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PALEOENVIRONMENT OF BROWN COAL FROM SANGATTA COAL MINES, EAST BORNEO, INDONESIA

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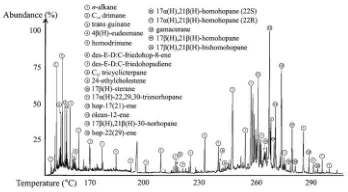
Graphical abstract



Abstract

Organic geochemical studies on brown coal (lignite) located in Inul area were carried out, an area that is located in Sangatta coal mines, East Borneo, which is a part of the Balikpapan formation, aged as old as Middle Miocene to Late Miocene. Aliphatic hydrocarbon biomarker compounds which were identified by using the GC-MS analysis showed a presence of *n*-alkane (*n*-C_{12}-*n*-C_{36}) with bimodal distribution, which described the sources of organic compounds that originated from two different sources. These sources of organic compounds are phytoplankton, zooplankton and higher plants terrestrial. The Pr/Ph ratio of 1.3, the dominance of C_{31}-homohopane and a high ratio of Tm/Ts indicated that the process of peat depositions took place in an oxic environment. The existence of hopanoid contents showed that there were dominant activities of microbes and biolipids organic compounds such as ββ-hopane and hop-17(21)-ene inside the samples of olean-12-ene and α-cadinene, which inidicated that they are organic compounds that came from higher plants such as Angiosperm and immature coals. The existence of 24-ethylcholestene and 5β-cholest-24-ene found in the coal samples, which are categorised as steranes, also indicated a low level of carbonization from the coal itself.

Keywords: Brown coal, Sangatta coal mines, hopene, GCMS

1.0 INTRODUCTION

The Sangatta coalmine is a part of Balikpapan Formation, Kutai Basin, which is estimated to be aged around Middle Miocene to Late Miocene. The Balikpapan Formation that lies comfortably on top of the Pulubalang Formation, is dominated by clay, silt and sandstones. The distinctive features of Balikpapan Formation in Sangatta coalfield are the absence of kalkareus sandstone, thicker seam, more fluviatil and the presence of coral limestone lens. The Balikpapan Formation is deposited by using the delta system on the delta plain up to the delta front and contains the main coal seam (the main coal-bearing strata). The layers with more economic values in this formation are located in the West of Pinang Dome. The calorific value of the coals in Kutai basin lies in the range of 5800-7100 cal/g [1,2]. However, the lignite coals located in the Inul area, which is a part of the Sangatta coalfield, have not been used optimally due to its low calorific value (ca. 4379cal/g).

In the case of using the coal for energy sources, the shift to coal-fired generation in the ASEAN region-particularly in Malaysia and Thailand — is driven by the development of independent power projects and energy security considerations that are leading to a shift from lignite and oil to sub-bituminous and/or bituminous coal-fired generation and, to a lesser extent, natural gas in the fuel mix [3]. And Indonesian coal is environmentally friendly (low mineral matter and low sulfur) [4].

In the Indonesia Energy Outlook 2014, the coal comsumption for industry increased at a lower average rate of 7,4% per year. Other needs for coal comsumption is as a raw material to produce CTL (coal to liquid), which is estimated to start in 2030 with the amount of coal reaching 4,5 million tons per year until the end of 2035. As a raw material to produce CTL, low calorie brown coals (lignites) will be used [5]. One of the low calorie brown coal deposits in Indonesia are located in Inul pit in the Sangatta coalmine, Balikpapan Formation, Kutai basin, which are estimated to be aged as old as Middle Miocene to Late Miocene. In order for the brown coal to be used more economically, the process of diversification needs to be done, one of them is by coal liquefaction (the process of turning coal to liquid). Before the process of coal liquefaction took place, biomarker analysis on the liquefied lignite coal needed to be done. This strengthens the reason to reveal the characteristics of the coal having such low calorie as lignite coal.

