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# Gas chromatography and gas chromatography–mass spectrometry study of hydrocarbons in Vlasta oil (Adriatic Basin) as the basis for geochemical interpretation

A. ALAJBEG*, A. TODORIĆ and S. ŠVEL-CEROVEČKI

*INA-Oil Industry, Research and Development, Zagreb (Yugoslavia)*

and

M. ŠUSTĚRČIĆ

*Naftaplin, Zagreb (Yugoslavia)*

## ABSTRACT

In order to elucidate the chemistry and geochemistry of Vlasta oil (central Adriatic Basin) a gas chromatography and gas chromatography–mass spectrometry study of hydrocarbon composition and structure was performed, as well as some global geochemical characterization. Twenty-one components of the light end of the oil, 83 components of the whole-oil sample and 17 components of the heavy end of the oil were identified by gas chromatography and by a gas chromatography–mass spectrometry coupled system. The light components are represented by straight and branched alkanes, cycloalkanes and aromatics, whereas thioethers are found to be whole-oil components. The heavy components are represented by pentacyclic triterpanes. The obtained results have shown algal and bacterial biomass to be the most probable origin of the Vlasta oil, which was deposited in anoxic hypersaline in carbonate beds during the Triassic period. Oil was released from related kerogen in the early stage of maturity. It underwent no significant biodegradation.

## INTRODUCTION

The composition of an oil (petroleum) reflects the origin and deposition of precursors, the stage of maturation of the related source rock and the history of oil migration and trapping in geological strata [1,2]. In studying oils, modern analytical chemistry offers the possibility of detailed investigation at the level of interest.

In order to obtain global composition characteristics, oils are investigated by NMR [3,4], liquid chromatography, thin-layer chromatography [5] and other techniques for group analysis. Many valuable geochemical parameters depend upon individual constituents.

Many efforts have been made to indentify oil components [6,7], and many geochemical rules enable the conversion of analytical data into geochemical parameters, which are important in studying oils and oil basins.

Oil constituents can be identified by gas chromatographic–mass spectrometric (GC–MS) analysis of whole oil [8] as well as of oil fractions. In addition to full mass

spectra, mass fragmentograms help to discriminate between compounds classes and improve individual component identification [9–12].

Biomarkers [13], which are important molecular geochemical indicators, are frequently studied by fragmentograms, such as $m/z$ 191 for terpenoids and $m/z$ 177 for biodegraded terpenoids [14]. Terpenoids, as well as some other important classes of biomarkers, are present in oils as complex mixtures of isomers and homologues in very low concentration and elute at the heavy end of the gas chromatogram.

In order to increase the concentration, some separation procedures may help [1], *e.g.* asphaltene precipitation and maltene fractionation into saturated and non-
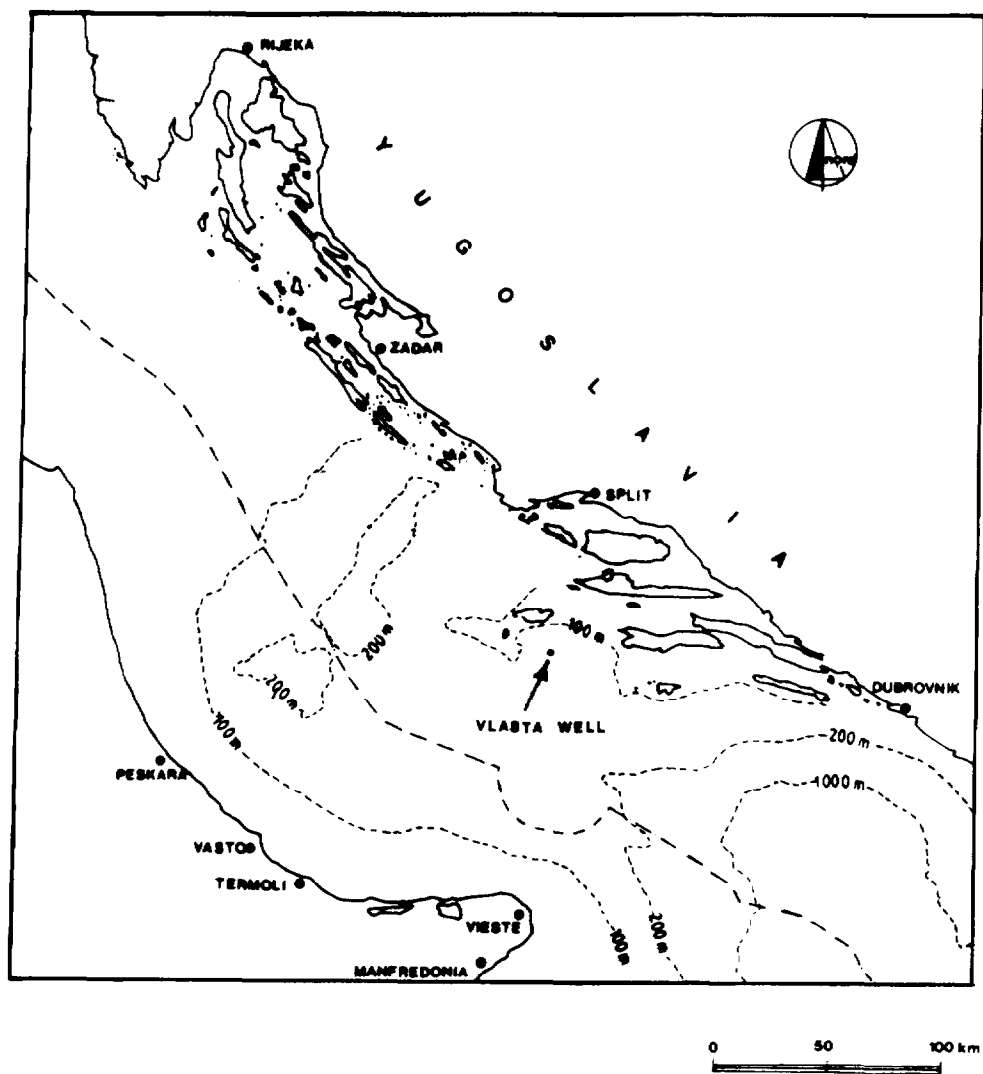


