COMPONENTS OF PLANTS OF THE FAMILY EMETRACEAE. V. ESTERS FROM *Empetrum* SPECIES

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In the course of the study of the chemical composition of the lipophilic fraction of the crowberry [1], which possesses an anticonvulsive activity, we have isolated the total esters, and the present communication is devoted to a study of these.

When a hexane extract of crowberry was separated by column chromatography on silica gel L (100-160 μm), treatment of the sorbent with boiling chloroform led to a white powder (yield 3.5%). It was dissolved in benzene–ethanol (1:1), and the addition of an alcoholic solution of KOH gave a precipitate which was washed to neutrality and was purified by preparative TLC on Silufol. Elution with chloroform yielded a mixture of substances which was investigated by spectral methods.

The IR spectrum [$\nu_{max.}^{KBr}$ 1745 (C=O), 1200 cm^{-1} (C–O–C)] showed the presence of an ester group, which was confirmed by the hydroxamic reaction with copper sulfate. The PMR spectrum (100 MHz, $CDCl_3$, δ, ppm): 0.86 (terminal CH_3 groups); 1.3 (m, CH_2 groups of a long alkyl chain); triplets at 2.27 and 4.03 (CH_2 groups at C=O and C–O– of esters). It followed from the ratio of the integral intensities of these signals that the molecule consisted of 50-60 carbon atoms. Titration of this sample with the lanthanoid shift reagent $Eu(FOD)_3$ showed that it consisted of a group of esters, while the absence of shifts of the signal at 0.86 ppm due to the addition of the $Eu(FOD)_3$ showed the presence of a terminal methyl group no closer than six methylene groups from the ester bond [2].

In the mass spectrum of the sample obtained (MKh 1310, 70 eV), taken in the temperature interval of 473-573 K, three groups of fairly widely spaced signals were observed. The first group included a set of groups of fragmentary ions characteristic for esters of monobasic carboxylic acids with aliphatic substituents (m/z 59, 60, 61, 73, 74, 75, ..., 115, 116, 129, 143) and the fragments of an unbranched C_3-C_{10} hydrocarbon chain (41, 43, 55, 57, ..., 141) [3, 4]. The second group consisted of five intense triplets with an interval of 28 a.m.u. corresponding to ions of the $(RCOO)^+$ and $(RCO)^+$ types. The fragmentation of the esters took place at the β-bonds, since the strongest peaks began from a mass of 393.

The third group of peaks consisted of M^+ and fragmentary ions of the type of $(M-1)^+$ and $(M-15)^+$; the seven strongest peaks of the molecular ions differed from one another by 28 a.m.u. and belonged to esters with the same substituents ($C_nH_{2n+1}-\underset{\underset{O}{\|}}{C}-O-C_nH_{2n+1}$). Between the strong peaks there were weaker ones assigned to esters the length of the substituents of which differed by one methylene group.

Thus, on the basis of chemical and spectral characteristics it has been established that the sample obtained consisted of the homologous series of unbranched aliphatic esters, seven of which with equal alkyl substituents from C_{24} to C_{30} made up about 90% of the sample. The remaining five esters (10% of the sample) contained $C_{24}-C_{25}$, $C_{25}-C_{26}$, $C_{26}-C_{27}$, $C_{27}-C_{28}$, and $C_{28}-C_{29}$ substituents differing by one methylene group, $C_nH_{2n+1}-\underset{\underset{O}{\|}}{C}-O-C_{n+1}H_{2n+3}$.

REFERENCES

1. N. N. Red'kina, O. V. Bryanskii, E. A. Krasnov, A. A. Semenov, and E. V. Ermilova, Khim. Prir. Soedin., 719 (1989).

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2. V. D. Ogorodnikov, Instrumental Methods of Investigating Petroleum [in Russian], Nauka, Novosibirsk (1987), p. 49.
3. A. A. Polyakova and R. A. Khmel'nitskii, Mass Spectrometry in Organic Chemistry [in Russian], Khimiya, Leningrad (1972).
4. H. Budzikiewicz, C. Djerassi, and D. Williams, Interpretation of Mass Spectra of Organic Compounds, Holden-Day, San Francisco (1964) [Russian translation], Mir, Moscow (1966), p. 26.