CHAPTER VI

RESULTS

Twelve oil samples from different reservoirs and subunits of Sirikit Oilfield were analysed in this study (Table 8). The objective of the study was to reveal the biomarkers characteristic used for geochemical correlation of source, depositional environment, maturity and other alteration reactions of the oils. Most biomarkers were analysed by GC, GC-ITD, and the triple stage quadrupole GC/MS. Chromatogram for the RIC, m/z 123, and m/z 191 of all samples are shown in an Appendices 2, 3 and 4. The distribution and carbon-numbered identification of all terpane biomarkers of the Sirikit oil in this study are shown in Figure 22 and Table 9. Each of the biomarker characteristics will be described in the following sections.

BIOMARKER CHARACTERISTICS

Normal alkanes

Normal alkanes and their precursors are the most common biomarkers which are widely distributed among the plant kingdom and are biosynthesized along combining with fatty acids and alcohols. N-alkanes can also originate from saturation and/or defunctionalization of saturated and unsaturated monocarboxylic acids present in stored

Table 9. Crude Oils Examined in this Study.

Sample	Subunit Reservoir	Depth Interval (m)
TA-1	M30	1445-1451
LB-1	L10/20/30	1894-2118
TC-1	L0/L40	1842-1975
SD-4	M30/40	1525-1753
LD-4	L0/LL	1779-1972
TE-7	M20	1593-1666
LF-7	LL	1848-1980
TG-2	M30	1568-1637
TK-2	M20	no information
SK-6	M30	1594-1701
SL-3	M30	no information
TP-2	M30	no information

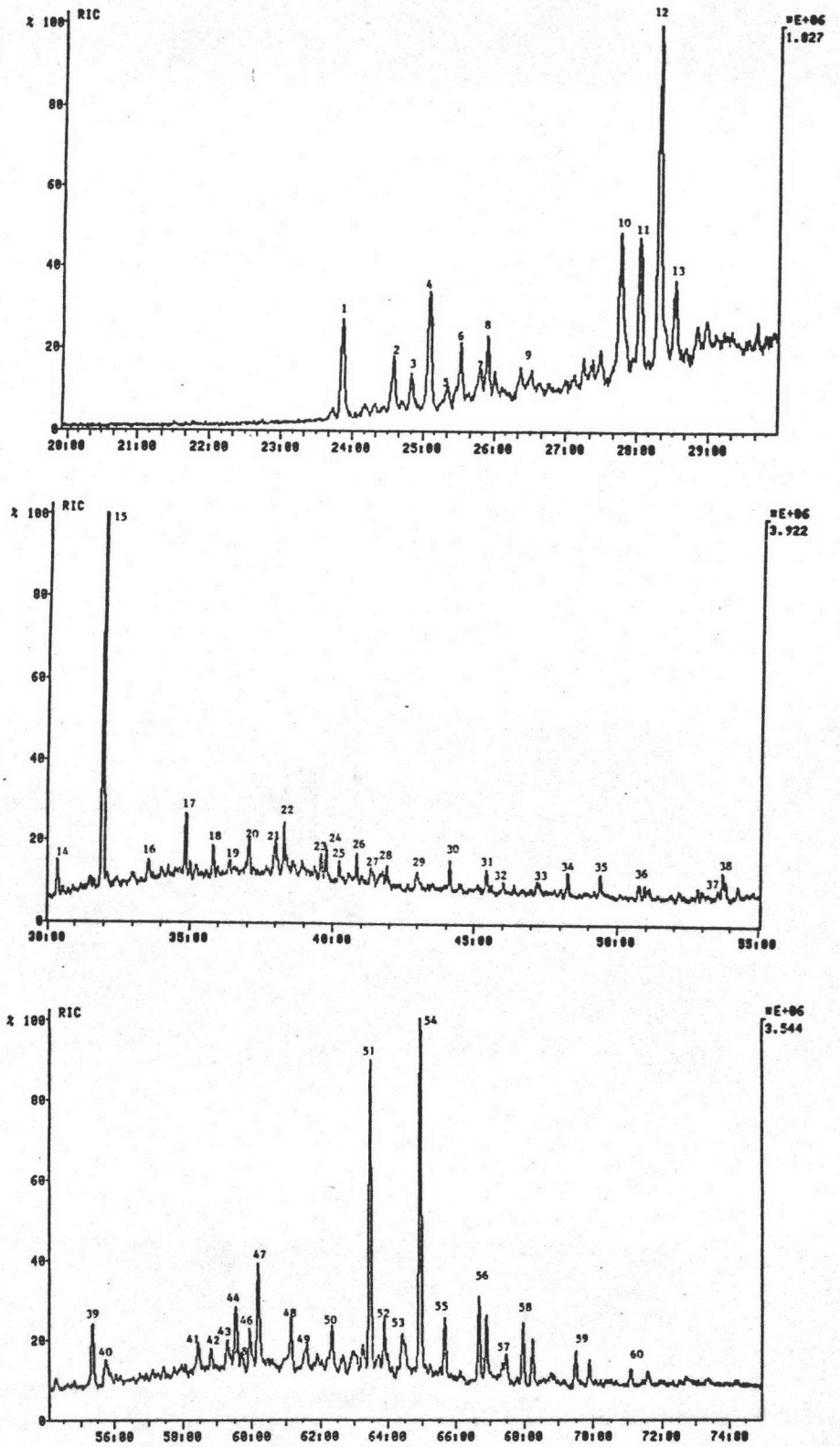

Figure 22. Mass chromatogram of biomarkers distribution of Sirikit crude oil.

