The IR and UV spectra and an analysis of the conversion products, together with the absence of a depression of the melting point with an authentic sample, enabled glycoside I to be identified as kaempferol 3-O-α-L-rhamnofuranoside-7-O-α-L-rhamnofuranoside, which has been reported previously under the names "kaempferitrin" and "lespedin" [2, 3].

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LUTEOLIN FROM THE LEAVES OF DIGITALIS CILIATA

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In the preparation of cardiac glycosides from the leaves of *Digitalis ciliata* Trautv. we isolated a yellow crystalline substance [1] giving all the reactions for flavonoids. In the cyanidin test, an octanol-extractable orange-red pigment was formed, which shows the aglycone nature of the compound [2]. When the substance was subjected to paper chromatography in the butanol–acetic acid–water (4 : 1 : 5) system it gave a single spot, while in each of the systems ethyl acetate–formic acid–water (10 : 2 : 3) and benzene–ethyl acetate–acetic acid (74.5 : 23.5 : 2) systems it gave two spots. On them the main component appeared at the level of an authentic sample of luteolin, and a small spot in the region of apigenin.

To separate the combined flavonoids into the individual compounds we chromatographed them on a polyamide sorbent. Pure luteolin was isolated by washing the column with a mixture of chloroform and ethanol (1 : 1). After its recrystallization from dilute ethanol, long yellow acicular crystals, $C_{15}H_{10}O_6$, with mp 330–332° C were obtained. It gave no depression with standard luteolin. The acetate of the substance melted at 226–231° C. The IR and UV spectra of the flavonoid and its acetate coincided completely with literature data for luteolin and its acetate [3, 4].

REFERENCES

1. E. P. Kemertelidze, KhPS [Chemistry of Natural Compounds], 1, 379, 1965.
2. E. T. Brrejant, J. Am. Pharm. Assoc., 39, 481, 1956.
3. I. P. Kovalev and E. V. Titov, Infrared Absorption Spectra of Some Groups of Natural Compounds (Atlas of Spectra) [in Russian], Khar'kov, 1966.
4. V. I. Litvinenko and N. P. Maksyutina, KhPS [Chemistry of Natural Compounds], 1, 420, 1965.

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LUTEOLIN 7-GLUCOSIDE FROM CAMPANULA LACTIFLORA

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The chromatography of an ethanolic-aqueous extract from the leaves of *Campanula lactiflora* M. B. in the BAW (4 : 1 : 5) system showed the presence of three substances of a flavonoid nature. One of them, with the composition $C_{20}H_{20}O_{11}$, mp 256–258° C (from ethanol), $[\alpha]_D^{20}$ −58° (c 0.528; methanol–pyridine (3 : 2)), mol. wt. 259, is a flavone glycoside as was shown by the results of color reactions.

UV spectrum: λ_{max} 352, 255 mμ; $\lambda_{max}^{AlCl_3}$ 400, 275 mμ; $\lambda_{max}^{CH_3COONa}$ 355, 258; $\lambda_{max}^{CH_3COONa+H_3BO_3}$ 380, 258 mμ; $\lambda_{max}^{CH_3ONa}$ 407, 265 mμ; $\lambda_{max}^{AlCl_3+HCl}$ 390, 275 mμ. The elementary composition found corresponds to that calculated.

On acid hydrolysis, the yield of aglycone was 63%, which indicates that the substance is a monoglycoside. The aglycone, $C_{15}H_{10}O_6$, had mp 325–328° C (from ethanol); UV spectrum: λ_{max} 355, 260 mμ; $\lambda_{max}^{AlCl_3}$ 400, 270 mμ, λ $\lambda_{max}^{CH_3COONa}$ 375, 265 mμ; $\lambda_{max}^{CH_3COONa+H_3BO_3}$ 375, 265 mμ; $\lambda_{max}^{AlCl_3+HCl}$ 390, 270 mμ; $\lambda_{max}^{CH_3ONa}$ 400, 280 mμ. On the basis of these results and a mixed melting point, the aglycone was identified as luteolin. The addition of sodium acetate to the glycoside did not lead to a bathochromic shift of the absorption bands, which shows that the sugar component (glucose) is attached to the aglycone in the $C_{(7)}$position. The osazone had mp 204–206° C (from 50% ethanol). The acetate of the aglycone had mp 222–226° C (from petroleum ether–chloroform) and gave no depression of the melting point in admixture with the acetate of a sample of luteolin obtained from willow [1].

The glucoside was subjected to hydrolysis with an enzyme preparation from Aspergillus oryzae, which showed the β configuration of the glycosidic bond. The results of differential IR spectroscopy and also a comparison of (M) for the glycoside with (M) for phenyl β-D-glucopyranoside showed that in the glycoside isolated the glucose is in the β-D-glucopyranose form. Consequently, the glycoside is 5, 3', 4'-trihydroxyflavone 7-O-β-D-glucopyranoside (luteolin 7-β-D-glucopyranoside).

REFERENCES

1. B. A. Kompantsev and A. L. Shinkarenko, KhPS [Chemistry of Natural Compounds], 4, 380, 1968.
2. I. P. Kovalev and V. I. Litvinenko, KhPS [Chemistry of Natural Compounds], 1, 233, 1965.

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KAEMPFEROL 7-RHAMNOSIDE FROM ACONITUM ORIENTALE

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By chromatographing the total material from an ethanolic extract of the leaves [1, 2] of Aconitum orientale Mill., collected in the Teberdina reserve, on a column of polyamide sorbent, we have isolated, using 45% ethanol, an individual substance with composition $C_{21}H_{20}O_{10}$, mp 232–233° C, $[\alpha]_D^{20}$ −165° (c 0.42; methanol). A positive cyanidin reaction showed its flavonoid nature.

On acid hydrolysis, an aglycone (yield 67%) and a sugar component were obtained. The latter was identified by paper chromatography as L-rhamnose (melting point of the osazone 178–180° C).

After recrystallization from ethanol, the melting point of the aglycone was 273–275° C and that of its acetyl derivative 180–182° C. The substance was identified by a mixed melting point as kaempferol (3, 5, 7, 4'-tetrahydroxyflavone).

In the UV region of the spectrum the glycoside had λ_{max} 370, 258 mμ (methanol). The absence of a bathochromic shift of band I of the glycoside on the addition of CH_3COONa shows that the hydroxyl group at $C_{(7)}$ is glycosidated.

Hydrolysis with an enzyme preparation from Aspergillus oryzae [5] did not lead to the cleavage of the glycoside, which shows the absence of a g-glycosidic linkage.

On comparing the molecular rotation of the glycoside isolated and the appropriate phenyl rhamnosides [6], it was found that the L-rhamnose was attached by an α-glycosidic bond and is present in the furanose form.

The results obtained and also the IR spectrum, permit the glycoside isolated to be regarded as kaempferol 7-O-α-L-rhamnofuranoside.

REFERENCES

1. V. I. Litvinenko, N. P. Maksyutina, and D. G. Kolesnikov, Med. prom. SSSR, no, 3, 40, 1962.
2. V. I. Litvinenko, Farm. zh., no. 5, 20, 1963.
3. T. A. Geissman, The Chemistry of Flavonoid Compounds, Pergamon Press, N. Y., 1962.