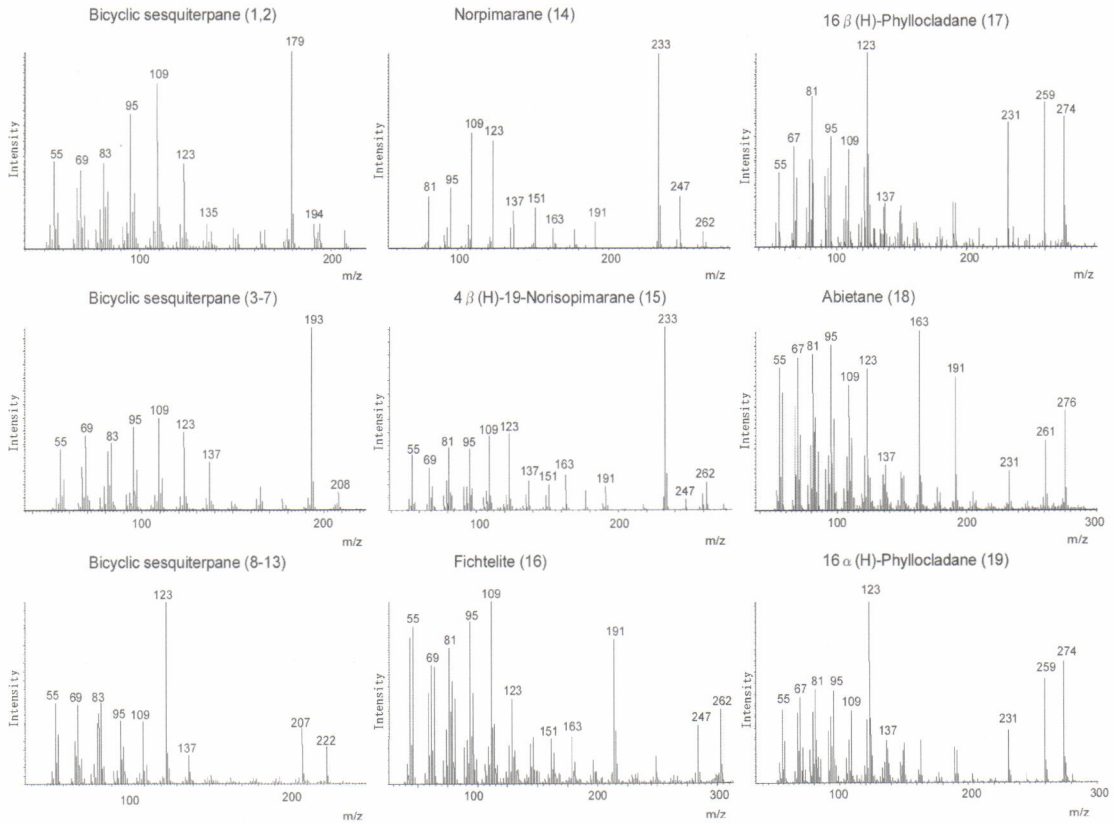


Fig. 3. Representative mass spectra of bicyclic sesquiterpanes and diterpanes detected in the saturate fractions of organic matter isolated from the early Late Paleocene-Middle Eocene sediments from the MITI Sanriku-oki borehole and the oils from the Yufutsu field and adjacent offshore wildcats, and from the Sagara field.

ursatetraene, tetramethyloctahydropicenes, 8,14-seco-oleanoid, isopropylpropanomethylchrysene, and trimethyltetrahydropicenes were assigned based on comparison with mass spectra from the literatures (Spyckerelle *et al.*, 1977; Wakeham *et al.*, 1980; Chaffee and Fookes, 1988;

