

ANALYSIS OF HYDROFORMYLATION PRODUCTS OF HIGHER *n*-ALKENES BY CAPILLARY GAS CHROMATOGRAPHY

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A mixture of alcohols obtained by hydroformylation of C_{10} – C_{13} *n*-alkenes was analyzed by capillary gas chromatography using Carbowax 20M stationary phase, and acetates prepared from the alcohols were analyzed on capillary columns using Carbowax 20M and Apiezon L stationary phases. The capillary gas chromatography and gas chromatography-mass spectrometry treatment gave evidence that all of the 24 alcohols that could form by the hydroformylation reaction mechanism were present.

Hydroformylation of *n*-alkenes with higher numbers of carbon atoms gives rise to a mixture of alcohols which occur as intermediates in the production of detergents. Since the alcohol mixtures are highly complex, gas chromatography and its combination with infrared spectrometry¹ or mass spectrometry² are employed for their analysis.

Octanols prepared by hydroformylation of 1-heptene were analyzed by Kanski and coworkers³ on packed columns with Apiezon L stationary phase, and 1-heptene, *n*-octanol, and isooctanol only were identified. The abundances of the isomeric alcohols in the hydroformylation products were investigated by Nachikova and coworkers⁴. A group analysis was performed on the hydroformylation products of C_{11} – C_{14} *n*-alkenes by Prokopenko and coworkers^{5–9}. NMR spectroscopy was used by Hájek and coworkers¹⁰ for the identification of primary and secondary alcohols in hydroformylation products.

Packings with polyethylene glycol liquids suit best to the chromatographic analysis of alcohols¹¹. For analysis of alcohols on supports wetted with nonpolar stationary liquids, highly inert support surfaces must be employed. Acetates or silyl ethers of the alcohols are therefore more suitable for the analysis on packings with nonpolar stationary phases¹².

The aim of this work was to analyze alcohols obtained by hydroformylation of C_{10} – C_{13} *n*-alkenes by gas chromatography. Since all the positional and steric isomers were present in the *n*-alkene mixture, 24 alcohols could be expected in the reaction product. The mixtures of alcohols and of acetates derived from them were

analyzed by capillary gas chromatography. With the acetates, the gas chromatography-mass spectrometry combination was used for the identification of the positional isomers of the alcohols.

TABLE I

Basic characteristics of the columns used and conditions for the analysis of the alcohols and acetates

Characteristics and conditions	Column			
	A	B	C	D
Length, m	87	120	3	3
Inner diameter, mm	0.25	0.25	2	2
Stationary phase	C-20M	Ap-L	3%C-20M	20% DEGJ
Temperature, °C	130–140	130–140	100–120 ^a	160
Carrier gas	hydrogen	nitrogen	helium	helium
Flow rate, ml min ⁻¹	0.5	0.5	15	15

^a Temperature program with a gradient of 8°C min⁻¹.

TABLE II

Survey of alcohols expected in the hydroformylation product of C₁₀–C₁₃ n-alkenes and their labelling used in this paper

Alcohol	Label	Alcohol	Label
1-Undecanol	10–1	2-Methyl-1-dodecanol	12–2
2-Methyl-1-decanol	10–2	2-Ethyl-1-undecanol	12–3
2-Ethyl-1-nonanol	10–3	2-Propyl-1-decanol	12–4
2-Propyl-1-octanol	10–4	2-Butyl-1-nonanol	12–5
2-Butyl-1-heptanol	10–5	2-Pentyl-1-octanol	12–6
1-Dodecanol	11–1	1-Tetradecanol	13–1
2-Methyl-1-undecanol	11–2	2-Methyl-1-tridecanol	13–2
2-Ethyl-1-decanol	11–3	2-Ethyl-1-dodecanol	13–3
2-Propyl-1-nonanol	11–4	2-Propyl-1-undecanol	13–4
2-Butyl-1-octanol	11–5	2-Butyl-1-decanol	13–5
2-Pentyl-1-heptanol	11–6	2-Pentyl-1-nonanol	13–6
1-Tridecanol	12–1	2-Hexyl-1-octanol	13–7

EXPERIMENTAL

Apparatus

A Fractovap 2350 gas chromatograph (Erba, Milan) equipped with a flame ionization detector and a sample splitter was used. Nitrogen for lamps and electrolytic hydrogen served as the carrier gases, and electrolytic hydrogen and oxygen were used as the additive gases. The alcohols and acetates were analyzed on glass capillary columns containing Carbowax 20M (column A) and Apiezon L (column B); their basic characteristics are given in Table I.

