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TOMATOSIDE A FROM THE SEEDS OF *Lycopersicum esculentum*

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Results are given which confirm the structure of the furostanol glycoside from tomato seeds forming wastes of the preserving industry. From a butanolic extract of the seeds of *Lycopersicum esculentum* Mill. we have isolated the furostanol glycoside tomatoside A (I) the structure of which has been established as 25(S)-5α-furostan-3β,22α,26-triol 26-O-β-D-glucopyranoside 3-O-[O-β-D-glucopyranosyl-(1→2)-O-β-D-glucopyranosyl-(1→4)-β-D-galactopyranoside]. At the same time, by enzymatic and chemical transformations three new spirostanol glycosides of neotigogenin have been obtained: tomatoside B (III), which is 25(S)-5α-spirostan-3β-ol 3-O-[O-β-D-glucopyranosyl-(1→2)-β-D-galactopyranoside], 25(S)-5α-spirostan-3β-ol 3-O-[O-β-D-glucopyranosyl-(1→4)-β-D-galactopyranoside] (V), and 25(S)-5α-spirostan-3β-ol 3-O-β-D-galactopyranoside (IV).

We have reported previously [1] that the seeds of *Lycopersicum esculentum* Mill. (tomato) contain about 0.3% of neotigogenin (II). Continuing a study of tomato seeds, from the total extractive substances we have isolated two compounds with similar R_f values (Ia/Ib). A positive reaction with the Ehrlich reagent [2], the presence in the IR spectrum of a broad band of low intensity at 900 cm^{-1} [3] with the absence of bands indicating that the compounds belong to the spirostan series [4, 5] and a characteristic behavior on two-dimensional TLC [6] permit these substances to be assigned to the furostanol glycosides.

It is known that 22-OH furostanols, on being heated with methanol, form the 22-O-methyl ethers which readily undergo the reverse transition [7, 8]. When the combined glycosides (Ia/Ib) were heated in water and methanol, the individual compounds (Ia) and (b) were isolated. The PMR spectrum of glycoside (Ib) has a three-proton singlet at 3.12 ppm [3]. In the PMR spectrum of compound (Ia) there are no resonance signals of the protons of methoxy groups. Consequently, substance (Ia) is a 22-OH furostanol glycoside. This is a native compound and we have called it tomatoside A. Compound (Ib) is its 22-O-methyl ether. Because of the ease of interconversion of glycosides (Ia) and (Ib), the subsequent operations to prove the structure of tomatoside A (Ia) were performed with the product (Ia/Ib).

In 1973, Japanese workers [9], who were interested in the bitter principal of tomato seeds, described the structure of a new tetraside of the furostan series which they called TFI. The marked difference in the melting points of tomatoside A (Ia) and TFI (247-250°C and 217-220°C, respectively) caused some doubts as to the complete identity of the structures of these glycosides. The aim of the present work was to establish the structure of tomatoside A (Ia) and to obtain a number of model glycosides of neotigogenin.

The complete acid hydrolysis and methanolysis of product (Ia/Ib) led to neotigogenin [1, 2] and a mixture of carbohydrates. Analysis of the hydrolysates by TLC and GLC [11] showed the presence of D-glucose and D-galactose in a ratio of 3:1.

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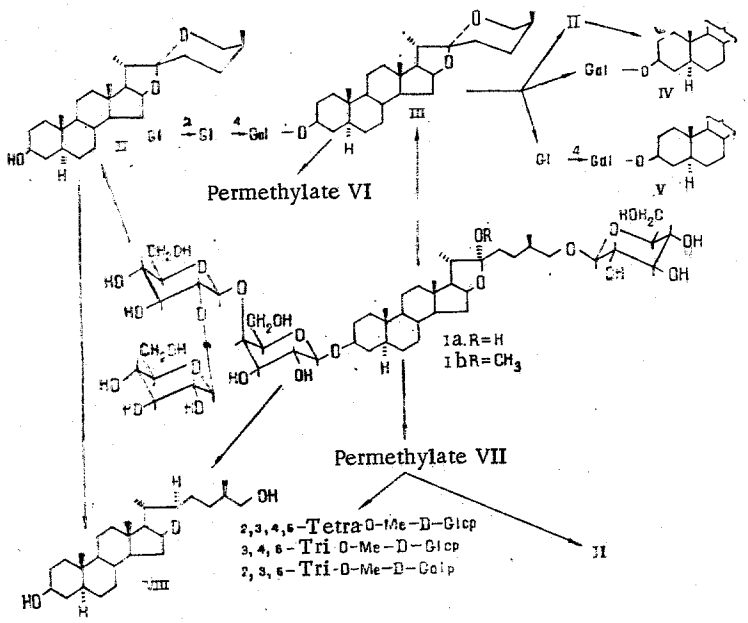