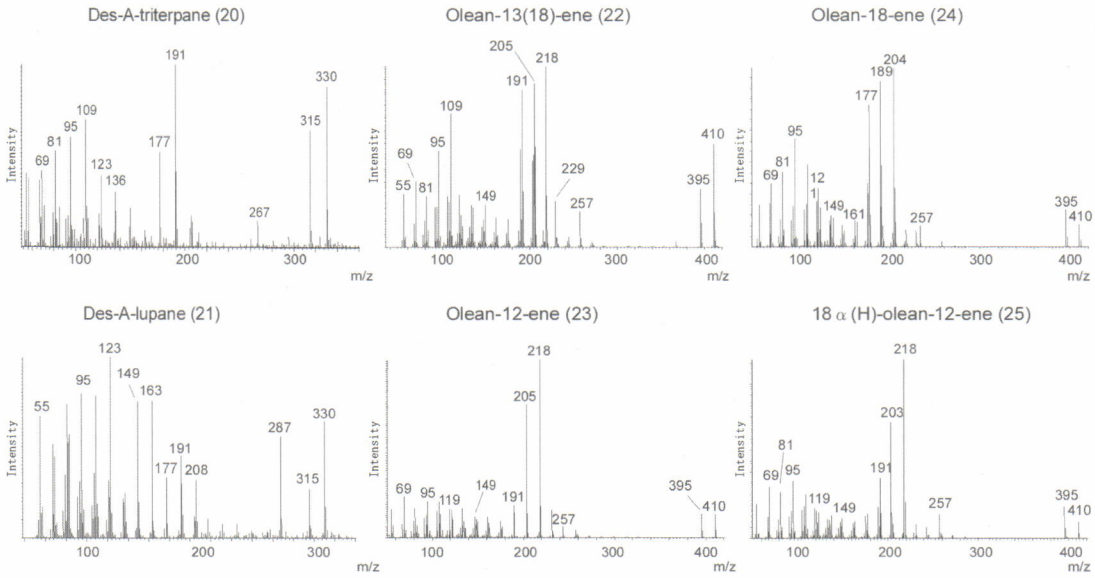


Fig. 4. Representative mass spectra of saturate and unsaturated triterpanes of higher plant origin detected in the saturate fractions of organic matter isolated from the early Late Paleocene-Middle Eocene sediments from the MITI Sanriku-oki borehole and the oils from the Yufutsu field and adjacent offshore wildcats, and from the Sagara field.

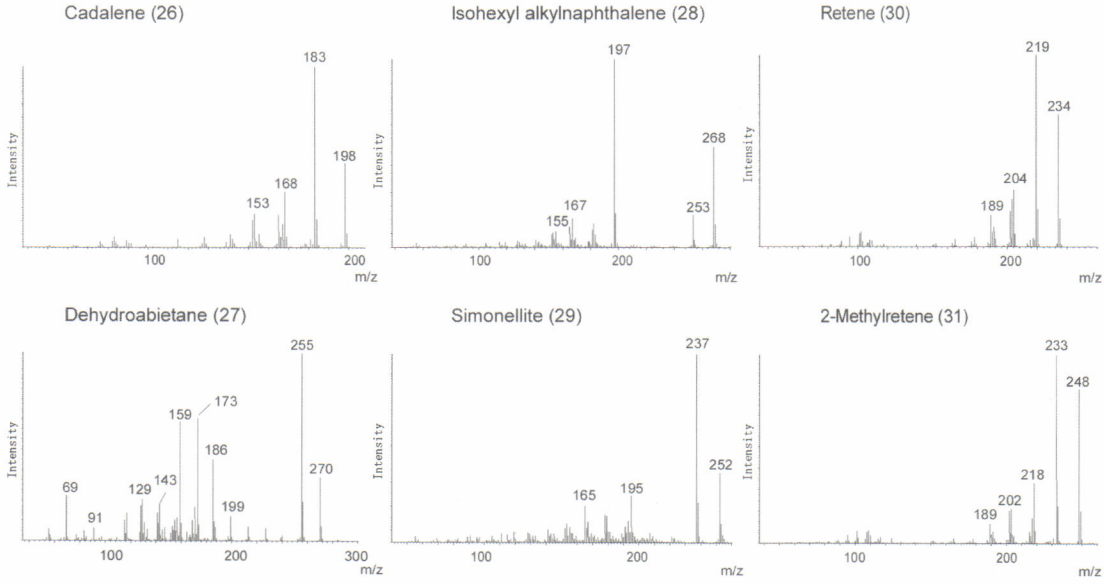


Fig. 5. Representative mass spectra of sesqui- and diterpenoids of higher plant origin detected in the aromatic fractions of organic matter isolated from the early Late Paleocene-Middle Eocene sediments from the MITI Sanriku-oki borehole and the oils from the Yufutsu field and adjacent offshore wildcats, and from the Sagara field.