The mass spectra of the acetates were obtained with a GC-MS MAT-111 instrument (Varian) using the energy of ionizing electrons 80 eV, ionization current 270 μ A, ion source temperature 200°C, carrier gas separator temperature 200°C, and connecting tube temperature 190°C. Packed columns C and D (Table I) were used in this instrument.

Samples

The alcohol sample was prepared by hydroformylation of C_{10} – C_{13} n-alkenes. The 24 alcohols expected and the symbols used for them in this paper are listed in Table II.

The alcohols were converted into the corresponding acetates by heating the mixture with excess acetyl chloride and evaporating the latter in a nitrogen stream. 1-Decanol, 1-undecanol, 1-dodeca-

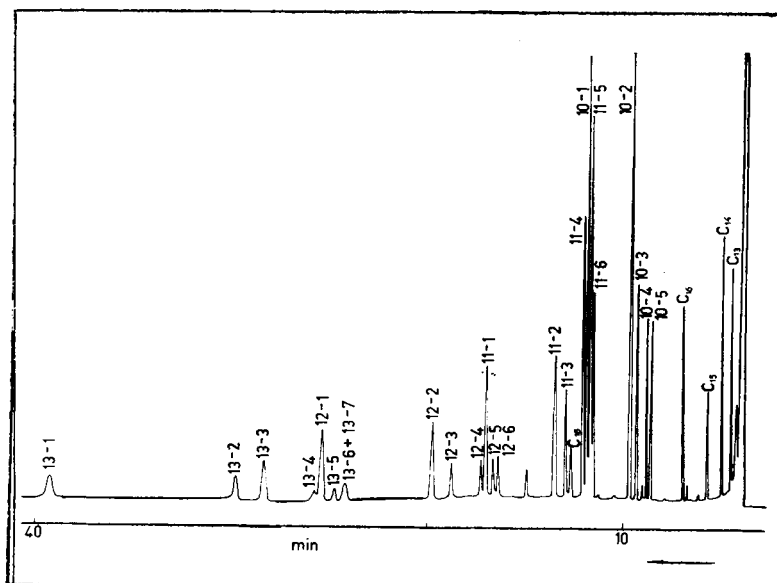


FIG. 1

Separation of a mixture of C_{13} – C_{18} n-alkenes and hydroformylation products of C_{10} – C_{13} n-alkenes in a capillary column with Carbowax 20M (column A) at 130°C

nol, 1-tridecanol and 1-tetradecanol, and secondary alcohols prepared by addition of water to C_9 – C_{14} n-alkenes under the catalytic effect of H_2SO_4 were analyzed as model samples.

RESULTS AND DISCUSSION

Separation of Alcohols and Their Acetates

Published data and our preliminary experiments indicated that isomeric alcohols are insufficiently resolved on packed columns. Capillary columns were therefore used for the alcohols and the related acetates; polyethylene glycol 2000 (Carbowax 20M) appeared to be a suitable stationary liquid for the C_{10} – C_{14} alcohols.

A chromatogram for the mixture of n-alkanes and alcohols separated on Carbowax 20M is shown in Fig. 1. The peaks of the alcohols are symmetrical and their number is as was expected based on the reaction mechanism. Problems occur with the resolution of the non-even carbon "central" isomers (11–5 and 11–6, and 13–6 and 13–7 pairs).

