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STEROID GLYCOSIDES FROM Solanum tuberosum SEEDS

TUBEROSIDES C AND D

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UDC 547.918+547.917

No investigations of the presence of steroid glycosides in the seeds of Solanum tuberosum L. have previously been made. In the present communication we give information on the isolation and determination of the structures of steroid glycosides from potato seeds, which we have called tuberosides C and D.

After the elimination of alkaloids by precipitation with ammonia, a methanolic extract was subjected to repeated chromatography on a column of silica gel, as a result of which individual glycosides were obtained. The separation was monitored by thin-layer chromatography in the chloroform–methanol–water (65:35:10, lower layer) system.

Tuberoside C (I), with mp 236-238°C, $[\alpha]_D^{20}$ −63° (c 1.7; Py) and tuberoside D (II), with mp 266°C, $[\alpha]_D^{20}$ −70°, gave positive reactions with the Sannié reagent and negative reactions with the Ehrlich reagent [2], which permitted them to be assigned to the spirostanol glycosides. Their IR spectra contained absorption bands at 845, 890 < 920, and 980 cm^{-1}, which are characteristic for spiroketal chains of the (25S)-series.

On complete acid hydrolysis a single aglycon was isolated, which was identified as yamogenin, the identification being confirmed by physicochemical methods (mp 201°C; $[\alpha]_D^{20}$ (c 1.0; $CHCl_3$), $[M^+]$ 414).

With the aid of gas–liquid chromatography of the acetates of the aldononitrile derivatives of the sugars [3] the presence of the following monosaccharides in the given ratios was established: for tuberoside C – rhamnose and galactose (1:1); and for tuberoside D – rhamnose and glucose (2:1).

By means of partial hydrolysis a number of progenins were obtained, and these were investigated by physicochemical methods. For tuberoside C – a progenin with mp 230-233°C, $[\alpha]_D^{20}$ −91° (c 1.0; CH_3OH); for tuberoside D – progenins with mp 264°C, $[\alpha]_D^{20}$ −97° (c 1.0; CH_3OH) – yamogenin glucopyranoside – and with mp 241-243°C, $[\alpha]_D^{20}$ −57° (Py) – yamogenin rhamnoglucopyranoside [2].

The positions of attachment of the carbohydrate units to one another were revealed by the methanolysis of permethylates of tuberosides C and D, obtained by Hakomori's method [4]. By GLC in the presence of markers, for glycoside C we identified methyl 2,3,4-tri-O-methyl-

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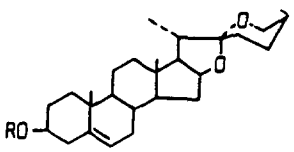
L-rhamnopyranoside and methyl 3,4,6-tri-O-methylgalactopyanoside, and for glycoside D methyl 2,3,4-tri-O-methyl-L-rhamnopyranoside and methyl 3,6-di-O-methyl-D-glucopyranoside. The presence of the dimethylglucose derivative showed branching of the carbohydrate chain. The configurations of the glycosidic centers were determined from molecular rotation differences of the initial glycosides, their progenins, and the aglycon in accordance with Klyne's rule [5].

On the basis of the facts given, the following structures are proposed for tuberosides C and D:



I. Rha $1\xrightarrow{\alpha}2$ Gal$\xrightarrow{\beta}$

II. Rha $1\xrightarrow{\alpha}4$
Rha $1\xrightarrow{\alpha}2$ Glc$1\xrightarrow{\beta}$

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ALKALOIDS OF Liriodendron tulipifera

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Continuing a systematic study of the alkaloids of the plant Liriodendron tulipifera, L., family Magnoliceae, [1, 2] according to vegetation periods, we have investigated the leaves gathered in the flowering phase in the Botanical Garden of the Uzbek SSR Academy of Sciences (Tashkent).

The dry comminuted raw material was extracted with methanol. The evaporated methanolic extract was treated with chloroform. The total alkaloids (0.30% on the dry weight of the plant) were obtained from the chloroform solution in the usual way, and they were separated into phenolic and nonphenolic fractions. The alkaloids were separated chromatographically on a column of silica gel. Remerine, lirinidine, nornuciferine, nuciferine, and glaucine were isolated from the nonphenolic fraction, and lirinidine, caaverine, isocorypalmine, N-methylcrotsparine, and bases (I) and (II) from the phenolic fraction. All the alkaloids isolated, with the exception of bases (I) and (II), were identified by direct comparison with authentic samples obtained previously from this plant species [1, 2].

Base (I) – $C_{19}H_{21}NO_4$, mp 156-158°C (acetone). Its UV spectrum had an absorption maximum at 286 nm ($\log\varepsilon$ 3.70). The PMR spectrum of (I) (CF_3COOH, δ scale) showed the signals of two methoxy groups (3.52 ppm, s, 3H, and 3.55 ppm, s, 3H) and of four aromatic protons (6.66 ppm, s, 2H; 6.50 ppm, s, 1H; 6.56 ppm, s, 1H). The mass spectrum of the alkaloid contained the following main ion peaks: m/z 327 (M^+), 326 $(M-1)^+$, 296 $(M-31)^+$, 178 (100%), 176, 150, 135. The PMR and mass spectra of (I) are characteristic for tetrahydroprotoberberine alkaloids containing two hydroxy and two methoxy groups [2, 3]. The peak of an ion with m/z 178 showed the presence of a methoxy and a hydroxy group in ring D. The peak of the $(M-OCH_3)^+$ ion with an intensity of 16%, analogous to that in the spectrum of isocorypalmine [2] showed the presence of a methoxy group at C_9. After the partial methylation of

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