Among the carbohydrate derivatives of diglycerides, representing an extremely widespread class of natural glycolipids [1], a special place is occupied by compounds containing uronic acid residues. Glycolipids of this type were discovered comparatively recently: 3-O-β-D-glucopyranuronosyl-sn-1,2-diglyceride was detected in the cell lipids of Pseudomonas rubescens [2], and later a glucuronosyldiglyceride anomeric to it was found in the lipids of Pseudomonas diminuta [3]. Subsequently lipids of analogous structure were isolated from halophilic bacteria [4-7], from actinomycetes [8], as well as from Bacillus cereus T [11]. Moreover, diglyceruronosides of more complex structure have been found in pseudomonads and actinomycetes: the carbohydrate portion of the molecule of these glycolipids is a residue of isoaaldobionic acid [3,10,11].

It is suggested that under definite conditions of development of certain microorganisms, glucuronosyldiglycerides may perform the function of phospholipids as structural components of the cytoplasmic membrane [3,9]. In connection with this, a further study of the distribution of uronosyldiglycerides among microorganisms takes on interest. However, in most cases the content of these lipids in the total cell lipids is small, and their isolation in the individual state in large quantities is difficult, which creates serious obstacles to their identification.

In one of our previous communications [12] it was shown that the use of mass spectrometry in the study of monohexosyldiglycerides permits a determination of the structure with a minimum expenditure of time and the investigated material. It might be expected that the use of a mass spectrometric method of analysis in the identification of natural diglyceruronosides will have the same advantages in comparison with the method usually used [2-11].

As was shown by our experiments with natural and synthetic glucuronosyldiglycerides, the treatment of these glycolipids (in deionized form) with diazomethane, followed by acetylation, leads to methyltriacetyl derivatives of the type of (I) and (II), which prove to be convenient objects for mass spectrometric study. We established the basic pathways of fragmentation of the molecular ions of the indicated derivatives under electron impact in an investigation of the mass spectra of synthetic methyl esters of 1,2-di-O-acyl-3-O-(2',3',4')-tri-O-acetyl-β-D-glucopyranuronosyl-L-glycerins (I)-(IV).* This communication cites the results of this investigation.†

*The synthesis of these derivatives of glucuronosyldiglycerides will be described in a separate communication.
†The mass spectra were taken on an LKB-9000 instrument; the investigated samples were introduced directly into the ion source, temperature of the ion source 140°, energy of ionizing electrons 70 eV, accelerating voltage 3.5 kV.
The decomposition of molecular ions (MI) of compounds (I) and (II) (see Figs. 1 and 2, as well as schemes 1-5) is largely similar to the fragmentation of MI of hexapyranosyl diglycerides under electron impact [12]. One of the basic pathways of decomposition is the cleavage of bonds at the glycoside oxygen atom, as a result of which a "diglyceride" ion 1 and an ion a₄ (see scheme 1a) including the carbohydrate portion of the molecule, are formed. The formation of the ion a₄ was observed in the mass spectra of all the previously investigated derivatives of methyl-2,3,4-tri-O-acetylglucuronate [13-15].

SCHEME 1

\[ R = n-C_{17}H_{33}, \ R' = \text{Me}, \ R'' = \text{Ac (I)}; \ R = n-C_{17}H_{31}, \ R' = \text{Me}, \ R'' = \text{Ac (II)}; \]
\[ R = n-C_{17}H_{33}, \ R' = \text{CD}, \ R'' = \text{Ac (III)}; \ R = n-C_{17}H_{31}, \ R' = \text{Me}, \ R'' = \text{CD}_{2} \text{CO (IV)} \]

*The values of m/e of ions according to the mass spectra of the deuteromethyl derivative (III) and the deuteroacetate (IV) are indicated in parentheses.
†One of the possible structures of the ions a₂ and a₄ is cited; however, all that is stated in the text is also correct for the remaining structures.