Table 10. Identification of terpanes in the Sirikit crude oil chromatogram shown in figure 22

Peak No.	Biomarker Identification
1.	C_{14}-Bicyclic Sesquiterpane
2.	
3.	
4.	C_{14}-Bicyclic Sesquiterpane
5.	C_{14} and C_{15}-Bicyclic Sesquiterpanes
6.	C_{15}-Bicyclic Sesquiterpane
7.	C_{15}-Bicyclic Sesquiterpane
8.	C_{15}-Bicyclic Sesquiterpane
9.	C_{15}-Bicyclic Sesquiterpane
10.	C_{14}-Bicyclic and C_{14}-Tricyclic Diterpanes
11.	C_{14}-Bicyclic and C_{14}-Tricyclic Diterpanes
12.	C_{14}, C_{15} and C_{16}-Bicyclic Sesquiterpane
13.	
14.	
15.	Pristane
16.	C_{18}-Bicyclic Sesquiterpane
17.	Phytane
18.	C_{17} and C_{18}-Tricyclic Diterpanes
19.	C_{18}-Tricyclic Diterpane
20.	C_{17} and C_{18}-Tricyclic Terpanes
21.	C_{19}-Tricyclic Diterpanes and C_{20}-Bicyclic Sesquiterpane
22.	C_{19}-Tricyclic Diterpane
23.	C_{19}-Tricyclic Terpane
24.	C_{19}-Tricyclic Terpane
25.	
26.	C_{21}-Bicyclic Sesquiterpane
27.	C_{20}-Tricyclic Terpane
28.	C_{20}-Tricyclic Terpane
29.	
30.	C_{21}-Tricyclic Terpane
31.	C_{21}-Tricyclic Terpane
32.	C_{22}-Tricyclic Terpane
33.	
34.	C_{23}-Tricyclic Terpane
35.	C_{24}-Tricyclic Terpane
36.	C_{24}-Tetracyclic Terpane
37.	C_{26}-Tricyclic Terpane
38.	C_{24}-Tetracyclic and C_{26}-Tricyclic Terpanes
39.	C_{27}-8,14-Secohopane
40.	C_{27}-8,14-Secohopane

(continue)

(Table 10.)

Peak No.	Biomarker Identification
41.	C_{29}-8,14-Secohopane
42.	C_{29}-8,14-Secohopane
43.	C_{28} and C_{29}-8,14-Secohopane
44.	C_{28} and C_{29}-8,14-Secohopane
45.	C_{29}-8,14-Secohopane
46.	C_{30}-8,14-Secohopane
47.	C_{28}-Trisnorhopane (Ts)
48.	C_{28}-Trisnorhopane (Tm)
49.	C_{30} and C_{31}-8,14-Secohopanes
50.	C_{30}-8,14-Secohopane
51.	C_{29}-Norhopane [17α(H),21β(H)]
52.	
53.	C_{29}-Normoretane [17β(H),21α(H)]
54.	C_{30}-Hopane [17α(H),21 (H)]
55.	C_{30}-Moretane [17β(H),21α(H)]
56.	C_{31}-Homohopanes [22S and 22R]
57.	C_{30}-Gammacerane
58.	C_{32}-Bishomohopane

Table 11. Compositional Analysis Data of the Sirikit Oil Samples.

Sample	% Saturates	% Aromatics	% NSO's	% Asphaltene
TA-1	46.76	10.53	17.34	25.37
LB-1	39.27	8.66	14.66	37.41
TC-1	50.04	12.29	17.40	20.27
SD-4	48.88	11.87	16.06	23.19
LD-4	52.73	12.54	12.47	22.26
TE-7	41.87	8.70	19.15	30.28
LF-7	46.45	10.63	19.07	23.85
TG-2	45.51	10.75	18.10	25.64
TK-2	44.61	10.06	13.82	31.51
SK-6	45.39	5.15	24.34	25.12
SL-3	53.92	15.23	11.26	19.59
TP-2	62.21	7.96	19.46	10.37
mean	48.14	10.36	16.93	24.57

fats and phospholipids of alga membranes. Most of the oil samples examined in this study contained high proportion of saturated hydrocarbons (Table 10) and have a n-alkane distribution in the C_{10} to C_{40} range (Appendix 5). The n-alkanes show bimodal distribution with the first rang maxima in the between C_{16}-C_{18} and the second between C_{21} and C_{29}. The first range in the C_{16} to C_{18} is predominated by odd-carbon number n-C_{17} peak. The abundance between n-C_{21} and C_{29} indicates their derivation from terrigineous material in the depositional environment by direct synthesis, or via defunctionalization of even-carbon numbered acids, alcohols and esters (TISSOT and WELTE, 1978). However, a strong odd-carbon number dominance of n-alkanes, especially in the range C_{23} to C_{35} can be decreased by bacterial action during diagenesis, either by bacterial reworking or by the contribution of n-alkanes from bacteria themselves (TISSOT and WELTE, 1984; ALBAIGES et al., 1985). A marked odd/even predominance in the n-alkane distributions can be converted into a distribution with little or no odd/even preference as the maturity level of the sample increases as a result of further degradation and thermal cracking.

