

## PARAFFINIC HYDROCARBONS FROM DEVONIAN, TRIASSIC AND JURASSIC SEDIMENTS OF NORTHERN BULGARIA

G.KOVAČEV<sup>a</sup>, D.DELOVA<sup>a</sup> and K.STRÁNSKÝ<sup>b</sup>

<sup>a</sup>*Geological Institute, Bulgarian Academy of Sciences,  
Sofia 13, Bulgaria*

<sup>b</sup>*Institute of Organic Chemistry and Biochemistry,  
Czechoslovak Academy of Sciences, Prague 6*

Received January 17th, 1972

Fractions of saturated hydrocarbons from five samples of sediments were analyzed by gas chromatography and mass spectrometry. Besides the naturally occurring homologous series of n-alkanes (in all cases with a balanced proportion of odd- and even-numbered homologues) also 2-methyl and 3-methyl alkanes were identified.

In connection with petroleum prospecting and exploration we were interested in the composition of five samples of bitumens<sup>1</sup> originating from Devonian, Triassic and Jurassic sediments in Northern Bulgaria. The present communication describes the analysis of higher saturated aliphatic hydrocarbons contained in the samples.

### EXPERIMENTAL

*Material.* Samples 1 and 2 originate from a borehole in a Triassic sediment near Pleven. Sample 3 comes from another borehole in the same area. Sample 4 is from Devonian sediments from the neighbourhood of Varna and sample 5 from Jurassic sediments from the neighbourhood of Mihalovgrad (Table I, Scheme 1).

*Extraction.* The samples were disintegrated and ground dry in a ball grinder (particle size 0.25–1 mm) and extracted with chloroform in a Soxhlet apparatus for 50–70 h.

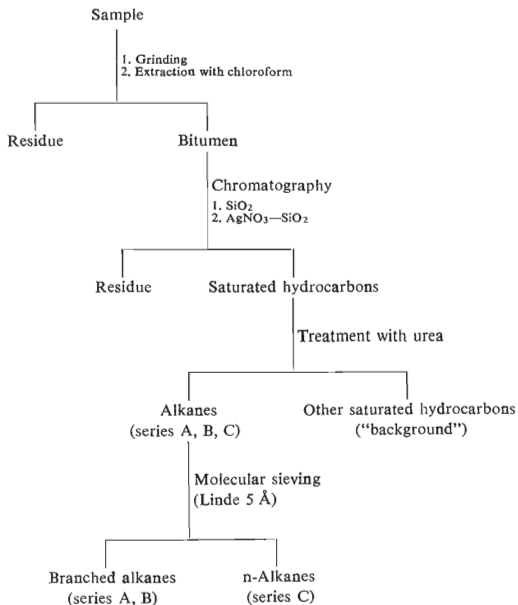
*Hydrocarbon fraction<sup>2</sup>.* The individual extracts were adsorbed to a small amount of silica gel and chromatographed on a column of silica gel PHH (0.10–0.25 mm, 100-fold excess) with light petroleum (b.p. 45–65°C). The fractions with hydrocarbons were pooled and rechromatographed in light petroleum on a column of silica gel, impregnated with 15% AgNO<sub>3</sub>. For further separation only fractions containing saturated hydrocarbons were used.

*Treatment of saturated hydrocarbons.* The treatment with urea was done as described before<sup>2,3</sup>. Saturated hydrocarbons obtained from urea clathrates were dissolved in 2,2,4-trimethylpentane and refluxed for 7 h with a 20-fold excess of the molecular sieve Linde 5 Å.

*Gas chromatography* was done in a Pye series 104 Chromatograph, Model 24 with flame-ionization detectors and a dual system of glass columns (0.4 × 150 cm). The liquid phase was 3% SE-30 on Gas-Chrom Z (100–120 mesh). For a qualitative evaluation we used the linear relationship between the number of carbon atoms and the logarithm of the retention volume.

The quantitative evaluation of the chromatograms was done in such a way as to compare the products of the retention times and of the corresponding wave heights (without using correction factors).

*Mass spectrometry* was done in a MS 902 AEI Mass spectrometer (70 eV, ion source temperature 250°C) connected with a gas chromatograph (Pye series 104 Chromatograph, Model 64). The liquid phase was 3% SE-30 on Gas-Chrom Q (100–120 mesh); 100–250°C, programmed at 4°C/min, helium flow 60 ml/min.