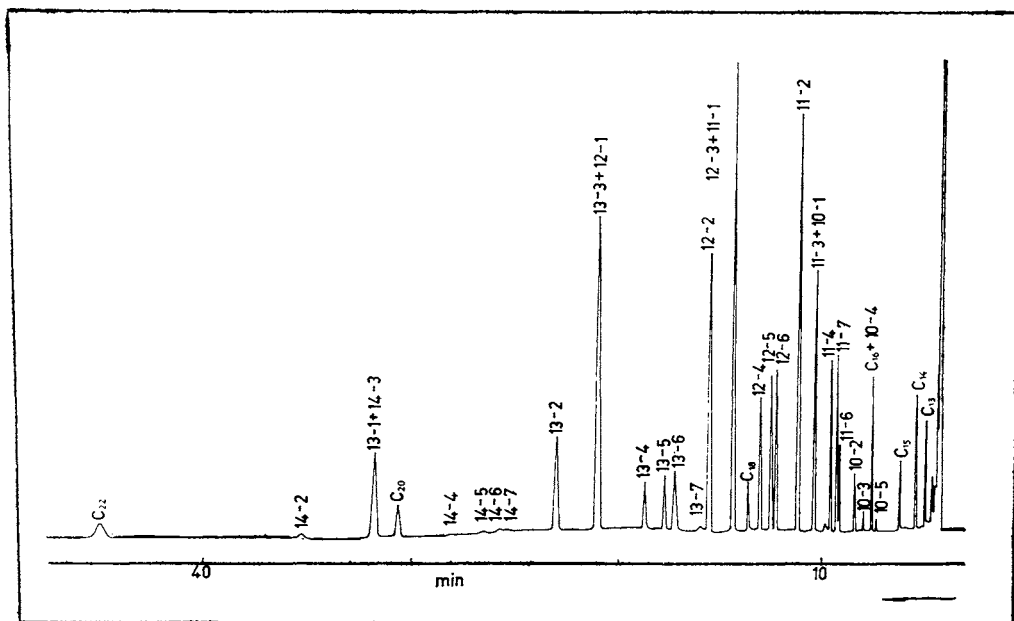


FIG. 2

Separation of a mixture of C_{13} – C_{22} n-alkanes and acetates derived from alcohols obtained by hydroformylation of C_{10} – C_{13} n-alkenes in a column with Carbowax 20M (column A) at $130^\circ C$

The record for the corresponding acetates is shown in Fig. 2. Since hydrogen bonds with the stationary phase cannot occur any more as the hydrogen in the hydroxy group is substituted by the acetyl group, the acetates elute considerably faster than the alcohols, as documented by the chromatograms in Figs 1 and 2 and by the values of the Kováts indices in Tables III and IV. The peak pairs labelled 10-1 + 11-3, 11-1 + 12-3, 12-1 + 13-3, and 13-1 + 14-3 in Fig. 2 could not be resolved even if programmed temperature was used. Figs 1 and 2 document that low boiling acetates evaporate together with acetyl chloride in the nitrogen stream.

The column properties were altered by surface treatment and by increasing the thickness of the stationary liquid film. If the column surface was modified by an interlayer of BaCO_3 , the alcohols eluted considerably more slowly (compare the records in Figs 3 and 1), which points to a higher polarity of the column with the interlayer. Since modification of the surface and the Carbowax 20M film thickness has a marked effect on the capillary column properties, these phenomena were investigated in detail in a separate study¹³.

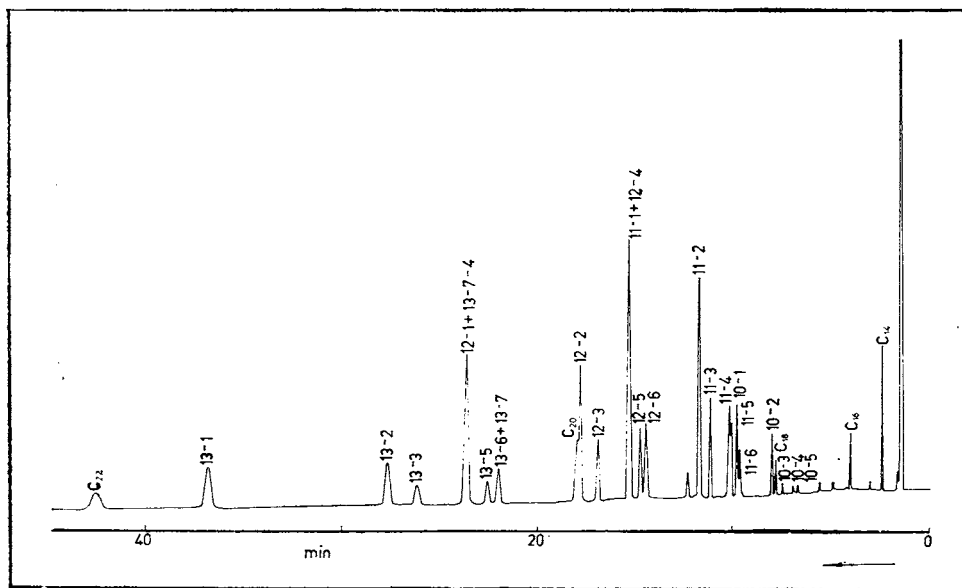


FIG. 3

Separation of a mixture of C_{14} — C_{22} n-alkanes and hydroformylation products of C_{10} — C_{13} n-alkenes in a column whose surface was modified with a BaCO_3 interlayer and which contained Carbowax 20M as the stationary phase at 142°C

In the process of separation of the acetates in capillary columns with a nonpolar stationary phase, interactions of the nonpolar alkyl parts of the compounds with the stationary phase liquid play the major part. So all the acetates derived from the alcohols listed in Table II could be resolved in a capillary column containing the Apiezon Lp phase.