In addition to the source materials, biodegradation can also influence the distribution of n-alkanes in crude oils. The first stage of bacterial degradation will remove low molecular weight n-alkanes, followed by alkanes in the n-C_{16} to n-C_{25} range and

finally by these above n-C_{25} (POWELL and MCKIRDY, 1972). However, biodegradation is sometimes accompanied by water washing which can also effect the distribution of n-alkanes in crude oil (MILNER et al., 1977) and produce distribution similar to those resulting from biodegradation. Most oil samples show no biodegradation and/or water washing effect because no removal evidence of n-alkane had been observed. This is also supported by the characteristics of the other biomarkers.

Isoprenoids

One of the first uses of biomarkers for recognition of depositional environments was based on the relative amounts of pristane and phytane (PHILP, 1987 and ref. therein). It has been proposed that phytol side chain of chlorophyll-A is produced by diagenetic hydrolysis of chlorophyll and subsequent oxidation, decarboxylation and reduction will produce pristane, Dehydration and reduction of phytol will, in more reducing conditions, result in phytane. Therefore, the relative abundance of pristane to phytane will depend on the initial reducing character of the local environment (TISSOT and WELTE, 1978). High abundance of pristane relative to phytane is believed to be indicative of an oxidizing environment. It can be seen in gas chromatograms of saturate fractions of all the Sirikit crude oil samples (Appendix 6) that there is a clear predominance of C_{19} isoprenoid, pristane, over the C_{20}

isoprenoid, phytane. The Pr/Ph ratios of these oils are between 2.7 and 3.7 (Table 11). It is probably concerned to an oxidizing depositional environment in early stage of diagenesis and the environmental type. This is understandable as conditions are dependent on the geological setting, the lacustrine depositional environment, which was shallow, large lake. Therefore, it is reasonable to assume that the condition "shallow lake" of this basinal environment might also had been very well oxygenated. The Pr/Ph ratios are then in agreement with the geological setting data.

Bicyclic sesquiterpanes

The source precursor of bicyclic sesquiterpanes in geological sample is as not well established. There are the reports which have suggested that these compounds may result from degradation of steroids or triterprenoid hydrocarbons of plants (ANDER et al., 1971; BENDORAITIS 1973). The most abundant and well studied bicyclic sesquiterpanes are drimane and eudesmane. Drimane has been reported to have a widespread occurrence in Ordovician samples. Their precursors were not land plant derived but can be attributed to degradation of steranes, hopanes or onoceranes (ALEXANDER et al., 1985), whereas eudesmane has been proposed to be derived from higher plant precursor, eudesmanol, and is always present in non-marine, land plant source oils (PHILP et al., 1981, 1985). For oils from Sirikit Oilfields, they show a high

Table 12. The Biomarker Parameters of the Sirikit Crude oil Compositions.

Sample	OEP	Pr/Ph	Pr/n-C_{17}	Ph/n-C_{18}
TA-1	0.96	2.70	0.24	0.09
LB-1	0.98	3.00	0.26	0.09
TC-1	1.01	3.00	0.25	0.09
SD-4	1.10	4.00	0.30	0.09
LD-4	0.91	2.80	0.29	0.11
TE-7	1.05	3.50	0.29	0.09
LF-7	1.03	2.91	0.27	0.10
TG-2	0.95	3.45	0.30	0.10
TK-2	1.05	3.56	0.29	0.09
SK-6	1.10	3.57	0.29	0.10
SL-3	0.98	3.50	0.29	0.09
TP-2	1.10	3.71	0.28	0.09
mean	1.01	3.31	0.28	0.09

variable concentration of bicyclic sesquiterpanes in C_{14}-C_{16} range (Appendix 7). The distribution is different from the sesquiterpane distribution in non-marine Australian oils proposed by PHILP (1981). By GC/MS/MS analysis of the mass ion m/z 123, comparing the MID and daughter/parent mode, it can suggest that these oil which also have material precursors are terrigenous higher plants. Both drimane and eudesmane could not be identified exactly in these oils because their distributions are not identical to other previous studies (ALEXANDER et al., 1983; PHILP et al., 1981; BENDORAITIS, 1973). Therefore, the identification of sesquiterpanes in this study was based on the carbon number comparison to a spectrum of MID and daughter/parent mode. Many spectrums represented C_{14}-C_{16} bicyclic sesquiterpanes in these oils may represent the stereoisomeric compounds. Five C_{14}, three C_{15} and one C_{16}-carbon numbers stereoisomers of sesquiterpanes have been seen in these oils. Examination by looking at daughter ion m/z 123 and 109 in a daughter/parent mode suggests the possible structure for those isomers of C_{14} probably are eudesmane structure rather than drimane structure, whereas some of C_{15} isomers may have drimane structures. The presence of drimanes in the oils are probably concerned to the bacteria contribution in the depositional environment. ALEXANDER et al.(1983) analysed bicyclic sesquiterpanes of crude oil from worldwide . sources which were not identical in their

distribution but all contained drimane compounds. They suggested that drimanes may be derived from a ubiquitous source, except that the possibility of its being derived from higher plant precursors. They state that the most likely conclusion is a microbial origin. In addition, drimanes can arise either from microbial degradation of higher terpanes such as hopanes or from direct formation of a compound or compounds containing the bicyclic ring system. This is a direct contrast with eudesmane which was found in land plant-based crude and undoubtedly reflects its higher plants origin.

