

## NEW DATA ON THE CARBOXYLIC ACIDS AND RELATED COMPOUNDS CONTAINED IN KUKERSITE SEMICOKING OIL

Ada SUMBERG and Kaarli UROV

Eesti Teaduste Akadeemia Keemia Instituut (Institute of Chemistry, Estonian Academy of Sciences), Akadeemia tee 15, EE-0026 Tallinn, Eesti (Estonia)

Presented by Ü. Lille

Received June 1, 1993; accepted June 11, 1993

**Abstract.** Using chromatography-mass spectroscopy a series of aliphatic saturated and unsaturated as well as cyclic carboxylic acids were identified in the oil obtained by processing kukersite shale in an industrial vertical retort. Correlations between chemical structures of the hydrocarbons, carboxylic acids, and ketones present in the oil are discussed.

**Key words:** semicoking oil, kukersite, mass spectrometry.

### INTRODUCTION

Though industrial processing of Estonian oil shale "kukersite" into oil has continued for more than 70 years already, we still have but very little information on the composition of the carboxylic acids contained in the oil, and the existing data on the subject are 40 years old or older. It has been established that saturated aliphatic carboxylic acids  $C_5$ — $C_{15}$  and, tentatively, unsaturated acids are present in the oil [1–3]. Fatty acids  $C_1$ — $C_5$  have been identified in the shale processing waste water [4]. In the present work an attempt has been made to obtain additional information on the above and related compounds using more modern equipment.

### EXPERIMENTAL

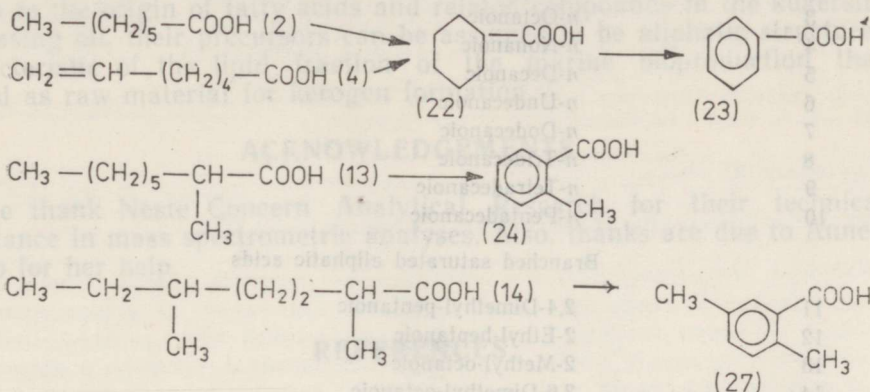
A sample of the methylated acidic compounds that were separated from the oil obtained by processing kukersite in an industrial retort (so-called generator, Kohtla-Järve Shale Processing Plant) was used. Its composition was investigated by a Hewlett Packard 5971A gas chromatographic-mass spectrometric system with fused silica capillary column DB-5, 30 m $\times$ 0.32 mm, temperature programmed 50 °C  $\xrightarrow{5^\circ\text{C}/\text{min}}$  320 °C; helium served as the carrier gas.

### RESULTS AND DISCUSSION

A chromatogram of acids obtained by a mass-selective detector is presented in the Figure; the identification of the peaks is given in the Table. In most cases, a compound has been considered to be present in the mixture under study when the probability of its identification exceeded 80%.

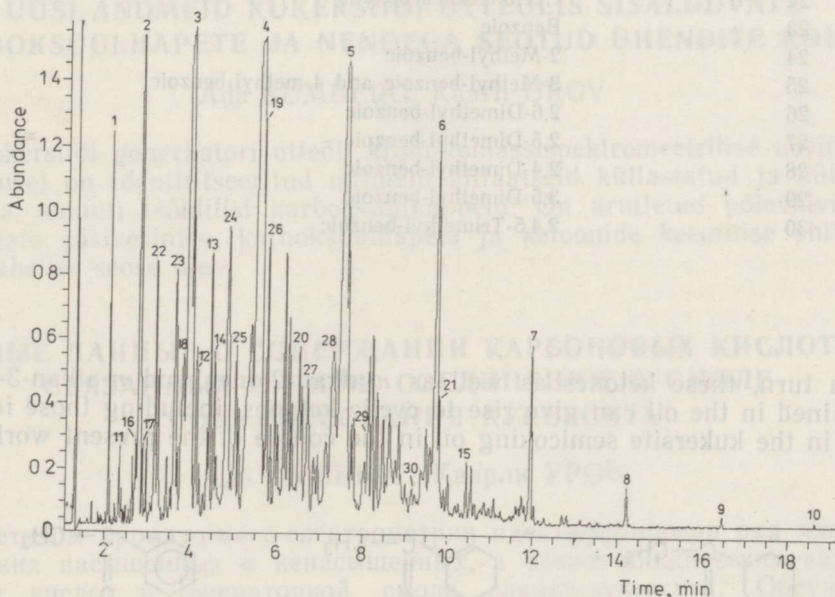
It is evident from the data presented that, in addition to the saturated fatty acids identified earlier in the kukersite thermolysis oil, it contains a series of iso- and unsaturated as well as cyclic acids.

It is interesting to note that in the branched acids the alkyl substituent is preferentially in the  $\alpha$ -position with respect to the carboxylic group. One can easily observe the formation of some cyclic acids by cyclization of aliphatic ones, for example (the compound's number according to the Table is given in parentheses):



At the same time, some neutral oxygen compounds and hydrocarbons contained in the oil also seem to be derived from the corresponding acids.