Understanding the characteristics of coal can be studied through biomarkers compounds it contains. In the past, petrological and palaeobotanical data were the primary sources of information about the coal forming environment and ecology of peat formation. In more recent times, biomarkes analysis of the soluble organic matter of coal has increasingly contributed to the understanding of the palaeoenvironment in the mires and has provides clues to the botanical input involved in their formation [6,7]. Biomarkers compounds also provide information about the facies variations during the deposition and transformation process as well as the degradation of organic compounds during diagenesis pathway and the relationship of fossil organic compounds with depositional environment [8-13].

Studying the biomarker compounds by involving aliphatic hydrocarbon compounds could give us information about the depositional environment of the coal. The presence of *n*-alkanes with a range from C_{13} to C_{33} indicated that the organic compound derived from two different sources. The existence of long-chain saturated hydrocarbon in the coal implied that the organic materials came from higher plants, particularly from the *Ficus elastica*, which is an organic material specifically suited for the tropical regions of Indonesia, whereas the presence of short-chains indicated the presence of phytoplankton and zooplankton sources. On the other hand, the dominance of unsaturated hydrocarbons on the coal could give us information about the immature coals [14-17]. The compositions of terpenoid biomarkers (particularly cadinane and eudesmane-type sesquiterpenoids, and oleanane and ursane-type triterpenoids found in low grade coals indicated an abundant contribution of Angiosperm plants on the deposition of coal organic compounds. The existence of hopanoids compounds indicated that there were activities of microbes, whilst the presence of isoprenoids pristane and phytane compounds indicated the redox environment [9]. The combinations of the origins of the organic coals and ancient environment and the relations of the existence of organic materials with their ancient environment could explain the evolutions that took place on coals. This background will be the reason as to why the existence of the aliphatic hydrocarbon compounds needed to be studied for this research. This journal presents the geochemical characteristics, especially the aliphatic hydrocarbon biomarkers that originated from the brown coal deposits located in the Inul area in the Sangatta coalmine. This study is expected to be able to explain the low calorie coal characteristics in the Inul area in the Balikpapan Formation.

2.0 EXPERIMENTAL

Samples

One type of coal samples used in this research came from the Inul area coalmine in the Sangatta coalfield, East Borneo, Indonesia. The Inul coal area is part of the Kutai basin in the Balikpapan Formation, which is estimated to be aged as old as Middle Miocene to Late Miocene. The location of Inul area located at the north of Pinang Dome (Appendix).

Methodology

Coal powder (ca. 100 g) was extracted in a 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 GF_{254}, with KOH/isopropylalcohol and eluted sequentially into three fractions using diethylether (neutral fraction), diethylether/formic acid (98/2 v/v, acid fraction) and $CH_2Cl_2/MeOH/H_2O$ (60/25/4 v/v/v, polar fraction). Neutral fractions refractionated into hydrocarbons fractions, cetone fractions and alcools fractions using thin layer chromatography (TLC) over activated silica gel in dichloromethane as eluent. Hydrocarbon fractions separated into hydrocarbon aliphatic fractions and hydrocarbon aromatic fraction using thin layer chromatography (TLC) over activated silica gel and eluting with n-hexane. In this study, only hydrocarbon aliphatic fractions were analyzed.

