B. In a quartz flask, 1 g ($4 \cdot 10^{-4}$ mole) of (I) was dissolved in dioxane and, with stirring, a solution of 0.4 ml ($8 \cdot 10^{-4}$ mole) of $Br_2$ in dioxane was added dropwise over 0.5 h. The reaction was performed with illumination by a UV lamp with a power of 250 W at 100°C for 4 h. The solution was worked up in a similar way to experiment A. Yield 81%.

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# COMPLEXES OF THE PORPHYRINS OF KARAZHANBASS PETROLEUM WITH TRANSITION-METAL IONS

R. N. Nasirov

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The possibility and prospects of the use of petroleum porphyrins isolated from Karazhanbass petroleum for the synthesis of complex compounds of the transition metals has been shown.

Complexes of porphyrins with transition metal ions are effective homogeneous catalysts of a number of chemical processes [1]. The high cost of synthetic porphyrins is dictating the necessity for finding new sources of these substances. One of the possible natural sources is petroleum with a high content of metalloporphyrins.

As has been shown [2, 3] the mineral oils of the Buzachi anticline contains porphyrins in the form of complexes with nickel and vanadyl in concentrations of up to 1 kg per ton and can be considered as a full-value substitute for expensive and poorly available biological porphyrin compounds.

It has been shown previously [3] by the methods of electronic and PMR spectroscopy that the vanadylporphyrins of the Karazhanbass petroleum are represented by a set of homologs relating mainly to two series, M and M-2. The vanadylporphyrins from the Karazhanbass obtained from borehole 851 were isolated by a combined extraction-chromatographic method [4]. To determine the total content of vanadylporphyrin complexes in the petroleum and to extract them completely they were isolated from the petroleum directly by the procedure of Bogomolov et al. [5] with the aid of hot ethanol—acetone extraction. For the quantitative determination of the vanadylporphyrins the optical density of the extract at 572 nm was measured with the aid of a Specord UV-Vis spectrophotometer. Table 1 gives the results of a study of the influence of the selectivity of the solvents on the extraction of the vanadylporphyrins from the oil of the Karazhanbass deposit. The most effective extractant proved to be dimethylformamide (DMFA). Since the petroleum of the Karazhanbass deposit and DMFA have almost identical densities (0.95 g/cm$^3$), to achieve phase separation we used the preliminary dilution of the petroleum with hexane to decrease its density.

With the aim of detecting homologs of the vanadylporphyrins from the Karazhanbass petroleum we made a mass-spectrometric investigation on a MS-30 instrument at an ionization energy of 70 eV and with the gradual heating of the sample from 50 to 325°C. Analysis of the mass

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TABLE 1. Influence of the Selectivity of Solvents on the Extraction of Vanadylporphyrins from the Petroleum of the Karazhanbass Deposit, Borehole 851 (mg/100 g of petroleum)

| Solvent | Number of the extract | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | sum |
| N,N-Dimethylformamide | 26,2 | 4,70 | 2,34 | 33,24 |
| Acetone | 21,0 | 3,04 | 1,17 | 25,21 |
| Ethanol and acetone (hot extraction) | 22,4 | 13,02 | – | 35,42 |

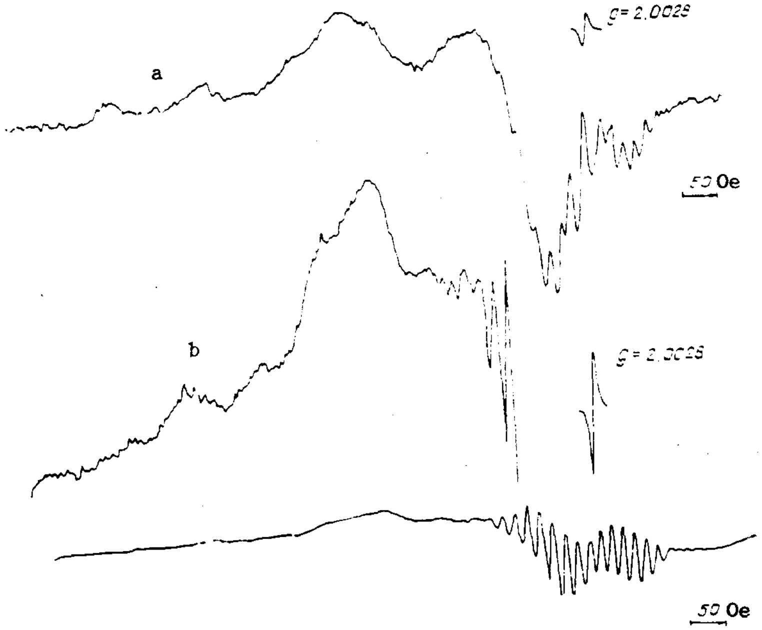

Fig. 1. ESR spectrum of the complexes $Cu^{2+}$-DPEP (a) and $Cu^{2+}$-OEP (b) at −196°C.