Diterpanes

Diterprenoids form a large group of compounds which are widely distributed in the plant kingdom. Tricyclic diterprenoids are abundant in higher plants and are major constituents of conifer resins. The diterprenoids usually occur as diterpane compounds in sediments and in crude oils (PHILP et al.,1983; LIESEY et al.,1984) which can be use for terrestrial source biomarkers. These diterprenoids had been buried and had undergone diagenesis or early catagenesis. Despite the increased use of diterpanes as geochemical markers for higher plants in sediment, coal and crude oil, there remains some ambiguity regarding their structures. DOUGLAS and GRANTHAM (1974) analysed the distribution of the diterprenoids in various fossil resins and reported the major diterprenoid in saturate fraction of retinite

was fichtelite and the minor component was an unidentified C_{19}-norditerpanes.

In this study the distribution of tricyclic diterprenoid compounds was analysed by GC/MS at the mass ion m/z 123, 191 in daughter/parent and MID mode. In daughter/parent mode, the parent ions were set at the mass ion m/z 220 of C_{16}-diterpane to m/z 304 of C_{22}-diterpane. By comparing the daughter ions at m/z 123 and 191, the mass chromatograms of the carbon number of tricyclic diterprenoids in these oil were shown in Appendix 8. No significant distinguished distribution of diterpanes could be seen in these oils. The major compounds are C_{19}-diterpanes of the parent ion at m/z 262. Combinations between tricyclic diterprenoid and bicyclic compounds in the same retention time contribute an ambiguous peak identification. But by comparison with published data (DOUGLAS and GRANTHAM, 1974; SIMONEIT, 1977; PHILP et al., 1981; RISHARDSON and MILLER, 1982; LIESEY et al., 1984), the major peaks which have molecular ion at m/z 262 are confirmed to be C_{19}-tricyclic norditerpanes. The proposed structure of 4 peaks of C_{19}-tricyclic norditerpanes have been reported in sediments from an offshore (Labrador) well by LIESEY et al.(1984) were C_{19}-norpimarane or norisopimarane and norabietane skeletons. A relatively low concentration of diterprenoid compounds in these oils made it difficult to identify exactly. However, the presence of these compounds in the oil samples can infer to a terrigenous

higher plant or, more specificially, of a resin to the source material. BARRICK and HEDGES (1984) suggested that the C_{19}-diterpanes may sometimes be produced by different diagenetic pathways, and further noted a lack of correlation between the occurrence of plant wax n-alkane and diterprenoid hydrocarbon. Therefore, a better knowledge of the diagenetic pathway of diterprenoid compounds for indication is desperately needed.

Tricyclic terpanes

The homologous serie of tricyclic terpanes present in most samples was found in range from $C_{19}H_{34}$ to $C_{30}H_{56}$ (AQUINO NETO et al., 1983). Presently, they have been accepted to extend to $C_{45}H_{86}$ (MOLDOWAN et al., 1983) and have been reported as appearently absent in recent sediments. This absence implies the formation of these terpanes during maturation rather than diagenesis. The major tricyclic terpanes series which have been reported in sediment and petroleum are C_{19} and C_{20} members, which probably are degraded from tricyclohexaprenane. A likely biological precursor of this compound could be tricyclohexaprenol which is formed anaerobically from cyclication of a universal cell constituent, regular hexaprenol unlike C_{19} and C_{20} diterprenoids, e.g. abeitane primalane and norabeitane which are also tricyclic compounds but derived from terrestrial material. The extended tricyclic terpanes (C>20) are believed to be derived from a marine source (SIMONEIT et

al., 1980) but AQUINO NETO et al. (1983) reported the tricyclic terpanes were presented in all oils except those derived from terrestrial source material. This ubiquity implied a microbial or algae origin of tricyclic terpanes.

The identification of the C_{19}-C_{28} tricyclic terpanes in this study is based on the mass fragmentogram at mass ion m/z 191 of GC/MS/MS analysis. By comparison, the molecular ion in MID and daughter/parent mode, the C_{19} homologous serie is clearly a predominated member of tricyclic terpanes in these oil samples. The abundance of lower molecular weight tricyclic may be a function of maturity due to cracking of the side chain of higher molecular weight homologue (AQUINO NETO et al., 1981). As mentioned earlier, they tend to be more abundant in oil derived from marine source material, than terrestrial originated source. This has been suggested that they may have natural precursors specific to marine environments. The distribution and carbon number of tricyclic terpanes in Sirikit crude oils are shown in Appendix 9.

