PHENOLIC COMPOUNDS OF THE BARK OF Syringa vulgaris

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According to the literature, the bark of common lilac Syringa vulgaris L. (family Oleaceae) contains the secoiridoids oleuropein and ligustroside, and also derivatives of hydroxycinnamic acid – syringin [2] and coniferin [1].

The freshly gathered bark of common lilac procured in May 1987 in the Moscow oblast was exhaustively extracted with methanol, and the extract obtained was evaporated in vacuum to a viscous residue which was then chromatographed on various sorbents. Ten substances of phenolic nature were isolated: derivatives of phenethyl alcohol (compounds III-VI), phenylpropanoids (I, II, VII, and VIII), a coumarin (IX), and a flavonoid (X).

To identify the substances isolated we used the results of chemical transformations (acetylation and acid, enzymatic, and alkaline hydrolysis), and also the results of UV, IR, PMR, and mass spectroscopies and a direct comparison with authentic samples (in the case of compounds III, V, IX, and X).

Syringin (I). White acicular crystals with the composition $C_{17}H_{24}O_9$, mp 190-192°C (water), λ_{max} 266 nm.

Coniferin (II). White crystals with the composition $C_{16}H_{22}O_8$, mp 184-185°C (ethanol), λ_{max} 266 sh, 258 nm.

On enzymatic hydrolysis with β-glucosidase, compounds (I) and (II) gave the same carbohydrate fragment, glucose, and, as aglycons, sinapyl alcohol (M^+ 210) and coniferyl alcohol (M^+ 180), respectively. Neither substance reacted with diazotized sulfanilic acid (aromatic OH group glycosylated) and they had a characteristic deep-blue coloration after treatment on Silufol plates with a 16% solution of sulfuric acid (110°C).

Tyrosol (4-Hydroxyphenylethanol) (III). Colorless crystals of the composition $C_8H_{10}O_2$ (M^+138), mp 91-92°C (chloroform).

3,4-Dihydroxyphenylethanol (IV). Light-yellow amorphous substance of the composition $C_8H_{10}O_3$ (M^+ 154). The presence in the molecule of (IV) of an orthodihydroxy grouping was confirmed by the results of UV spectroscopy (bathochromic shift with boric acid).

Salidroside (V). Colorless acicular crystals with the composition $C_{14}H_{20}O_7$, mp 160-162°C (chlf–MeOH (4:1)).

O-(3,4-Dihydroxyphenethyl) β-D-Glucopyranoside (VI). Light-yellow syrupy substance with the composition $C_{14}H_{20}O_8$.

On acid and enzymatic (β-glucosidase) hydrolysis, compounds (V) and (VI) formed glucose and aglycons identical with substances (III) and (IV), respectively.

Acetoside (VII) and Forsythiaside (VIII). Light-yellow amorphous substances with the same composition, $C_{29}H_{30}O_{15}$, and UV spectrum (λ_{max} 330 nm).

On the basis of the results of acid and alkaline hydrolysis it was concluded that compounds (VII) and (VIII) contained the same fragments (hydroxytyrosol (IV), caffeic acid (M^+ 180), glucose, and rhamnose) and differed by the structure of the carbohydrate moiety (rungioside and rutinoside, respectively). A comparison of the results of chemical transformations and also those of UV, IR, PMR, and mass spectroscopies enabled compounds (VII) and (VIII) to be identified as acetoside and forsythiaside, respectively [3, 4].

Esculetin (IX). Light-yellow crystals with the composition $C_9H_6O_4$, M^+ 178, mp 248-249°C (chlf–MeOH).

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Astragalin (X). Yellow crystals with the composition $C_{21}H_{20}O_{11}$, mp 236-238°C (aqueous ethanol). On acid and enzymatic hydrolysis it was split into glucose and kaempferol (M^+ 286).

This is the first time that compounds (III), (IV), (VI), (VIII), and (IX) have been isolated from common lilac. It is interesting that compounds (V) and (VII) have been isolated previously from the flowers of this plant [3], and compound (X) from lilac leaves, in which, among the flavonoids, rutin predominates [5].

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STEROID GLYCOSIDES OF THE ROOTS OF Capsicum annuum.

IV. STRUCTURE OF CAPSICOSIDES C_2 AND C_3

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Several chromatographically homogeneous fractions containing glycosides – gitogenin, tigogenin, and diosgenin – close in structure and difficult to separate have been isolated previously from the roots of bush red pepper Capsicum annuum L. [1]. Continuing an investigation of the glycosidic fractions of the roots of this plant remaining after the separation of capsicoside C_1, we have isolated another two glycosides, and we give structures for them.

The isolation of individual glycosides of tigogenin and diosgenin by the direct method was unsuccessful, and therefore to separate the mixture of these glycosides the double bond of the diosgenin moiety was epoxidated. The fully acetylated glycosidic fraction obtained was treated with m-chloroperbenzoic acid [2]. The completeness of epoxidation was determined with the aid of TLC and IR spectroscopy. As a result, a new diosgenin glycoside derivative was obtained – an oxirane (I), with mp 135-137°C, $[\alpha]_D^{20}$ −43° (c 1.0; $CHCl_3$), readily separable from the tigogenin glycoside peracetate (II), mp 117-119°C, $[\alpha]_D^{20}$ −68° (c 1.0; $CHCl_3$), by chromatography on a column of silica gel in the solvent system chloroform–acetone–methanol (45:5:2).

The individual peracetate (II) was saponified, and a glycoside was isolated which we have called capsicoside C_2 (III), mp 270-272°C, $[\alpha]_D^{20}$ −40° (c 1.0; CH_3OH). The complete acid hydrolysis of this glycoside gave tigogenin as the aglycon.

The peracetate (I) was then treated with chlorotrimethylsilane and sodium iodide in acetonitrile [3]. The diosgenin glycoside peracetate obtained was purified by chromatography, and saponification led to an individual diosgenin glycoside – capsicoside C_3 (IV), mp 263-265°C, $[\alpha]_D^{20}$ −60° (c 1.0; CH_3OH). Hydrolysis of glycoside (IV) gave one alycon, identical in its physicochemical constants with diosgenin.

To determine the compositions and relative amounts of the monosaccharides in the carbohydrate moieties of the glycosides we studied a hydrolysate of each glycoside with the aid of PC and GLC [4].

In each of the hydrolysates of (III) and (IV), galactose, glucose, and xylose were detected in a ratio of 1:1:1.

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