Fig. 1. Sample location (central Adriatic Basin).

saturated components. The former could be used to prepare samples for a terpenoid study.

To avoid a loss of information caused by the overlapping of light-component peaks during whole-oil analysis (under reasonable working conditions), the light-oil fraction may be studied separately.

In order to facilitate the geochemical oil classification, some global properties, such as elemental composition, stable isotope depletion and aliphatic to aromatic ratio, may provide useful complementary data in a hydrocarbon study.

A geochemical study of Croatian oils started recently [15–20]. The oils from the Adriatic Basin are rarely studied in detail. This paper is a study of Vlasta oil. Its aim is to determine the origin, precursor deposition environment, kerogen maturation level and biodegradation rank of oils in the central part of the Adriatic Basin.

EXPERIMENTAL

Vlasta oil originates from the central Adriatic Basin (Fig. 1). It was brought with the well mud from the Triassic layers in the interval between 5200 and 5500 m. During collection and transportation the sample may have suffered some loss of light components. The oil was dewatered and mineral particles removed. It then underwent an analytical procedure (Fig. 2), which involved GC and GC–MS analyses, as well as some complementary global geochemical characterization, such as elemental analysis
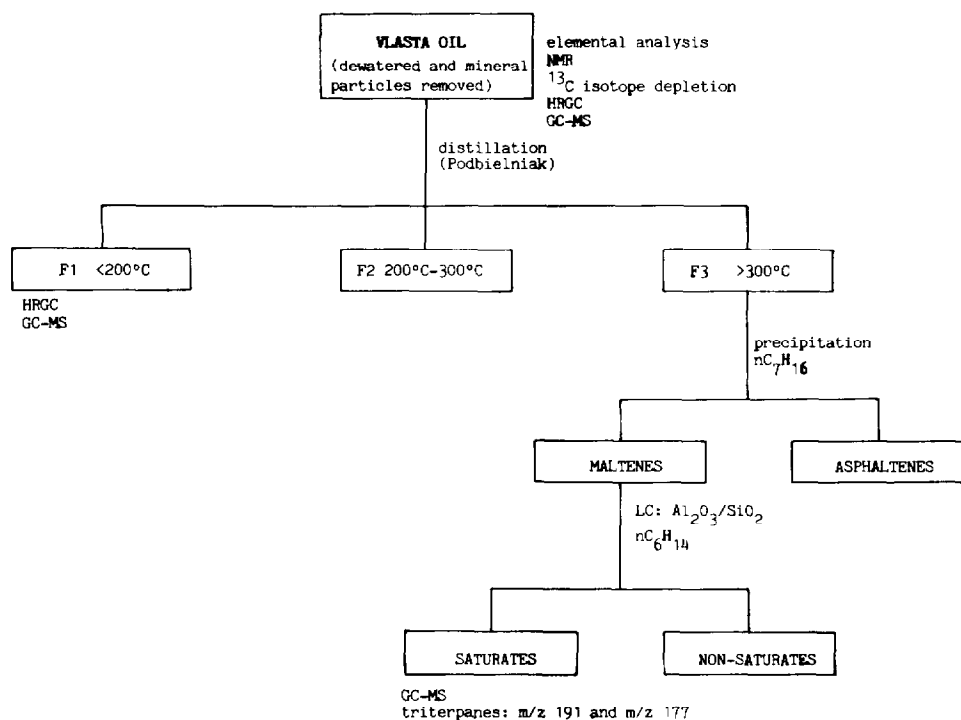


Fig. 2. Analytical procedure scheme.

