The mass spectra of four guaianolides with epoxy groups of C1-C2 have been studied. A mechanism is proposed for the formation of the main ions. The origin of the secondary fragments has been confirmed by measurements of elementary compositions.

In spite of the existence of a considerable number of sesquiterpene lactones of the guaiane type, there is extremely little information on the mass spectra of these compounds [1-4]. Continuing a study of the pathways of the fragmentation of lactones of sesquiterpene lactones, in this paper we consider the mass spectra of four lactones with a guaiane skeleton representing the 1,2-epoxyguaianolides — chrysartemin B (I) [5], rupin A (II) [4], ajafinin (III) [6], and biebsanin (IV) [7].

The intensities of the peaks of the molecular ions of (I-IV) are very low in comparison with the main peak of the spectra (Fig. 1), which is obviously due to the relative instability of the guaiane skeleton, aggravated by the presence of the epoxy groups. In the case of rupin A and biebsanin, the peaks of the ions of the protonated forms (M+1)+ with m/e 295 (C15H21O4) and 331 (C15H29O6Cl), respectively, have a higher intensity. A similar phenomenon has been observed in the spectra of lactones, when the vapor pressure of the substances rises in the ion source of the mass spectrometer [8].

In contrast to the germacranolides [9], the presence of several OH groups does not lead to an appreciable increase in the role of the splitting out of substituents. At the same time, in the spectra of chrysartemin B (I) and rupin A (II) there are ions with m/e 111, the
intensity of the peaks of which far exceeds all the others. Irwin and Geissmann [4], comparing the spectra of rupin A and another 1,2,2,4-diepoxyguaianolide — anin (I') — suggested that this ion is formed as the result of the localization of the charge on the oxygen of the 3,4-epoxy group with the subsequent splitting out of rings B and C (Scheme 1).

A comparison of the spectra of the diepoxyguaianolides (I) and (II) in the spectra of compounds (III) and (IV), in the molecules of which the 3,4-epoxy groups are hydrated and hydrochlorinated, respectively, forced us to reconsider the mechanism of the appearance of the ion with m/e 111 suggested by Irwin and Geissman [4]. The spectra of (III) and (IV) each contain intense peaks of fragments with m/e 129 (111 + H₂O) and 147/149 (111 + HCl) (see Fig. 1). As an analysis of metastable transitions by the method of ion beam defocusing shows, the ions with m/e 111 in the spectra arise from the ions mentioned above by the elimination of a molecule of water (III) or of hydrogen chloride (IV).

It is natural to assume that the initial act of the fragmentation of the molecular ions of compounds (I-IV) by the direction considered is the cleavage of the C₁-C₁₀ bond with the localization of the charge on the oxygen of the 1,2-epoxy group (see Scheme 1). The process is activated by the presence of an OH group at C₁₀.

The analogy in the positions of the OH groups in rupin A and biebsanin, and also in ajafinin and biebsanin, permits us to observe other, less characteristic, processes of the cleavages of the bonds in the skeletons in the spectra of these pairs of compounds. Thus, as the result of the 1,2-elimination of a molecule of water at the expense of the 8-OH—7-H atoms, activated by the formation of a conjugated chain, the cleavage of the C₉—C₁₀ and C₈—C₁₀ bonds may take place, leading to the formation of ions of medium intensity with m/e 122 and 123 (see Scheme 1). The splitting out of water with the participation of the hydroxyl at C₈ in ajafinin and biebsanin initiates the fragmentation of rings B and C and the formation of ions with m/e 141 (III) and 159/161 (IV), as shown in the scheme.

Other, second-degree, methods of fragmentation of the guaiane skeleton of compounds (I-IV), as a rule accompanying the splitting out of substituents, are characterized briefly in Table 1. All the directions of fragmentation discussed have been confirmed by measurements of the elementary compositions of the ions. The processes of splitting out of the substituents are reflected directly in Fig. 1.

We have also analyzed the compositions of the ions (M — 35)⁺ and (M — 36)⁺ in the biebsanin spectrum and have established that the loss of Cl and HCl is responsible for 50% and 5%,