Tetracyclic terpanes

Tetracyclic terpanes have not been widely reported in crude oils or source rocks. Their origin has been proposed as the thermal evolution from pentacyclic triterpane, thus these terpanes have a role for thermal maturity indicators. Tetracyclic terpanes usually are detected in crude oil and source rock by using GC/MS and

MID of the characteristic ion at m/z 191 in the C_{24} to C_{27} range. The naturally occurring compounds have been suggested as possible precursors, as has the degradation of hopanoids by the clevage of the C_{17}-C_{21} bond. The abundance of tetracyclic terpanes in these oils show a low concentration at mass ion m/z 191 (Appendix 9). Identification of these compounds was based on a comparison of molecular ion m/z 191 and 123 of C_{21} to C_{27} compounds in daughter/parent and MID mode in GC/MS/MS experiment. The occurrence of 17,21-secohopanes or tetracyclic terpanes in these oils may suggest the following study of TRENDEL et al. (1982) that (i) a thermo-catalytic degradation of pentacyclic hopane precursors geologically matured, or (ii) a microbial opening of ring-E hopanoids e.g. oxidation of hop-17(21)-enes at the early stage of diagenesis followed later by a geochemical reduction to the corresponding alkanes occurred, or (iii) a cyclization of precursor squalene stoping at ring-D, leading to tetracyclic precursors which could be further reduced by the geochemical processes developed. These tetracyclic hopanoids could in this case also represent a novel class of bacteria constituent in these oils.

8,14-Secohopanes

The 8,14-tetracyclic secohopanes are believed to be derived from the pentacyclic terpane by ring-C opening. They can be analyzed by monitoring the mass ion

at m/z 123 of GC/MS and MID mode. This is the mass ion difference for identifying between regular tetracyclic terpanes, 17,21-secohopanes, and 8,14-secohopanes. The mass spectra of 8,14-secohopanes in these oils were analyzed by daughter/parent and MID mode of the GC/MS/MS. The results of homologous serie of 8,14- secohopanes were observed, ranging from C_{27} to C_{31}, and corresponding to the molecular ion ranging from m/z 372 to 428. The chromatograms are shown in Appendix 10. The 8,14-secohopanes which have been previously reported were observed in C_{27} to C_{29} carbon-numbered range (SCHMITTER et al., 1982). The origin of 8,14-secohopanes is at present unclear, although RULLKOTTER (1982) proposed the biodegradation effect. These compounds may have a thermal origin as the 8,14 bond might posess the lowest energy (SCHMITTER et al., 1982). The lack of evidence of crude oil biodegradation effect and maturity of these oils, may be correspondent toward the microbial degradation effect in the early stage of diagenesis.

Pentacyclic triterpanes

All crude oil samples studied in this topic illustrate a similar distribution chromatogram of pentacyclic hopanes in the range of C_{27} to C_{35}. The identification was based on chromatogram description in PHILP (1985; and ref. therein) and comparing the molecular ion m/z 370 to 496 to a daughter ion m/z 191 in daughter/parent and MID mode of GC/MS/MS experiment.

Table 13. The Biomarker Parameters from Triterpane Distribution of the Sirikit Oil Samples.

Sample	Tm/Ts	$\frac{C_{30}\ Hopane}{C_{29}\ Hopane}$	$\frac{22S C_{31}\ Hopane}{22R}$	$\frac{C_{30}\ Moretane}{C_{30}\ Hopane}$
TA-1	0.48	1.41	1.16	0.15
LB-1	0.50	1.35	1.30	0.16
TC-1	0.54	1.56	1.22	0.13
SD-4	0.60	1.39	1.30	0.17
LD-4	0.61	1.43	1.36	0.16
TE-7	0.41	1.27	1.38	0.16
LF-7	0.58	1.38	1.27	0.15
TG-2	0.71	1.37	1.45	0.15
TK-2	0.58	1.45	1.41	0.17
SK-6	0.57	1.34	1.32	0.16
SL-3	0.53	1.36	1.21	0.16
TP-2	0.67	1.41	1.12	0.15
mean	0.56	1.39	1.28	0.16

Undoubtedly, the carbon-numbered was identified because of their relatively high concentration compared to the other biomarkers. The distribution chromatogram of hopanes of these oils are shown in Appendix 11. The ratios of C_{27} hopane, Tm, 17α(H)-22,29,30-trisnorhopane and Ts, 18α(H)-22,29,30-trisnorhopane are from 0.41 to 0.67 range. As reported by AQUINO NETO et al. (1981), in a heating experiment, with increasing thermal maturity the hopane series will shift to the more stable (Tm) low molecular weight C_{27} homologous. This means the abundances of Tm, Ts and norhopane to hopane are concerned to maturity of crude oil samples. Ts has been reported ubiquitously occurring in most every crude oil (PYM et al., 1975).

The stereoisomer configuration of hopanes has also been reportedly effected by maturation. In these oils, the main stereoisomer is the 17α(H),21β(H) configuration. This configuration is mentioned to be a thermodynamic configuration processed by the majority of hopane in crude oil and mature source rock. It was affected by diagenesis. The maturation of the organic precursors leads to defunctionalization and formation processes. The 17β(H),21α(H)-diastereomers are also presented in minor amount in these oils whereas the C_{30} hopanes are dominated over C_{29} hopanes. Generally, the predominance of C_{29} hopanes in source rock or crude oil has been found in such samples derived from an evaporite-carbonate source. The ratios of C_{30}/C_{29} hopanes of

Sirikit oils are from 1.27 to 1.56 range. The epimer configurations, 22S and 22R, of C_{31}-hopanes of these oils are predominated by 22S epimers. The ratio of 22S/22R C_{31} hopanes are ranged from 1.12 to 1.45. C_{30} Moretane/hopane ratios are from 0.13 to 0.17 range which are rarely high in general crude oil. This ratio was observed less than 0.1 for some sediments or crude oils from Tertiary basins (GRANTHAM, 1986). The parameters from pentacyclic hopanes are shown in Table 12.

