



The Oxygenated Biomarker as an Indicator of Origin and Maturity of Miocene Brown Coal, Sangatta Coal Mines, East Kalimantan

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Abstract - The Middle to Late Miocene brown coal extracted from Inul area, Sangatta coal mines, East Kalimantan, was studied to recognize the distribution of ketone and acid biomarkers. Samples were extracted using soxhlet method and separated by column chromatography and thin layer chromatography. Acetylation of acid fractions by BF_3/MeOH produced an ester compound which is an acid derivative. The distributions of fatty acid methyl esters were analyzed with gas chromatography-mass spectrometry (GC-MS). The distributions of ketones included compounds in *n*-alkan-2-one, amyrin-derived ketone, and friedeline derivatives as well as olean-13(18)-en-3-one with oleanane skeleton. Distributions of fatty acids included compounds in the range from *n*-methylhexadecanoate (*n*-C₁₆) to *n*-methyltriacontanoate (*n*-C₃₀) with dominating compounds from *n*-methylhexadecanoate (*n*-C₁₆) to *n*-methyldococanoate (*n*-C₂₂). The most obvious feature is predominance of compounds with even-over-odd-carbon-atom-number in a molecule, which come from vascular plant fatty acids. The distributions of these biomarker compounds are used as an indicator of higher plant and oxic depositional environment, as well as the involvement of bacteria in diagenesis stage which indicates immature coals.

Keywords: GC-MS, ketone, fatty acid biomarkers; brown coal, Sangatta coalmines

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INTRODUCTION

Ketone is one of biomarker compounds in coal samples and other geological sediments that can be used as an indicator of the maturity level of the coal. Because of its molecular structures, ketones can evolve into an alkane (Ikan *et al.*, 1973). Ketone biomarkers can also provide information about the origin of organic matter during coalification, depositional environment,

type of vegetation, climate, facies variations of deposition, and alteration process as well as degradation of organic compounds during diagenesis pathway, and also the relationship of fossil organic compounds with depositional environment (Azevedo *et al.*, 2001; Burhan *et al.*, 2002; Fabiańska, 2004; Tuo and Li, 2005). Lehtonen and Ketola (1990) found a long-chain acyclic methylketone, *n*-alkane-2-ones (range $n\text{C}_{17}$ - $n\text{C}_{35}$), and isoprenoidal methylketone in peat soil. The

presence of methylketone in peat soils indicates the source of organic matter in coal derived from grass and moss. The straight chain of *n*-alkane-2-ones and isoprenoidal methylketone found abundant in lipid sediments also suggests that the coal was derived from higher plants (Cranwell *et al.*, 1987). The predominance of odd carbon in homologous series of long-chain *n*-alkyl methyl ketone (in range nC_{19} - nC_{33}) in the soil sediments also indicates that this compound was not generated from primary plant, but it was generated by the oxidation of *n*-alkane by microbial (Volkman *et al.*, 1980; Albaiges *et al.*, 1984).

Fatty acids in the sediments are also used as precursors of aliphatic hydrocarbon compounds, the main component in the petroleum and coal bitumen. These compounds were a main source of organic compounds in organism tissues from marine/lacustrine kerogen, peat, and brown and bituminous coals. Therefore, the source of organic compounds derived from terrestrial and marine environment based on the existence of fatty acids can be compared (Fabińska, 2004). Fatty acids dominated by long chains of carbon atoms (nC_{22} - nC_{32}) are the characteristic of cutin and suberin from higher plants. Nor even chain-lengths predominance or long chain esters are found in sedimentary organic matter of marine origin (Mita *et al.*, 1998; Fabianska, 2004). Thermal maturity of the coal can also be identified through the content of fatty acid biomarkers. The maturity of coal increases with the decrease of fatty acids. Fatty acids are relatively more stable and can survive until the middle of catagenesis, thus it is used as an indicator of the maturity of sediment samples.