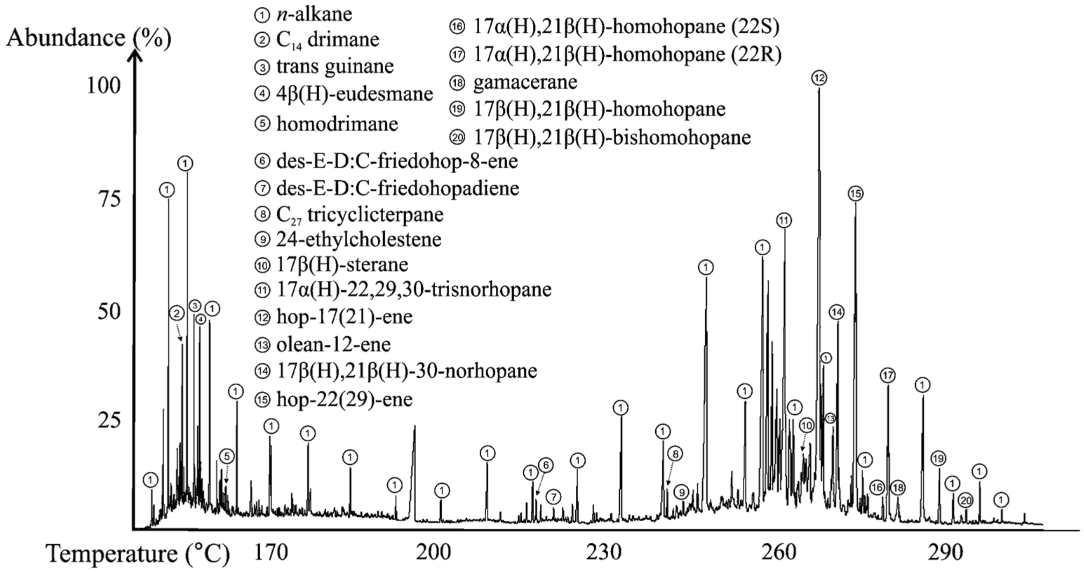


Figure 1 The gas chromatography-mass spectrometry (GC-MS) of the total ion chromatograms (TIC) of the aliphatic hydrocarbon fractions which shows the distribution of aliphatic hydrocarbon compounds

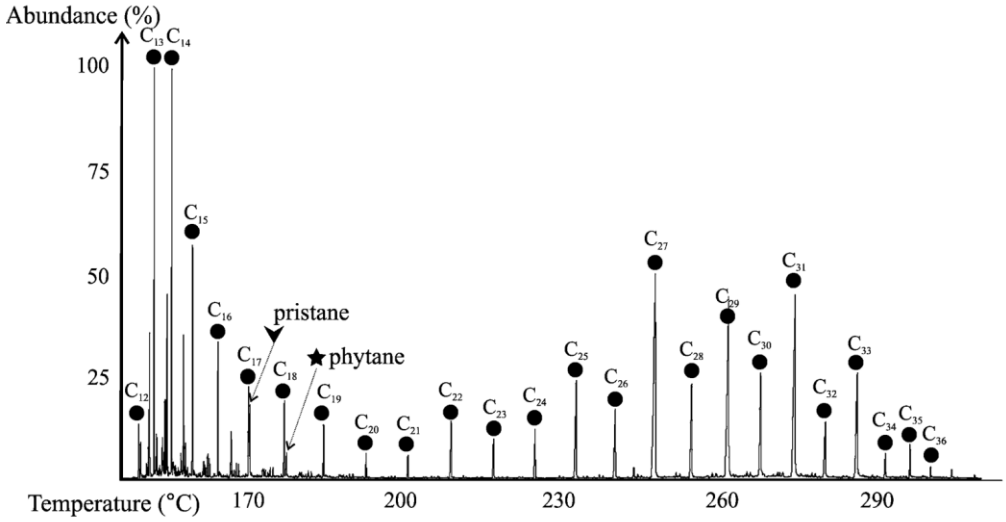


Figure 2 The m/z 57 fragmentogram which shows the *n*-alkane aliphatic hydrocarbon and isoprenoid compounds

The gas chromatography-mass spectrometry analysis was done by using the GC-MS Agilent 122-5561. The GC used the DB-5 MS columns, 60 m x 0.25 m, with column thickness of 0,1 µm. The spectrometer was operated by using the electron energy of 70 eV. The operational condition for hydrocarbon aliphatic fractions is as follows: Helium carrier gas with a flow rate of 1,2 mL/min; isothermal temperature control at 70°C for 1 minute; temperature increase from 70-150°C at a temperature increase rate of 10°C/min, from 150-290°C at a temperature increase rate of 2°C/min and from 290-300°C at a temperature increase rate of 5°C/min; isothermal temperature for 6 minutes.