Steranes

Steranes have proved to be very useful as biomarkers (MACKENZIE et al., 1982) and are generally studied by monitoring at mass ion m/z 217. All crude oils in this study were analyzed by the distribution of sterane by GC/MS/MS at daughter/parent and MID mode, including short chain sterane region, C_{21} and C_{22} compounds. The relatively sterane concentration in these oils is anomalously low when compared to hopane concentrations. There is no presence of C_{30} steranes which are held to be diagnostic of marine environments (MOLDOWAN, 1985). The lack of steranes in lacustrine freshwater depositional environments has been noted from analyses of oils from Brazil, China, Sudan and Australia (MOLDOWAN et al., 1985; MCKIRDY et al., 1986; MELLO et al., 1988). The possible explanation has been suggested by MELLO et al., (1988) that its due to the living organism in such a habitat, using lipids other than

Table 14. The Biomarker Parameters from Steranes Distribution of The Sirikit Oil Samples.

Sample	$C_{27}:C_{28}:C_{29}$	$\frac{C_{29}}{C_{27}}$ ($\alpha\alpha\alpha$ 20R)	$\frac{\alpha\alpha 20S C_{29}}{20S+20R}$	$\frac{\alpha\beta\beta 20 C_{29}}{\alpha\alpha\alpha}$	Hopane ster	C_{29} Dia Ster
TA-1	1:1.9:4.0	4.04	0.30	0.58	30.7	0.62
LB-1	1:2.6:6.1	6.09	0.30	0.67	32.1	0.79
TC-1	1:1.8:4.9	4.85	0.26	0.86	47.5	1.00
SD-4	1:2.7:7.1	7.10	0.26	0.72	30.8	0.65
LD-4	1:3.7:7.9	7.86	0.31	0.71	28.1	0.69
TE-7	1:2.0:4.0	4.15	0.25	0.72	30.8	0.94
LF-7	1:3.6:8.0	8.00	0.29	0.82	35.9	0.89
TG-2	1:3.5;5.8	5.80	0.28	0.82	26.7	0.79
TK-2	1:2.7:5.4	5.40	0.23	0.67	33.1	0.77
SK-6	1:2.1:5.2	5.15	0.25	0.79	28.4	0.97
SL-3	1:2.2:4.5	4.47	0.28	0.75	34.7	0.70
TP-2	1:2.6:6.5	6.50	0.28	0.69	44.1	0.73
mean	1:2.6:5.8	5.78	0.27	0.73	33.6	0.80

sterols as rigidifier and as a protector of cell wall materials. This protection is necessary for terrestrial and freshwater plants which live under higher oxygenated condition than their saline counterparts and therefore require greater protection for their cells. In addition, all crude oils examined in this study illustrated the anomalously low concentration of isomers of C_{29} sterane. Many crude oils from Tertiary source rocks have been reported due to an incomplete sterane isomerization that contribute relatively low concentration of isomer ratios (GRANTHAM, 1986). An insufficient time controlled reaction rate of the incompletion of isomerization reactions has been suggested to these Tertiary oils. The other proposal was suggested to deltaic land-plant-containing source rocks generated crude oils under low heating condition and non-indigenous organic matter contribution during oil migration along immature source rock. Rapid burial of sediments under high heating rate condition and a mixing of mineral matrix or dispersed coals in the source rock affected the reaction rate of isomerization of sterane were proposed by STRACHAN et al. (1988, 1989). Hence, the constraints on the use of C_{29} sterane isomer ratios as maturity indicator might be affected by source material and heating rate of such depositional environment.

The parameters of different steranes and different isomers of Sirikit crude oils are shown in Table 13. The predominance of C_{29} related to C_{27} and C_{28}

steranes can be seen in most oil samples in this study. Therefore, this is indicative a higher plant input or characteristic of a non-marine source of the Sirikit oil samples. Nevertheless, the interpretation must be made with caution since MELLO et al. (1988) found a dominance of C_{27} steranes in lacustrine/freshwater Brazilian offshore oils and C_{29} steranes have also been reported found increasingly in marine oils (WALTERS and CASSA, 1985) and recent marine sediments (VOLKMAN et al., 1981).

An appearance of rearranged steranes or diasteranes can be seen in most samples inspite of a several relatively low concentration. There was some evidence from the thermal maturation experiments using hydrous pyrolysis of LEWAN et al. (1986) that the abundance of C_{27}-C_{29} regular steranes will decrease with increasing maturity. By increasing temperature, the decrease in an abundance of regular steranes will be related to diasterane concentration. It is believed that diasterane is a more thermally stable than regular sterane. The identifications of short chain steranes and C_{27}-C_{29} steranes are shown in Appendix 12 and 13. They were based the description of PHILP (1985) and GC/MS/MS analysis in daughter/parent and MID mode at mass ion m/z 217. However, it should be noted that because of a relatively low concentration and a low sensitivity in the distribution, a problem of baseline in a calculating ratios of sterane epimers occurs.