Inul area, one of Sangatta coal mining areas, East Kalimantan, is known to have a lower grade coal (CV of ca. 4379 kcal/kg adb and Rv of 0.31%) as compared to other areas in Sangatta, so it has not been exploited optimally. The low calorific value of brown coal in the Inul area is related to its origin of the formation of vegetation and coalification process. The objective of this study was to use biomarker distribution, ketone, and acid biomarkers to characterize the respective maturity, origin, and depositional environment of coal samples.

REGIONAL GEOLOGY OF KUTAI BASIN

The coal used in this study is the one in Inul area, in Kaltim Prima Coal (KPC) Sangatta working concession, District of East Kutai, East Kalimantan, Indonesia. The KPC Sangatta mining area is located in the Kutai Basin and included in Balikpapan Formation. The area of exploration, mining, and coal production reaches 90,960 hectares covering the area of Sangatta and Bengalon. There are two main groups of potential coal in Sangatta region, namely: Pinang Group and Melawan Group. Sangatta area stretches between the Bengalon River and the Sangatta River, and empties into the northeast towards the Makassar Strait. This area has the texture of undulating hills with the highest elevation reaching 330 m above sea level, which is the culmination of Pinang Dome. The areas that are around Pinang Dome have a bumpy morphology with small hills and are relatively flat in the South (Nas, 1994).

Sangatta coal mine geological structure consists of anticline, syncline, faults, and joints. Anticline and syncline fold axis are generally to the north-south direction, while the fracture is to the east-west direction. The two main anticlines, Pinang and Melawan, which are to the north-south direction occur in the west and the east of Sangatta mine. Between the two anticlines, there is a syncline directing to north-south (Nas, 1994). Pinang anticline directing to north-south forms a dome structure (dome), so that it is called Pinang Dome and is the dominant structural element in the Pinang area. Pinang Dome is estimated to be a diapiric shale (Gunawan, 1979; Mugeridge, 1987), and this diapiric structure can affect the pattern of coal rank in Sangatta area (Mugeridge, 1987).

Geologically, KPC Sangatta is located in the Kutai Basin, which is between Mahakam Delta and Mangkalihat High. Delta systems of Sangatta are formed simultaneously with the Mahakam Delta and are estimated to have been formed since the Early Miocene. Delta sedimentation reached the peak of development in the period of Late Miocene to Pliocene regression

in the Kutai Basin represented by the presence of Pamaluan, Bebulu, Pulubalang, and Balikpapan Formations (Christyahya, 2006). Together with Kampung Baru Formation except Bebulu Formation, those three formations are present as coal-bearing formation in the Kutai Basin as seen in Figure 1.

From the four coal-bearing formations, only Balikpapan Formation that contains the most economic coal seams. This formation is also found in

parts of West Pinang Dome, so the facies change from west to east in the dome (Sikumbang *et al.*, 1981). Pulubalang Formation which is dominated by mudstone, siltstone, and sandstones is overlain by Balikpapan Formation. The Balikpapan Formation is characterized by the absence of calcareous sandstone, thicker seam, more fluvial, and the presence of coral limestone. This Formation was deposited in the delta plain up to delta front system, Middle Miocene to Late Miocene in age.