The enzymatic hydrolysis of product (Ia/Ib) with the complex enzyme of the snail *Helix plectotropis* gave compound (III). A positive reaction with the Sanié reagent and a negative one with the Ehrlich reagent, and the presence in the IR spectrum of glycoside (III) of bands at 905 < 920 cm^{-1} [4, 5] shows that it belongs to the spirostanol glycosides of the 25(S) series. The methanolysis of compound (III) showed that its aglycone is neotigogenin (II) and in the carbohydrate moiety D-glucose and D-galactose are present in a ratio of 2:1.

Characteristic for saponin-bearing plants is the simultaneous presence of biogenetically related spirostanol and furostanol glycosides [7, 8], and we therefore did not subsequently exclude the possibility of detecting in tomato seeds the glycoside (III) which we have called tomatoside B.

A characteristic feature of all glycosides of the furostan series known up to the present time [7, 8] is the splitting off on enzymatic hydrolysis of one molecule of D-glucose attached to the hydroxy groups at C-26 of the aglycone, accompanied by the conversion of the furostanol glycoside into the corresponding spirostanol glycoside. Consequently, it may be assumed that one D-glucoside molecule in tomatoside A (Ia) is attached to the hydroxy group at C-26 of 25(S)-5α-furostan-3β,22α,26-triol, and a trisaccharide carbohydrate chain to the hydroxy group at C-3.

The partial acid hydrolysis of tomatoside B (III) gave, in addition to neotigogenin (III), the glycosides (IV) and (V). From the results of color reactions and IR spectroscopy, both compounds were assigned to the spirostanol glycosides of the 25(S) series. Methanolysis showed that in both cases the aglycone was neotigogenin (II). The carbohydrate chain of glycoside (IV) consisted of one D-galactose molecule, and that of glycoside (V) of D-galactose and D-glucose in a ratio of 1:1.

The structure of neotigogenin 3-O-β-D-galactopyranoside (IV) was confirmed by its synthesis from acetobromogalactose and neotigogenin (II) by the Koenigs-Knorr method in V. T. Chernobai's modification [12]. Consequently, D-galactose is attached to the hydroxy group at C-3 of the aglycone in tomatosides A (Ia) and B (III).

To determine the structure of the carbohydrate chain at C-3, the configurations of the glycosidic bonds, and the conformations of the carbohydrate rings, we carried out the Hakomori methylation [13] of the products (Ia/Ib) and (III), and obtained the permethylates (VII) and (VI), respectively. The IR spectra of these compounds lacked absorption due to the presence of hydroxy groups. The PMR spectrum of the permethylate (VII) has four resonance signals of the anomeric protons of sugars in the form of doublets with J = 7-8 Hz in the 4.12-4.69 ppm region.

A comparison of the chemical shifts of the signals of the anomeric protons of the sugars of the PMR spectra of the permethylates (VII) and (VI) permitted the doublet at 4.12 ppm in the PMR spectrum of compound (VII) (J = 7 Hz) to be assigned to the anomeric proton of the

D-glucose attached to the hydroxy group at C-26 of the aglycone of tomatoside A (Ia). The spin–spin coupling constants (J = 7-8 Hz) show the β-configuration of the glycosidic bonds [14] and the C1 conformation of the carbohydrate rings [15]. Calculation by the method of molecular rotation differences [16] confirms the β-configuration of the glycosidic bonds.

The complete acid hydrolysis of permethylate (VII) gave neotigogenin (II) and a set of methylated sugars. After its separating into individual components, 2,3,4,6-tetra-O-methyl-D-glucopyranose, 3,4,6-tri-O-methyl-D-glucopyranose, and 2,3,6-tri-O-methyl-D-galactose were identified in the presence of markers by TLC and GLC.

Thus, the terminal glucose molecule is attached to the hydroxy group at C-2 of the glucose molecule attached to the hydroxy group at C-4 of the galactose molecule present at C-3 of the aglycone. A trisaccharide of this structure (lycotrioside) is a fragment of the tetrasaccharide lycotetraoside [17]. The latter is the carbohydrate component of many natural glycosides [18].