3.0 RESULTS AND DISCUSSION

The aliphatic hydrocarbon biomarker compounds were identified based on the interpretation of their mass spectra and by comparing their mass spectra with the mass spectra data that have been published previously [18-22]. The analysis of biomarker hydrocarbon aliphatic fractions with the gas chromatography-mass spectrometry (GC-MS) method resulted in total ion chromatogram (TIC) as shown in Figure 1. The aliphatic hydrocarbon fractions show the different groups of compounds with the different structures and origins. These compounds are the *n*-alkanes, triterpenoids hopanoids, triterpenoid non hopanoids, sesquiterpenoids, sesterterpenoids and diterpenoids.

n-alkanes and Isoprenoids Biomarker

Based on the m/z 57 fragmentogram, the presence of *n*-alkanes as seen in Figure 2, shows that the *n*-alkane hydrocarbons homolog compounds are distributed along the range of *n*-C_{12} to *n*-C_{36} with the bimodal distribution type.

The maximum concentration was shown by the *n*-C_{13}-*n*-C_{15} and *n*-C_{27}-*n*-C_{31} range. The relative percentages of the two groups of alkanes that were shown by the *n*-C_{13}-*n*-C_{14} and *n*-C_{27}-*n*-C_{31} range are related to the two different sources. The first group showed the origins of phytoplankton and zooplankton organic compounds, and the second group came from the higher vascular plants. The high abundance of short-chain *n*-alkanes of *n*C_{13} and *n*C_{14} indicated that the organic compounds came from phytoplankton and zooplankton. The dominant formation of short-chain *n*-alkanes may also be caused by the temperature increase and indicated that it is an immature coal [13, 23, 24]. The high abundance of long-chain *n*-alkanes of *n*-C_{27}-*n*-C_{31} showed that the organic compounds originated from the wax cuticle layer of terrestrial higher vascular plant, notably *Ficus elastica* from the Moraceae family, which is a typical for the tropical regions of Indonesia [14, 17]. The dominance of odd carbon atoms over even carbon atoms, particularly in the *n*-C_{25}-*n*-C_{36} homolog indicated the presence of organic compounds of the terrestrial higher plants [20] with the oxic environment coming from the immature coal [25-27]. The pristane/phytane (pr/ph) ratio is generally used to test the oxicity of the depositional environment as a geochemistry parameter. The oxic depositional environment is supported by the pr/ph ratio with a value of 1.3 in the coal sample that was taken from the Inul area in the Sangatta coalmine, which indicated the oxic depositional environment. The pr/ph ratio increased as the amount of thermal maturity increases; hence the low level of pr/ph ratio is also an indication of immature coal [28].

Triterpenoid hopanoids and non hopanoids

The presence of hopanoid as pentacyclic triterpenoid biomarkers in the coal obtained from Inul area in the Sangatta coalfield is identified based on the fragmentogram m/z 191(Figure 3).

The presence of hopanoid compounds that were identified by using the m/z 191 fragmentogram and the standard mass spectrum had been publicized previously [18,29] in the Miocene coal samples, which were also obtained from the Sangatta coalfield in East Borneo, which was shown as C_{27}-C_{32} hopane series with the exceptions of bisnorhopane C_{28}. The small distributions of the pentacyclic triterpenoids homologous sequence is an indicator that the organic compounds were obtained from terrestrial environments [30]. The main hopanoid was