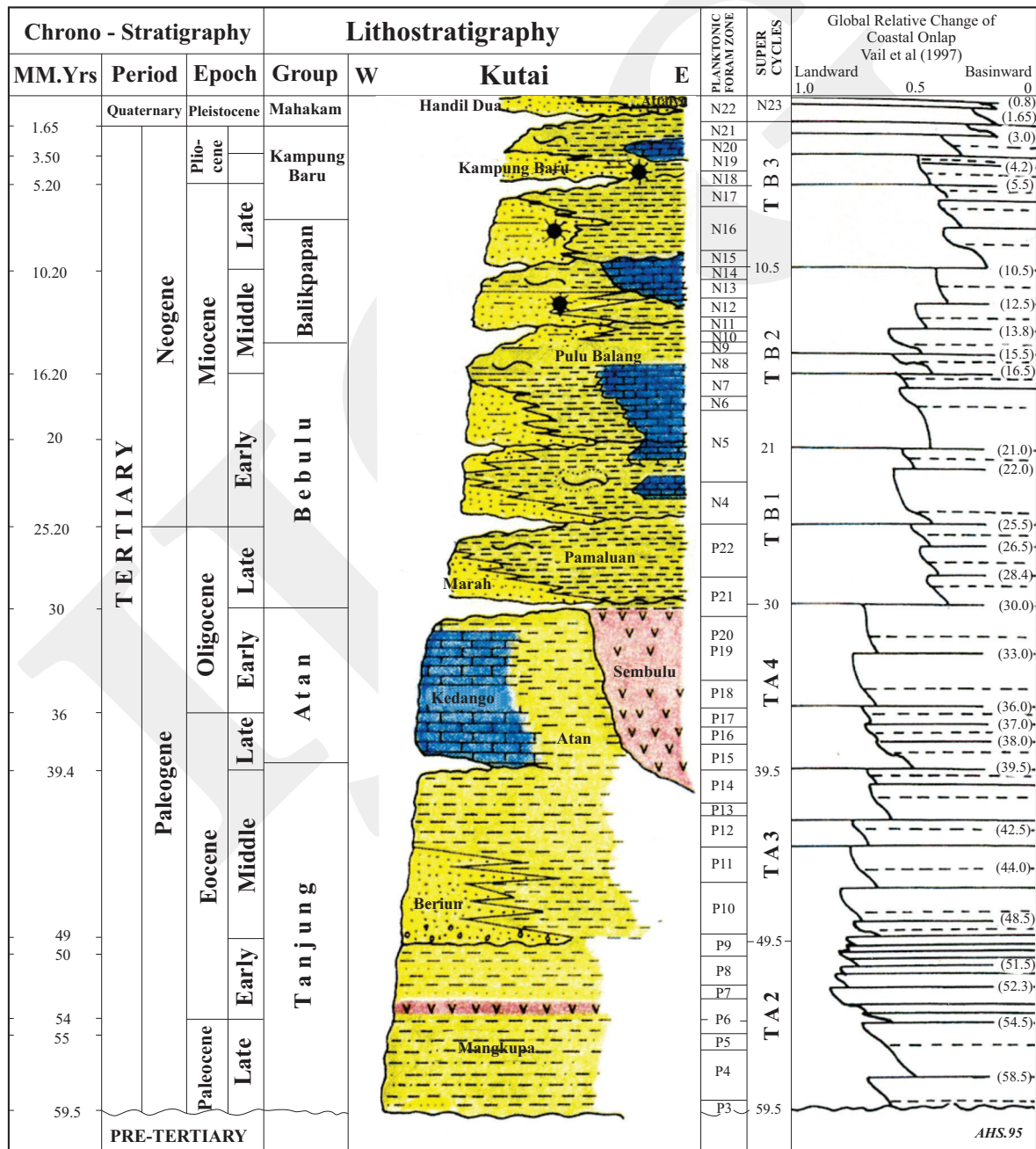


Figure 1. Lithostratigraphy of Kutai Basin (Courtney *et al.*, 1991).

SAMPLES AND METHODS

Samples

Samples were collected from Middle-Late Miocene Balikpapan Formation, located in Inul area, north of Pinang Dome, Sangatta coal mines, East Kalimantan, included in the Kutai Basin. The samples were taken from an open pit mining at depth of 74.80 m to 76.12 m from the original surface with total thickness of 1.32 m.

Methods

In this study, only one of coal samples was taken to determine the fraction of acid and ketone biomarkers contained in the coal. Around 100 gram crushed samples (120 mesh) was extracted in soxhlet apparatus for 48 h using an azeotropic mixture of acetone (47%), methanol (23%), and chloroform (30%). Solvent was removed with a rotary evaporator. The extracts were separated using column chromatography over activated silica gel GF₂₅₄, with KOH/isopropyl alcohol yielding neutral fraction (elution with diethyl-ether), acid fraction (elution with diethyl ether/formic acid (98/2), and polar fraction (elution with CH₂Cl₂/MeOH/H₂O (60/25/4)). The neutral and acidic fractions will further be analyzed to be reported in this paper. The acid fraction was esterified by BF₃/MeOH and separated by thin layer chromatography (TLC) over activated silica gel using dichloromethane as eluent. The band corresponding to monoester was scraped from the TLC plate after visualization under UV-light (254 nm). The monoester fractions were extracted by dichloromethane. Solvent was removed with a rotary evaporator and dried using N₂ gas.