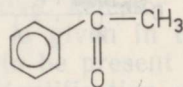
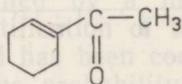
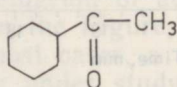
Thus, *n*-1-alkenes, which are characteristic of the kukersite semicoking oil, can be easily formed by decarboxylation of the corresponding unsaturated aliphatic acids (e.g. compounds 16, 20, and 21 in the Table). Besides, we have established that in the kukersite derived oil there is a series of aliphatic unsaturated ketones  $\text{C}_8 - \text{C}_{14}$  with the double bond in the  $\omega$ -position with respect to the carbonyl groups (from 7-octen-2-one to 13-tetradecene-2-one). It is probable that  $\omega$ -alken-2-ones and the corresponding fatty acids of types 16 and 21 have similar precursors in the shale organic matter.

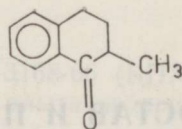
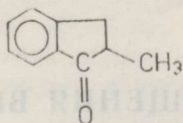
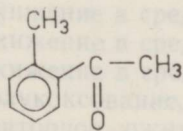


Chromatogram of the carboxylic acids fraction of kukersite oil. The numbers correspond to the compounds listed in the Table.

Peak number (see Fig.)	Compound
Unbranched saturated aliphatic acids	
1	<i>n</i> -Hexanoic
2	<i>n</i> -Heptanoic
3	<i>n</i> -Octanoic
4	<i>n</i> -Nonanoic
5	<i>n</i> -Decanoic
6	<i>n</i> -Undecanoic
7	<i>n</i> -Dodecanoic
8	<i>n</i> -Tridecanoic
9	<i>n</i> -Tetradecanoic
10	<i>n</i> -Pentadecanoic
Branched saturated aliphatic acids	
11	2,4-Dimethyl-pentanoic
12	2-Ethyl-heptanoic
13	2-Methyl-octanoic
14	3,6-Dimethyl-octanoic
15	2-Methyl-undecanoic
Unsaturated aliphatic acids	
16	<i>n</i> -Hepten-6-oic
17	<i>n</i> -Hepten-5-oic
18	<i>n</i> -Octen-4-oic
19	<i>n</i> -Nonen-7-oic
20	<i>n</i> -Decen-2-oic
21	<i>n</i> -Undecen-10-oic
Cyclic acids	
22	Cyclohexancarboxylic
23	Benzoic
24	2-Methyl-benzoic
25	3-Methyl-benzoic and 4-methyl-benzoic
26	2,6-Dimethyl-benzoic
27	2,5-Dimethyl-benzoic
28	2,4-Dimethyl-benzoic
29	3,5-Dimethyl-benzoic
30	2,4,5-Trimethyl-benzoic

In turn, these ketones as well as *n*-alkan-2-ones and *n*-alkan-3-ones contained in the oil can give rise to cyclic ketones, including those identified in the kukersite semicoking oil in the course of the present work:





As to the origin of fatty acids and related compounds in the kukersite processing oil, their precursors can be assumed to be aliphatic structures characteristic of the lipid fraction of the marine bioproduction that served as raw material for kerogen formation.

### ACKNOWLEDGEMENTS

We thank Neste Concern Analytical Research for their technical assistance in mass spectrometric analyses. Also, thanks are due to Anneli Hesso for her help.

### REFERENCES

1. Когерман П., Лютс К., Хюссе И. Химия эстонских сланцев. Госхимиздат, Москва—Ленинград, 1934, 52—58.
2. Броун А. С., Цейтлин А. С. Исследование кислых фракций гдовской сланцевой смолы. — Хим. тв. топл., 1936, 7, 2, 136—143.
3. Valdek, R. «Kiviõli» tunnelahjude põlevkiviõli kergeis fraktsioonides sisalduvaist karboonhappeist ja nende kasutamisevõimalustest. — ENSV TA Toim., 1953, 2, 2, 235—251.
4. Иванов Б. И., Шаронова Н. Ф. Химический состав подсмольной воды сланцев Прибалтийского месторождения. — In: Химия и технология продуктов переработки сланцев. Гостоптехиздат, Ленинград, 1954, 164—188.

### UUSI ANDMEIDI KUKERSIIDI UTTEÕLIS SISALDUVATE KARBOKSÜÜLHAPETE JA NENDEGA SEOTUD ÜHENDITE KONTA

Ada SUMBERG, Kaarli UROV

Kukersiidi generaatori utteõli kromatomassispektromeetrilise uurimise tulemusel on identifitseeritud mitmeid alifaatseid küllastatud ja küllastamata, samuti tsüklilisi karboksüülhappeid. On arutletud põlevkiviõlis leiduvate süsivesinike, karboksüülhapete ja ketoonide keemilise ehituse omavahelise seose üle.

### НОВЫЕ ДАННЫЕ О СОДЕРЖАНИИ КАРБОНОВЫХ КИСЛОТ И СВЯЗАННЫХ С НИМИ СОЕДИНЕНИЙ В СМОЛЕ ПОЛУКОКСОВАНИЯ КУКЕРСИТА

Ада СУМБЕРГ, Каарли УРОВ

Методом хромато-масс-спектрометрии идентифицирован ряд алифатических насыщенных и ненасыщенных, а также циклических карбоновых кислот в генераторной смоле сланца-кукерсита. Обсужден вопрос о корреляции химических структур содержащихся в смоле углеводородов, карбоновых кислот и кетонов.