Another proof that tomatoside A (Ia) belongs to the glycosides of the furostan series was obtained by the reduction of product (Ia/Ib) with sodium tetrahydroborate followed by the complete acid hydrolysis of the reaction mixture [6]. One of the compounds isolated proved to be identical with the product of the reduction of neotigogenin (II) by lithium tetrahydroaluminate in the presence of aluminum chloride [17] — dihydroneotigogenin (VIII).

Thus, the structure of tomatoside A corresponds to formula (Ia), and is therefore identical with the structure put forward for TFI [9]. The difference in the melting points of tomatoside A and TFI is due, in our opinion, to the fact that the Japanese authors [9] characterized as an individual glycoside a mixture of tomatoside A and its 22-O-methyl ether.

EXPERIMENTAL

General Observations. Thin-layer chromatography (TLC), preparative thin-layer chromatography (PTLC), and two-dimensional thin-layer chromatography (TTLC) were performed on KSK silica gel (63 μ) containing 15% of gypsum, and column chromatography on KSK silica gel (63-100 μ). For chromatography we used the following systems of solvents: 1) chloroform–methanol–water, a) (65:30:6), and b) (65:11:2); 2) chloroform–methanol, a) (10:1), b) (15:1), c) (20:1) d) (99:1); 3) benzene–methanol (10:1); and 4) butanol–ethanol–water (5:3:2).

The sapogenins and their derivatives were detected by the Sannié reagent, the glycosides by the Sannié and Ehrlich reagents, and the sugars with o-toluidine salicylate, the sugars being chromatographed on plates impregnated with a 0.3 M aqueous solution of NaH_2PO_4.

The glycosides were methanolyzed by boiling them in anhydrous methanol containing 5% of HCl for 12 h. The cooled reaction mixture was treated with an equal volume of water and the aglycone that deposited was separated off by filtration and was washed water and analyzed by TLC. Part of the filtrate after the elimination of the methanol was heated at 100°C for 4 h and, after neutralization with ÉDÉ-10 P anion-exchange resin, it was analyzed by TLC. Another part was neutralized with Ag_2CO_3, filtered, evaporated to dryness, and analyzed by GLC.

Gas–liquid chromatography was carried out on a Tsvet-4 chromatograph. Monosaccharides were chromatographed in the form of trimethylsilyl ethers of the methyl glycosides [11] on a column (3 m × 4 mm) filled with Chromaton N-AW impregnated with 5% of the silicone phase SE-30 (phase 1). The temperature of the thermostat was 190°C, the carrier gas here and below was helium, and the rate of flow of the gas was 45 ml/min. The methyl glycosides of the methylated sugars were obtained by boiling the methyl ethers in anhydrous methanol containing 5% of HCl for 4 h. The compounds obtained were chromatographed on a column (1 m × 4 mm) fille with Celite including 20% of poly(tetramethylene succinate) and also on a column (1 m × 4 mm) with Chromaton N-AW containing 10% of poly(phenyl ether) (phases 2 and 3, respectively) at thermostat temperatures of 160 and 180°C and a rate of flow of gas of 50 ml/min. The retention times T_{rel} for the methylated methyl glycosides were calculated with respect to the retention time of methyl 2,3,4,6-tetra-O-methyl-β-D-glucopyranoside [18].

Mass spectra were recorded on a MKh-1310 instrument at an ionizing voltage of 40 eV and a temperature of 110-160°C. Molecular weights were determined mass-spectrometrically. IR spectra were obtained on a UR-20 instrument in KBr or in paraffin oil. PMR spectra were obtained on a JNM-4H-100 instrument with HMDS as internal standard (δ scale).

Preparation of the Total Glycosides (Ia/Ib). Tomato meal — wastes from the preserving industry — was washed free from skin and fruit pulp with water and the seeds were dried in the

air, after which 1 kg of the comminuted and defatted seeds was exhaustively extracted with water-saturated butanol at the boiling point of the azeotropic mixture. The yield of combined extractive substances was 7%. The aqueous butanolic extract was evaporated to dryness and the residue was dissolved in water and was exhaustively extracted with petroleum ether and then with butanol. The butanolic extracts were evaporated to dryness, the residue was dissolved in methanol, and the saponins were precipitated with acetone. After reprecipitation with purification by column chromatography in system 1a, 5g of the combined glycosides (Ia/Ib) containing no other components were obtainedin the form of a white powder with R_f in system 1a 0.42 and 0.45, respectively, ν_{max}^{KBr}, cm^{-1}: 900 (weak broad band) 3300-3500 (OH).