SCHEME 1

## RESULTS AND DISCUSSION

*n-Alkanes.* The composition of alkanes forming clathrates with urea is shown in Table II. All the analyzed samples contained always three homologous series of alkanes A, B and C. The C series contained *n*-alkanes approximately from C<sub>14</sub> to C<sub>43</sub>. While most recent waxes<sup>4-9</sup> show a marked predominance of odd-numbered *n*-alkanes over the even-numbered ones, the fossil materials<sup>10-14</sup> show a rather

TABLE I  
Content of Hydrocarbons in Sediments from Northern Bulgaria

Sample	1	2	3	4	5
Geological period	Triassic	Triassic	Triassic	Devonian	Jurassic
Borehole depth, m	4 045	4 080	3 600	1 320	2 300
Sample weight, g	1 620	960	1 480	2 730	1 650
Extract weight, g	1·177	1·243	0·408	0·620	0·484
Hydrocarbons, mg	473	571	80	299	95
Clathrate-forming hydrocarbons, mg	75·3	89·5	13·9	3·6	0·5
Hydrocarbons after sieving, mg	20·1 <sup>a</sup>	26·3 <sup>a</sup>	—	—	—

<sup>a</sup>Since the treatment with urea before molecular sieving was done only once, a small fraction of "background" hydrocarbons is present.

balanced proportion between the two groups. On the contrary, n-alkanes produced by lower plants<sup>6,15-20</sup> show either a predominance of odd-numbered homologues or a fair balance. In the samples studied here the proportion is very even.

*Branched alkanes.* To study the composition of branched alkanes contained in homologous series A and B, samples 1 and 2 were treated with Linde's molecular sieve 5 Å where the n-alkanes (homologous series C) were mostly absorbed. The composition of the two samples after sieving is shown in Table III. The individual homologues of the A series show retention times corresponding to those of monomethylalkanes with branching in the middle of the chain such as have been identified in waxes before<sup>3,21-29</sup>. The mass spectra of two homologues (C<sub>29</sub>, C<sub>30</sub>) of this series were very unclear due to the low concentration of the compounds so that they could not be identified. Particularly in the region up to C<sub>30</sub>, hydrocarbons of the homologous series B were present. The retention times suggested that the individual homologues will be most likely iso- or anteiso-alkanes, or their mixtures. On the basis of mass spectra<sup>2,30-34</sup> obtained during gas chromatography of samples 1, it was found that the homologue C<sub>21</sub> represents a mixture of 2-methyl and 3-methyl-icosane, the homologue C<sub>23</sub> is 2-methyldocosane, the homologue C<sub>24</sub> is 2-methyl-tricosane, C<sub>25</sub> is 2-methyltetracosane and C<sub>26</sub> is a mixture of 2-methyl and 3-methyl-pentacosane. Since calibration runs were not performed it can only be assessed from the mass spectra of homologues C<sub>21</sub> and C<sub>26</sub> that the ratio of the iso- to anteiso-alkanes in the homologues is about 1. For the same reason, one cannot exclude the possible presence of small amounts of anteisoalkanes in the C<sub>23</sub>, C<sub>24</sub> and C<sub>25</sub> homologues.

It follows from the lack of symmetry of the waves of the individual homologues of the C series that almost every peak contains a mixture of at least two alkanes.