Neutral fractions were separated into hydrocarbon fractions, ketone, and alcohol fractions using thin layer chromatography (TLC) over activated silica gel in dichloromethane. Of the three neutral fractions obtained, only a fraction of ketone was taken and analyzed further to be reported in this paper. The band corresponding to ketone was scraped from the TLC plate after visualisation under UV-light (254 nm). The acid fractions and ketone fractions were analyzed by

gas chromatography-mass spectrometry using GC-MS Agilent 122-5561, DB-5 MS column (60 m x 0.25 m x 0.1 μm film thickness). Spectrometer was operated in the electron impact mode (ionization energy 70 eV). Operating condition using Helium carrier gas with a flow rate 1.2 mL/min; isothermal temperature control at 70°C for 1 minute increases in temperature from 70 - 150°C at 10°C/min, from 150 - 290°C at 2°C/min, and from 290 - 300°C at 5°C/min; isothermal temperature for 6 minutes.

RESULTS AND DISCUSSION

Ketone Biomarkers

Ketone biomarkers of coal samples are shown in Total Ion Chromatogram (TIC) (Figure 2). The group compounds identified are derivatives of 2-alkanon (ketone), derivatives of amyryn, and derivatives of friedeline.

Lesser amount of ketones (Figure 3) in geochemical samples is produced from biosynthe-

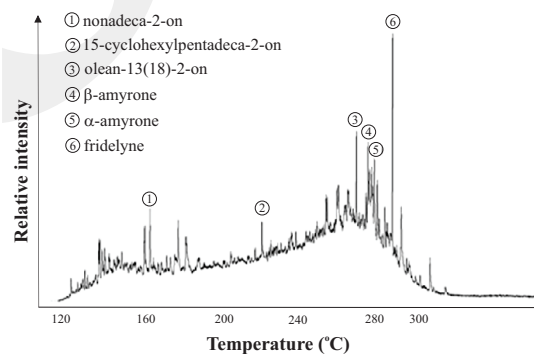


Figure 2. Total ion chromatogram (TIC) of ketone fractions shows the distribution of ketone compounds.

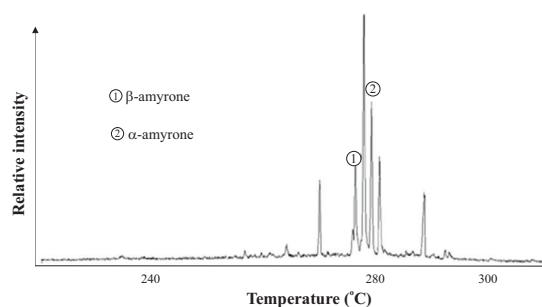


Figure 3. Fragmentogram *m/z* 218 ketone fractions.

sized of fatty acid by enzymatic reduction together with alcohol, branched alkanes, and aldehydes as shown in the following reaction (Killops and Killops, 2005):



n-nonadecanon, type of straight-chain 2-alkanon compound, was identified based on fragmentogram *m/z* 58 (Volkman *et al.*, 1980; Tuo and Li, 2005; Jaraula *et al.*, 2010). Whereas cyclic ketone which is identified based on *m/z* 83 is 15-cyclohexylpentadecan-2-on. Wide distribution of *n*-alkan-2-ones was found in soil samples, peats (Morisson and Bick, 1966), marine sediments (Cranwell, 1977; Simoneit, 1978), and lacustrine sediments (Rieley *et al.*, 1991). The existence of *n*-alkan-2-ones indicates that these compounds were formed from both microbially mediated β -oxidation of the corresponding *n*-alkanes in the sediments, and from microbial oxidation of higher plant-derived *n*-alkanes, prior to their incorporation in the sediments (Tuo and Li, 2005).