TABLE I

EXPERIMENTAL CONDITIONS FOR GC AND GC–MS ANALYSIS

*(A) For whole oil*

   (I)   GC conditions

| | |
|---|---|
| Gas chromatograph | Pye Unicam 304 |
| Column | Fused-silica, non-polar DB1, 30 m |
|   Temperature | 50°C for 5 min, 4°C/min to 300°C |
|   Carrier gas | Hydrogen |
|   Pressure | 0.21 MPa |
|   Flow-rate | About 1.2 ml/min |
| Sample size | 1 $\mu$l of ca. 10% oil solution in $nC_6H_{14}$ |
| Injection mode | Splitless, 30 s |
| Detection | Flame ionization |

   (II)  GC–MS conditions

| | |
|---|---|
| Gas chromatograph | Varian 3700 |
| Column, column temperature, flow, sample size and injection mode as in AI | |
| Carrier gas | Helium |
| GC–MS coupling | Open split |
| Mass spectrometer | Varian MAT 112S |
|   Scanning rate | 1 s/decade |
|   Interscan time | 0.2 s |
|   Resolution | 1:500 |
|   Ionization | Electron impact |
|   Electron energy | 70 eV |
|   Emission current | 0.7 mA |
|   Ion source temperature | 250°C |
|   Ion source pressure | $10^{-5}$ Pa |

*(B) For light end*

   (I)   GC conditions

| | |
|---|---|
| Gas chromatograph, column, carrier gas, pressure, flow and detection as in AI | |
| Column temperature | 30°C, Isothermal |
| Sample size | 0.1 $\mu$l |
| Injection mode | Splitting 50:1 |

   (II)  GC–MS conditions

| | |
|---|---|
| Column, flow, sample size and injection mode as in BI | |
| Column temperature | Room temperature |
| GC chromatograph, carrier gas, GC–MS coupling and mass spectrometer conditions as in AII | |

*(C) For heavy end*

   GC–MS conditions

| | |
|---|---|
| Column | Fused-silica, non-polar, DB1, 60 m |
|   Temperature | 150°C, 10°C/min to 300°C |
|   Flow-rate | About 1 ml/min |
| Sample size | 1 $\mu$l of ca. 10% solution of saturates in $nC_6H_{14}$ |
| Injection mode | Splitless, 30 s |
| The other conditions as in AII | |

Full-scan and mass fragmentograms ($m/z$ 191 and $m/z$ 177) were taken.

(ASTM D-1551), aliphatic to aromatic ratio (NMR [3]) and $^{13}$C isotope depletion [21].

$^1$H-NMR analysis was performed on a Varian EM 390 using tetramethylsilane (TMS) (Merck, Darmstadt, Germany) as standard. $^{13}$C isotope depletion was measured by a Finnigan MAT 250 mass spectrometer, using NBS 22 (NBS, Washington, USA) standard.

The oil was cut by Podbielniak distillation (ASTM D-2892) into fractions: F1 up to 200°C, F2 between 200°C and 300°C, and F3 above 300°C. F1 was analysed by GC–MS as well as by GC co-injection of reference compounds such as 2-methylpentane, 3-methylpentane, 2,4-dimethylpentane, 2-methylhexane, 2,3-dimethylpentane, 3-methylhexane, 1,3-dimethylcyclopentane (*cis*), 1,3-dimethylcyclopentane (*trans*) and 1,2-dimethylcyclopentane (trans) (all from PolyScience, IL, USA), under the conditions listed in Table IB.

Maltenes were isolated from the F3 fraction by precipitation of asphaltenes in *n*-heptane (and *n*-heptane evaporation). The concentrate of high-molecular weight saturates (normal- + iso- + cycloalkanes with boiling point above 300°C) was separated from maltenes by column chromatography with aluminium oxide–silicon oxide (Kemika, Zagreb, Yugoslavia), with *n*-hexane as eluent.

The concentrate of saturates was taken for a study of pentacyclic triterpanes (biomarkers) by GC–MS (under the conditions listed in Table IC). Full spectra and mass fragmentograms ($m/z$ 191 and $m/z$ 177) were used for identification of triterpanes.

The heights of GC or GC–MS or mass fragmentogram peaks were used for calculation of geochemical parameters, with no correction factors.

## RESULTS AND DISCUSSION

Global geochemical characterization points to the prevailing aliphatic character of Vlasta oil. NMR analysis showed not more than 3% of hydrogen atom to be bonded to aromatic rings. One-third of them were found to belong to phenyl groups, while two-thirds are attached to fused aromatic rings. Also, an average of 1.8 hydrogen atoms are attached to one carbon atom (elemental analysis).

Carbon isotope depletion, $\delta$ $^{13}$C, for whole oil was $-30.3‰$ and classifies the Vlasta oil sample as belonging to the Triassic group of Adriatic oils [20].

The gas chromatogram of the oil (Fig. 3; peak labels 1W to 83W relate to the same labels in Table II) shows that most of the prominent peaks belong to *n*- and isoalkanes. In the gas chromatograms of whole oil, *n*-alkanes are recognizable in the range from $n$-$C_8H_{18}$ (1W) up to $n$-$C_{30}H_{62}$ (83W) (the light end covered by a solvent added for splitless type of GC injection). Their distribution reaches a maximum at $C_{15}H_{32}$ (59W), with still reasonable $n$-$C_{17}H_{36}$ (68W). After reaching the maximum the *n*-alkane distribution rapidly diminishes in concentration, being rather low and constant after $n$-$C_{19}H_{40}$ (72W). This type of chromatogram is an indication for the marine algal origin of the oil [22]. There is a slight preponderance of *n*-alkanes with an even number of carbon atoms over those with an odd number carbon preference index [23] = 0.96), which might indicate that the biomass was deposited as oil precursor in a carbonate environment [22].