Wolff *et al.*, 1989 ; Stout, 1992). Monoaromatic (A-ring) triterpenoids include des-A-triterpenoid and dinorursatetraene (Fig. 6). Identification of des-A-triterpenoid by Stout (1992) was based on mass spectra interpretation. The base peak of this compound (m/z 187) is suggested to correspond to C-ring cleavage, at position of a C_{12} double bond. Monoaromatic compounds of similar type, like dinorursatetraene, are distinguished by characteristic ions at m/z 145 and 158, which have been interpreted to originate from A- and B-ring mono- and dimethyltetrahydronaphthalene fragments. Trimethyltetrahydrochrysene, 8,14-seco-oleanoid, and tetramethyloctahydropicenes are triaromatic compounds. Trimethytetrahydrochrysene has prominent ion fragments at m/z 218 and 274. The former one is due to rupture of the E-ring, while the latter one represents the molecular ion. C-ring cleaved structural configuration of 8,14-seco-oleanoid has been suggested based on the presence of base peak at m/z 169 (Chaffee and Fookes, 1988). Tetramethyloctahydropicenes have prominent molecular ions at m/z 342. Intense ion at m/z 257 in mass spectra of 2,2,4a,9-tetramethyl-1,2,3,4,4a,5,6,14b-octahydropicene is due to rupture of the E-ring. Tetraaromatic triterpenoids such as 1,2,9-trimethyl-1,2,3,4-tetrahydropicene and 2,2,9-trimethyl-1,2,3,4-tetrahydropicene also have prominent molecular ions, which are at m/z 324. The next most intense ions, in these com-

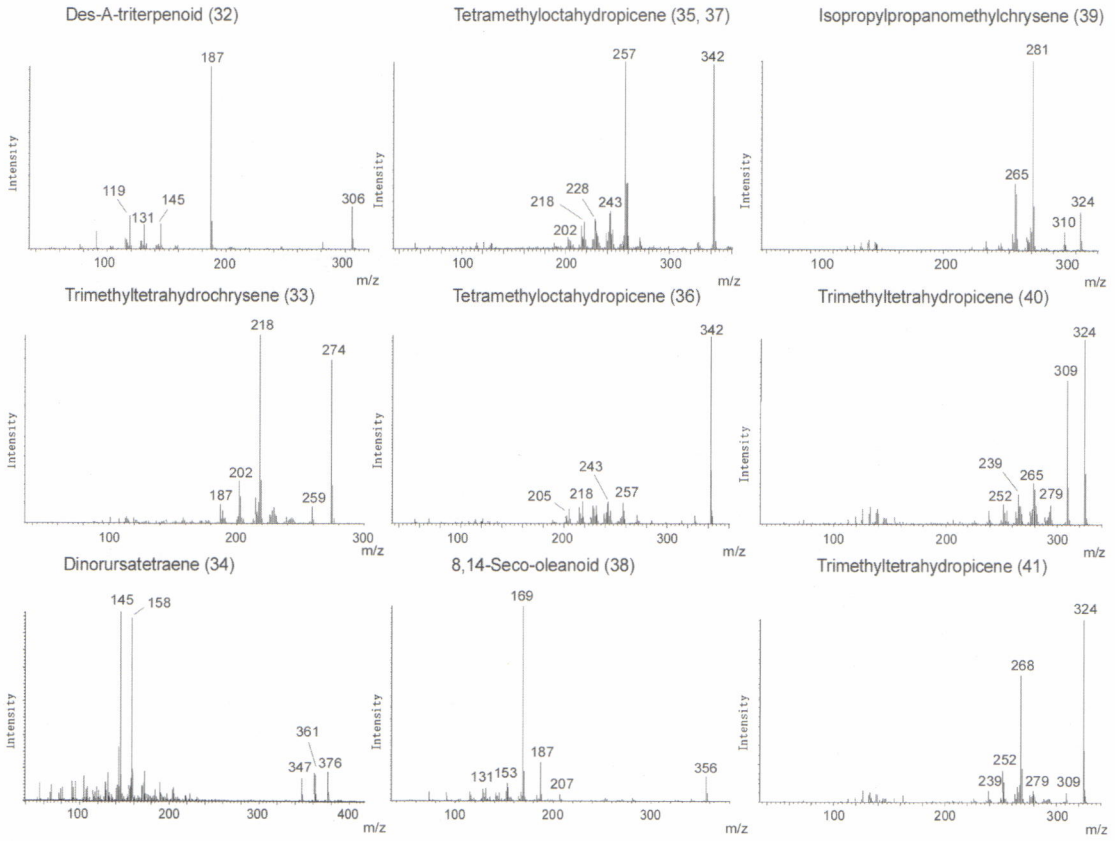


Fig. 6. Representative mass spectra of triterpenoids of higher plant origin detected in the aromatic fractions of organic matter isolated from the early Late Paleocene-Middle Eocene sediments from the MITI Sanriku-oki borehole and the oils from the Yufutsu field and adjacent offshore wildcats, and from the Sagara field.

pounds are at m/z 309 and 268, representing loss of methyl group and the rupture of the E-ring, respectively.

