2. L. Ferband, F. Labric, P. A. Kelly, and J. P. Raynaud, Biol. Reprod., 18, 99 (1978).
3. A. Segaloff and R. B. Gabbard, Steroids, 43, 111 (1984).
4. V. M. Rzheznikov, USSR Inventor's Certificate No. 1,395,639 (1988); Byull Izobret, No. 18, 99 (1988).

STEROID GLYCOSIDES OF Solanum tuberosum

II. TUBEROSIDE F

P. K. Kintya, T. I. Prasol, and N. E. Mashchenko

UDC 547.918+547.917

The presence of steroid glycosides in potato seeds has been reported previously [1]. In the present paper we give a proof of the structure of a new glycoside isolated from seeds of Solanum tuberosum L., which we have called tuberoside F (I).

Tuberoside F (mp 152-153°C, $[\alpha]_D^{20}$ −127°, c 2.5; MeOH), which was obtained in the individual state by the repeated chromatography on a silica gel column of a methanolic extract of potato seeds, gave a positive reaction with the Ehrlich reagent [2]. In the products of acid hydrolysis we identified yamogenin (mp 201°C, $[\alpha]_D$ −120° (c 1.0; $CHCl_3$); $[M^+]$ 414; IR spectrum: $890 < 920$ cm^{-1}), which was the basis for considering the aglycon of tuberoside F to be (25S)-furost-5-ene-3β,22α,26-triol.

GLC of the aldononitrile derivatives [3] of the monosaccharides of (I) showed the presence of galactose, rhamnose, and glucose in a ratio of 1:1:1.

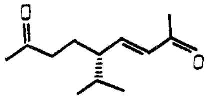
The methyl 3,4,6-tri-O-methyl-D-galactopyranoside, methyl 2,3,4-tri-O-methyl-L-rhamnopyranoside, and methyl 2,3,4,6-tetra-O-methyl-D-glucopyranoside obtained after the methanolysis of Hakomori-permethylated [4] tuberoside F showed the direct attachment of the galactose residue to the aglycon.

Methylation and the methanolysis of the permethylate of yamogenin rhamnogalactopyranoside (II), mp 236-238°C, $[\alpha]_D^{20}$ −63° (c 1.7; pyridine), obtained, together with yamogenin galactopyranoside (mp 230-233°C; $[\alpha]_D^{20}$ −91°, c 1.0; CH_3OH) and yamogenin, as the result of the mild hydrolysis of (I), showed the identity of (II) with tuberoside C [1].

A confirmation of the furostanol nature of (I) may be considered to be its oxidative cleavage [5] and the presence of free glucose and compound (II) in the products of the enzymatic hydrolysis of tuberoside F with β-glucosidase.

The configurations of the glycosidic centers were determined from the differences in the molar rotations of the initial glycosides, of the progenins, and of the aglycon [6].

According to all the facts presented, tuberoside F corresponds to the structure of (25S)-furost-5-ene-3β,22α,26-triol 26-O-β-galactopyranoside 3-O-[O-L-rhamnopyranosyl-(1 → 2)-β-D-galactopyranoside].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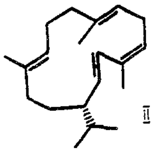
II

LITERATURE CITED

1. P. K. Kintya and T. I. Prasol, Khim. Prir. Soedin., No. 4 (1991).
2. S. Hijosawa, M. Huton, T. Komori, et al., Chem. Pharm. Bull., 16, 1162 (1968).

Institute of Ecological Genetics, Moldavian Academy of Sciences, Kishinev. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 730-731, September-October, 1991. Original article submitted October 29, 1990; revision submitted January 31, 1991.

0009-3130/91/2705-0646$12.50 © 1992 Plenum Publishing Corporation

3. V. V. Krokhmalyuk et al., Izv. Akad. Nauk MSSR, Ser. Biol. Khim. Nauk, 1, 85 (1975).
4. S. Hakomori, J. Biochem. (Tokyo), 55, 205 (1964).
5. M. E. Wall, H. E. Kenney, and E. S. Noronha, Tetrahedron Lett., 5141 (1968).
6. W. Klyne, Biochem. J., 47, No. 4, xli (1950).

