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Abstract

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CHEMISTRY

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CHALCONE GLYCOSIDES OF LICORICE–*GLYCYRRHIZA GLABRA* L.

(Presented by Academician A. I. Oparin, 2 IX 1963)

In studying the qualitative composition of the flavonoids of licorice, it was established that in the roots and rhizomes these compounds are represented mainly by two classes: flavonones and chalcones. Some of the pigments discovered were isolated by means of column chromatography on a polyamide sorbent (1).

The subject of the present work was the study of two of them, designated as substances L-7 and L-8. The isolated flavonoids are individual crystalline compounds, the physicochemical properties of which are shown in Tables 1 and 2.

The data presented indicate that substances L-7 and L-8 are chalcone monoglycosides of isoliquiritigenin (2,4,4′-trioxychalcone). From the spectral properties it was found that the sugar substituent is located in flavonoid L-7 at the 4 position, and in flavonoid L-8 at the 4′ position. One of the features of the chalcone derivatives under study is

Table 1

Physicochemical properties of chalcone glycosides and their derivatives

Properties and qualitative reactions	Isoliquiritin (9)	Substance L-8	Neoisoliquiritin (L-7)	Acetyl derivatives L-7	Acetyl derivatives L-8
M.p., °C	185–186	187–189	230–232	158–160	169–171
Mol. weight	418.0	418.0	418.0	670.0	670.0
Formula	$C_{21}H_{22}O_9$	$C_{21}H_{22}O_9$	$C_{21}H_{22}O_9$	$C_{33}H_{34}O_{15}$	$C_{33}H_{34}O_{15}$

Properties and qualitative reactions	Isoliquiritin ([9])	Substance L-8	Neoisoliquiritin (L-7)	Acetyl derivatives L-7	Acetyl derivatives L-8
Optical activity	−62.15° ([10]) (C 1.07, methanol)	−60.8° (C1 ethanol)	−61.5° (C 0.5, ethanol)	−12.8° (C1, acetone)	−13.5° (C 0.52, acetone)
Values of R_f					
1. *n*-Butanol—acetic acid—water (4 : 1 : 2)	0.52	0.52	0.56	—	—
2. 15% acetic acid	0.31	0.31	0.37	—	—
Color of spots with alkali	greenish-yellow	greenish-yellow	orange	—	—
Cyanidin reaction ([2])	positive in water	positive in water	positive in water	negative	negative
Reaction in $FeCl_3$	brown	brown	brown	negative	negative
Reaction with $SbCl_5$ ([3])	orange	orange	orange	negative	negative
Aglycone	isoliquiritigenin	isoliquiritigenin	isoliquiritigenin	isoliquiritigenin	isoliquiritigenin
Carbohydrate component	D-glucose	D-glucose	D-glucose	D-glucose	D-glucose

Table 2

Spectral properties of chalcone glycosides and their aglycone

Solutions and reagents	A. Isoliquiritin (L-8), band 1	A. Isoliquiritin (L-8), band 2	A. Isoliquiritin (L-8), Δλ, ½	B. Neoisoliquiritin (L-7), band 1	B. Neoisoliquiritin (L-7), band 2	B. Neoisoliquiritin (L-7), Δλ, ½	C. Isoliquiritigenin, band 1	C. Isoliquiritigenin, band 2	C. Isoliquiritigenin, Δλ, ½	Position of free phenolic hydroxyls, A	Position of free phenolic hydroxyls, B	Position of free phenolic hydroxyls, C
Solution in absolute ethanol, 0.5 · 10^{-5} molar	360	260	–	370	240	–	370	255	–	–	–	–
Ethanolic solution + sodium acetate	325375260		+150	295370250		0+10	380		+10 –	4+	4–	4+
Ethanolic solution + sodium ethylate	315395225280		+35+20	340445252280		+75+40	310350450	232	+60–2	4′ –	4′+	4′+
Ethanolic solution + aluminum chloride	315365240		+5–20	315375240	250	+50+10	315360230		–10–25	2+	2+	2+

Solutions and reagents	A. Isoliquiritin (L-8), band 1	A. Isoliquiritin (L-8), band 2	A. Isoliquiritin (L-8), Δλ, ½	B. Neoisoliquiritin (L-7), band 1	B. Neoisoliquiritin (L-7), band 2	B. Neoisoliquiritin (L-7), Δλ, ½	C. Isoliquiritigenin, band 1	C. Isoliquiritigenin, band 2	C. Isoliquiritigenin, Δλ, ½	Position of free phenolic hydroxyls, A	Position of free phenolic hydroxyls, B	Position of free phenolic hydroxyls, C
Ethanolic solution of acetyl derivatives	320	233	–	310	226	–	310	225	–	–	–	–

