Details of the $^{13}$C NMR spectra of glycyrrhizic acid and four of its derivatives are given, and on their basis the configurations of the anomeric centers of the carbohydrate chain have been redetermined and the $\beta$-configuration of the C-1' carbon atom has been suggested.

There is no information in the literature on the use of $^{13}$C NMR spectroscopy to establish the structure of a triterpene glycoside — glycyrrhizic acid — the active principle of an extract of liquorice Glycyrrhiza glabra. We have previously [1] reported the $^{13}$C NMR spectra of derivatives of the aglycon — glycyrrhetic acid. In the present paper we give details of the $^{13}$C NMR spectra of glycyrrhizic acid (I) and four of its esters (II-V) as the result of a study in which a stereochemical configuration of the carbohydrate moiety of the molecule is proposed.

The stereochemistry of the disaccharide moiety of glycyrrhizic acid was established by Lythgoe and Trippett [2] by hydrolysis and the subsequent methylation of the hydrolysis products with the use of optical rotation results. It was shown [2] that the bond between the glucuronic acids of the disaccharide part of glycyrrhizic acid has the $\beta$-configuration and the bond with the aglycon the $\alpha$-configuration.

Thus, according to results of previous work [2-4], glycyrrhizic acid has the structure of 38-$[O-\alpha-D$-glucopyranuronosyl-(1 + 2)$-\beta-D$-glucopyranuronosyloxy]$-11$-oxo$-(18\beta$H$)$-olean$-12$-en$-30$-oic acid.

We have investigated in detail the $^{13}$C NMR spectra of the glycoside (I) and its derivatives (II-V). Table 1 gives the $^{13}$C NMR chemical shifts for compounds (I-V). The multiplicity of the signals for compounds (II-V) fully agreed with the results for the spectrum of the acid (I).

The assignment of the signals of the C-atoms in the $^{13}$C NMR spectra of glycoside (I) and its derivatives was made on the basis of information for the genin and its derivatives [1, 6] and literature information for corresponding glycosides [8-12]. The triterpene moiety of the glycyrrhizin acid molecule is easily identified in the spectrum of (I) from a comparison with the $^{13}$C NMR spectrum of 18β-glycyrrhetic acid [1]. An exception is the signal of the C-3 carbinol carbon linked to the carbohydrate moiety of the molecule, which resonates at 90.74 ppm. In this case, the glycosylation effect amounts to 12 ppm and indicates the β-configuration of the O-C-3 bond [7], which is in harmony with the stereochemical structure of the aglycon of the glycyrrhizin acid molecule [3, 6].

The signals of the two carboxy groups of the carbohydrate moiety were observed in the weak-field region (172.29 ppm). Weak-field signals at 106.01 and 105.10 ppm, respectively, corresponded to the C-1' and C-1" carbon atoms of the glucuronic acid residues. The signal of the C-2' carbinol carbon atom linked to the second glucuronic acid residue of the disaccharide moiety of the molecule appeared in a weaker field (83.78 ppm) than those of the other carbon atoms of the carbohydrate moiety of the glycoside (72.85-77.35 ppm).

On the basis of literature results [7, 10], increments of the influence of substituents on the chemical shifts of D-glucuronic acid derivatives were obtained and were used in the calculation of the chemical shifts of the carbon atoms of the carbohydrate moiety of the molecule of the α- and β-configurations of the C-1' anomeric center. A comparison of the calculated and experimental figures gave unambiguous evidence in favor of the β-configuration of the C-1' anomeric center. In the case of the α-configuration of this center, the C-3' and C-5' signals should be observed in a stronger field ($\delta$calc C-3' = 72.5 ppm and $\delta$calc C-5' = 71.9 ppm) because of the contribution of the steric 1,3-diaxial interaction, as follows from stereocchemical models for the $\text{C}_{1}$ conformer that were considered. In the case of the $\text{C}_{6}$ conformer, diamagnetic shifts of practically all the carbinol signals would have been observed.

Similar information on the structure of the carbohydrate residue was obtained in a study of the $^{13}$C NMR spectra of cyclosieversioside H—a triglycoside from Astragalus sieversianus [8].

More characteristic is the spectrum of the pentaacetate of the trimethyl ester of glycyrrhizinic acid (II). The signals of the C-1' and C-1 anomeric protons (103.43 and 100.88 ppm, respectively) in the spectrum of (II) indicate the β-configurations of the glycosidic bonds.