TABLE II  
Composition of Alkanes Forming Clathrates with Urea

Number of C atoms	1			2			3			4			5		
	A <sup>a</sup>	B <sup>a</sup>	C <sup>a</sup>	A	B	C	A	B	C	A	B	C	A	B	C
14	—	—	0.3	—	—	0.4	—	—	—	—	—	—	—	—	—
15	—	+	0.5	—	+	1.3	—	—	—	—	—	—	—	—	—
16	—	+	0.7	—	+	2.8	—	—	—	—	—	—	—	—	—
17	—	+	2.0	—	+	3.8	—	—	—	—	—	—	—	—	—
18	—	+	4.3	—	+	4.8	—	—	—	—	—	—	—	—	—
19	—	+	5.7	—	+	6.3	—	—	—	—	—	—	—	—	—
20	—	+	7.1	—	+	7.2	—	—	—	—	—	—	—	—	—
21	—	0.1	7.9	—	0.1	7.8	—	—	—	—	—	—	—	—	—
22	—	0.2	8.7	—	0.2	8.6	—	—	—	—	—	—	—	—	—
23	—	0.2	8.0	—	0.3	7.9	—	—	—	—	—	—	—	—	—
24	—	0.4	7.1	—	0.1	6.8	—	—	—	—	—	—	—	—	—
25	+	0.5	6.0	—	0.5	5.7	—	—	—	—	—	—	—	—	—
26	+	0.6	5.0	—	0.4	4.9	—	—	—	—	—	—	—	—	—
27	+	0.5	4.6	—	0.3	4.7	—	—	—	—	—	—	—	—	—
28	+	0.5	4.0	—	0.5	3.7	—	—	—	—	—	—	—	—	—
29	+	0.5	3.9	—	+	3.5	—	—	—	—	—	—	—	—	—
30	+	+	3.3	—	+	2.9	—	—	—	—	—	—	—	—	—
31	+	+	3.0	—	+	2.6	—	—	—	—	—	—	—	—	—
32	0.2	+	2.1	—	0.1	1.8	—	—	—	—	—	—	—	—	—
33	0.2	+	1.7	—	+	1.6	—	—	—	—	—	—	—	—	—
34	0.2	+	1.2	—	0.2	1.1	—	—	—	—	—	—	—	—	—
35	0.3	+	1.0	—	0.2	0.9	—	—	—	—	—	—	—	—	—
36	0.2	+	1.2	—	0.3	0.8	—	—	—	—	—	—	—	—	—
37	0.3	+	0.8	—	0.2	0.8	—	—	—	—	—	—	—	—	—
38	0.3	+	0.8	—	0.5	0.6	—	—	—	—	—	—	—	—	—
39	0.3	+	0.8	—	0.5	0.6	—	—	—	—	—	—	—	—	—
40	0.3	—	0.8	—	+	0.5	—	—	—	—	—	—	—	—	—
41	0.4	—	0.5	—	—	+	—	—	—	—	—	—	—	—	—
42	0.2	—	0.4	—	—	—	—	—	—	—	—	—	—	—	—
43	+	—	+	—	—	—	—	—	—	—	—	—	—	—	—
Total	2.9	3.6	93.5	2.5	3.1	94.4	+	2.6	97.4	0.6	2.5	96.8	+	100	—
Ratio odd/even			1.00			1.01			1.05			1.05			0.95

<sup>a</sup> Designation of homologous series. + Traces.

Mass spectrometry of the  $C_{23}$ ,  $C_{24}$ ,  $C_{25}$  and  $C_{27}$  homologues of this series (sample 1) showed that one of the components are apparently n-alkanes not trapped in the molecular sieve.

TABLE III  
Composition of Alkanes after Molecular Sieving

Number of C atoms	1			2		
	A <sup>a</sup>	B <sup>a</sup>	C <sup>a</sup>	A	B	C
14	—	+	—	—	+	—
15	—	0.2	—	+	0.5	—
16	0.1	0.3	+	0.2	0.6	0.1
17	0.2	0.5	0.1	0.6	0.6	+
18	0.3	0.7	0.1	0.6	0.8	0.6
19	0.4	0.9	0.1	0.6	0.9	0.3
20	0.1	1.2	0.1	0.6	1.3	0.1
21	+	1.4	0.2	+	1.5	0.2
22	+	1.7	0.3	+	2.0	0.4
23	+	2.2	0.6	0.2	2.5	0.7
24	0.2	2.6	0.8	0.3	3.0	0.9
25	0.2	3.2	1.0	0.4	3.6	1.2
26	+	3.6	1.2	0.5	3.9	1.3
27	0.3	3.5	1.3	0.6	4.2	1.3
28	0.2	3.5	1.2	0.6	3.6	1.1
29	0.4	3.0	1.5	0.7	3.1	1.2
30	0.7	2.9	3.4	0.9	3.1	2.6
31	2.9	1.6	2.7	2.8	1.9	2.3
32	2.9	1.7	1.9	3.5	1.3	1.7
33	2.6	1.0	1.7	3.0	+	1.4
34	3.0	1.5	1.2	3.3	+	1.3
35	2.3	+	1.0	3.8	+	0.8
36	2.4	+	1.1	2.7	+	0.8
37	2.3	+	1.0	2.5	+	1.2
38	2.1	0.3	1.5	3.2	+	1.3
39	2.7	+	1.7	2.7	+	+
40	2.9	+	1.0	1.7	+	+
41	2.1	+	—	1.7	+	+
42	1.3	+	—	1.1	+	+
43	3.2	+	+	—	—	—
44	+	+	—	—	—	—
<i>Total</i>	35.8	37.5	26.7	38.8	38.4	22.8

<sup>a</sup>Designation of homologous series. + Traces.