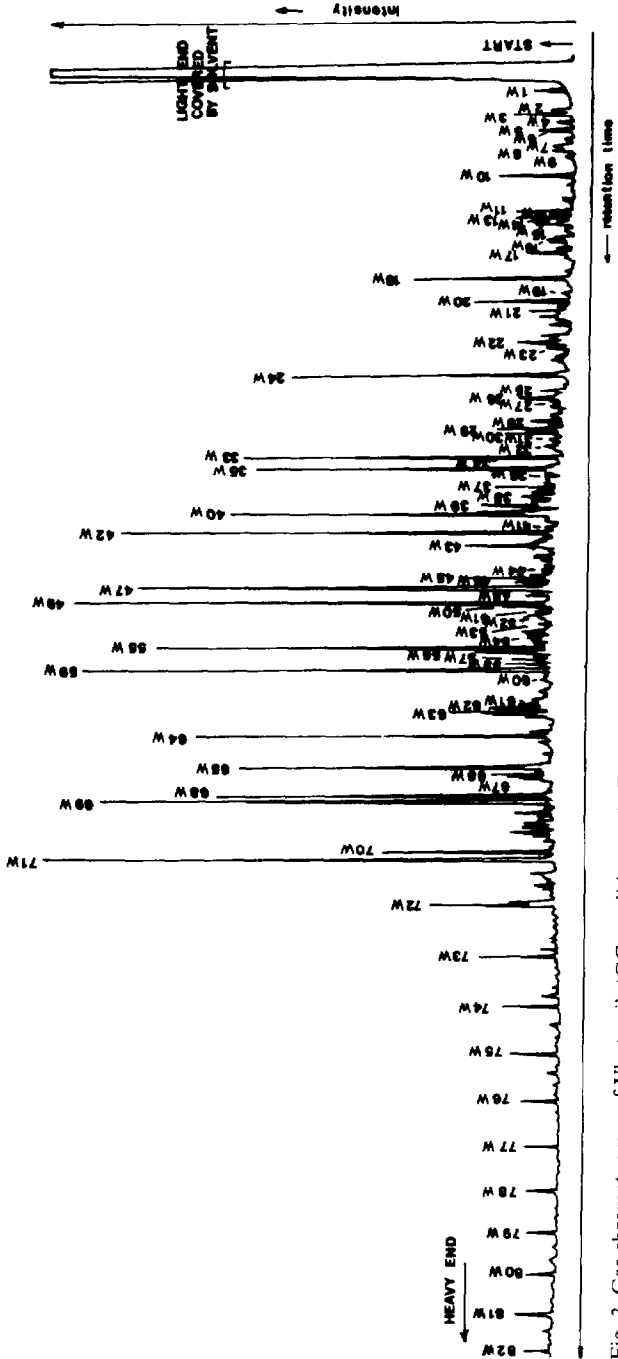Besides the prominent *n*-alkane homologues series, pristane (69W) and phytane

Fig. 3. Gas chromatogram of Vlasta oil. (GC conditions as in Table IA).

TABLE II

COMPONENTS IDENTIFIED IN OIL SAMPLE

| Label (as in Fig. 3) | Component | |
|---|---|---|
| 1W | n-Octane | $n$-$C_8H_{18}$ |
| 2W | 2,6-Dimethylheptane | |
| 3W | Isononane | iso-$C_9H_{20}$ |
| 4W | Ethylbenzene | |
| 5W | m-Xylene | |
| 6W | p-Xylene | |
| 7W | 4-Methyloctane | |
| 8W | o-Xylene | |
| 9W | Cyclohexylpropane | $C_3H_7$ |
| 10W | n-Nonane | $n$-$C_9H_{20}$ |
| 11W | Isodecane | iso-$C_{10}H_{22}$ |
| 12W | Propylbenzene | $CH_3$ |
| 13W | Cyclohexylbutane | $C_4H_9$ |
| 14W | 1-Methyl-3-ethylbenzene | |
| 15W | 1-Methyl-4-ethylbenzene | |
| 16W | 1,3,5-Trimethylbenzene | |
| 17W | 1,2,4-Trimethylbenzene | |