TTLC of Products Ia/Ib. A methanolic solution of the combined glycosides (Ia/Ib) in the form of a spot was deposited at the corner of a 17 × 17-cm plate and was chromatographed in system 1a. The plate was dried and was placed in a chamber saturated with methanol vapor for 24 h, after which it was again dried and was chromatographed in system 1a in the direction perpendicular to the first. Spraying revealed four spots arranged in the form of a square.*

Tomatoside A (Ia). A solution of 115 mg of product (Ia/Ib) in 50 ml of water was heated at 100°C for 16 h. Part of the water was evaporated off, 200 ml of acetone was added, and the precipitate that deposited was filtered off and dried. This gave 105 mg of tomatoside A (Ia), $C_{51}H_{86}O_{24}$, mp 247-250°C (decomp.), $[\alpha]_D^{20}$ −29.3 ± 2° (c 1.18; pyridine). The PMR spectrum contained no signals of methoxy protons.

22-O-Methyl Ether of Tomatoside A (Ib). A solution of 125 mg of the combined glycosides (Ia/Ib) in 50 ml of absolute methanol was heated at the boiling point for 16 h. The cooled solution was concentrated and 200 ml of anhydrous acetone was added, and the precipitate that deposited was filtered off and dried. This gave 110 mg of the 22-O-methyl ether of tomatoside A (Ib), $C_{52}H_{88}O_{24}$, mp 243-246°C (decomp.), $[\alpha]_D^{20}$ − 25.2 ± 2° (c 1.19; pyridine). PMR spectrum (C_5D_5N , δ, ppm): 3.12 (22-O-CH_3, s).

Complete Acid Hydrolysis of the Products (Ia/Ib). A solution of 250 mg of the combined glycosides (Ia/Ib) in a mixtureof 95 ml of water and 5 ml of concentrated sulfuric acid was heated at 100°C for 6 h. The precipitate that deposited was filtered off and washed with water, and the filtrate was neutralized with ÉDÉ-10 P anion-exchange resin and evaporated. D-Glucose and D-galactose in a ratio of 1.00:0.38 were detected to TLC (system 4) and GLC (phase 1).

The precipitate was purified by column chromatography in system 2c. The fractions homogeneous on TLC in system 2b were combined and recrystallized from acetone. This gave 30 mg of neotigogenin, $C_{27}H_{44}O_3$, mp 106-198°C, $[\alpha]_D^{20}$ −73.8 ± 2° (c 1.12; chloroform), ν_{max}^{KBr}, cm^{-1}; 853, 900 < 923 (spiroketal chain of the 25(S) series, 3540 cm^{-1} (OH); M^+ 416.

Tomatoside B. A solution of 1.5 g of product (Ia/Ib) in 150 ml of water was treated with 5 ml of the complex enzyme of the snail *Helix plectotropis* and the mixture was left at 20°C for 16 h. The precipitate that had deposited was filtered off, washed with water, dried and recrystallized from methanol. This gave 1.25 g of tomatoside B (III), $C_{45}H_{74}O_{18}$, mp 267-270°C (decomp.), $[\alpha]_D^{20}$ −50.5 ± 2° (c 0.99; pyridine), ν_{max}^{KBr}, cm^{-1}: 905 < 930 (spiroketal chain of the 25(S) series), 3300-3500 (OH).

Methanolysis (for conditions, see the General Remarks section) showed that the aglycone of tomatoside B (III) is neotigogenin (II) (TLC, system 2b), and the carbohydrate moiety includes D-glucose and D-galactose in a ratio of 1.00:0.46 (TLC, system 4; GLC, phase 1).

Partial Acid Hydrolysis of Tomatoside B (III). A solution of 0.73 g of glycoside (III) in a mixture of 146 ml of methanol, 146 ml of water, and 15 ml of 35.5% hydrochloric acid was heated at the boiling point for 2 h, and then 150 ml of water was added, the methanol distilled off, and the precipitate was filtered off; it weighed 0.63 g. After separation by column chromatography in system (Ib) and combining the chromatographically homogeneous eluates four fractions were obtained: a) 90 mg, b) 20 mg, c) 120 mg, and d) 235 mg. The weight of the fractions containing mixtures of compounds was 100 mg. TLC in system 2b showed that fraction a) consisted of neotigogenin (II) and fraction d) of the initial glycoside (III) (TLC in system 1b).

