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LIGNANS OF THE BARK OF Syringa volgaris

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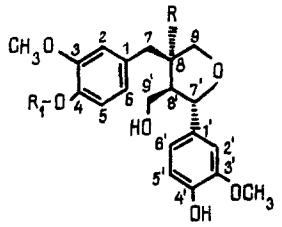
Two lignans have been isolated from the bark of Syringa vulgaris and identified: (+)-lariciresinol 4-β-D-glucopyranoside (I) and –olivil 4-β-D-glucopyranoside (II). This is the first time that glycoside (9) has been described.

We have previously reported the isolation from the bark of the common lilac (Syringa vulgaris L. family Oleaceae) of phenolic compounds [1] and of irodoids [2]. In a further study of the chemical composition of the bark of the common lilac, we have isolated two lignan glycosides (I and II). To establish the structure of the substances isolated we used UV, PMR, and mass spectroscopy and the results of chemical transformations, and also a direct comparison with authentic samples of the substances (compounds I and Ia).



I. R=H; R_1=β-*D*-Glc
Ia. R=R_1=H
II. R=OH; R_1=β-*D*-Glc
IIa. R=OH; R_1=H

Compounds (I) and (II) and also their aglycons (Ia) and (IIa), which were obtained on enzymatic analysis, formed a red coloration with diazotized sulfanilic acid (DSA), which is characteristic for phenolic substances. The fact that compounds (I) and (II) belonged to lignan monoglycosides was shown by their UV and PMR spectra and also by the mass spectra of the aglycons.

According to the PMR results, each of the two lignans contained two 1,2,4-substituted aromatic rings and two aromatic CH_3O groups. The acetylation of compounds (I) and (II) formed hexa- and heptaacetates, respectively, each of these derivatives having one aromatic acetoxy group (δ 2.30 in the PMR spectrum). It followed from the results of acetylation that the aglycon of (I) contained one free alcoholic OH group and that of (II) two such groups, one of them being of tertiary nature (singlet, δ 1.8, in the spectrum of the acetate). These facts permitted the assumption that compounds (I) and (II) were phenolic glycosides of lariciresinol and olivil. The ^1H NMR spectrum of compound (I) was completely identical with that of (–)-lariciresinol 4-β-D-glucopyranoside, which we had isolated previously from

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callus culture of Rhodiola rosea [3]. However, their aglycons differed with respect to the signs of their rotations ($[\alpha]_D$ −24.2° and +18.2°, respectively). The lignan (+)-lariciresinol is fairly widely distributed in plants, but only one of its glycosides, in which the nonphenolic $-CH_2OH$ group is glycosylated (lariciresinol 9'O-β-D-glucopyranoside), has been described [4]. Thus, we are the first to have isolated a phenolic glycoside of (+)-lariciresinol.

The ^1H NMR spectrum of compound (II) was practically identical with that of (I) except for a few signals in the strong field. In the spectrum of (I) there were the signals of four protons (2 H-7, H-8, and H-8') in the 2.7-3.2 ppm region. In the spectrum of (II), the three protons characteristic for the structure of olivil (IIa) resonated in the 3.0-3.6 ppm region – two doublets with J = 14 Hz (2 H-7) and a broadened double doublet of the H-8' proton.

The coupling constant of the anomeric proton (J = 6.5 hz) and the results of hydrolysis by β-glucosidase permitted the conclusion that a β-D-glucopyranoside fragment was attached to a phenolic hydroxyl (C-4 or C-4') in each of the two glycosides. The choice in favor of 4-glycosylation was made on the basis of a comparison of the physicochemical constants with literature information [3-8]. This conclusion was indirectly confirmed by the wide distribution of (-)-olivil 4-glucoside in plants [5-8], including related representatives of the family Oleaceae (Ligustrum japonicum [7] and L. obtusifolium [8]).

It must be mentioned that the structures of the isomeric 4-'glycosides cannot be excluded for (I) and (II). This question can be answered after additional investigations with the aid of ^{13}C NMR spectroscopy, which will permit a determination of the influence of glycosylation on the chemical shifts of the aromatic carbons C-1 (1') and C-3 (3') of the guaiacyl fragments [5, 6, 9].

Compounds (I) and (II) have not previously been isolated from the bark of common lilac, and we are the first to have described (+)-lariciresinol 4-glucoside (I).

EXPERIMENTAL

The spectral characteristics were obtained on varian HA-100D (100 MHz), Gemini 200 (200 MHz), and Bruker WM-250 (250 MHz) instruments – ^1H NMR (δ scale, 0 – TMS), a Varian CH-8 instrument at 70 eV (mass spectra), and a Specord M40 spectrometer (UV). Angles of rotation were determined on a Polamat A polarimeter at 546 nm and were recalculated to 589.3 nm. For enzymatic hydrolysis we used Serva β-glucosidase.