TABLE II (*continued*)
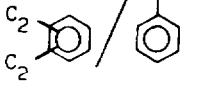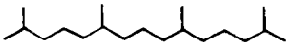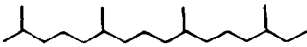
| Label (as in Fig. 3) | Component | |
|---|---|---|
| 18W | *n*-Decane | $n\text{-}C_{10}H_{22}$ |
| 19W | 1,2,3-Trimethylbenzene |  |
| 20W | Isodecane | $\text{Iso-}C_{10}H_{22}$ |
| 21W | 1-Methyl-3-sec-propylbenzene |  |
| 22W | Butylbenzene | $C_4H_9\text{—}$  |
| 23W | Isoundecane | $\text{iso-}C_{11}H_{24}$ |
| 24W | *n*-Undecane | $n\text{-}C_{11}H_{24}$ |
| 25W | Cyclohexylpentane | $C_5H_{11}\text{—}$  |
| 26W | Pentylbenzene | $C_5H_{11}$  |
| 27W | Diethylbenzene/sec-butylbenzene | $C_2$  |
| 28W | Pentylbenzene | $C_5H_{11}\text{—}$  |
| 29W | Naphthalene |  |
| 30W | Methylthioheptane | $C_7H_{15}\text{–S–CH}_3$ |
| 31W | Pentylbenzene | $C_5H_{11}\text{—}$  |
| 32W | Methylthioheptane | $C_7H_{15}\text{–S–CH}_3$ |
| 33W | Pentylbenzene | $C_5H_{11}$  |
| 34W | Cyclohexylheptane | $C_7H_{15}\text{—}$  |
| 35W | *n*-Dodecane | $n\text{-}C_{12}H_{26}$ |
| 36W | Isotridecane | $\text{iso-}C_{13}H_{28}$ |
| 37W | Cyclohexylheptane | $C_7H_{15}\text{—}$  |
| 38W | Methylthioheptane | $C_7H_{15}\text{–S–CH}_3$ |

TABLE II (*continued*)

| Label (as in Fig. 3) | Component | |
|---|---|---|
| 39W | Cyclohexyloctane | $C_8H_{17}$—⬡ |
| 40W | Isotetradecane (isoprenoid) | iso-$C_{14}H_{30}$ |
| 41W | Cyclohexyloctane | $C_8H_{17}$ ⬡ |
| 42W | n-Tridecane | n-$C_{13}H_{28}$ |
| 43W | Methylthiooctane | $C_8H_{17}$–S–$CH_3$ |
| 44W | Heptylbenzene | $C_7H_{15}$—⬡ |
| 45W | Cyclohexylnonane | $C_9H_{19}$—⬡ |
| 46W | Ethylthiooctane | $C_8H_{17}$–S–$C_2H_5$ |
| 47W | Isopentadecane (isoprenoid) | iso-$C_{15}H_{32}$ |
| 48W | Cyclohexylnonane | $C_9H_{19}$ ⬡ |
| 49W | n-Tetradecane | n-$C_{14}H_{30}$ |
| 50W | Hexylbenzene | $C_6H_{13}$ ⬡ |
| 51W | Ethylnaphthalene | $C_2H_5$—⬡⬡ |
| 52W | Ethylthiooctane | $C_8H_{17}$–SS–$C_2H_5$ |
| 53W | Ethylthiooctane | $C_8H_{17}$–S–$C_2H_5$ |
| 54W | Cyclohexyldecane | $C_{10}H_{21}$—⬡ |
| 55W | Isohexadecane (isoprenoid) | iso-$C_{16}H_{34}$ |
| 56W | Ethylthiooctane | $C_8H_{17}$–S–$C_2H_5$ |
| 57W | Cyclohexyldecane | $C_{10}H_{21}$—⬡ |
| 58W | Isotetradecane | $C_{14}H_{30}$ |
| 59W | n-Pentadecane | n-$C_{15}H_{32}$ |
| 60W | Methylthiodecane | $C_{10}H_{21}$–S–$CH_3$ |
| 61W | Methylethylnaphthalene | $C_1$, $C_2$ >⬡⬡ |
| 62W | Isohexadecane | iso-$C_{16}H_{34}$ |
| 63W | Isopentadecane | iso-$C_{15}H_{32}$ |
| 64W | n-Hexadecane | n-$C_{16}H_{34}$ |

TABLE II (*continued*)

| Label (as in Fig. 3) | Component | |
|---|---|---|
| 65W | Cyclohexylundecane | $C_{11}H_{23}$ ⬡ |
| 66W | Isohexadecane | iso-$C_{16}H_{34}$ |
| 67W | Cyclohexylundecane | $C_{11}H_{23}$ ⬡ |
| 68W | *n*-Heptadecane | *n*-$C_{17}H_{36}$ |
| 69W | Pristane | |
| 70W | *n*-Octadecane | *n*-$C_{18}H_{38}$ |
| 71W | Phytane | |
| 72W–83W | *n*-Alkane homologues from nonadecane to triacontane | *n*-$C_{19}H_{40}$–*n*-$C_{30}H_{62}$ |

(71W) also appear in a comparatively high concentration. These two isoprenoids, thought to be the fragments released from chlorophyll and/or from archae-bacterial lipids, are thought to be dependent on the concentration and on redox potential of the oil precursors' deposition environment [23]. The pristane–phytane ratio, which does not exceed 0.81, might be an indication that oil precursors were deposited mainly in anoxic conditions.

Regarding MS spectra (taken by GC–MS), isoprenoidal structure may be related to one tetradecane (40W), one pentadecane (47W) and one hexadecane (55W). For positive structure determination (head-to-head, tail-to-tail, head-to-tail), co-injection of the reference compounds is necessary. The nature of component 2W was confirmed (2,6-dimethylheptane, Aldrich, Milwaukee, WI, USA).

Isoprenoids in oils are the remnants of terpanes originating from biomass, which were partly preserved during their geological history. Partly cyclized terpane structures may be mirrored in fragments composed of cyclic and alkyl counterparts. The alkylcyclohexanes found in Vlasta oil (9W, 13W, 25W, 34W, 37W, 39W, 41W, 45W, 48W, 54W, 57W, 65W and 67W), may be related to them.

