COMPONENTS OF Haplophyllum latifolium

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We have investigated the plant Haplophyllum latifolium (Rutaceae) growing in the environs of Tashkent for its content of alkaloids and other extractive substances. It has been shown previously that the alkaloid skimmianine is present in the leaves (from 0.005 to 0.6% of the dry weight of the plant), in the seeds (0.047%), and in the roots (0.009%); haploperine (evoxine) only in the leaves (0.06%); haplopine in the seeds (0.024%); and dubamine in very small amount in the leaves [1].

In the separation of the combined alkaloids according to their basicities from an acid solution, when its pH was brought to 7, a glycoside deposited, the products of the hydrolysis of which by 10% hydrochloric acid contained D-glucose. The spectra of this glycoside (λ_{max} 230 and 280 nm, ν_{max} 1640, 1590, 1420 cm^{-1}) showed that it belonged to the lignan group.

The mother liquors remaining after the separation of the bases yielded six nitrogen-free substances by column chromatography on alumina with gradient elution (petroleum ether, ether, chloroform).

Substance (I) (0.006% in the leaves, 0.021% in the seeds) had the composition $C_{22}H_{26}O_6$, mp 127-128°C (MeOH or acetone), $[\alpha]_D^{23}$ −35.5° (c 2.14; chloroform); M^+ 386; $\lambda_{max}^{ethanol}$ 232 and 280 nm (log ε 4.20 and 3.79); ν_{max}^{KBr} (cm^{-1}) 1769 (CO of a γ-lactone), 1617, 1599, and 1525 (arom.). NMR spectrum ($CDCl_3$, δ, ppm); multiplet at 6.42-6.61 (6H, arom.), singlet at 3.75 (12H, $4\times OCH_3$), multiplet at 4.00 (CH_2 group in position 4), poorly resolved doublet at 2.88 and broad singlet at 2.48 (6H for H-2, H-3, 2H-5, and 2H-6).

The mass spectrum of substance (I) had the strong ions (m/e) M^+ 386 (100%), 177, 168, 151, and 137, which are characteristic for lignans with a γ-lactone ring. The facts given above correspond to the dimethyl ether of matairesinol (methyl ether of arctigenin), which has been isolated from Ptelea trifoliata [2]. Consequently, substance (I) is (8R, 8'R)-4,4'-dimethylguaialignan-9,9'-olide [3].

Substance (II) (0.015% in the leaves, 0.032% in the seeds) had the composition $C_{10}H_{10}O_2$, mp 137-138°C (ether); sublimes; M^+ 178; $\lambda_{max}^{ethanol}$ 210, 228-232, and 315-317 nm (log ε 3.95, 3.96, and 4.30), giving a bathochromic shift of 50 nm in the presence of alkali (para position of an OH group relative to a second substituent in a benzene nucleus); ν_{max}^{KBr}, cm^{-1} 3390, broad band (associated hydroxyl), 1630 (double bond), 1700 (ester CO), 1608, 1600, 1590 (arom.), 840 and 805 (para-substituted benzene nucleus); $\nu_{max}^{chloroform}$, cm^{-1} 3590 and 3400-3300 (OH group participating in intramolecular hydrogen bonds).

The methylation of substance (II) with dimethyl sulfate (with heating) gave a methyl derivative $C_{11}H_{12}O_2$ with mp 89-90°C [4] in the IR spectrum of which the absorption band of the OH group had disappeared and the maximum of the CO group had shifted by 12 cm^{-1}. The mass spectrum of the initial substance (II) had strong ions (m/e) M^+ 178 (100%), 147 (150%) (M^+-OCH_3), and 119 (40%) [$(M^+-OCH_3)-CO$].

The NMR spectrum ($CDCl_3$) of (II) (δ, ppm) had two doublets at 6.90 and 7.47, J = 10 Hz (4H, arom.), two doublets at 6.46 and 7.75, J = 15 Hz (2H, trans-olefinic protons), and a singlet at 4.08 (OCH_3). In the methyl derivative of (II) there was a six-proton doublet at 3.71 ($2\times OCH_3$). The properties of substance (II) permit it to be considered as methyl p-coumarate (in the cis form) [6], and this was confirmed by the results of a chromatographic comparison with an authentic sample.

Substance (III), mp 135°C, on the basis of its IR spectrum (ν_{max}^{KBr}, cm^{-1}: 3160, 1750, 1720, 1630, 1520, 1270, 1231, 1220, 1160, 1139 and 2850) can apparently be assigned to the guaialignans with a γ-lactone ring.

Substances (IV) with mp 211-212°C, (V) with mp 170-172°C, and (VI) with mp 264°C are being studied.

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