Characterization of the Alcohols and the Corresponding Acetates

It is convenient to formally consider the CH_2OH grouping as the functional group of the alcohols. All the alcohols obtained by hydroformylation of n-alkenes (except

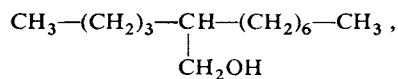
TABLE III

Kováts indices (I), temperature increments ($\Delta I/10^\circ\text{C}$), and structure increments (H) for the C_{11} – C_{14} alcohols measured in a capillary column with Carbowax 20M at 130°C

Alcohol ^a	I	s^b	$\Delta I/10^\circ\text{C}$	H
10–5	1 681.6	0.29	1.4	681.6
10–4	1 689.8	0.06	0.9	689.8
10–3	1 708.7	0.06	2.0	708.7
10–2	1 720.3	0.29	1.4	720.3
10–1	1 781.0	0.35	1.4	781.0
11–6	1 774.2	0.17	0.2	674.2
11–5	1 777.4	0.24	0.9	677.4
11–4	1 785.9	0.35	1.2	685.9
11–3	1 805.5	0.06	1.6	705.5
11–2	1 817.8	0.12	1.1	717.8
11–1	1 878.3	0.17	1.8	778.3
12–6	1 869.1	0.24	1.0	669.1
12–5	1 872.6	0.17	1.2	672.6
12–4	1 882.4	0.17	1.3	682.4
12–3	1 902.5	0.06	1.5	702.5
12–2	1 914.4	0.35	1.7	714.4
12–1	1 975.3	0.17	2.1	775.3
13–7	1 963.9	0.17	2.0	663.0
13–6	1 963.9	0.17	2.0	663.9
13–5	1 968.9	0.17	1.4	668.9
13–4	1 978.5	0.12	0.9	678.5
13–3	1 999.5	0.24	0.7	699.5
13–2	2 010.7	0.24	2.6	710.7
13–1	2 070.4	0.24	3.9	770.4

^a See Table I; ^b standard deviation of I obtained from triplicate measurements.

for nonbranched 1-ols) can be then regarded as analogues of secondary alcohols. For instance, 2-butyl-1-nonanol,



is structurally akin to 5-dodecanol, and we label it 12-5 to indicate the number of the carbon atoms in the alkyl chain by the first figure and the position of the $-\text{CH}_2\text{OH}$ group in this chain by the second figure (Table II).

TABLE IV

Kováts indices (I), temperature increments ($\Delta I/10^\circ\text{C}$), and structure increments (H) for the $\text{CH}_3\text{COOCH}_2$ -group of acetates derived from the C_{11} - C_{14} alcohols, measured in a capillary column with Carbowax 20M at 130°C

Acetate ^a	I	$\Delta I/10^\circ\text{C}$	H
10-5	—	—	—
10-4	1 600.0	0.0	600.0
10-3	1 623.6	4.4	623.6
10-2	1 644.5	4.0	644.5
10-1	1 718.5	4.4	618.5
11-6	1 676.9	3.0	576.9
11-5	1 681.0	3.2	581.0
11-4	1 692.2	4.5	592.2
11-3	1 718.5	4.4	618.5
11-2	1 740.8	3.9	640.8
11-1	1 814.9	3.8	614.9
12-6	1 769.8	3.0	569.8
12-5	1 775.1	3.2	575.1
12-4	1 787.5	3.5	587.5
12-3	1 814.9	3.8	614.9
12-2	1 837.4	3.6	637.4
12-1	1 911.4	4.4	611.4
13-7	1 863.8	4.0	563.8
13-6	1 863.8	2.8	563.8
13-5	1 870.6	3.0	570.6
13-4	1 883.4	3.2	583.4
13-3	1 911.4	4.4	611.4
13-2	1 933.9	3.6	633.9
13-1	2 007.9	2.2	607.9

^a See Table I.