The relatively high concentration of the isoalkanes and cyclohexyl alkanes cannot be definitely attributed to biodegradation, which in preference destroys *n*-alkanes [1,2]. The explanation may be found at an early stage of the kerogen maturity at the time when the release of Vlasta oil occurred. At an early stage of maturation, the kerogen (cross-linked macromolecular oil and gas precursor) may have had a better yield of fragments by cracking the bonds related to the tertiary carbon atoms, since they appear to be weaker, than the bonds between secondary carbon atoms.

Aromatic compounds are found in low concentration. In the sample of whole
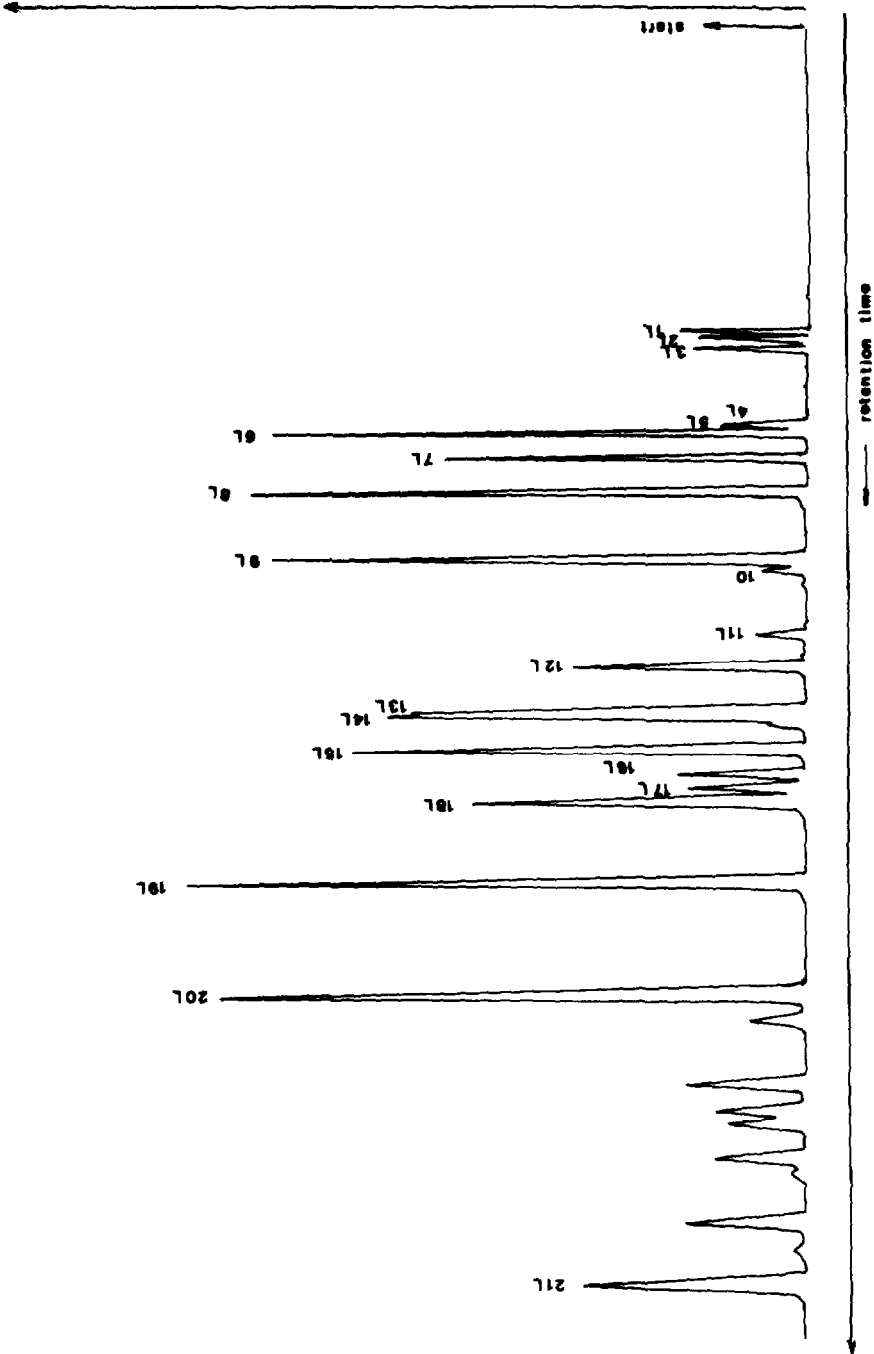
Fig. 4. Light-end chromatogram (GC conditions as in Table 1B).