Beside *n*-alkan-2-ones, the presence of amyirin derivatives in coal samples which is estimated as olean-13(18)-en-3-one with oleanane skeleton was formed during diagenesis of β -amyirin, characteristic for Angiosperms (Alberdi and Lopez, 2000; Hanisch *et al.*, 2003). Therefore, this biomarker compound was used as an indicator of Angiosperms (Nytoft *et al.*, 2002; Fabianska and Kurkiewicz, 2013). The other compounds of amyirin derivatives in coal analysed are β -amyrone and α -amyrone, formed by oxidation of squalane contained in wax leaf-higher plant.

The existence of amyrone compound indicates the source of organic matter of coal samples originated from higher plant in tropical environment (Volkman *et al.*, 1980; Alberdi and Lopez, 2000; Hanisch *et al.*, 2003; Bakar *et al.*, 2011; Fang Yu *et al.*, 2013). Besides, there was also friedelan-3-one produced by oxidation of friedelin. Therefore, the existence of these biomarker compounds is potentially used as an indicator of higher plant origin and oxic depositional environment, as well as the involvement of bacteria in diagenesis stage.

Acid Biomarkers

Acid biomarkers identified in the form of monoester derivatives have been obtained from esterification of carboxylic acid by BF_3/MeOH . The total ion chromatogram of the monoester fraction is shown in Figure 4.

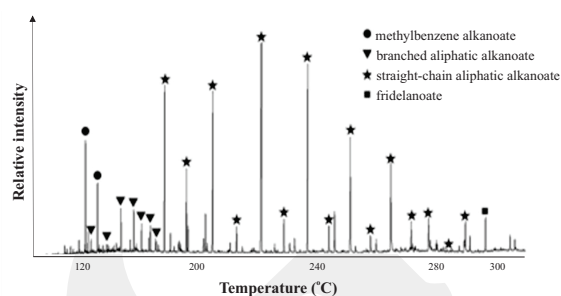


Figure 4. Total ion chromatogram monoester fractions.

The identification of biomarkers based on fragmentogram *m/z* 74 showed the presence of straight-chain aliphatic alkanooate (*n*-alkanoate) and branch-chain aliphatic alkanooate (*iso*-alkanoate). This identification of biomarkers is also based on a former published literature (Matsuda and Koyama, 1977; Fabiańska and Kurkiewicz, 2013) as shown in the following figure.

The distribution of $n\text{C}_{16}$ - $n\text{C}_{30}$ shows the existence of straight-chain aliphatic alkanooate. Short chain *n*-alkanoate ($n\text{C}_{16}$ - $n\text{C}_{20}$) indicates the contribution of plankton and bacteria, whereas long chain ($>n\text{C}_{20}$) displays the contribution of higher plant (Duan, 2000).

The predominance of even-over-odd carbon in monoester, as shown in Figure 5, CPI = 0.17, indicates the source of organic matter from terrestrial higher plant (Simoneit, 1977; Fabiańska

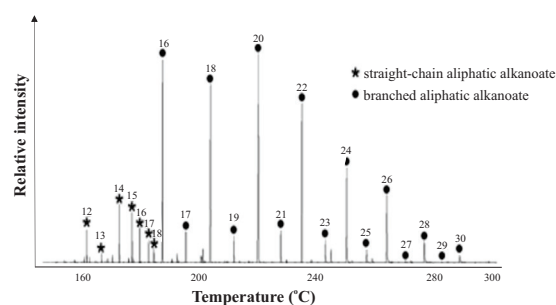


Figure 5. Fragmentogram *m/z* 74 monoester fraction.

and Kurkiewicz, 2013). This trend is related to the formation of fatty acid with even carbon number in wax higher plant which is derived from acetic acid biosynthesis (Simoneit, 1977; Parrish *et al.*, 2000). This indicates that the organic matter of coal did not alter as much during peatification until the formation of coal and also indicates the immature coal. One of straight-chain monoester alkanoate compounds is $\text{CH}_3(\text{CH}_2)_{18}\text{COOCH}_3$ ($n\text{-C}_{20}$), as shown in Figure 6.