TABLE V

Kováts indices (I) and structure increments (H) for the $\text{CH}_3\text{COOCH}_2$ -group of acetates derived from the C_{11} – C_{14} alcohols, measured in a capillary column with Apiezon L at 140°C

Acetate ^a	I	H	Alcohol ^a	I	H
10–5	1 362.6	362.5	12–5	1 555.5	355.5
10–4	1 372.1	372.1	12M4	1 567.4	367.4
10–3	1 395.3	395.3	12–3	1 592.5	392.5
10–2	1 414.0	414.0	12–2	1 612.5	412.5
10–1	1 473.3	473.3	12–1	1 672.7	472.7
11–6	1 455.1	355.1	13–7	1 645.5	345.5
11–5	1 458.5	358.5	13–6	1 647.0	347.0
11–4	1 469.4	369.4	13–5	1 650.1	350.1
11–3	1 494.0	394.0	13–4	1 665.6	365.6
11–2	1 513.2	413.2	13–3	1 691.2	391.2
11–1	1 573.2	473.2	13–2	1 711.5	411.5
12–6	1 551.3	351.3	13–1	1 772.4	472.4

^a See Table I.

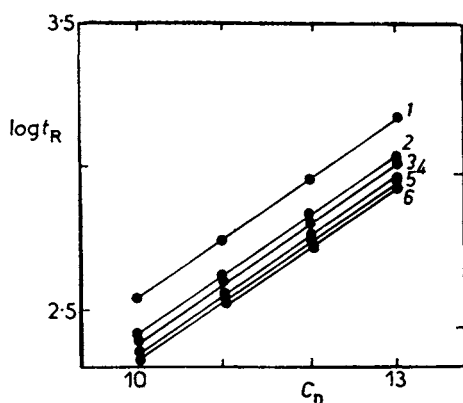


FIG. 4

Dependence of $\log t_R$ on the number of carbon atoms C_n in acetates derived from the C_{11} – C_{14} alcohols, for a capillary column with Carbowax 20M (column A) at 140°C

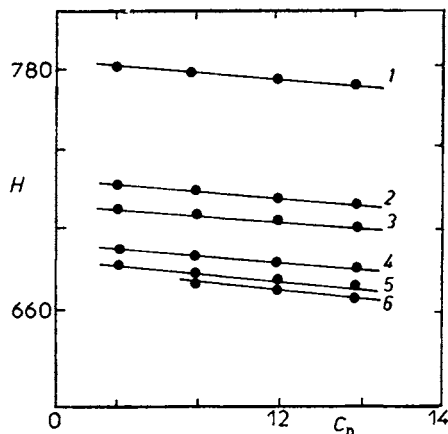


FIG. 5

Dependence of the structure increments (H) for the $-\text{CH}_2\text{OH}$ group on the number of carbon atoms the C_{11} – C_{14} alcohols, for a capillary column with Carbowax 20M at 140°C

This formal similarity between the alcohols in the hydroformylation product and secondary alcohols was utilized for the characterization of the former based on the published elution data for the latter and for the corresponding acetates.

Fig. 4 shows the semilogarithmic dependence of the corrected retention times on the number of carbon atoms, obtained by analyzing alcohols (standards and alcohols in the sample) on a capillary column with Carbowax 20M at 140°C. Similar linear relations were obtained for the acetates using Carbowax 20M and Apiezon L. The dependences of t'_R on C_n were used for a tentative characterization of the $-\text{CH}_2\text{OH}$ and $-\text{CH}_2\text{OCOCH}_3$ group in the alkyl chain. The Kováts indices were

TABLE VI

Kováts indices (I) for acetates derived from the C_{11} – C_{14} alcohols, measured at 140°C in capillary columns with Carbowax 20M and with Apiezon L, and their differences (ΔI)

Acetate ^a	I		ΔI
	Carbowax 20M	Apiezon L	
10–5	—	1 362·6	—
10–4	1 600·0	1 372·1	227·9
10–3	1 628·0	1 395·4	232·7
10–2	1 648·5	1 414·0	234·5
10–1	1 722·9	1 473·3	249·6
11–6	1 679·9	1 455·1	224·8
11–5	1 684·2	1 458·5	225·7
11–4	1 696·7	1 469·4	227·3
11–3	1 722·9	1 494·0	228·9
11–2	1 744·7	1 513·2	231·5
11–1	1 818·7	1 573·2	245·5
12–6	1 772·8	1 551·3	221·5
12–5	1 778·3	1 555·5	222·8
12–4	1 791·0	1 567·4	223·6
12–3	1 818·7	1 592·5	226·2
12–2	1 841·0	1 612·5	228·5
12–1	1 915·8	1 672·2	243·1
13–7	1 863·6	1 645·5	218·1
13–6	1 866·6	1 647·0	219·5
13–5	1 873·6	1 653·1	220·5
13–4	1 886·6	1 665·6	221·0
13–3	1 915·8	1 691·2	224·6
13–2	1 937·5	1 711·5	226·0
13–1	2 010·1	1 772·4	237·7

^a See Table I.

also employed and compared with the published data for secondary alcohols and the related acetates¹⁴.

