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# D-MANNITOL FROM THE ROOTS OF GLYCYRRHIZA ECHINATA

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An aqueous extract of the roots (117 g) of Glycyrrhiza echinata L. collected by T. P. Nadezhina in June, 1967 in the floodlands of the Volga river in the Astrakhan Oblast was treated with boiling ethanol. At room temperature, the ethanolic extract deposited crystals (0.7 g) with mp 165–166° C (from ethanol) and the composition $C_6H_{14}O_6$.

The substance gave no depression of the melting point with a sample of D-mannitol [1]. The IR spectra of an authentic sample of D-mannitol and the substance under investigation were identical.

Acetylation of the substance gave a hexaacetate having mp 119–120° C and $[\alpha]_D^{20}$ + 25.4° (c 0.59; chloroform), which are identical with the properties of D-mannitol hexaacetate given in the literature [3]. This is the first time that D-mannitol has been isolated from the roots of Glycyrrhiza echinata.

The roots of this plant are sometimes sweetish to the taste, which is possibly due to the presence of this alcohol in them.

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# ISOMERIZATION DURING HYDROGENATION

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We have studied the chemistry of the hydrogenation of cottonseed oil at 80, 100, and 120° C on a disperse nickel-copper catalyst (Ni : Cu = 1 : 1) with 0.2% of total metals on the weight of the oil.

The fatty acids of the hydrogenizate were separated by Twitchell's method into solid and liquid fractions, and then the solid acids were separated by the mercury adduct method [1] into saturated and unsaturated acids. The liquid fatty acids and the unsaturated acids isolated from the solid acids were oxidized by Hilditch's method [2]. The position of the double bonds in the mono- and dicarboxylic acids obtained was judged from their composition. The composition of the initial fat of the oxidized fragments was established by GLC.

In the oxidation products were found $C_5$—$C_{10}$ monocarboxylic and $C_3$—$C_5$ and $C_8$—$C_{13}$ dicarboxylic acids. This shows that the double bonds of the acids migrate mainly by one $CH_2$ group to the right and to the left of their original position, and more rarely by two groups.

From the results of UV spectroscopy (absorption band at 234 mμ), dienes with a conjugated system of double bonds are formed in the fatty acid fraction. Bands at 950, 970, and 990 $cm^{-1}$ were found in the IR spectra of the same fraction. The presence of bands at 950 and 990 $cm^{-1}$ shows the cis-trans and trans-cis configuration of the dienes, and a band at 970 $cm^{-1}$ the presence of trans-monoenic and trans,trans-dienic acids with isolated double bonds.

In addition to position and geometric isomerization, triglyceride isomerization was studied. By using the results of enzymatic hydrolysis of the glycerides, we calculated the content of saturated (S) and unsaturated (U) fatty-acid radicals in the α, α'- and β-positions in the hydrogenizates obtained at the very beginning of the process, after 10 and 30 min.

We established that during hydrogenation, and particularly intensively in its initial stage, glyceride isomerization takes place through the intermolecular migration of fatty-acid radicals in the following way: SSU ⇌ SUS and SUU ⇌ ⇌ USU, so that the total of the disaturated-monounsaturated and of the monosaturated-diunsaturated glycerides remain constant in all samples. A proof of this is the fall in the ratio of the amount of S-acids in the $\alpha,\alpha'$-position to their amount in the $\beta$-position from 4.59 to 1.09 and a rise in the same ratio for the U-acids from 1.50 to 2.71.

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# FUROCOUMARINS OF DICTAMNUS DASYCARPUS

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It is known [1] that some species of the genus Dictamnus L. cause dermatitis.

We have studied D. dasycarpus Turcz., collected in the region of Khabarovsk in order to investigate the presence of furocoumarins with a photosensitizing activity in it. The substances with a coumarin nature were isolated by the following method: the coumarins were extracted from the comminuted leaves and stems with 50% ethanol, the extract was evaporated to an aqueous residue, and this was treated with chloroform. The chloroform extract was evaporated and transferred to a column of acidic alumina [2]. The column was eluted with petroleum ether containing different concentrations of benzene. Two substances were isolated—(I) and (II).

Psoralen (I) was eluted from the column with petroleum ether containing 30–50% of benzene. A substance, $C_{11}H_6O_3$, crystallized from ethanol in the form of needle-like crystals with mp 161–163° C.

In its physicochemical properties, $R_f$ values in various systems of solvents, fluorescence before and after treatment of a methanolic solution with alkali, and melting point of a mixed sample, substance (I) was identified as psoralen.

Xanthotoxin (II) was eluted from the column with petroleum ether containing 50–70% of benzene, mp 143–145° C (from ethanol), $C_{12}H_8O_4$.

It was identified in a similar manner to psoralen (I), the complete identity of substance (II) with xanthotoxin being shown.

These compounds have been detected by paper chromatography in the fruit of D. dasycarpus and in the epigeal part and fruit of D. gymnastylis Stev.

Thus, it may be assumed that the dermatitises caused by these plants are due to the presence of psoralen and xanthotoxin in them.

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