*As in Russian original — Publisher.

Neotigogenin 3-O-β-D-Galactopyranoside from (III). The recrystallization of fraction b) from acetone gave 12 mg of glycoside (IV), $C_{33}H_{54}O_8$, mp 276-279°C (decomp.) $[\alpha]_D^{20}$ −69.6 ± 2° (c 0.69; pyridine), ν_{max}^{KBr}, cm^{-1}: 853, 900 < 927 (spiroketal chain of the 25(S) series), 3300-3500 (OH); M^+ 578.

Methanolysis shows that the aglycone of glycoside (IV) was neotigogenin (II) (TLC, system 2b), and the carbohydrate moiety contained one molecule of D-galactose (GLC, phase 1).

Neotigogenin 3-O-[O-β-D-Glucopyranosyl-(1→4)-β-D-galactopyranoside] (V). Recrystallization of the fraction from methanol yielded 95 mg of compound (V), $C_{39}H_{64}O_{13}$, mp 272-275°C (decomp.), $[\alpha]_D^{20}$ −55.2 ± 2° (c 1.16; pyridine), ν_{max}^{KBr}, cm^{-1}: 854, 900 < 925 (spiroketal chain of the 25(S) series), 3300-3500 (OH); M^+ 740.

Methanolysis showed that the aglycone of glycoside (V) was neotigogenin (II) (TLC, system 2b), and the carbohydrate moiety of the molecule contained D-glucose and D-galactose in a ratio of 1.00:0.78 (TLC, system 4; GLC, phase 1).

Neotigogenin 3-O-β-D-Galactopyranoside (IV) from (II). Neotigogenin (II) (416 mg) was dissolved in 50 ml of toluene and, after 10 ml of the solvent had been distilled off 0.5 g of CaO and 2.0 g of Ag_2CO_3 were added in portions to the boiling solution. Then, with the continuous distillation of the toluene, a solution of 1.2 g of acetobromogalactose in 20 ml of toluene was added dropwise in such a way that the volume of the reaction mixture remained constant. Then it was boiled for another 4 h with the addition of toluene at the same rate as that at which it was distilled off. The resulting precipitate was filtered off and was carefully washed with chloroform and the filtrate was evaporated to dryness. The dry residue was dissolved in 10 ml of methanol and then 2 ml of methanol saturated with ammonia was added and the mixture was left at 20°C for 15 h. After this, the ammonia and the methanol were driven off in vacuum and the residue was separated by column chromatography in system 2d. This gave 300 g of the initial neotigogenin (II) and 70 mg of the glycoside (IV), $C_{33}H_{54}O_8$, mp 274-277°C (decomp.) (methanol), $[\alpha]_D^{20}$ −70.0 ± 2° (c 1.22; pyridine); ν_{max}^{KBr}, cm^{-1}: 855, 900 < 925 (spiroketal chain of the 25(S) series, 3300-3500 cm^{-1} (OH); M^+ 578.

Permethylate of Tomatoside B (VI) from (III). With stirring, 350 mg of the glycoside (III) was dissolved in 25 ml of dimethyl sulfoxide (DMSO) and then 290 mg of sodium hydride was added in portions, and after 15 min 4 ml of methyl iodide was run in over 15 min. After 3 hours, the reaction mixture was poured into water and exhaustively extracted with chloroform. The extract was washed with saturated aqueous sodium thiosulfate and then with water and it was dried over anhydrous sodium sulfate and evaporated to dryness. After purification by column chromatography in system 3, 150 mg of the white amorphous permethylate (VI) was obtained: $C_{55}H_{94}O_{18}$, $[\alpha]_D^{20}$ −55.4 ± 2° (c 1.13; chloroform); ν_{max}^{Nujol}, cm^{-1}: 855, 900 < 925 (spiroketal chain of the 25(S) series). PMR spectrum ($CDCl_3$, δ, ppm): 0.69 (3H at C-18, s), 0.95 (3H at C-19, s), 0.92 (3H at C-27, d, J = 6 Hz), 1.07 (3H at C-21, d, J = 5 Hz), 3.40-3.50 (signals of 10 methoxy groups), 3196 (H at C-16, m), 4.26, 4.61, 4.69 (3H — anomeric protons of sugars, d, J = 7-8 Hz). M^+ 1042.

