IRIDOIDS OF THE BARK OF Syringa vulgaris

V. A. Kurkin, G. G. Zapesochnaya,
and N. A. Grinenko

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We have previously reported the isolation from the bark of common lilac of 11 substances of phenolic nature – derivatives of cinnamyl and phenylethyl alcohols, of caffeic acid, and of other compounds [1].

Further investigations of the bark of common lilac have led to the isolation of four iridoids (compounds (I)-(IV)).

Oleuropein (I) – $C_{25}H_{32}O_{13}\cdot H_2O$, $[\alpha]_D^{20}$ –165° (0.5; ethanol); λ_{max}^{EtOH} 232, 282 nm.

Demethyloleuropein (II) – white crystals with the composition $C_{24}H_{30}O_{13}$, mp 145-147°C (from alcohol), $[\alpha]_D^{20}$–157° (0.4; ethanol); λ_{max}^{EtOH} 232, 282 nm. On acetylation it gave an amorphous hexaacetate with the composition $C_{36}H_{42}O_{19}$, mp 71-74°C, which, according to NMR results, contained two aromatic acetoxy groups.

Ligustroside (III) – $C_{25}H_{32}O_{12}\cdot H_2O$, $[\alpha]_D^{20}$ –175° (0.2; ethanol); λ_{max}^{EtOH} 227, 278 nm.

Nüzhenide (IV) – $C_{31}H_{44}O_{17}\cdot 2H_2O$, $[\alpha]_D^{20}$ –150° (0.7; ethanol); λ_{max}^{EtOH} 227, 278 nm.

In the PMR spectra of all four compounds and their full acetates the signals of the protons characteristic for the secoiridoid group [2-7] were readily identified, the basis of their structure being oleoside (V), which is a glucoside of a secoiridoid diacid [3]: broadened singlet at 6.4 ppm (H-1), singlet at 7.7 ppm (H-3), quartet (7 Hz) at 6.2 ppm (H-8), and doublet (7 Hz) at 1.7 ppm (3 H-10).

On saponification with 2% NaOH, compounds (I) and (II) yielded 3,4-dihydroxy-β-phenylethanol (3-hydroxytyrosol), compound (III) gave 4-hydroxy-β-phenylethanol (tyrosol), and compound (V) gave the tyrosol glycoside salidroside (4-hydroxy-β-phenylethyl β-D-glucopoyranoside). The identification of the "alcohol" moieties of the molecule was made by comparison with authentic samples isolated previously [1].

The saponification of compounds (I-IV) also led to an acid (V) which, after methylation with diazomethane and acetylation under the conditions of [3], gave a product that was characterized in each case as dimethyloleoside tetraacetate (VI). Its PMR spectrum ($CDCl_3$) contained the singlet signals of two methoxycarbonyl groups at 3.73 and 3.63 ppm and of four aliphatic acetoxy groups (2.02-2.09 ppm). The signal at 3.63 ppm, which was absent from the spectra of the initial compounds (I-IV), related to the saturated methoxycarbonyl group (at C-6), while the signal at 3.73 related to the unsaturated methoxycarbonyl group at C-4 [2, 4]. Consequently, in compounds (I), (III), and (IV), the PMR spectra of the acetates of which each contained the three-proton singlet at 3.73, the COOH group at C-4 was methylated, while in compound (II) it was free. When the acetate of compound (II) was methylated with diazomethane it was converted into the acetate of compound (I) (and the signal at 3.73 ppm appeared).

It follows from the results obtained that the 7-COOH group of oleoside was esterified by salidroside in compound (IV), by tyrosol in compound (III), and by hydroxytyrosol in compounds (I) and (II). The possibility of the formation of an ester through the phenolic hydroxyls was excluded by the positive reaction with diazotized sulfanilic acid and by the presence of aromatic acetoxy groups in the acetates according to the PMR spectra (δ 2.30 ppm). Consequently, in compounds (I-III) the ester bond was formed by the phenylethanolic alcohol group. So far as concerns compound (IV), in it salidroside has formed an ester bond with oleoside through the glucose hydroxyl at C-6: in the PMR spectrum of (IV) the signal of the glucose methylene group (2 H-6, $^2J = 12$ Hz) was displaced downfield (δ 4.80).

The facts presented permitted the compounds isolated to be identified as follows: I) oleuropein; III) ligustroside; IV) nüzhenide; while for compound (II) the structure of demeth-

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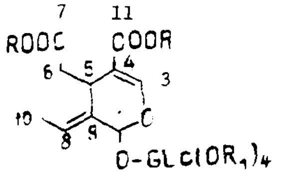
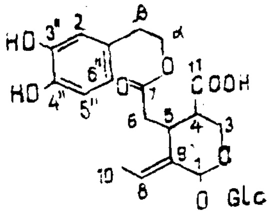
yloleuropein is proposed. The NMR spectra of compounds (I), (III), and (IV) corresponded to those given in the literature [2-7].

We are the first to have isolated compound (II) and (IV) from common lilac bark, (IV) having been isolated previously only from Ligustrum lucidum and L. japonicum L. [2], while demethyloleuropein (II) is a new natural compound.



V $R = R_1 = H$

VI $R = CH_3$; $R_1 = Ac$



II

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COMPONENTS OF Artemisia santolinifolia

F. B. Zhonkhozhaeva, I. D. Sham'yanov,
D. Batsuren, S. Kh. Zakirov,
B. M. Malikov, and A. Abdusamatov

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Artemisia santolinifolia Turcz. is one of the common species of wormwood growing on Mongolian territory. According to the results of an analysis that we have performed by K. S. Rybalko's method [1], this species contains lactones. To isolate the lactones, the epigeal part of Artemisia santolinifolia (5 kg), gathered in the environs of Gurvan-Saikan Ula, South Gobi aimak, in the flowering stage was extracted four times with chloroform (1:5). The evaporated extract was treated with 50% aqueous ethanol. After the precipitate had been removed, the lactones were extracted from the filtrate with chloroform. The dry residue (68 g) obtained by vacuum evaporation was separated on a chromatographic column containing KSK silica gel (ratio 1:30), with elution by hexane—ethyl acetate solvent systems containing increasing concentrations of the latter. As a result of the chromatographic separation, four crystalline substances were isolated (I-IV):

I) $C_{15}H_{20}O_3$, mp 117-118°C (from hexane), M^+ 248; II) $C_{15}H_{20}O_3$, mp 109-110°C (from hexane), M^+ 248; (III) $C_{29}H_{50}O$. mp 140-141°C (from acetone), M^+ 414; (IV) $C_9H_6O_3$, mp 228-230°C (from benzene), M^+ 162.

The IR spectrum of (I) had absorption bands at (cm^{-1}) 1775 (γ-lactone) and 1715 (C=O in a six-membered ring); the UV spectrum had no maxima characteristic of conjugation; in the PMR spectrum of (I) the signals of three methyl groups were characteristic: a doublet at 1.16 ppm, a singlet at 1.26 ppm (methyls on tertiary and quaternary carbon atoms) and a singlet

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