Chromatographic monitoring was carried out by TLC on Silufol UV 254 plates in the chloroform–methanol–water (26:14:3) and chloroform–methanol (4:1) systems and by a PC (for the identification of sugars) in the butanol–acetic acid–water (4:1:2) system. Detection (TLC) was by means of UV 254 nm and with diazotized sulfanilic acid (DSA) in an alkaline medium.

Isolation of the Substances. In the course of a study of phenolic and iridoid compounds [1, 2] from a methanolic extract of common lilac bark, two substances of lignan nature (I) and (II) were isolated in minor amounts. The purification of compounds (I) and (II) was achieved by repeated chromatography on Sephadex LH-20, Woelm polyamide, and silica gel L 40/100 using eluent mixtures of chloroform and ethanol (100:0) → (85:15)).

(+)-Lariciresinol 4-O-β-D-glucopyranoside (I), light yellow amorphous powder with the composition $C_{26}H_{34}O_{11}$, $[\alpha]_D^{21}$ −20.5° (0.29; ethanol λ_{max}^{EtOH} 227, 280 nm. ^1H NMR spectrum (C_5D_5N, 250 MHz, δ: 7.53 (d, 8.7 Hz, H-5'), 7.25 (d, 2 Hz, H'2'), 7.14 (d, 8.7 Hz, H-5), 7.08 (dd, 8.7 and 2 Hz, H-6'), 6.93 (d, 2 Hz, H-2), 6.82 (dd, 8.7 and 2 Hz, H-6), 5.63 (d, 6.5 Hz, H'1"), 5.27 (d, 6 Hz, H-7'), 4.47 (dd, 12 and 2 Hz, H-6"), 4.4-3.9 (m, 5H of glucose + 2H-9 + 2H-9'), 3.70 (s, CH_3O), 3.66 (s, CH_5O), 3.17 (dd, 14 and 5 Hz, H-7), 2.95 (m, H-8), 2.7 (m, H-7, H-8').

The Hexaacetate of (I). Colorless amorphous substance, $[\alpha]_D^{23}$ −15.3° (c 1.2; ethanol), ^1H NMR spectrum ($CDCl_3$, 100 MHz), δ: 3.82 (s, 6H, $2CH_3O$), 2.30 (c, 3H, Ac–arom.), 2.08 (s, 6H, 2Ac), 2.03 (s, 9H, 3Ac).

Enzymatic Hydrolysis of (I); Isolation of (+)-Lariciresinol (Ia). Glycoside (I) (10 mg) was hydrolyzed with β-glucosidase by the usual method. This gave rise to glucose and the aglycon (+)-lariciresinol (Ia): white amorphous powder, $[\alpha]_D^{19}$ + 18.2° (c 0.67; ethanol), λ_{max}^{EtOH} 230, 282 nm. Mass spectrum (m/z, %): 360 (M^+ $C_{20}H_{24}O_6$, 100%), 194(23), 180(19), 175(16), 153(23), 151(52), 150(18), 137(90).

(−)-Olivil 4-O-β-D-glucopyranoside (II). Light yellow amorphous powder with the composition $C_{26}H_{34}O_{12}$, $[\alpha]_D^{21}$ −64.2° (c 0.52; ethanol), λ_{max}^{EtOH} 227, 280 nm. ^1H NMR spectrum (C_5D_5N, 200 MHz), δ: 7.68 (d, 2 Hz, H-2'), 7.57 (d, 8.5 Hz, H-5'), 7.39 (dd, 2 and 8.5 Hz, H-6'), 7.36 (d, 2 Hz, H-2), 7.25 (d, 8.5 Hz, H-5), 7.17 (dd, 2 and 8.5 Hz, H-6), 5.68 (d, 6.5 Hz, H-1"), 5.33 (d, 6 Hz, H-7'), 4.56 (dd, 12 and 2 Hz, H-6"), 4.5-3.9 (m, 5H of glucose + 2H − 9 + 2H-9'), 3.72 (s, $2CH_3O$), 3.60 and 3.40 (doublets, J = 14 Hz, 2H-7), 3.05 (br, dd, 6 and 12 Hz, H-8').

Heptaacetate of (II). Amorphous white powder, $[\alpha]_D^{23}$ −32.8° (c 0.9; ethanol). ^{1}NMR spectrum ($CDCl_3$, 100 MHz), δ: 3.83 (s, 6H, $2CH_3O$), 2.30 (s, 3H, Ac–arom.), 2.10 (s, 6H, 2Ac), 2.04 (s, 9H, 3Ac), 1.80 (s, 3H, Ac).

Enzymatic Hydrolysis of (II); Isolation of (−)-Olivil (IIa). Glycoside (II) (10 mg) was hydrolyzed with β-glucosidase by the usual method. This led to glucose and the aglycon (−)-olivil (IIa); white amorphous powder, $[\alpha]_D^{19}$ −23.9° (c 0.38; ethanol), λ_{max}^{EtOH} 231, 282 nm. Mass spectrum (m/z, %): 376 (M^+ $C_{20}H_{24}O_7$, 7%), 358(3), 196(19), 180(24), 137(100).

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