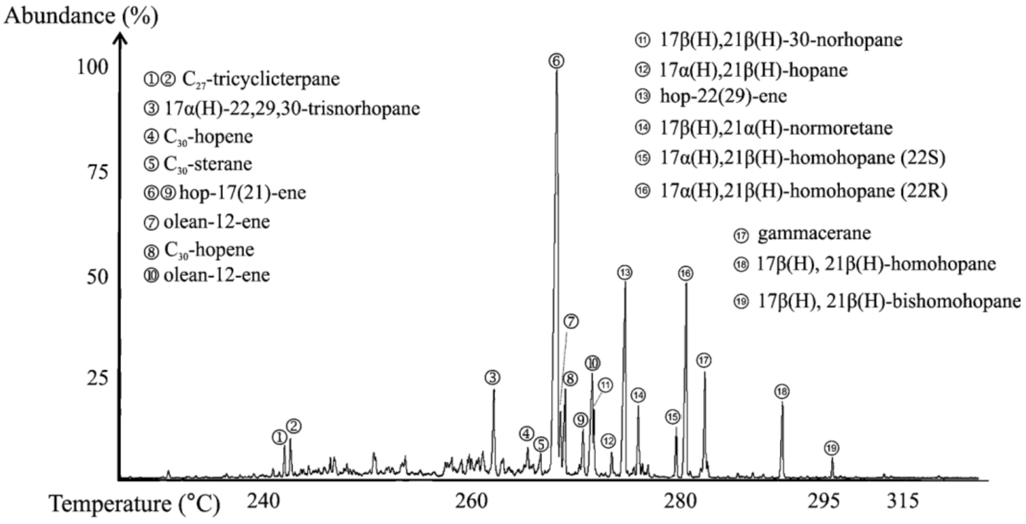


Figure 3 The m/z 191 fragmentogram which showed the triterpenoid cyclic compounds

identified as hop-17(21)-ene; hop-22(29)-ene; 17α(H),21β(H)-homohopane (22R); gammacerane, and 17β(H),21β(H)-homohopane. The hop-17(21)-ene compound is a biomarker compound with a relatively more dominant intensity, besides from the hop-22(29)-ene and C30-hopene which were unsaturated hopanoids. The presence of hopene with high abundance indicated the low maturity of coal [7,30]. The biological sources of the hop-17(21)-ene compound could not be explained in more details, even though its existence was known to be found in samples of immature coal. The direct inputs of this compound into the sediments are from bacteria or from ferns and moss [7]. Hop-22(29)-ene is thought to originate from diplopterol which were found in several eukaryotic phyla (e.g. ferns, mosses, lichens, fungi), just like bacteria that produced hopanoid [7, 31, 32]. Diploterol was also thought to be a forming precursor of hop-17(21)-ene compound [33]. This compound was probably formed as an effect of microbial activity activities in the coalification stage during the process of peat forming [7].

The 17α(H), 21β(H)-homohopane (22R) compound along with its17α(H), 21β(H)-homohopane (22S) isomer were also identified in the Miocene coal samples that were taken from the Sangatta coalfield in East Borneo. The presence of this compound is thought to be formed through the oxidation reaction followed by the decarboxylation reaction of its bacteriohopanetetrol precursor [23]. The high abundance of C_{31} homohopane indicated the presence of oxic environment during the forming of coal organic compunds which was also supported by the pr/ph ratio. The low abundance of 22S compared to the 22R suggested a low maturity of the coal [30].

The discovery of hopane compounds with ββ configurations such as 17β(H),21β(H)-30-norhopane; 17β(H),21β(H)-homohopane and 17β(H),21β(H)-bishomohopane is common, because living organisms mostly synthesize hopanes with ββ configuration and very rarely βα configurations. During the geology transformation, the ββ structure will undergo a change into forming a more thermodynamically stable sctructure, which is the form of isomer αα. Hence the stereochemistry of this type of hopane structure can be used as a degree of metamorphism indicator of the geology sample [19]. The presence of hopane with the ββ configuration indicated the low maturity level of the analysed samples and it also indicated that the coal organic compounds originated from bacteriohopanetetrol which have been synthesized only by bacteria [14, 34]. The role of bacteriohopanetetrol showed by the presence of biomarker hopanoid compounds was also strengthen by the distribution of *n*-alkane hydrocarbon compounds with bimodal distribution type during the process of forming coal organic compounds. The discovery of relatively high concentration of 17α(H)-22,29,30-trisnorhopane(Tm) compounds, but on the other hand no 17β(H)-22,29,30-trisnorhopane(TNH) and 18α(H)-22,29,30-trisnorneohopane(Ts) compunds that were found in the Miocene coals that were obtained from Sangatta coalfield in East Borneo, is a typical for some peat and coal [9]. The exclusive presence of 17α(H)-22,29,30-trisnorhopane (Tm) implied that the high Tm/Ts ratio indicated the presence of oxic environment during the sedimentation process [9, 35]. This analysis corresponds to the pr/ph ratio which indicated the presence of oxic environment during the making of the coal currently being analysed. The correlations between the oxic environment with the pr/ph ratio can be seen on the reactions in Figure 4 below [28].