Acknowledgments

We thank Japan Petroleum Exploration Co Ltd (JAPEX) and Japan Oil, Gas and Metals National Corporation (JOGMEC) for providing the oil and sediment samples and permission to publish this paper. Special thanks to Mr. H. Saito for his sampling of oils in Sagara oil field. Thanks are also due to Drs. K Sawada and N. Ratnayake for their constructive suggestion and help in preparatory work. We are grateful to Professor Shuichi Yamamoto of Soka University and one anonymous reviewer for their comments, which substantially improved the manuscript.

References

Anders, D. E and Robinson, W. E. (1971) Cycloalkane constituents of the bitumen from Green River Shale. *Geochim. Cosmochim. Acta* **35**, 661-678.

Barrick, R. C. and Hedges, J. I. (1981) Hydrocarbon geochemistry of the Puget Sound region II. Sedimenatary diterpenoid, steroid and thiterpenoid hydrocarbons. *Geochim. Cosmochim. Acta* **45**, 381-392.

Bastow, T. P., Singh, R. K., VAN Aarssen, B. G. K., Alexander, R. and Kagi, R. I. (2001) 2-Methylretene in sedimentary material : a new higher plant biomarker. *Org. Geochem.* **32**, 1211-1217.

Bendoraitis, J. G. (1974) Hydrocarbons of biogenic origin in petroleum - aromatic triterpenes and bicyclic sesquiterpenes. In : Tissot B. and Bienner F. (Eds.), *Advan. in Org. Geochem.* 1973, pp.209-224. Editions Technip.

Chaffee, A. L. and Fookes, C. J. R. (1988) Polycyclic aromatic hydrocarbons in Australian coals-III. Structural elucidation by proton nuclear magnetic resonance spectroscopy. *Org. Geochem.* **12**, 261-271.

Ellis, L., Singh, R. K., Alexander, R. and Kagi, R. I. (1996) Formation of isohexyl alkylaromatic hydrocarbons from aromatization-rearrangement of terpenoids in the sedimentary environment : A new class of biomarker. *Geochim. Cosmochim. Acta* **60**, 4747-4763.

Hirano, S., Araki, Y., Wada, H. and Sagara Drilling Program Scientific Party (2003) Lithology and physical properties of core samples obtained from the Sagara oil field, central Japan : Preliminary results of the Sagara Drilling Program (SDP). In : IFREE Report for 2001-2002, *Frontier Research on Earth Evolution*, Vol.1, pp.253-257.

Japan National Oil Corporation (JNOC) (2000) *Report on the MITI Sanriku-oki drilling.* (in Japanese), pp.48.

Moldowan, J. M., Dahl, J., Huizinga, B. J., Fago, F. J., Hickey, L. J., Peakman, T. M. and Taylor, D. W. (1994) The molecular fossil record of oleanane and its relation to angiosperms. *Science* **265**, 768-771.

Noble, R. A., Alexander, R., Kagi, R. I. and Knox, J. (1985) Tetracyclic diterpenoid hydrocarbons in some Australian coals, sediments and crude oils. *Geochim. Cosmochim. Acta* **49**, 2141-2147.

Noble, R. A., Alexander, R., Kagi, R. I., and Knox, J. (1986) Identification of some diterpenoid hydrocarbons in petroleum. *Org. Geochem.* **10**, 825-829.

Peters, K. E., Walters, C. C. and Moldowan, J. M. (2005) The Biomarker Guide : Volume 2, Biomarkers and Isotopes in Petroleum Systems and Earth History. Cambridge University Press, pp.475-1155.

Philp, R. P. (1985) Fossil fuel biomarkers. Applications and spectra. *Meth. in Geochem. and Geoph.* **23**, 1-294.