Permethylate of Tomatoside A (VII) from Product (Ia/Ib). The methylation of the combined glycosides (Ia/Ib) was carried out as described for glycoside (III), was performed with the following amounts of reagents: product (Ia/Ib), 500 mg; DMSO, 75 ml; NaH, 450 mg; CH_3I, 7 ml. After purification by column chromatography in system 3, 400 mg of the white amorphous permethylate (VII) was obtained the IR spectrum of which contained no absorption characteristic for hydroxy groups. Composition: $C_{66}H_{116}O_{24}$, $[\alpha]_D^{20}$ −41.1 ± 2° (c 1.13; chloroform). PMR spectrum ($CDCl_3$, δ, ppm): 0.62 (3H at C-18, s), 0.77 (3H at C-19, s), 0.90 (6H at C-21 and C-27, d, J = 6 Hz), 3.45-3.55 (signals of 15 methoxy groups), 4.02 (H at C-16, m), 4.12 (anomeric proton of D-glucose at C-26, d, J = 7 Hz), 4.27, 4.62, 4169 (3H — anomeric protons of sugars at C-3, d, J = 7-8 Hz). M^+ 1292.

Products of the Hydrolysis of the Permethylate (VII). A solution of 300 mg of compound (VII) in 100 ml of 50% aqueous methanol containing 5 vol. % of concentrated sulfuric acid was heated at the boiling point for 6 h. Then 50 ml of water was added to the cooled reaction mixture, the methanol was distilled off, and the aglycone that had deposited was filtered off, washed with water, and dried. TLC in system 2 showed the identity of the aglycone of the permethylate (VII) with neotigogenin (II).

The filtrate was heated at 100°C for 6 h, after which it was cooled and neutralized with ÉDÉ-10 P anion-exchange resin, and the methylated sugars were separated by PTLC in system

2a. As a result of comparison with the authentic samples on TLC in system 2a and by GLC of the methyl glycosides, the following methylated sugars were identified:

	T_{rel}			
	Phase 2		Phase 3	
2,3,4,6-Tetra-O-methyl-D-glucopyranose	1.00:	1.45	1.00:	1.34
3,4,6-Tri-O-methyl-D-glucopyranose	3.17;	3.87	1.65;	2.21
2,3,6-Tri-O-methyl-D-galactopyranose	3.24;	3.85	1.59;	2.11
	4.51;	4.90	2.52;	2.56

Reduction of Product (Ia/Ib) with Sodium Tetrahydroborate. A solution of 1.6 g of the combined glycoside (Ia/Ib) in 200 ml of water was treated with 0.97 g of sodium tetrahydroborate. The mixture was left at 20°C for 16 h, and then 12.5 ml of concentrated sulfuric acid in 37.7 ml of water was added, after which it was heated at 100°C for 6 h. The reaction mixture was cooled, and the precipitate was washed with water and dried. This gave 620 mg of combined aglycones the separation of which by column chromatography in system 2c yielded 24 mg of dihydroneotigogenin (VIII), $C_{27}H_{46}O_3$, mp 169-170°C (acetone), $[\alpha]_D^{20}$ −19.5 ± 2° (c 1.12; chloroform), ν_{max}^{KBr}, cm^{-1}: 3400 (OH); M^+ 4.8.

Dihydroneotigogenin (VIII) from (II). In portions, 0.45 g of lithium tetrahydroaluminate was added to a solution of 5 mg of aluminum chloride in absolute ether in an ice bath, and then, in the course of 15 min, a solution of 0.5 g of neotigogenin (II) in 40 ml of absolute ether was run in. All the operations were carried out with stirring. Then the reaction mixture was boiled for 2 hours. After this, 200 ml of dilute hydrochloric acid solution was added and the ethereal layer was separated off. The aqueous layer was extracted with ether. The combined ethereal solution was washed with $NaHCO_3$ solution and with water and was dried over anhydrous sodium sulfate and evaporated to dryness. Repeated recrystallization from acetone yielded 0.28 g of dihydroneotigogenin (VIII), $C_{27}H_{46}O_3$, mp 170-171°C, $[\alpha]_D^{20}$ −20.8 ± 2° (c 1.12; chloroform); ν_{max}^{KBr}, cm^{-1}: 3400 (OH). PMR spectrum ($CDCl_3$, δ, ppm): 0.73 (3H at C-18, s); 0.78 (3H at C-19, s), 0.88 (3H at C-27, d, J = 6 Hz), 0.96 (3H at C-21, d, J = 6 Hz), 3.39 (4H at C-3, C-22, and C-26, m), 4.12 (H at C-16, m); M^+ 418.

