aqueous ethanol. In this way, substances (I) and (II) were isolated. Substance (I) formed light yellow acicular crystals with mp 254°C. UV spectrum λ_{max}, nm; C_2H_5OH: 255, 266 sh., 350; C_2H_5ONa: 262, 300 sh., 396; $AlCl_3$: 274, 300 sh., 330, 432; $AlCl_3$ + HCl: 274, 294 sh., 358, 386; CH_3COOH: 258, 266 sh., 365 sh., 405; CH_3COONa + H_3BO_3: 260, 372. Acid hydrolysis yielded luteolin and D-glucose. The substance was identified as luteolin 7-β-D-glucopyranoside. Substance (II) formed pale yellow crystals with mp 178-180°C. UV spectrum, λ_{max}, nm; C_2H_5OH: 268, 335; C_2H_5ONa: 269, 386; $AlCl_3$: 276, 300, 348, 386; $AlCl_3$ + HCl: 277, 299, 340, 382; CH_3COONa: 267, 355, 386. Acid hydrolysis yielded apigenin and D-glucose. The substance was identified as apigenin 7-β-D-glucoside.

We have detected caffeic acid in the same plant by paper chromatography.

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THE STRUCTURES OF ISOFLAVONE C-GLYCOSIDES FROM *Lupinus luteus*

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Continuing a chemical study of the flavonoids of *Lupinus luteus* L. (European yellow lupine) [1], from its flowers we have isolated two isoflavone glycosides.

Compound (I). $C_{21}H_{20}O_{10} \cdot H_2O$, mp 185-189°C (aq. MeOH), $[\alpha]_D^{20}$ + 24° (c 1; MeOH); λ_{max},

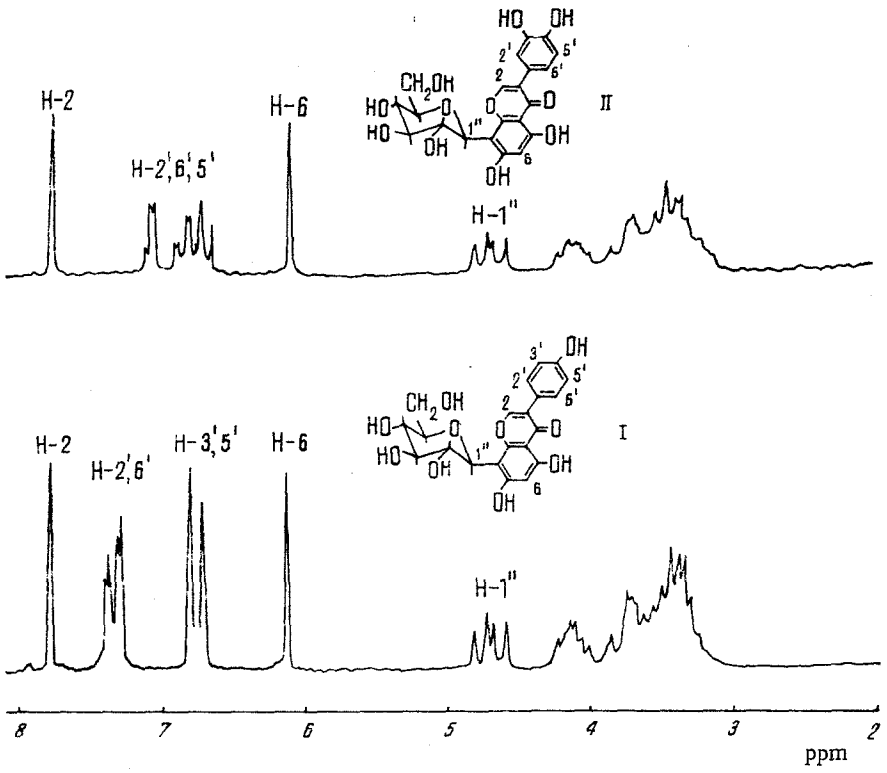

Fig. 1. NMR spectra of the trimethylsilyl ethers of genistein 8-C-β-D-glucopyranoside (I) and of orobol 8-C-β-D-glucopyranoside (II) in CCl_4.