The other pentacyclic triterpenoid non hopanoid compounds that were identified in the coal samples that were taken from the Inul area in the Sangatta coalfield were gammacerane. This compound is a biomarker characteristic for high-salinity lakes and marine sediments. The discovery of this sample indicated that marine and lake environments with a relatively high salinity level contributed to the peat deposition environment [27]. The presence of marine and lake environments with high salinity level was due to the high distribution level of short-chain alkane hydrocarbon nC_{13} and nC_{14}, which is an indicator of organic compounds that originated from phytoplanktons and zooplanktons contained in the coal samples being analysed [16].

The presence of unsaturated oleanane compounds, such as olean-12-ene, which was identified based on the m/z 191 fragmentogram, indicated an organic compound that originated from ®-amyrin precursors of Angiospermae higher plants.

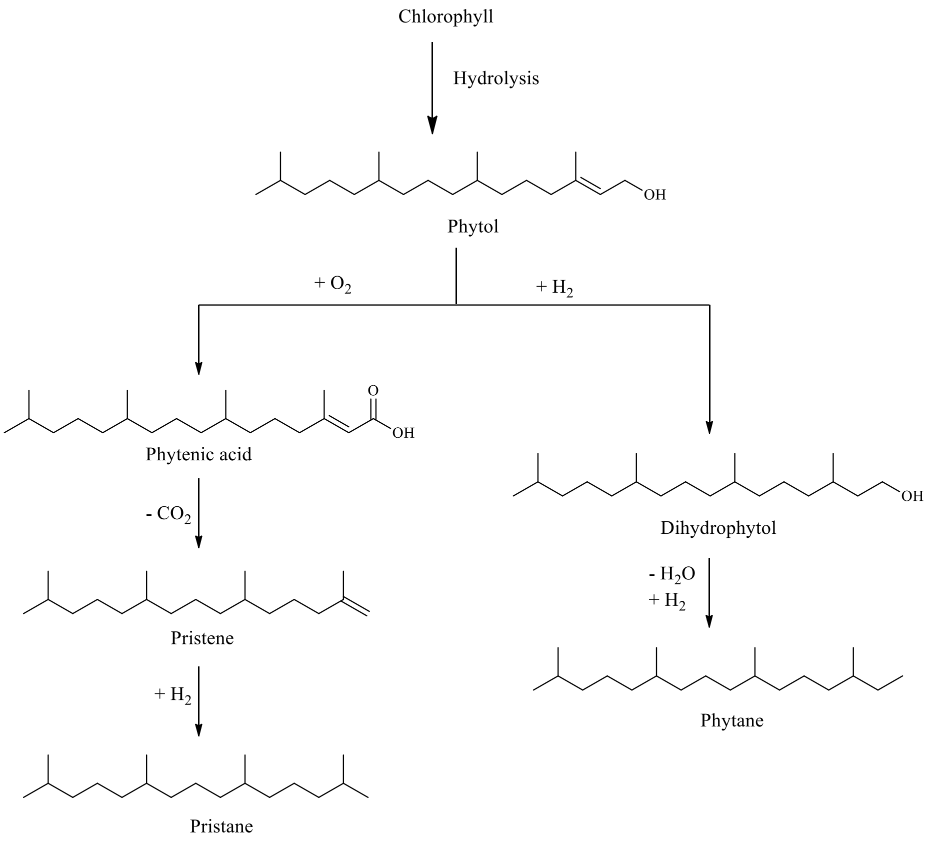


Figure 4 Diagenetic origin of pristane and phytane from phytol (derived from side chain of chlorophyll)

During the catagenesis stage, the olean-12-ene compound will transform further to form 18β-oleanane and 18α-oleanane which were not found in the sample being analysed. Hence this explains why there were not any samples of 18β-oleanane and 18α-oleanane compounds being found, however, the discovery of a sample of olean-12-ene compound indicated that the coal is immature [23].

The presence of sterane groups which were identified based on the m/z 257 fragmentogram indicated the existence of 5β-cholest-24-ene and 24-ethylcholestene compounds. These unsaturated sterane skeleton compounds are generally found in the coal samples with low carbonization. Only low rank coals that contain unsaturated hydrocarbon compounds [17, 36].

