Results of a Spectral Study of the Flavonoids of Solidago canadensis

Substance No.	Substance	Mp, °C	Empirical composition	Absorption bands	UV spectra				
					λ, mμ, of the initial solution	the same + sodium acetate	the same + sodium methoxide	the same + boric acid + sodium acetate	the same + aluminum chloride
(I)	Quercetin	311—314	$C_{15}H_{10}O_7$	I	370	385*	332	385	456
						322			330*
					300*			300*	
					270**				
					255	273	245*	258	271
(II)	Kaempferol	280—285	$C_{15}H_{10}O_6$	II	365	375	407	365	422
					320*		321*	520*	347*
					300*	305*			305*
					267	273	275	267	270
(III)	Rhamnetin	188—192	$C_{27}H_{30}O_{16}$	I	356	395	408	375	430
						322*	325*		
					295*			300*	300*
					265**				
					258	273	271	261	271
(IV)	Isorhamnetin	303—308	$C_{16}H_{12}O_7$	II	367	380	333	368	428
						320*			355*
					300*			305*	300*
					267*				
					254	275	245*	253	263
(V)	Isorhamnetin 3-glucorhamnoside	165—170	$C_{28}H_{32}O_{16}$	I	355	393	412	355	405
						320*	330**		365*
					300*			298*	302*
					265**			267**	
				II	255	273	272	255	267

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*Low-intensity absorption bands

**Shoulder

Substance IV differs only slightly from quercetin in its behavior with additions of sodium acetate and methoxide. With the addition of boric acid and sodium acetate, band I of the UV spectrum of substance IV, unlike the same band in the case of quercetin, undergoes no change in comparison with the initial solution. This fact permits the assumption that the hydroxyl group in position 3' is etherified. From its physicochemical properties and by means of paper chromatography, substance IV has been identified as 3,5,7,4'-tetrahydroxy-3'-methoxyflavone (isorhamnetin). A mixture of substance IV and isorhamnetin gave no depression of the melting point.

Substance V consists of a diglycoside of isorhamnetin. From the products of the acid hydrolysis of substance V we have isolated isorhamnetin and, as sugar components, glucose and rhamnose. The UV spectra show that the sugar components are present in position 3.

The sample of isorhamnetin was given to us by N. F. Komissarenko.

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FLAVONOIDS OF AFLATUNIA ULMIFOLIA

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Aflatunia ulmifolia (Franch.) Vass. is a shrub of the family Rosaceae distributed in the mountain of Central Asia and Kazakhstan. The raw material for the investigation was branches freed from leaves collected in the fruit-bearing phase in the Tereksai gorge of the Talas Ala-Tau.

An aqueous extract of the dry ethanolic extract was extracted successively with petroleum ether, ether, and ethyl acetate. The residue after the evaporation of the ethyl acetate was recrystallized from aqueous ethanol giving a substance having the composition $C_{21}H_{20}O_{11} \cdot 2H_2O$, mp 187–189° C, with a yield of 0.4%. Its acid hydrolysis led to equimolar amounts of quercetin with mp 317 (pentaacetate with mp 194–195° C) and rhamnose (osazone with mp 180.5–182° C), and methylation with dimethyl sulfate and subsequent splitting off of the carbohydrate part of the molecule led to 3-hydroxy-5,7,-3',4'-tetramethoxyflavone with mp 193–194° C. On the basis of the chemical reactions mentioned and the IR spectra and R_f values of the substance in several systems of solvents, it was identified as quercetin 3-rhamnoside (quercitrin). A mixture of quercitrin and the derivatives obtained with authentic samples [1] gave no depression of the melting points.

The evaporated ethereal fraction was chromatographed on polyamide, and 30% ethanol eluted 0.02% of a colorless crystalline substance with mp 227–229° C. It gave positive reactions for flavones with alkali, sodium borohydride in an acid medium [2], with Mg + HCl (crimson), with Zn + HCl (transient crimson), $FeCl_3$ (brown), and with concentrated HNO_3 (red). The substance was soluble in aqueous Na_2CO_3, which shows the presence of acid phenolic groups in it (for example 7-OH). The compound underwent no change on acid hydrolysis, but alkaline degradation yielded products differing from the products of the decomposition of hesperetin. Microanalysis showed that its molecule contained one CH_3O group. Its IR spectrum showed absorption bands of hydroxyl groups at 3440 (sharp), 3320 (unsharp), 3140 (broad) cm^{-1}, the carbonyl of a γ-pyrone probably bound by a hydrogen bond with the 5-OH [3] at 1633 cm^{-1}, and also bands at 843 and 817 cm^{-1} characteristic for CH– with a 3',4'-substituted B ring. Evidently one OH group is methylated, since the difference in the intensities of these bands is marked [4]. The IR spectrum is characteristic for flavanones or isoflavanones [5] and, in contrast to those of the flavones, has one strong and one ill-defined maximum: λ_{max} 292, 331 mμ (log 4.30, 3.69, respectively). The bathochromic shift of the short-wave maximum under the influence of sodium acetate (λ_{max} 328 mμ, log ε 4.46), sodium ethoxide (λ_{max} 328 mμ, log ε 4.47), and aluminum chloride (λ_{max} 312 mμ, log ε 4.43) permits the compound isolated to be assigned to the flavanones having free OH groups in positions 5 and 7 [5]. The study of the compound isolated is continuing with the aim of elucidating the position of the substituents in ring B.

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THE PRESENCE OF α-TERPINENE IN THE TURPENTINES OF VARIOUS CONIFERS

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We have previously [1] reported that the Δ^3-carene fraction of the turpentines from Pinus silvestris L. (Scotch pine) [1], and also the turpentines of other conifers, contain a monoterpene of unknown structure the relative retention time of which in GLC corresponds to α-terpinene (p-mentha-1,3-diene).

In the present investigation, we have shown that this monoterpene is in fact α-terpinene.

The α-pinene and part of Δ^3-carene were distilled off from the oleoresin turpentine of Pinus silvestris L. through a column with an efficiency of 18 theoretical plates at a reflux number (R. No.) of 20. From the distillation residue (Fig. 1, a)* by rectification with a column of 50 theoretical plates at a R. No. of 50 was isolated the α-terpinene fraction

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*The analysis of the turpentines and their fractions was carried out on KhV-2 instrument with a column (6000 × 4 mm) filled with Inza deactivated diatomite brick impregnated with tricresyl phosphate (10%) with hydrogen as carrier gas.