ALKALOIDS OF THE CORMS OF Colchicum laetum

O. I. Popova, D. A. Murav'eva, and O. N. Tolkachev

UDC 547.944.6

There is limited amount of information in the literature on the alkaloid composition of Colchicum laete Stev. [1-3]. Colchicine has been isolated from the corms of this plant [3]. In order to study its alkaloids, the plant was gathered in the flowering period in September, 1988 in the Apsheron region, Stavropol' krai.

The fresh comminuted corms together with the juice (1.3 kg) were acidified to pH 3-4 with tartaric acid and were extracted with toluene (fraction 1-2.42 g), and they were then made alkaline with ammonia to pH 9-10 and were again treated with toluene (fraction 2-1.68 g). Fraction 3 (1.75 g) was obtained by the chloroform treatment of the meal left after the isolation of fraction 2. Column chromatography was used for the isolation of individual bases.

As a result of the treatment of toluene fraction 1 with petroleum ether and then with ethyl acetate, we isolated base (I) (0.76 g) with the composition $C_{22}H_{25}NO_6$, mp 155-156°C (ethyl acetate), $[\alpha]_D^{20}$ −121° (c 0.879; chloroform), which was identified as colchicine from its physicochemical properties [4], its IR spectrum, and direct comparison with an authentic sample.

The ethyl acetate mother liquor after the separation of base (I) was chromatographed on a column of silica gel with elution by benzene and then by benzene—methanol (9:1) and (1:1). This led to the isolation of base (II) (0.35 g), with the composition $C_{21}H_{23}NO_6$, mp 178-180°C (chloroform), $[\alpha]_D^{20}$ −137° (c 1.0; chloroform). Its UV spectrum showed two maxima, at 243 and 355 nm, and its mass spectrum contained the peak of the M^+ 385 ion, corresponding to a dimethylated colchicine derivative [4-6]. The PMR spectrum of the base taken in deuterochloroform with tetramethylsilane as internal standard contained the signals of three methoxy groups (at 4.10, 3.90, and 3.66 ppm), of an N-acetyl group (1.99 ppm), and of four aromatic protons in the form of singlets at 6.52 and 7.61 ppm (H-3 and H-8), and also doublets at 6.77 and 7.38 ppm, dd, J = 10 Hz (H-11 and H-12). By comparison with literature information, base (II) was identified as 2-demethylcolchicine [5, 6].

The treatment of fraction 2 with acetone led to the precipitation of base (III) (0.24 g), with the composition $C_{21}H_{25}NO_5$, mp 184-186°C (ethanol), $[\alpha]_D^{20}$ −127° (c 1.0; chloroform). Its mass spectrum had the molecular ion M^+ with m/z 371. From these constants it was identical with colchamine [4, 5]. A mixture of the isolated base (III) with an authentic sample of colchamine gave no depression of the melting point.

On a column of Al_2O_3, the acetone mother liquor after the isolation of base (III) yielded base (IV), with the composition $C_{21}H_{21}NO_6$, mp 263-264°C (ethyl acetate), $[\alpha]_D^{20}$ −106° (c 0.68; chloroform). PMR spectrum: 1.96 ($NH{-}CO{-}CH_3$); 3.80 (C-1, OCH_3); 5.98 ($O{-}CH_2{-}O$) and 6.45 (H-4). The mass spectrum contained peaks with m/z 383 (M^+), 355, 340, 312, 296, 281, 265, and 251. A comparison of the results obtained with the literature permitted base (IV) to be identified as cornigerine [5, 7].

Fraction 3 yielded a base (V) having the composition $C_{22}H_{25}NO_6$, mp 183-185°C (ethanol), $[\alpha]_D^{20}$ −304° (c 1.0; chloroform). Its UV spectrum (in alcohol) had maxima at (nm) 224, 266,

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