

PARAFFINIC HYDROCARBONS FROM CRUDE OIL FROM NORTHERN BULGARIA

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Received January 9th, 1975

Using gas chromatography and mass spectrometry the hydrocarbon fraction of Bulgarian crude oil was analysed. In addition to homologous n-alkanes with a balanced ratio of even and odd numbered homologues four isoprenoid alkanes were also identified.

In connection with the prospection of crude oils and their utilization¹⁻³ we investigated the chemical composition of the crude oil found in the northern part of Bulgaria. This paper presents the results of the analysis of the hydrocarbons.

EXPERIMENTAL

Material. The crude oil was obtained from a site 3960–4040 m deep in Gorna Gnoenica in North Bulgaria from a medium trias layer; d_4^{20} 0.7843, n_D^{20} 1.4342, sulfur content 0.003%.

Preparation of hydrocarbons. The sample was first diluted with a 40-fold amount of n-pentane and allowed to sediment. After 12 hours sedimentation insoluble asphaltenes were eliminated and the residue was distilled on a 22 TP column to eliminate the components boiling up to 200°C. The distillation residue was chromatographed on a silica gel column (Reanal, Hungary; 2.5 × 120 cm) with light petroleum (b.p. 45–65°C), giving the hydrocarbon fraction (Fig. 1A).

The separation of hydrocarbons was carried out using the urea clathrate method^{3,4} and sorption on the molecular sieve⁴ Linde 5A and following a procedure described earlier³. n-Alkanes were separated from the molecular sieve by dissolving it in hydrofluoric acid (Fig. 1B).

Gas chromatography was carried out on a Becker 419 chromatograph provided with flame ionisation detectors and a dual column system (0.2 × 100 cm) containing 10% of SE-30 on Chromosorb W—H.P. (80–100 mesh). Qualitative and quantitative evaluation was carried out in the same manner as before³.

Mass spectrometry was carried out on an A.E.I. MS 902 apparatus (70 eV, ion source temperature 150°C) combined with a PYE series 104 Chromatograph, Model 64 (3% SE-30 on Gas-Chrom Q, 60 ml/min He (programme 100°C, 1°C per min up to 160°C), using a Watson-Biemann separator.

RESULTS AND DISCUSSION

n-Alkanes (Fig. 1B) represent a homologous series in the C_{11} – C_{34} range, with the maximum at C_{16} and with a balanced ratio of even and odd members. This balance is common in n-alkanes of fossil origin and this fact was mentioned several times in the literature^{1,3,5-7}. In contrast to this n-alkanes from recent sources are characterized by a strong predominance of odd homologues over the even ones⁷.

The representation of the hydrocarbons which did not give adducts with urea is shown in Fig. 1C. The chromatogram illustrates the often met confusion wave⁴ of the so-called chromatographic background from which commonly shaped chromatographic peaks emerge. Using combined gas chromatography-mass spectroscopy method and studying the typical fragmentation⁸⁻¹² C_{16} and C_{18} alkanes were identified as 2,6,10-trimethyltridecane and 2,6,10-trimethylpentadecane, and C_{19} and C_{20} alkanes as 2,6,10,14-tetramethylpentadecane (pristane) and 2,6,10,14-tetramethylhexadecane (phytane). The mass spectra of other alkanes could not be interpreted satisfactorily in consequence of the disturbing effect of the chromatographic background.

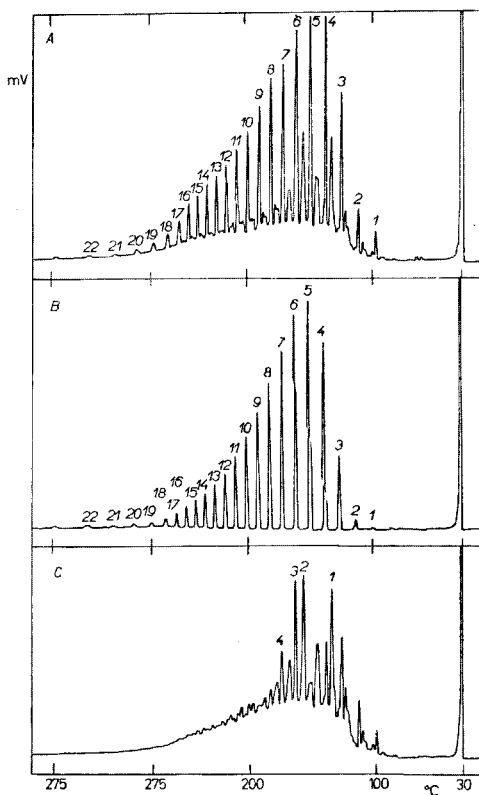


FIG. 1

Gas Chromatograms

A. Total hydrocarbons; B. n-Alkanes sorbed on the molecular sieve, 1—21 n- C_{12} —n- C_{32} , 2—22 n- C_{13} —n- C_{33} . C. Hydrocarbons which do not form adducts with urea 1 2,6,10-Trimethyltridecane, 2 2,6,10-trimethylpentadecane, 3 2,6,10,14-tetramethylpentadecane (pristane), 4 2,6,10,14-tetramethylhexadecane (phytane).

REFERENCES

1. Meinschein W. G. in the book: *Organic Geochemistry* (G. Eglinton, M. T. J. Murphy, Eds), p. 330. Springer, Berlin, Heidelberg and New York 1969.
2. Speers G. C., Whitehead E. V. in the book: *Organic Geochemistry* (G. Eglinton, M. T. J. Murphy, Eds), p. 638. Springer, Berlin, Heidelberg and New York 1969.
3. Kovačev G., Delova D., Stránský K.: *This Journal* 37, 4106 (1972).
4. Stránský K., Streibl M., Šorm F.: *This Journal* 33, 416 (1968).
5. Oró J., Nooner D. W., Zlatkis A., Wikström S. A., Barghoorn E. S.: *Science* 148, 77 (1965).
6. Hoeven W. V., Maxwell J. R., Calvin M.: *Geochim. Cosmochim. Acta* 33, 877 (1969).
7. Clark C., jr: *Occurrence of Normal Paraffin Hydrocarbons in Nature*. Technical Report No 66—34, Woods Hole Oceanographic Institution, p. 56. Woods Hole, Mass. 1966.
8. Burlingame A. L., Schnoes H. K. in the book: *Organic Geochemistry* (G. Eglinton, M. T. J. Murphy, Eds), p. 89. Springer, Berlin, Heidelberg and New York 1969.
9. Eglinton G.: *Proc. Soc. Anal. Chem.* 4, 111 (1967).
10. Johns R. B., Belsky T., McCarthy E. D., Burlingame A. L., Haug P., Schnoes H. K., Richter W., Calvin M.: *Geochim. Cosmochim. Acta* 30, 1191 (1966).
11. Kovjazin V. E., Hála S.: *This Journal* 38, 2938 (1973).
12. Hoeven W. V., Haug P., Burlingame A. L., Calvin M.: *Nature* 211, 1361 (1966).

Translated by Ž. Procházka.