More recently, V. Yu. Bagirov et al. [5] have isolated from the resin of the roots of *Ferula malacophylla* new sesquiterpene lactones which they called malaphyll and malaphyllin. The corrected structure of diversolide and the structure of malaphyll are identical. The NMR spectra of these compounds coincide in detail. Their IR and UV spectra [1, 5] are also identical. However, the melting point of diversolide (185–186°C) is lower than that of malaphyll (204–205°C) by 19°C. A check on the individuality of diversolide on Silufol UV-254 plates in the system used by Bagirov et al. [5] showed a single spot. Chromatography in the hexane–benzene–methanol (5:4:1) system permitted the presence of talassin A as an impurity to be detected (the R_f values of diversolide and of the talassin were 0.22 and 0.166, respectively. A 1% solution of $KMnO_4$ was used as the revealing agent). After purification by preparative separation on Silufol UV-254 plates and recrystallization from ethanol, diversolide had mp 201-203°C.

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TRITERPENE GLYCOSIDES OF *Androsace septentrionalis*. STRUCTURE OF ANDROSEPTOSIDES A, B, C, AND D

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In a preceding communication [1] we gave the results of a preliminary study of the glycosides from *Androsace septentrionalis* L. (northern rock jasmine). We have established that the plant contains glycosides of oleanolic acid and of primulagenin A. On isolation of the main individual glycosides by column chromatography on silica gel, we obtained a fraction containing the six least polar glycosides. By repeated column chromatography in the chloroform–methanol–water (65:35:10) and chloroform–methanol (8:2) systems we obtained individual glycosides, which were called androseptosides A (I), B (II), C (III), and D (IV); (I) – mp 165–167°C, $[\alpha]_D^{20}$ –20°(c 1.0; CH_3OH); (II) – mp 221–223°C, $[\alpha]_D^{20}$ –80° (c 1.0; CH_3OH); (III) – mp 175–176°, $[\alpha]_D^{20}$–10.5° (c 1.5; CH_3OH); (IV) – mp 258–261°C, $[\alpha]_D^{20}$–120°, (c 1.0; CH_3OH).

When androseptosides A and B were subjected to complete acid hydrolysis with 2.5% sulfuric acid, glucose was identified in the neutralized hydrolysate by paper chromatography in the butanol–benzene–pyridine–water (5:1:3:3) system, while glucose and arabinose were detected in the hydrolysates of the glycosides C and D, their ratio, according to the gas-liquid chromatography of the acetates of the corresponding aldononitriles, being 1:1.

From its physicochemical constants, the aglycone of compounds (I) and (III) was identified as oleanolic acid (mp 305–307°C, $[\alpha]_D^{20}$ + 80° (c 1.0; CH_3OH)), and for compounds (II) and (IV) the algycone was found to be primulagenin A (mp 248-250°C, $[\alpha]_D^{20}$ +55°) (c 1.0; $CHCl_3$). The IR spectra of standard samples and of the genins obtained coincided completely.

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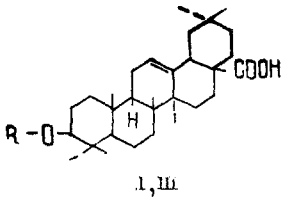
As a result of methylation followed by methanolysis of the permethylated androseptosides A and B, methyl 2,3,4,6-tetra-O-methyl-D-glucopyranoside was obtained, while androseptosides C and D yielded methyl 2,3,6-tri-O-methyl-D-glucopyranoside and methyl 2,3,4-tri-O-methyl-L-arabinopyranoside. The partial hydrolysis of biosides (III) and (IV) with 1% sulfuric acid on the boiling water bath for 1 h gave glycosides (I) and (II), respectively. Consequently, androseptoside C is a bioside of oleanolic acid and androseptoside D a bioside of primulagenin A.

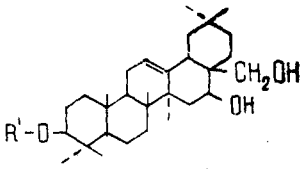
The alkaline saponification of (I) and (III) (10% aqueous ethanolic solution of KOH, 100°C, 5 h) did not change the chromatographic mobilities of the glycosides in a thin layer, which indicates the absence of a O-acyl glycosidic bond and consequently the attachment of the carbohydrate moieties to C_3 of the aglycone. The locations of the carbohydrate chains in (II) and (IV) have not been determined experimentally, and our conclusion relative to the positions of their attachment is based on analogy with other glycosides of the β-amyrin series.

The configurations of the glycosidic centers were established from molecular rotation differences between the initial glycosides and their progenins and are in harmony with Klyne's rule [2].

On the basis of the result obtained, glycosides A (I), B (II), C (III), and D (IV) can be assigned the following structures:

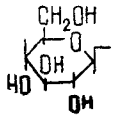


I, III

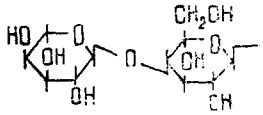


II, IV

for I and II, R = R' =



for III and IV R = R' =



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