Richardson, J. S. and Miller, D. E. (1982) Identification of dicyclic and tricyclic hydrocar-

bons in the saturate fraction of crude oil by gas chromatography/mass spectrometry. *Anal. Chem.* **54**, 765-768.

Rullkötter, J., Peakman, T. M. and TEN Haven, H. L. (1994) Early diagenesis of terrigenous triterpenoids and its implications for petroleum geochemistry. *Org. Geochem.* **21**, 215-233.

Simoneit, B. R. T. (1977) Diterpenoid compounds and other lipids in deep-sea sediments and their geochemical significance. *Geochim. Cosmochim. Acta* **41**, 463-476.

Simoneit, B. R. T. (1986) Cyclic terpenoids of the geosphere. In : Johns, R. B. (Eds.), *Meth. in Geochem. and Geoph.* **25**, Elsevier.

Schmitter, J. M., Arpino, P. J. and Guiochon, G. (1981) Isolation of degraded pentacyclic triterpenoid acids in a Nigerian crude oil and their identification as tetracyclic carboxylic acids resulting from ring A cleavage. *Geochem. Cosmochim. Acta* **45**, 1951-1955.

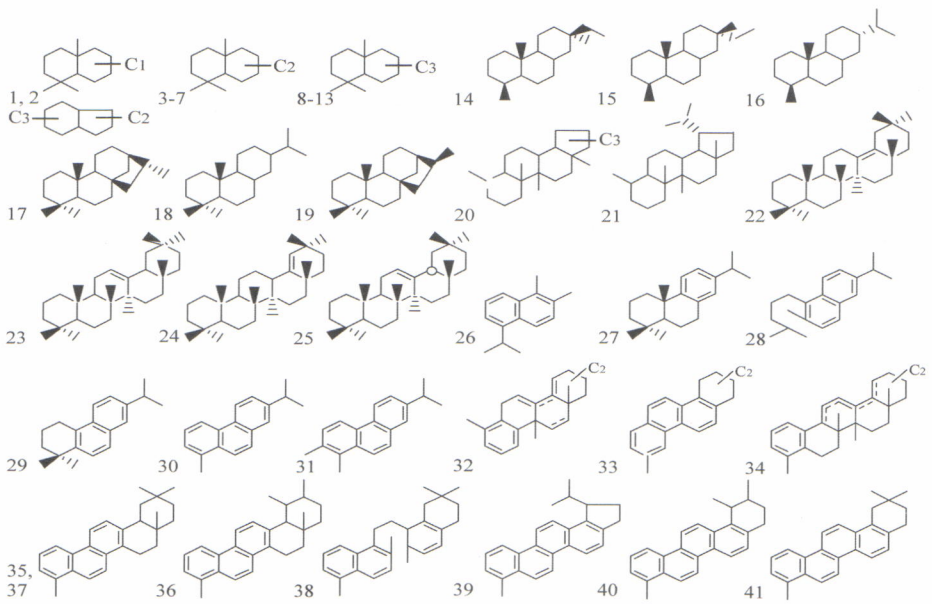
Spyckerelle, C., Greiner, A., Ch., Albrecht, P. and Ourisson, G. (1977) Aromatic hydrocarbons from geological sources. III. A tetrahydrochrysene derived from triterpenes in recent and old sediments : 3,3,7-trimethyl-1,2,3,4-tetrahydrochrysene. *J. Chem. Res.* (M), 3746-3777.

Stout, S. A. (1992) Aliphatic and aromatic triterpenoid hydrocarbons in a Tertiary angiospermous lignite. *Org. Geochem.* **18**, 51-66.

Wakeham, S. G., Schaffner, C. and Giger, W. (1980) Polycyclic aromatic hydrocarbons in recent lake sediments-II. Compounds derived from biogenic precursors during early diagenesis. *Geochem. Cosmochim. Acta* **44**, 415-429.

Wolff, G. A., Trendel, J. M. and Albrecht, P. (1989) Novel monoaromatic triterpenoid hydrocarbons occurring in sediments. *Tetrahedron* **45**, 6721-6728.

Woolhouse, A. D., Oung, J. N., Philp, R. P. and Weston, R. J. (1992) Triterpanes and ring-A degraded triterpanes as biomarkers characteristic of Tertiary oils derived from predominantly higher plant sources. *Org. Geochem.* **18**, 23-31.



Appendix. Chemical structures in the text.