spectra showed that the vanadylporphyrins were represented by an uninterrupted set of homologs of several series, 90-95% of the total amount of vanadylporphorins belonging to the M and M-2 series and the M-2/M ratio being 0.96.

The molecular masses of the homologs of the M series ranged between 459 and 627, the maximum peak height relating to a mass of 529 in which the number of carbon atoms in the side chains was 11; the molecular masses of the homologs of the M-2 series ranged between 457 and 625, the highest content relating to a mass of 541 with 12 carbon atoms in the side chains.

With the aid of the procedure of demetallization and chromatographic separation, the vanadylporphyrin concentrates of the Karazhanbass petroleum yield free porphyrins of two types: deoxophylloerythroetioporphyrin (DPEP) and etioporphyrin (EP) [3]. The purity of the porphyrins isolated was determined from the absorption band at 400 nm (Soret band) and also on the basis of the absence of background absorption in the 400-640 nm region. The degrees of purity of the samples obtained ranged between 85 and 95%.

The free porphyrins that had been isolated were used to obtain complex compounds of nickel and copper. A complex of bivalent nickel with EP was synthesized by the interaction of anhydrous $NiCl_2$ with EP in benzene in the presence of acetic acid as catalyst with heating on the water bath. The electronic spectrum of the complex showed the three absorption bands characteristic for this compound: 394, 515, and 553 nm (the ratio α/β − 3.0 [6]):

Complexes of bivalent copper were obtained by the interaction of the anhydrous salt $CuCl_2$ with DPEP in dry chloroform at room temperature for 24 h. Fig. 1a, shows the ESR spectrum of $Cu^{2+}$-DPEP at −196°C. A similar spectrum was obtained from the complex of bivalent copper with the isolated EP that we had prepared.

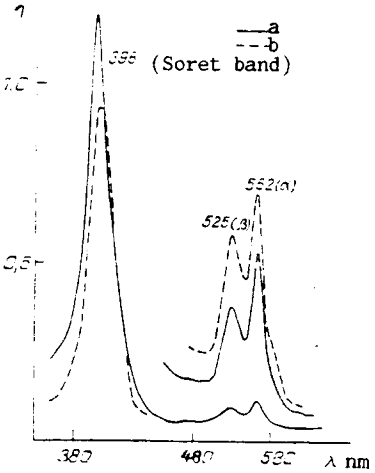

Fig. 2. Absorption spectra in the visible region of $Cu^{2+}$-EP (a) and of $Cu^{2+}$-DPEP (b) in chloroform.

Figure 1b gives the ESR spectrum of the complex of $Cu^{2+}$ with octaethylporphyrin (OEP) of synthetic origin. In both spectra, in the $g_I$ region hyperfine splitting is observed from the interaction of the unpaired electron with the $^{63,65}Cu$ nuclei and with four $^{14}N$ atoms. From an analysis of the isotropic spectrum of $Cu^{2+}$–OEP ($g_{iso}$ = 2.101, $a_{Cu}$ = 102.5 Oe, and $a_N$ = 12.5 Oe) and the spectrum in the Fig. 1b, we obtained the values $g_I$ = 2.083; $g_{II}$ = 2.137; $A_I^{Cu}$ = 115 Oe, $A_{II}^{Cu}$ = 77.5 Oe, $A_I$ = 15 Oe.

A comparison of the pattern of hyperfine splitting of the $g_I Cu^{2+}$ signals of $Cu^{2+}$-DPEP and of $Cu^{2+}$-OEP permitted the assumption of a closeness of the spectral characteristics of these complexes, which agrees with information on the influence of the structure of the porphyrins on their ESR spectra [7, 8].