The authors express their thanks to Dr L. Dolejš and Dr K. Ubik for measurement and interpretation of the mass spectra and to Mrs J. Dusová for technical assistance.

## REFERENCES

1. Vuchev V. T., Howells W. G., Burlingame A. L. in the book: *Advances in Organic Geochemistry*, p. 365. Pergamon Press, Oxford, Braunschweig 1972.
2. Stránský K., Streibl M., Šorm F.: This Journal 33, 416 (1968).
3. Stránský K., Streibl M., Kubelka V.: This Journal 35, 882 (1970).
4. Clark R. C., jr: Technical Report, Reference No 66—34, p. 56., Woods Hole Oceanographic Inst. 1966.
5. Douglas A. G., Eglinton G. in the book: *Comparative Phytochemistry* (T. Swain, Ed.), p. 57. Academic Press, London and New York 1966.
6. Stránský K., Streibl M., Herout V.: This Journal 32, 3213 (1967).
7. Mazliak P. in the book: *Progress in Phytochemistry*, (L. Reinhold, Y. Liwschitz, Eds), p. 49, Vol. 1. Interscience, London, New York, Sydney 1968.
8. Stránský K., Streibl M.: This Journal 34, 103 (1969).
9. Kolattukudy P. E.: *Lipids* 5, 259 (1970).
10. Stevens N. P., Bray E. E., Evans E. D.: *Habitat of Oil*, Am. Assoc. Petro. Geologists 1958, 779.
11. Oró J., Nooner D. W., Zlatkis A., Wikström S. A., Barghoorn E. S.: *Science* 148, 77 (1965).
12. Oró J., Nooner D. W.: *Nature* 213, 1082 (1967).
13. Smith H. M.: *J. Am. Oil Chem. Soc.* 44, 680 (1967).
14. Meinschein W. G. in the book: *Organic Geochemistry* (G. Eglinton, M. T. J. Murphy, Eds), p. 330. Springer, Berlin, Heidelberg, New York 1969.
15. Ciereszko L. S., Attaway D. H., Wolf M. A.: *Am. Chem. Soc. Petrol. Res. Fund.* 8th Ann. Rep. 1963, 33.
16. Clark R. C., jr: *M. S. Thesis*. Massachusetts Institute of Technology 1966.
17. Clark R. C., jr, Blumer M.: *Limnol. Oceanogr.* 12, 79 (1967).
18. Patterson G. W.: *J. Phycol.* 3, 22 (1967).
19. Oró J., Tornabene T. G., Nooner D. W., Gelpi E.: *J. Bacteriol.* 93, 1811 (1967).
20. Youngblood W. W., Blumer M., Gillard R. L., Fiore F.: *Mar. Biol.* 8, 190 (1971).
21. Mold J. D., Means R. E., Stevens R. K., Ruth J. M.: *Biochemistry* 5, 455 (1966).
22. Stránský K., Streibl M., Šorm F.: This Journal 31, 4694 (1966).
23. Hutchins R. F. N., Martin M. M.: *Lipids* 3, 250 (1968).
24. Arnold M. T., Blomquist G. J., Jackson L. L.: *Comp. Biochem. Physiol.* 31, 685 (1969).
25. Tartivita K., Jackson L. L.: *Lipids* 5, 35 (1970).
26. Jackson L. L.: *Lipids* 5, 38 (1970).
27. Gelpi E., Schneider H., Mann J., Oró J.: *Phytochemistry* 9, 603 (1970).
28. Cavill G. W. K., Clark D. V., Howden M. E. A., Wyllie S. G.: *J. Insect Physiol.* 16, 1721 (1970).
29. Nelson D. R., Sukkestad D. R.: *Biochemistry* 9, 4601 (1970).
30. Mold J. D., Stevens R. K., Means R. E., Ruth J. M.: *Biochemistry* 2, 605 (1963).
31. Mold J. D., Means R. E., Ruth J. M.: *Phytochemistry* 5, 59 (1966).
32. Hunter G. L. K., Brogden W. B., jr: *Phytochemistry* 5, 807 (1966).
33. Gülz P. - G.: *Phytochemistry* 7, 1009 (1968).
34. Enzel C. R., Rosengren A., Wahlberg I.: *Tab. Sci.* 13, 127 (1969).

Translated by A. Kotyk.