SUMMARY

The structure of a furostanol glycoside from the seeds of *Lycopersicum esculentum* Mill. has been confirmed; it is 25(S)-5α-furostan-3β,22α,26-triol 26-O-β-D-glucopyranoside 3-O-[O-β-D-glucopyranosyl(1→2)-O-β-D-glucopyranosyl-(1→4)-β-D-galactopyranoside].

Three new spirostanol glycosides of neotigogenin have been obtained: tomatoside B (25(S)-5α-spirostan-3β-ol 3-O-[O-β-D-glucopyranosyl-(1→2)-O-β-D-glucopyranosyl-(1→4)-β-D-galactopyranoside]), 25(S)-5α-spirostan-3β-ol 3-O-[O-β-D-glucopyranosyl-(1→4)-β-D-galactopyranoside], and 25(S)-5α-spirostan-3β-ol 3-O-β-D-galactopyranoside.

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STRUCTURE OF LEDERINE

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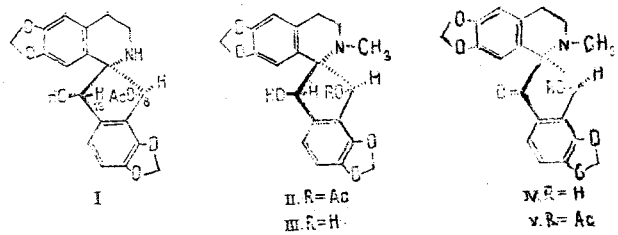
The new spirobenzylisoquinoline base lederine with mp 208-209°C (methanol), $[\alpha]_D$ +13° (c 0.84; chloroform) has been isolated from *Corydalis ledebouriana* Kar et Kir and *Dicentra peregrina* (Rudolphi) Fedde. Its structure has been established on the basis of spectral characteristics and chemical reactions.

Continuing the separation of the total alkaloids from the epigeal part of *Corydalis lederbouriana* Kar et Kir collected at Baraldaisae (KazSSR) 1 , from the nonphenolic-fraction we have isolated a new optically active base with mp 209-209°C, which we have called lederine (I). Lederine has also been isolated from the nonphenolic combined ether-extractable alkaloids of *Dicentra peregrina* (Rudolphi) Fedde collected on the island of Sakhalin.

The IR spectrum of the base contains absorption bands at (cm^{-1}) 3600-3150 (active hydrogen), 1760 (ester C=O), 1605 and 1500 (aromatic ring), and 1050 and 940 (CH_2O_2). The NMR spectra of (I) contains a three-proton singlet at 1.90 ppm ($COCH_3$), a one-proton singlet at 5.23 ppm, and two pairs of one-proton doublets at 5.86, 5.89, and 6.00, 6.03 ppm (J ∿ 2 Hz), ($2CH_2CO_2$). In the aromatic region of the spectrum there are one-proton singlets at 6.18, 6.51, and 6.66 ppm and a two-proton singlet at 6.78 ppm. The remaining protons are represented by a multiplet in the 2.40-3.65 region.

Methylation by Craig's method [2] yielded N-methyllederine (II). The saponification of (II) gave O-deacetyl-N-methyllederine (III), identical with severcinine (severzinine).

According to the facts given, lederine is a spirobenzylisoquinoline alkaloid [4]. To determine the position of the acetyl group in lederine we obtained O-acetylsibiricine (V) by acetylating sibiricine (IV) [5-7] with acetic anhydride in pyridine. The reduction of (V) with sodium tetrahydroborate led to O-acetyldihydrosibiricine, identical with N-methyllederine. Consequently, the acetyl group in lederine is located at C_8.



EXPERIMENTAL

For chromatography we used type KSK silica gel. For TLC we employed the following solvent system: 1) benzene—ethanol (9:1) and 2) chloroform—ethanol (9:1). IR spectra were recorded on a UR-10 instrument (tablets with KBr) and NMR spectra in $CDCl_3$ on a JNM-4H-100/100 MHz instrument with HMDS as standard (δ scale), and mass spectra on a MKh-1303 instrument.

Lederine, mp 208-209°C (methanol), $[\alpha]_D$ +13° (c 0.84; chloroform).

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