4-Methylsteranes

4-Methylsteranes examined in this study were analyzed on the mass ion m/z 231 in MID and daughter/parent mode. The molecular ions were analyzed at m/z 386, 400 and 414 for C_{28} to C_{30} methylsteranes. The distribution of methylsteranes of these oil samples are shown in Appendix 14. A presence of 4-methylsteranes in sediment and crude oil has been reported in some studies (MACKENZIE et al., 1980; MOLDOWAN et al., 1985). They are believed to be derived from the 4-methylsterols produced by dinoflagellates (DE LEEUW et al., 1983; MCKIRDY et al., 1986). Although dinoflagellates are common in both lacustrine and marine environments, they are reported that an appearance of high concentration of 4-methylsteranes in oils is associated with lacustrine source rocks (VOLKMAN, 1988, ref.therein). All Sirikit oil samples analysed in this study show a significant concentration of C_{30} 4-methylsteranes relatively to other biomarkers.

Aromatic Compounds

The biomarkers of aromatic hydrocarbons in this study were analysed by the GC-ITD in MID mode. The mass ions were based on naphthalene, phenanthrene and aromatic sterane compounds. The chromatograms and peak identification are shown in Appendix 15. The monoaromatic and triaromatic steranes could not be seen in significant concentration in these samples. The more

abundances are naphthalene and phenanthrene compounds. However, naphthalene and alkylnaphthalene are less concentrated than phenanthrene and alkylphenanthrene. The distribution of aromatic steranes in crude oils are determined by their maturity levels. An absence of monoaromatic and triaromatic steranes in the samples have been suggested referring to the low maturity level (SHI et al., 1981). The relative amount of naphthalene and alkylnaphthalene are usually higher than phenanthrene or other aromatic steranes and triterpanes in oils and particular condensates (HALL et al., 1985). For these oils the distribution of aromatic compounds used to be maturity biomarker is therefore based on phenanthrene and alkylphenanthrene compounds (Table 14). The MPR parameter based on 2-methylphenanthrene/1-methylphenanthrene ratios are 0.9 to 1.5 range. The MPI1 and MPI2 are 0.46 to 1.37 range and 0.54 to 1.55 range. These ratios are based on a different combination of four isomeric methylphenanthrene and phenanthrene compounds which are depend upon their maturity levels. Based on the MPI parameter, it is suggested by the assumption that 2- and 3-methylphenanthrene are derived not only from 1- and 9-methylphenanthrene by rearrangement but they are also derived from phenanthrene through methylation reaction. Therefore, the presence of 2- and 3-methylphenanthrene in a relative amount to other three compounds means to a potential of organic precursor and maturity level of three latter compounds.

Table 15. The Biomarker Parameters of Aromatic Hydrocarbon Fraction of the Sirikit Oil Samples.

Sample	MNR	MPR	MPI1	MPI2
TA-1	0.87	0.90	0.70	0.54
LB-1	-	0.98	0.66	0.68
TC-1	0.86	1.04	0.86	0.90
SD-4	1.53	1.50	1.06	1.31
LD-4	-	1.18	1.13	1.05
TE-7	-	1.15	0.95	1.10
LF-7	-	1.10	0.61	0.65
TG-2	-	1.33	0.46	1.27
TK-2	-	1.20	1.22	1.25
SK-6	-	1.28	1.17	1.19
SL-3	-	1.48	1.13	1.30
TP-2	-	1.32	1.37	1.55
mean	-	1.21	0.94	1.06

MNR = β-Naphthalene / α-Naphthalene

MPR = 2-m-Phenanthrene / 1-m-Phenenthrene

$$MPI1 = \frac{1.5 \times (2\text{-m-Phenanthrene} + 3\text{-m-Phenanthrene})}{\text{Phenanthrene} + 1\text{-m-Phenanthrene} + 9\text{-m-Phenanthrene}}$$

$$MPI2 = \frac{3 \times (2\text{-m-Phenanthrene})}{\text{Phenanthrene} + 1\text{-m-Phenanthrene} + 9\text{-m-Phenanthrene}}$$

STABLE CARBON ISOTOPES

In this study ^{13}C isotopic compositions were determined in the saturate and aromatic fractions (Table 15). A Sofer-type plot (SOFER, 1984) was also constructed for the $\delta^{13}C$ (permil) values of these saturate and aromatic fractions and is shown in Figure 23. The $\delta^{13}C$ values of saturate fraction range from -29.43 ‰ to -31.44‰ and -29.11‰ to -31.07‰ for the aromatic fraction. The average values of saturates of K and L reservoir are -30.00‰ and -30.84‰ respectively and -29.53‰ and -30.14‰ for the aromatic hydrocarbon. The average values of both fractions from different reservoirs are not much different since the crude oils are believed to be derived from same sources. Nevertheless, $\delta^{13}C$ values of saturate and aromatic fractions of Sofer-type plot fall in the region of non-waxy or oils derived from marine sources (Figure 23). The Canonical Variable (CV) values also range from -2.2 to -0.5 which refer to marine source oils. This phenomenon has also been observed in waxy crude oils from Indonesia (SOFER, 1984) and Australia (MCKIRDY et al., 1986). SOFER suggested to an uncommon occurrence sources of contemporaneous group of marine organisms that can synthesize long, straight-chain waxy hydrocarbon or/and the maturation affected this anomaly. An alternative source, C_{34}-botryococcane, generated high molecular alkanes which might affected such phenomena, has been proposed to be the source of oils from Australia.