It must be mentioned that the spectral parameters of the ESR spectra of the complexes of DPEP and EP with $Cu^{2+}$ are very close, and therefore the solutions of the complexes obtained were studied with the aid of electronic spectroscopy on a Specord UV-Vis instrument. Figure 2 shows the absorption spectra of these complexes in the visible region. As can be seen from Fig. 2a, b, they differ by the ratio of the intensities of the α- and β-bands: for $Cu^{2+}$-EP the ratio $\alpha/\beta$ = 1.7, and for $Cu^{2+}$-DPEP, $\alpha/\beta$ = 1.3.

It must be mentioned that in the visible region $Cu^{2+}$-EP and $Cu^{2+}$-OEP have similar spectra, the slight difference in the spectra being due to the different numbers of $CH_2$ groups in the alkyl substituents of the porphyrin ring.

## EXPERIMENTAL

The electronic absorption spectra of nickel etioporphyrin and also the spectra of the free porphyrins were taken on a Specord UV-vis spectrophotometer at room temperature. The mass spectra of the extracted vanadylporphyrins were measured on a MS-30 mass spectrometer at an ionizing voltage of 70 V with gradual heating of the sample from 323 to ~598 K. The samples entered the ion source through a direct introduction system. The ESR spectra were taken on a Varian E-12 radiospectrometer.

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# MONOTERPENOIDS (3-CARENE AND α-TERPINENE) IN ELECTROPHILIC DISULFIDE ADDITION REACTIONS

L. E. Nikitina and V. V. Plemenkov

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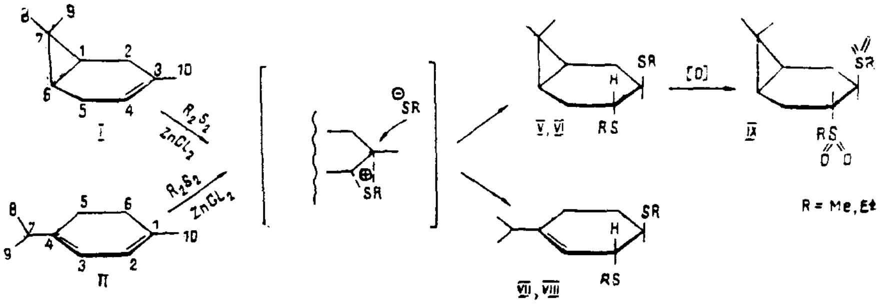
The reactions of 3-carene and α-terpinene with dialkyl disulfides have been studied.

The reactions of 3-carene (I) and of α-terpinene (II) with dialkyl disulfides (III, R = $CH_3$; IV, R = $C_2H_5$) are, primarily, a convenient method for introducing sulfur-containing functions into terpene hydrocarbons. In addition, these reactions open up a route to the use of this method as an analytical procedure for determining the positions of double bonds in terpenes and their derivatives.

We have established that the methods of introducing two sulfide functions described in the literature [4, 5] for other classes of compounds cannot be used in the case of the terpenes (I) and (II), since they lead to the total isomerization of (I) and (II) into p- and m-cymene. At the same time, the interaction of 3-carene (I) and α-terpinene (II) with the disulfides (III) and (IV) in the presence of $ZnCl_2$ has led to the formation of the addition products (V-VIII) as the main products with small amounts (not more than 5%) of p- and m-cymene as impurities. The structures of compounds (V-VIII) have been confirmed by PMR spectroscopy (Table 1). The results of elementary analysis correspond to the calculated figures. The structure of the adduct (V) was confirmed by mass spectroscopy.



To establish the stereochemistry of the addition of the disulfides to 3-carene (I), 3β-4α-di(methylthio)carane (V) was oxidized to the corresponding sulfone (IX), the crystalline structure of which has been determined by x-ray structural analysis. According to these results the sulfone group at the $C^3$ atoms was present in the cis- position and the sulfone group at the C4 atom in the trans- position to the cyclopropane ring, which indicates the observation of Markovnikov's rule in this reaction. The crystals of compound (IX) were rhombic; at 20°C, a = 6.526(2), b = 9.691(2), c = 22.941(5); Z = 4 (calc.), 1.348 g/cm$^3$; space group $P2_1$-$2_12_1$.

A characteristic feature of the addition of the disulfides (III) and (IV) to α-terpinene (II) is the high degree of chemoselectivity – the reaction takes place exclusively at the

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