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nm; MeOH, 264; NaOac, 280. On acetylation it gave a heptaacetate with mp 122-125°C the NMR spectrum of which contained the signals of four alipatic acetoxy groups (1.74 ppm, 3H; 2.02 ppm, 3H; 2.05 ppm, 6H) and of three aromatic acetyoxy groups (2.3, 2.37, and 2.41 ppm).

Compound (II). $C_{21}H_{20}O_{11} \cdot H_2O$, mp 190-193°C $[\alpha]_D^{20}$ 0° [MeOH—pyridine (1:1)]; λ_{max}, nm: MeOH, 264; NaOAc, 275. Acetylation formed an octaacetate with mp 132-134°C the NMR spectrum of which contained the signals of four aliphatic acetoxy groups (1.76 ppm, 3H; 2.02 ppm, 3H; 2.05 ppm, 6H) and four aromatic acetoxy groups (2.3 ppm, 6H; 2.39 ppm, 3H; 2.43 ppm, 3H).

The compounds were assigned to the isoflavone group on the basis of qualitative reactions and UV and PMR spectra that the substances are monoglycosides, and since they do not undergo hydrolysis by acids and enzymes they were assigned to the C-glycosides. Cleavage with ferric chloride, Kiliani's sugar mixture, and hydriodic acid under the conditions described by Laman and Volynets [1] showed that the carbohydrate moiety of both compounds was glucose, while the aglycone of compound (I) was genistein (4',5,7-trihydroxyisoflavone), $C_{15}H_{10}O_5$, M^+ 270, mp 303-306°C; and in compound (II) it was orobol (3',4',5,7-tetrahydroxyisoflavone), $C_{15}H_{10}O_6$, M^+ 286, mp 313-317°C.

In the PMR spectra (see Fig. 1), the signals of the aromatic protons correspond to genistein and orobol having substituents at position 8 in each case (H-6 singlets at 6.11 and 6.14 ppm). The signal of the 1"-proton of glucose appears in the form of a doublet with J = 10 Hz corresponding to diaxial coupling with H-2", i.e., to a β bond with the aglycone, in each case. The doubled doublet may be due to hindered rotation around the C_8—C_1" bond as a consequence of the steric hindrance of the voluminous trimethylsilyl substituting groups of the sugar and of the isoflavone nucleus (the existence of two possible rotation isomers has been reported previously for acetylated G-glucosides [2]). In the PMR spectrum of the free compound (I) taken in deuteropyridine, the anomeric proton resonates in the form of a sharp doublet with J = 10 Hz; likewise, no splitting of the signal of the protons at C-2',6' is observed.

The facts presented permit compound (I) to be regarded as genistein 8-C-β-D-glucopyranoside and (II) as orobol 8-C-β-D-glucopyranoside (the structures are shown in Fig. 1).

In the PMR spectra of the full acetates, a diamagnetic shift is observed of the signal of one acetyl group [1.74 ppm in (I) and 1.76 ppm in (II)], which is considered to be the 2"-acetyl group since it may be subject to the magnetic anisotropy of the aromatic ring [2]; simultaneously this is a proof of the equatorial orientation of these acetoxy groups [3], i.e., it is evidence in favor of the Cl conformation of the D-glucopyranose.

The suggested structures also correspond to the mass spectra, in which the main ions are the benzyl ions A (m/e 283 and 299 for compounds (I) and (II), respectively), while the presence of ions B (m/e 312 and 328) is evidence in favor of the C—8-glucosidic structure [4]. ions, but their mass spectra contain in considerable intensity the peaks of the ions $M - H_2O$, $M - 2H_2O$, and $M - 3H_2O$ [respectively, m/e 414 (59%), 396 (11%), and 378 (7%) for (I) and 430 (27%), 412 (10%), and 394 (36%) for (II)].

Compounds (I) and (II) are new, not having being described in the literature.

We have previously isolated from the roots of the European yellow lupine a genistein C-monoglucoside [1] which has now proved to be identical with compound (I).

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