**TABLE III**

**LIGHT-END COMPONENTS**

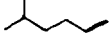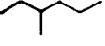| Label<br>(as in Fig. 4) | Components | |
| --- | --- | --- |
| 1L | *n*-Butane | |
| 2L | Isopentane | iso-$C_5H_{12}$ |
| 3L | *n*-Pentane | |
| 4L | Cyclopentane | |
| 5L | 2,3-Dimethylbutane | |
| 6L | 2-Methylpentane | |
| 7L | 3-Methylpentane | |
| 8L | *n*-Hexane | |
| 9L | Methylcyclopentane | |
| 10L | 2,4-Dimethylpentane | |
| 11L | Benzene | |
| 12L | Cyclohexane | |
| 13L | 2-Methylhexane | |
| 14L | 2,3-Dimethylpentane | |
| 15L | 3-Methylhexane | |

TABLE III (*continued*)

| Label (as in Fig. 4) | Components | |
| --- | --- | --- |
| 16L | 1,3-Dimethylcyclopentane (*cis*) | |
| 17L | 1,3-Dimethylcyclopentane (*trans*) | |
| 18L | 1,2-Dimethylcyclopentane (*trans*) | |
| 19L | *n*-Heptane | |
| 20L | Methylcyclohexane | |
| 21L | Toluene | |

oil alkylbenzenes ranging up to heptylbenzene (44W) were found. Among them mono-, di- and trialkylbenzenes were identified. Besides naphthalene (29W), alkyl-naphthalenes with two (51W) and three (61W) aliphatic carbon atoms were found in the mixture, as complex as oil is. Sulphur compounds such as methyl- and ethylthioethers were identified (30W, 32W. 38W, 43W, 46W, 52W, 53W, 56W and 60W). They reflect the highly reducing environment of the precursor depostion in which anaerobic microbial reduction of (inorganic) sulphate to sulphite took place [24]. In the case of a lack of heavy metal ions, $S^{2-}$ groups are incorporated within kerogen before entering the early-maturity stage. (According to elemental analysis sulphur comprises 2.5% of the mass of the oil.)

At the light end of the Vlasta oil (F1 analysed under the conditions shown in Table IB), 21 components were identified by mass spectra and/or reference compound(s) co-injection (components shown in Fig. 4 and Table III, labelled 1L to 21L). They are *n*-alkanes (1L, 3L, 8L and 19L) starting from *n*-butane; isoalkanes (2L, 5L-7L, 10L, 13L–15L); cycloalkanes including cyclopentane (4L), cyclohexane (12L) and their alkyl- and dialkyl homologues (9L, 16L–18L and 20L), as well as two aromatics: benzene (11L) and toluene (21L).

The components in Vlasta whole oil, including the light end, represent the majority of the oil (*e.g.* the oil portion which is able to pass through the GC column under conditions as shown in Table I).

The heavy end of the Vlasta oil consists of components which dramatically diminish in concentration. Among the components, terpenoids were studied, as they can serve as biomarkers of oil source [13]. precursor deposition environment [22],

TABLE IV

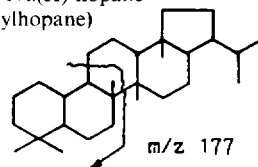PENTACYCLIC TRITERPANE BIOMARKERS

$m/z$ 191 = pentacyclic triterpanes, for example $C_{30}$ hopane

| Label (as in Fig. 5) | Component |
|---|---|
| 1t | 22,29,30-Trisnorneohopane, Ts |
| 2t | 22,29,30-Trisnorneohopane, Tm |
| 3t | $17\alpha(H),21\beta(H),30$-Norhopane |
| 4t | $C_{30}$-Cheilantane |
| 5t | $17\alpha(H),21\beta(H)$-Hopane |
| 6t | $17\alpha(H),21\beta(H)$-Hopane (moretane) |
| 7t | $17\alpha(H),21\beta(H),29$-Homohopane 22S |
| 8t | $17\alpha(H),21\beta(H),29$-Homohopane 22R |
| 9t | Gammacerane |
| 10t | $17\alpha(H),21\beta(H),29$-Bishomohopane 22S |
| 11t | $17\alpha(H),21\beta(H),29$-Bishomohopane 22R |
| 12t | $17\alpha(H),21\beta(H),29$-Trishomohopane 22S |
| 13t | $17\alpha(H),21\beta(H),29$-Trishomohopane 22R |
| 14t | $17\alpha(H),21\beta(H),29$-Tetrakishomohopane 22S |
| 15t | $17\alpha(H),21\beta(H),29$-Tetrakishomohopane 22R |
| 16t | $17\alpha(H),21\beta(H),29$-Pentakishomohopane 22S |
| 17t | $17\alpha(H),21\beta(H),29$-Pentakishomohopane 22R |
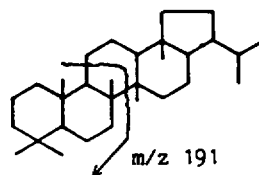
$m/z$ 177 = 25-Norhopane (10-desmethylhopane), no significance

$C_{29}$ 25-Nor-$17\alpha(H)$-hopane (10-desmethylhopane)

maturity stage [25], and aerobic biodegradation of oil [20]. Since they are present in a very low concentration in the complex mixture, a fragmentogram $m/z$ 191 was taken to study pentacyclic triterpanes (hopanes) and $m/z$ 177 for their biodegraded derivatives (Fig. 5, Table IV, components labelled 1t to 15t).