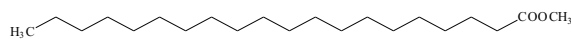


Figure 6. Methyl-icosanoate

Straight-chain monoester alkanoate biomarkers are shown in Table 1.

Straight-chain alkanolic acid is derived from oxidation of n -alkanes by microorganisms in oxidative environment (Okoh, 2006). The distribution of branched-chain alkanolic acid biomarker (iso-alkanoate) showed the lighter intensity than n -alkanoate. Distribution of iso-alkanoate is shown in the range of $iso\text{-C}_{12}$ to $iso\text{-C}_{18}$, with

the dominance of even-over-odd carbon number (Figure 7).

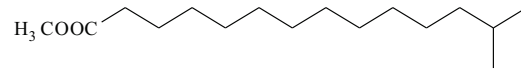


Figure 7. Methyl-isopentadecanoate

The existence of iso-alkanoate in coal is an indicator of bacterial involvement in a coalification process. The distribution of iso-alkanoate is shown in Table 2.

Subsequent identification based on fragmentogram m/z 105 shows the existence of methylbenzene monoester (Garcette-Lepecq *et al.*, 2000). Two compounds identified in methylbenzene alkanoate are 6-methyl toluilhexadecanoate and 7-methyl-toluilheptadecanoate. The existence of these biomarkers in coal samples indicates the presence of microorganisms and organic compounds derived from carotenoids during coalification. These biomarker compounds formed through alteration of carotenoid by microorganisms that occur at diagenesis stage that produce

Table 1. Straight-chain Monoester Alkanoate Biomarkers in Brown Coal of Inul Area

No	Number of Carbon	Structure	Mol. Mass	Compound
1	$n\text{-C}_{16}$	$\text{CH}_3(\text{CH}_2)_{14}\text{COOCH}_3$	270	n -methyl hexadecanoate
2	$n\text{-C}_{17}$	$\text{CH}_3(\text{CH}_2)_{15}\text{COOCH}_3$	284	n -methyl heptadecanoate
3	$n\text{-C}_{18}$	$\text{CH}_3(\text{CH}_2)_{16}\text{COOCH}_3$	298	n -methyl octadecanoate
4	$n\text{-C}_{19}$	$\text{CH}_3(\text{CH}_2)_{17}\text{COOCH}_3$	312	n -methyl nonadecanoate
5	$n\text{-C}_{20}$	$\text{CH}_3(\text{CH}_2)_{18}\text{COOCH}_3$	326	n -methyl icosanoate
6	$n\text{-C}_{21}$	$\text{CH}_3(\text{CH}_2)_{19}\text{COOCH}_3$	340	n -methyl hencosanoate
7	$n\text{-C}_{22}$	$\text{CH}_3(\text{CH}_2)_{20}\text{COOCH}_3$	354	n -methyl docosanoate
8	$n\text{-C}_{23}$	$\text{CH}_3(\text{CH}_2)_{21}\text{COOCH}_3$	368	n -methyl tricosanoate
9	$n\text{-C}_{24}$	$\text{CH}_3(\text{CH}_2)_{22}\text{COOCH}_3$	382	n -methyl tetracosanoate
10	$n\text{-C}_{25}$	$\text{CH}_3(\text{CH}_2)_{23}\text{COOCH}_3$	396	n -methyl pentacosanoate
11	$n\text{-C}_{26}$	$\text{CH}_3(\text{CH}_2)_{24}\text{COOCH}_3$	410	n -methyl hexacosanoate
12	$n\text{-C}_{27}$	$\text{CH}_3(\text{CH}_2)_{25}\text{COOCH}_3$	424	n -methyl heptacosanoate
13	$n\text{-C}_{28}$	$\text{CH}_3(\text{CH}_2)_{26}\text{COOCH}_3$	438	n -methyl octacosanoate
14	$n\text{-C}_{29}$	$\text{CH}_3(\text{CH}_2)_{27}\text{COOCH}_3$	452	n -methyl nonacosanoate
15	$n\text{-C}_{30}$	$\text{CH}_3(\text{CH}_2)_{28}\text{COOCH}_3$	466	n -methyl triacontanoate