Table 16. The Stable Carbon Isotope ($\delta^{13}C$) of Saturate and Aromatic Fraction of the Sirikit Oils.

Sample	$\delta^{13}C$Saturates	$\delta^{13}C$Aromatics	CV Value
TA-1	-31.44	-31.07	-1.08
LB-1	-30.81	-30.26	-0.88
TC-1	-30.96	-30.26	-0.50
SD-4	-29.87	-29.30	-1.13
LD-4	-30.72	-30.05	-0.64
TE-7	-29.63	-29.12	-1.33
LF-7	-30.85	-29.98	-1.15
TG-2	-29.75	-29.11	-1.01
TK-2	-29.56	-29.15	-1.58
SK-6	-29.43	-29.28	-2.19
SL-3	-30.22	-29.71	-1.50
TP-2	-30.11	-29.48	-0.92
mean	-30.28	-29.73	-1.16

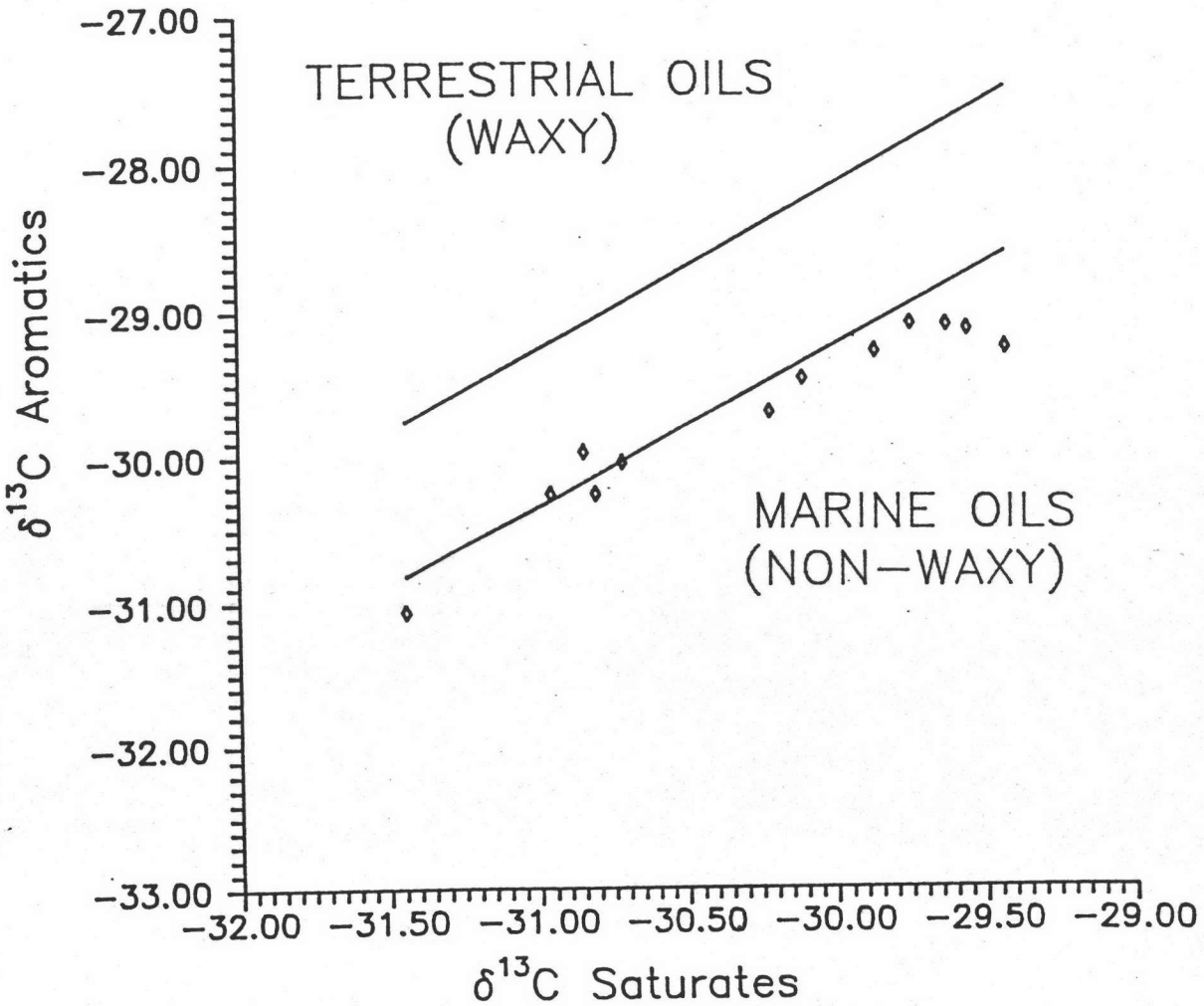

Figure 23. $\delta^{13}C$ isotopic compositions of saturate and aromatic hydrocarbon fractions of Sirikit oil samples followed Sofer type plot.