Sesquiterpenoids, Sesterterpenoids, and Diterpenoids

The presence of bicyclic sesquiterpane and sesterterpenoid compounds which were identified based on the m/z 123 fragmentogram and by comparing it with compound mass spectrum was already published previously [18, 37]. The five peaks identified in the fragmentogram are indicated as C_{15} bicyclic sesquiterpane such as C_{14} drimane; trans-guinane; 4β(H)-eudesmane; C_{16} homodrimane and sesterterpenoid des-A-lupane. The presence of bicyclic sesquiterpene biomarkers in the analyzed coal samples that were taken from the Inul area in the Sangatta coalfield, indicated that there were contributions of terrestrial higher plants resins and prokaryotic bacterias [38, 39].

The structure of eudesmane compounds are related to the carbon terpenoids skeleton which originated from terrestrial higher plants, whilst the drimane and homodrimane compounds were assumed to be derived from C_{35} bacteriohopanetetrol [30]. On the other hand, the drimane compounds could also be derived from drimenol which was produced by higher plants. The drimane compounds as well as the homodrimane compounds could also originate from hopane precursors, which indicated that there was a presence of bacteria entering the samples. The samples of drimane and homodrimane compounds have a steric similarities with the with A/B ring on the hopane compounds. Hence the discovery of drimanes as well as homodrimanes and hopanes indicated that both compounds originated from the same precursor, which is C_{35} bacteriohopanetetrol (Figure 5). This compound was produced by degrading C_{35} bacteriohopanetetrol through microbial activities during the diagenesis stage [40].

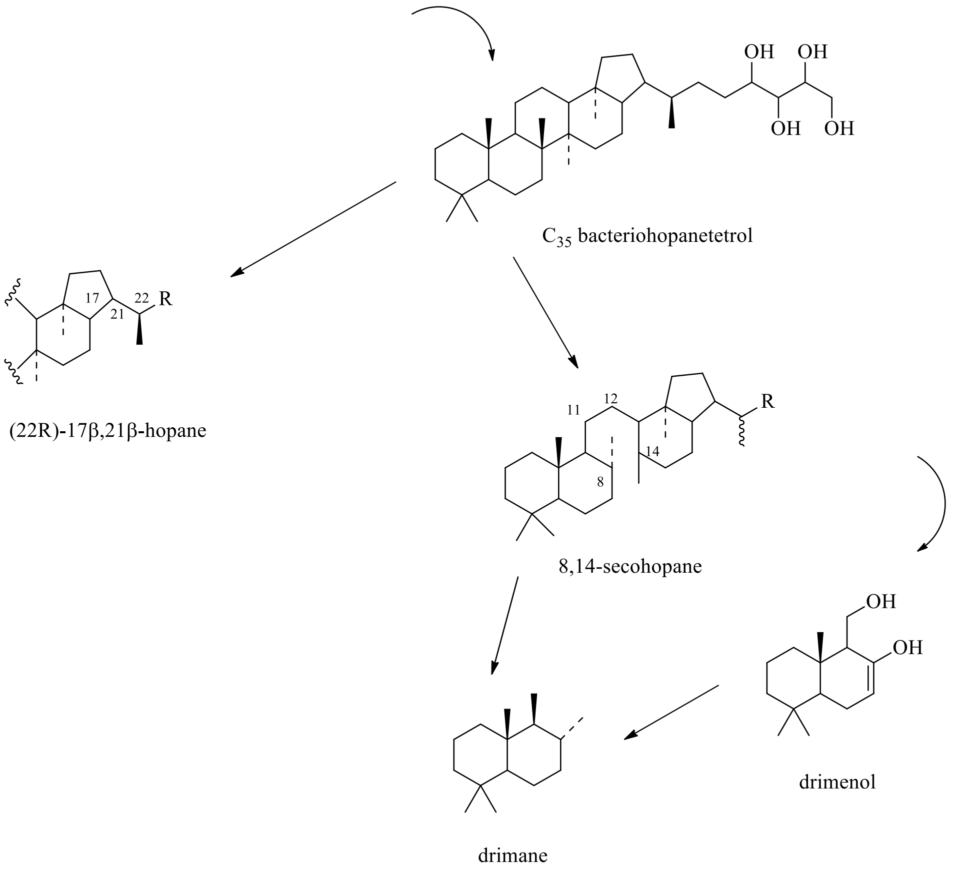


Figure 5 The biosynthesis paths of drimane and hopane compunds from bacteriohopanetetrol [23]