The Kováts indices, their standard deviations, and the temperature, and structure increments for the alcohols are given in Table III. The standard deviation estimates were calculated from the variance. The temperature increments are affected by errors of measurement, and so relation between $\Delta I/10^\circ\text{C}$ and the structure of the alcohols is difficult to evaluate. The dependence of the structure increments H on the number of the carbon atoms is linear over the range in question (Fig. 5), and this can be used to characterize the position of the $-\text{CH}_2\text{OH}$ group in the alkyl chain.

The corresponding values for the acetates measured with capillary columns containing Carbowax 20M (130°C) and Apiezon L (140°C) are given in Tables IV and V, respectively. The differences in the Kováts indices for the two phases, $\Delta I = I_{\text{Carb}} - I_{\text{Ap}}$, are given in Table VI. Characteristic of the acetates, the ΔI values for a given position of the $-\text{CH}_2\text{OCOCH}_3$ group in the chain decrease with increasing number of carbon atoms in the molecule.

The alcohols in the hydroformylation product of n-alkenes were characterized by their mass spectra obtained from the gas chromatography-mass spectrometry treatment. Although the acetates separated considerably more poorly on packed columns than on capillary columns, the substances in the mixed peaks could be identified by taking the mass spectra for various sections of the peaks.

Similarly as acetates derived from secondary alcohols¹⁵, the acetates under study do not display their molecular ions in the mass spectra; nevertheless, the molecular weights could be determined from the $[\text{M}-60]^+$ fragments. The position of the $-\text{CH}_2\text{OCOCH}_3$ group, on the other hand, could not be established unless standards were available.

Using the procedures described, all the 24 alcohols listed in Table II were thus identified in the product of hydroformylation of C_{10} — C_{13} n-alkenes.

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REFERENCES

1. Belafy-Rethy K., Kantor M.: *Erdoel Kohle Erdgas Petrochem. Bernst-Chem.* 24, 12 (1971).
2. Arpino A., Fedeli E., Borsary G. B., Bvosi E., Fuochi E. P.: *Riv. Ital. Sostanze Grasse* 8, 254 (1974).
3. Kaňski R., Vdovin A.: *Chem. Anal. (Warsaw)* 13, 252 (1968).
4. Nachikova P. R., Rud A. N., Ivanov V. V., Temberg G. A.: *Neftepererab. Neftekhim. (Moscow)* 8, 51 (1981).
5. Prokopenko N. A., Dubrova N. A., Kirsch T. P.: *Neftepererab. Neftekhim (Moscow)* 1, 43 (1980).

6. Prokopenko N. A., Dubrova N. A., Maiorova R. V., Borodavko V. A., Rane H., Stevenz D.: Zh. Anal. Khim. 33, 1228 (1978).
7. Prokopenko N. A., Dubrova N. A., Mairova R. V., Borodavko V. A., Rane H., Stevenz D.: Zh. Anal. Khim. 33, 1196 (1978).
8. Prokopenko N. A., Maiorova R. V., Dubrova N. A., Maltinskaya S. M.: Neftepererab. Neftekhim. (Moscow) 3, 33 (1978).
9. Prokopenko N. A., Maiorova R. V., Dubrova N. A.: Neftepererab. Neftekhim. (Moscow) 7, 36 (1978).
10. Hájek M., Vodička L., Vlková Y.: Chem. Listy 75, 870 (1981).
11. Schomburg G. in the book: *Advances in Chromatography* (J. C. Giddings, R. A. Keller, Eds), Vol. 6, p. 211. Dekker, New York 1968.
12. Littlewood A. B.: *Gas Chromatography*. Academic Press, New York 1970.
13. Krupčik J., Matisová E., Garaj J., Soják L., Berezkin V. G.: Chromatographia 16, 166 (1982).
14. Krupčik J., Tesařík K., Hrivňák J.: Chromatographia 8, 553 (1975).
15. Holotík Š., Leško J., Krupčik J., Tesařík K.: Chromatographia 9, 443 (1976).

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