In the preceding communications [1-3] we have shown that gypsoside (I), a triterpenoid saponin isolated from the roots of Gypsophila pacifica (Kom.) [1], is a gypsogenin naoside, the carbohydrate part of which contains one residue each of D-galactose (Gal), D-glucose (Gl), L-arabinose (Ar), D-fucose (Fu), L-rhamnose (Rha), and D-glucuronic acid (Glur) and three residues of D-xylose (Xy) [2, 3]. When (I) was exhaustively methylated and the product (II) was hydrolyzed, we obtained two molecular proportions of 2,3,4-tri-O-methyl-D-xylose and one molecular proportion each of 2,3,4-tri-O-methyl-L-arabinose, 2,3,4,6-tetra-O-methyl-D-glucose, 2,3,6-tri-O-methyl-D-glucose, 2,4-di-O-methyl-D-fucose, 3-O-methyl-L-rhamnose, and methyl 2-O-methyl-D-glucuronate [2, 3]. On the basis of results presented in this paper it has been established that gypsoside has the structure (I). In the partial hydrolysis of gypsoside (I) with 10% aqueous oxalic acid as the main products we obtained lactose and the typsogenin trioside (III), which was purified by chromatography on silica gel. As a result we obtained a chromatographically homogeneous substance (Fig. 1); in its acid hydrolysis we identified glucose, galactose, and glucuronic acid. In the exhaustive methylation of (III) with methyl iodide in dimethylformamide in presence of silver oxide [4] (IV), the fully methylated trioside (III), was formed. The methanolysis of (IV) with a 1:10 mixture of 72% HClO₄ and CH₃OH with subsequent acid hydrolysis of the methyl glycosides formed gave 2,3,4,6-tetra-O-methyl-D-galactose, 2,3,6-tri-O-methyl-D-glucose, and methyl 2,3-di-O-methyl-D-glucuronate. The structure of the latter was proved as follows. (IV) was reduced with lithium aluminum hydride, and the residue of methylated glucuronic acid was then converted into the corresponding residue of methylated glucose. In the methanalysis of the product of the reduction of (IV) 2,3- or 2,4-di-O-methyl-D-glucose should be formed. The choice between these variants was made as follows. By the reduction of the di-O-methyl-D-glucose with sodium borohydride we obtained the corresponding di-O-methylsorbitol, by the oxidation of which with sodium periodate we obtained 2,3-di-O-methyl-L-threose, and not 2,4-di-O-methyl-L-xylose, as would be expected in the

*In the further treatment the abbreviations given above for the monosaccharides will be used.
In the further study of the structure of the carbohydrate chain of gypsoside (I) we oxidized it with sodium periodate. We have already stated briefly [3] that only the xylose, rhamnose, fucose, and glucuronic acid residues are preserved unchanged in the periodate-oxidation product (V). Attempts to bring about the cleavage of (V) with phenylhydrazine by Barry's method [5] led to the formation of a difficultly purifiable glycoside of gypsogenin phenylhydrazone, in the hydrolyzate of which we identified glucuronic acid, xylose, rhamnose, and fucose by paper chromatography. As the presence of a phenylhydrazine residue in the product of Barry breakdown greatly complicated work on the establishment of its structure, we looked for other ways of bringing about the degradation of (V). As a result, it was found that by the reduction of (V) with sodium borohydride and the subsequent partial hydrolysis of the product (VI) by the action of 0.2 N H$_2$SO$_4$ two glycosides (VII) and (VIII) were formed (see Fig. 1), and after chromatographic purification these were obtained in the pure state. On acid hydrolysis the glycoside (VII) gave hederagenin (IX), the formation of which resulted from the reduction of the CHO group in gypsogenin into the CH$_2$OH group by the action of sodium borohydride on (V); also by paper chromatography we identified rhamnose, fucose, and glucuronic acid. (VII), therefore, is a hederagenin trioside. In a similar way it was shown that the molecule of the glycoside (VIII) contains hederagenin and residues of rhamnose, fucose, glucuronic acid, and xylose. Methylation data for gypsoside show that of the three xylose residues two are terminal and must therefore be broken down in periodate oxidation, and therefore (VIII) contains one xylose residue and is a hederagenin tetraoside.

\[(\text{III}) \quad R = \text{D-Gal-pyr-1} \rightarrow 4-\text{D-Gl-pyr-1} \rightarrow 4-\text{D-Glu-pyr-1} \rightarrow; \quad R' = \text{COOH}; \quad R'' = \text{CHO}; \quad (\text{VII}) \quad R = \text{D-Glu-pyr-1}; \quad R' = \text{D-Fu-pyr-1} \rightarrow 4-L-\text{Rha-pyr-1} \rightarrow; \quad R'' = \text{CH$_2$OH}; \quad (\text{VIII}) \quad R = \text{D-Glu-pyr-1} \rightarrow;\]

\[R' = \frac{D-\text{Fr-pyr-1}}{3}_{\text{H}} \rightarrow; \quad R'' = \text{CH$_2$OH};\]

\[(\text{IX}) \quad R = \text{H}; \quad R' = \text{COOH}; \quad R'' = \text{CH$_2$OH}; \quad (\text{X}) \quad R = 2,3,4-\text{tri-O-methyl-D-Gl-pyr-1} \rightarrow; \quad R' = \text{R''} = \text{CH$_2$OH}; \quad (\text{XI}) \quad R = \text{H}; \quad R' = \text{R''} = \text{CH$_2$OH}. \quad \text{All the sugars are in the pyranose form.}\]

In the methylation of the tetraoside (VIII) and the subsequent methanalysis and hydrolysis we identified 2,3,4-tri-O-methyl-D-xylose, 2,3,4-tri-O-methyl-D-fucose, 3-O-methyl-L-rhamnose, and methyl 2,3,4-tri-O-methyl-D-glucuronate. Reduction of methylated (VIII) with lithium aluminum hydride gave the glycoside (X) and the reduced trisaccharide (XI). In the hydrolysis of (X) 2,3,4-tri-O-methyl-D-glucose was formed, which confirmed

\[\text{*pyr} = \text{pyranose.}\]