A fichtellite compound is a diterpane with abietane basic skeleton found in a low level of concentration. Fichtelite compounds are mostly used as terrestrial plant indicators as well as retene and ionene, which were found as crystalline depositions in lignites [40, 41]. The α-cadinene compounds are unsaturated structures of cadinanes found in high abundance from fichtellite and are an indicator of immature coal [36]. These cadinane compounds were found in higher plants dammar resin of Angiospermae, particularly Dipterocarpaceae, which a lot of them grow in South East Asia. One type of Dipterocarpaceae genus is *Shorea*, which is a typical plant of modern tropical ombrogenous areas that grows in swamps located in the low areas of Indonesia, particularly Sumatra and Borneo. Hence, Dipterocarpaceae plants are used as an indicator of the origins of Tertiary coal and peat origins in Indonesia [9].

Des-A-lupane compounds [identification based on: 18, 29] with sesterterpenoid skeleton which were identified by comparing the present results of the compound mass spectrum with the previous results of the compound mass spectrum that have been published previously [18, 29], were found in small concentrations inside the samples of Miocene coal that were obtained from the Sangatta coalfield. The sesterterpenoid compounds were not the main natural product, so their existence in the sediments are very limited [41]. The *des*-A-lupane compounds are considered as a photochemical or photomimetic product which experienced degradation in ring A. The reaction started with the oxygen functionalization at the C-3 atom positions of non-hopanoid triterpenoids from higher plants [41,42]. The *des*-A-lupane compounds are also considered as non-hopanoid triterpene which can also form due to microbial activities during the process of coal forming; hence their existence is proportional to the abundance of hopanoid compounds [43]. The existence of *des*-A-lupane compounds as well as *des*-A-oleanane and *des*-A-ursane in the sediment samples also indicated the vegetation dominance of Angiospermae plants in the era of Early Eocene [16]. The existence of *des*-A-lupane compounds could also originate from lupane type pentacyclic triterpene produced by *Eleocharis sp*., which is a species that inhabits in the lake environment. Since the other types of triterpene compounds could not be produced by this particular *Eleocharis sp*. species, then the existence of *des*-A-lupane is used as an indicator of the specific environment conditions in the process of making coal [44, 45]. The *des*-A-triterpenes compounds also provide information on the diagenesis process and used as an indicator of environment change. A couple of des-A-triterpenoids are found in Holocene peat deposits [45,46], and some others are found in older sediments [47,48]. Only a small amount of the existence of *des*-A-lupane as well as des-A-ursane and *des*-A-oleanane were reported to be found in the sediment samples. *Des*-A-lupane compounds are more widely distributed compared to the des-A-ursane and des-A-oleanane. This may be caused due to their resistance during the diagenesis stage [45].

4.0 CONCLUSION

- The brown coal that came from the Sangatta coalmine in the Balikpapan formation is estimated to be aged as old as Middle Miocene-Late Miocene, is an immature coal and orignated from Angiospermae higher plants. The coal is deposited in an oxic environment and the activities of microbes have effects on the process of forming coal organic compounds. The bimodal distribution is indicated by the distribution of short-chain *n*-alkanes hydrocarbon is an indicator of phytoplankton and zooplankton, and the distribution of long-chain *n*-alkanes hydrocarbon indicated that the coal organic compounds originated from Angiospermae higher plants.
- The domination of long-chain *n*-alkanes compared to the short-chain *n*-alkanes, and the presence of the unsaturated hydrocarbon compounds such as hopene, oleanane compounds, 5β-cholest-24-ene, 24-ethylcholestene and ββ-hopane compounds, are both can be potentially used as immature coal indicators with low calorific values. Hence, with the discovery of the biomarker compounds in the coals, then there is a possibility for the coals to be diversified. One of the ways of doing so is through the process of coal liquefaction (the process of turning coal to liquid).

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