Table 3

Comparison of molecular rotations of chalcone glycosides

Glycosides	$[M]_D$ of glycosides	$[M]_D$ of acetyl derivatives
Isoliquiritin (L-8)	−254.0°	−86.0°
Neoisoliquiritin (L-7)	−257.0°	−90.5°
Phenyl-β-D-glucopyranoside	−182.0°	−123.0°
Phenyl-α-D-glucopyranoside	+402.0°	+688.0°

a hypsochromic shift, observed upon addition of aluminum chloride to alcoholic solutions of glycoside L-8 and isoliquiritigenin, instead of the expected bathochromic shift (^{4}). This is apparently due to the influence of the free hydroxyl group in position 4, conjugated with the carbonyl group.

The carbohydrate component, according to its physicochemical properties (m.p. 145–147°, $[\alpha]_D^{20} + 51.5°$ in water, etc.), was characterized as *D*-glucose.

According to enzymatic hydrolysis data and by the method of molecular-rotation differences (^{5}, ^{6}), it was determined, as shown in Table 3, that *D*-glucose is linked to the aglycone in both glycosides by a β-bond.

The geometrical isomerism of the chalcones was investigated by spectral methods; the results of these studies are given in Table 4.

From the data obtained it is evident that the absorption maxima of band 1 of the chalcone derivatives are considerably more intense than the maxima of band 2, which is characteristic of trans-chalcones ([7], [8]). Irradiation of the oxy derivatives of chalcones with ultraviolet light did not lead to the formation of an equilibrium mixture of cis- and trans-isomers. To confirm the geometrical isomerism of the glycosides under investigation and of isoliquiritigenin, their acetyl derivatives were synthesized and studied; after irradiation with ultraviolet light for 15 min at a distance of 20 cm from the radiation source (PRK-4), these form a mixture of isomers. This is clearly shown in Table 4 by the change in intensity of the absorption maxima in bands 1 and 2.

Table 4

Spectroscopic study of the geometrical isomerism of chalcone derivatives
(maxima (λ, mµ) and absorption intensity)

Compounds	Before irradiation with UV light, band 1: λ	Before irradiation with UV light, band 1: ϵ	Before irradiation with UV light, band 2: λ	Before irradiation with UV light, band 2: ϵ	After 15-min irradiation, band 1: λ	After 15-min irradiation, band 1: ϵ	After 15-min irradiation, band 2: λ	After 15-min irradiation, band 2: ϵ
Isoliquiritin (L-8)	360	35990	260	10000	360	35990	260	10000
Acetyl derivative of L-8	320	22000	233	20500	320	14500	233	12500
Neoisoliquiritin (L-7)	370	27540	240	10230	370	27540	240	10230
Acetyl derivative of L-7	310	18620	266	19940	310	12200	226	10700
Isoliquiritigenin	370	33910	255	3390	370	13910	255	3390

Compounds	Before irradiation with UV light, band 1: λ	Before irradiation with UV light, band 1: ϵ	Before irradiation with UV light, band 2: λ	Before irradiation with UV light, band 2: ϵ	After 15-min irradiation, band 1: λ	After 15-min irradiation, band 1: ϵ	After 15-min irradiation, band 2: λ	After 15-min irradiation, band 2: ϵ
Acetyl derivative of isoliquiritigenin	310	26300	225	19950	310	15850	225	18620

On the basis of the data obtained, the following structural formula may be proposed for the chalcone glycosides studied: in L-8, $R—H$ and R'— a glucosyl residue, whereas in L-7 R— a glucosyl residue and $R'—H$.

Therefore the flavonoid L-8 should be designated as trans-isoliquiritigenin-4′-β-D-glucopyranoside, identified with isoliquiritin (^{9}), and the flavonoid L-7 as trans-isoliquiritigenin-4-β-D-glucopyranoside.

$$\mathrm{RO{-}C_6H_3(OH){-}CO{-}CH{=}CH{-}C_6H_4{-}OR'}$$

For the latter we propose the trivial name —neoisoliquiritin.

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