Hopanes are supposed [26] to be derived from bacteriohopanetetrol (origin from prokaryotes) as a result of anaerobic bacterial activity. The more anoxic the environment, the higher the preservation, *i.e.* the relative concentration of tetra- and pentakishomohopanes as the largest derivatives. Higher homohopanes were well preserved in hypersaline conditions [27]. In the fragmentogram, homohopanes gradually decrease in concentration until tetrakishomohopanes (14t and 15t), suggesting low redox potential in the geochemical environment during and immediately after the deposition of the Vlasta oil source.

The presence of gammacerane (9t) as a highly specific biomarker [22] supports the idea of the hypersaline deposition environment prevailing in the Vlasta oil precursor. The ratio between Ts and Tm is (regardless of the influence of depostion environment [28] a relevant maturity parameter [22], since Tm is found to diminish in concentration as a result of maturation, while Ts is rather stable. Expressed as Ts/
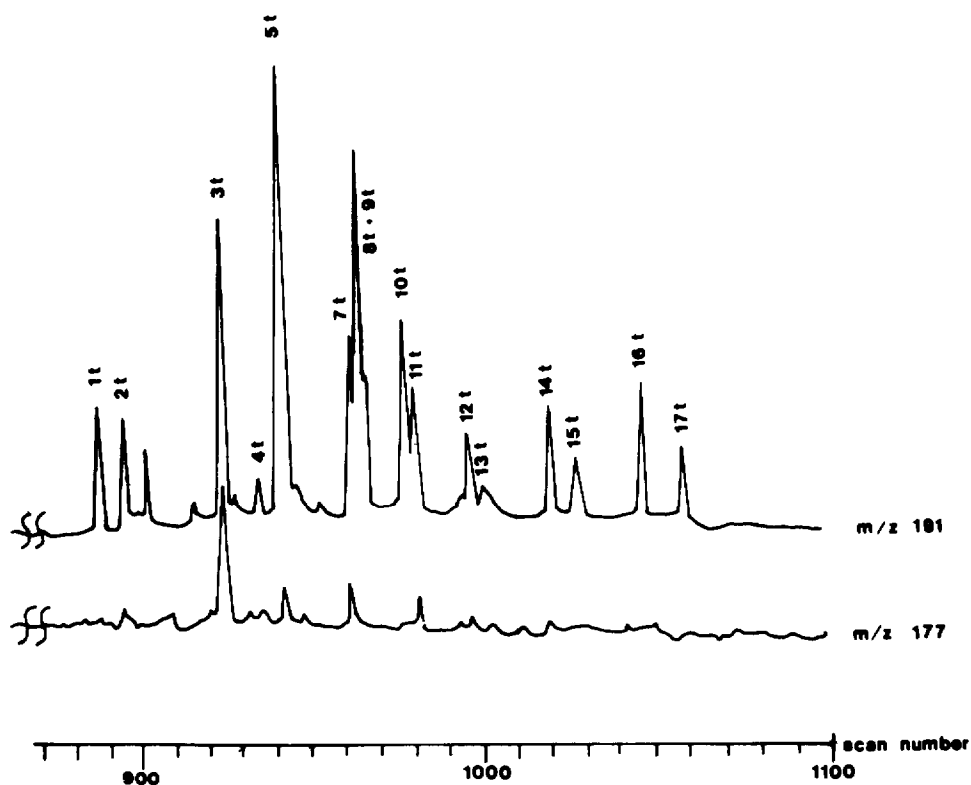
Fig. 5. Mass fragmentograms (GC–MS conditions as in Table 1C): $m/z$ 191 = pentacyclic triterpanes; $m/z$ 177 = 10-desmethylhopanes.

(Ts + Tm) this parameter reaches 0.50 during an early stage of maturity. For Vlasta oil it is found to be 0.55. The additional support for maturity level is the ratio of 22$S$/22$S$ + 22$R$) diastereoisomers of homohopanes. This parameter reaches an equilibrium of 0.62 at an early maturity stage [25]. For the Vlasta oil it is recorded at 0.60 for bishomohopanes (10t and 11t).

Oleanane, which suggests the terrestrial source input [22], has not been identified in the Vlasta oil.

Masses $m/z$ 177 may indicate the presence of 25-norhopanes (10-desmethylhopanes) which were the result of aerobic biodegradation of oils [29]. In Vlasta oil $C_{29}$-25-nor-17$\alpha$(H) hopane, the anticipated representative of 25-norhopanes, was not detected, and neither were its homologues. This suggests that Vlasta oil was very well preserved in a geological reservoir and that no apparent biodegradation took place.

CONCLUSIONS

The study of hydrocarbons in the Vlasta oil (121 components identified or characterized) offered a good insight into structural composition, as well as a reasonable basis for the study of its origin, deposition environment, maturity level and biodegradation rank.

The identified components indicate that Vlasta oil is composed of straight and branched alkanes, cycloalkanes and polycyclics, often with their aliphatic counterpart(s), and aromatics and thioethers. In terms of content, alkanes are found to prevail, while aromatic and sulphur compounds are found in low proportions.

Vlasta oil originates from marine organic matter, probably algae and/or bacteria. The biomass was deposited during the Triassic period in an anoxic hypersaline environment in a carbonate mineral matrix. Vlasta oil appears to be released from the related kerogen at its early maturation stage. The oil shows no significant biodegradation.

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