Table 2. Iso-alkanoate Biomarkers in Brown Coal of Inul Area

No	Number of Carbon	Structure	Mol. mass	Compound
1	<i>iso</i> -C ₁₂	(CH ₃) ₂ CH(CH ₂) ₈ COOCH ₃	214	methyl-isododecanoate
2	<i>iso</i> -C ₁₃	(CH ₃) ₂ CH(CH ₂) ₉ COOCH ₃	228	methyl-isotridecanoate
3	<i>iso</i> -C ₁₄	(CH ₃) ₂ CH(CH ₂) ₁₀ COOCH ₃	242	methyl-isotetradecanoate
4	<i>iso</i> -C ₁₅	(CH ₃) ₂ CH(CH ₂) ₁₁ COOCH ₃	256	methyl-isopentadecanoate
5	<i>iso</i> -C ₁₆	(CH ₃) ₂ CH(CH ₂) ₁₂ COOCH ₃	270	methyl-isohexadecanoate
6	<i>iso</i> -C ₁₇	(CH ₃) ₂ CH(CH ₂) ₁₃ COOCH ₃	284	methyl-isohexadecanoate
7	<i>iso</i> -C ₁₈	(CH ₃) ₂ CH(CH ₂) ₁₄ COOCH ₃	298	methyl-isooctadecanoate

alkylbenzene and alkylnaphthalene (Haug *et al.*, 1971), but alkylnaphthalene was not identified in the coal samples analyzed. Carotenoids are pigments found in plants, bacteria, and algal (Summons and Powell, 1987; Dong *et al.*, 1993). Biomarker *n*-alkanoic can also be derived from oxidation of straight-chain *n*-alkanes, cyclic, and monoaromatic in the presence of bacteria. This biodegradation occurs through oxidation of the methyl group terminal or subterminal from alcohol, followed by subsequent oxidation that produces carboxylic acids via aldehyde. This carboxylic acid presents in metabolic pathways through β -oxidation (Okoh, 2006).

The existence of methyl friedelanoate, friedelane derivatives, is identified based on fragmentogram *m/z* 273 (Bakar *et al.*, 2011). Biomarker that is identified in coal analyzed is 3,4-*seco*-friedelane-3-oic (Figure 8.), derived from oxidation of friedelane. The potential origin of these natural

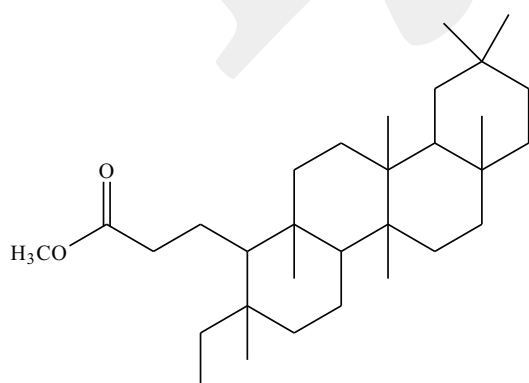


Figure 8. 3,4-*Seco*-friedelane-3-oate.

products may be from the known precursors by oxidation or from a direct source. Thus, all friedelane derivatives are inferred to derive from higher plants in this tropical environment (Killops and Killops, 2005; Bakar *et al.*, 2011).

CONCLUSION

The molecular distributions of homologous aliphatic lipid and ketones biomarker in brown coal, Inul area, Sangatta coal mines, East Kalimantan, have been investigated. The samples contains *n*-alkan-2-ones, derivatives of amyryl, derivatives friedelane, *n*-alkanoic acids, and iso-alkanoic acid. The distributions of these compounds in the samples indicate an input of terrestrial plant in this tropical environment. The presence of oxygenated products of alkane and triterpenoids indicating organic matter in brown coal is preserved mainly under oxic conditions. Therefore, the existence of these biomarker compounds is potentially used as an indicator of higher plant and oxic depositional environment, as well as the involvement of bacteria in diagenesis stage which indicates immature coals.

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