Constituents of *Lilium candidum* L.

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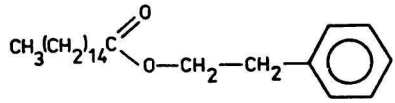
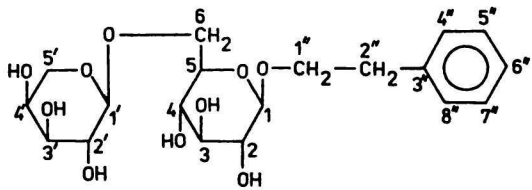
2-Phenylethyl palmitate and 2-phenylethyl α-L-arabinopyranosyl-(1 → 6)-β-D-glucopyranoside were isolated from petals of *Lilium candidum* L. (*Liliaceae*). These compounds, the presence of which has hitherto not been reported in this plant species, were separated by chromatography on silica gel and their structures were deduced from spectral data.

Из лепестков *Lilium candidum* L. (*Liliaceae*) были выделены 2-фенилэтилпальмитат и (2-фенилэтил)-α-L-арабинопиранозил-(1 → 6)-β-D-глюкопиранозид. Эти соединения, нахождение которых в этом виде растений до сих пор не было описано, были хроматографически разделены на силикагеле, и, исходя из спектральных данных, были установлены их структуры.

So far, we reported the presence of organic acids [1], kaempherol [2], alkaloids [3—5], and 3,5,7,4′-tetrahydroxy-8-(3″-methylsuccinyl)flavone [6] in petals of *Lilium candidum* L. This paper concerns the isolation of 2-phenylethyl palmitate (*I*) and 2-phenylethyl α-L-arabinopyranosyl-(1 → 6)-β-D-glucopyranoside (*II*). These compounds have not been reported in this plant material as yet.



I



II

Compound *I* exhibited a maximum in the UV region at $\lambda = 260$ nm, characteristic of an aromatic ring. The IR spectrum also displayed absorptions indicative of an aromatic ring at $\tilde{\nu}/cm^{-1}$: 700, 720, and 755, C—O—C and carbonyl groups at $\tilde{\nu}/cm^{-1}$: 1170 and 1730, respectively. The mass spectrum showed peaks of the molecular radical ion at $m/z = 360.3060$, corresponding to the formula $C_{24}H_{40}O_2$ (calculated 360.3028), fragment ions at $m/z = 104$ (C_8H_8, base peak) characterizing the phenylethyl grouping and other ions indicative of a 2-phenylethyl palmitate fragmentation pattern.

The structure of compound *II* was deduced from the ^1H and ^{13}C NMR spectral data of its peracetyl derivative *III*. The particular signal positions in the ^1H NMR spectrum of compound *III* were assigned by means of the 2D-homocorrelated experiment [7]. Their analyses revealed this compound to be a glycoside consisting of a disaccharide and an aglycone having an aromatic ring. The coupling constant values $J_{1,2}$ up to $J_{4,5}$ (> 8.1 Hz) of the first saccharide unit — hexose — evidence the axial arrangement of the respective protons identifying the carbohydrate as β-D-glucopyranose. Due to acetylation the H-2, H-3, and H-4 proton signals were in average by 1.7 ppm downfield shifted when contrasted with analogous signals of β-D-glucopyranose [8], whilst the H-1, H-6a, and H-6b proton signals were shifted less than 0.25 ppm. Consequently, the β-D-glucopyranose in compound *II* had to be linked through oxygen to carbons C-1 and C-6. The second saccharide unit — pentose — occurred in a pyran form, since the signal positions of H-5′a and H-5′e excluded acetylation at C-5′, which would occur with the furan form. Similarly, acetylation at C-1′ could neither take place, because of its linkage by a glycosidic bond. Analysis of ^1H coupling constants of this unit [8] showed this segment to be α-L-arabinopyranose. Also here a characteristic deshielding of H-2′, H-3′, and H-4′ protons was observed when compared with the free α-L-arabinopyranose [8], and therefore, the structure of 6-*O*-α-L-arabinopyranosyl-β-D-glucopyranoside has been proposed for the saccharide moiety of the molecule.

Further signals in the ^1H NMR spectrum of *III* were due to the aglycone counterpart: an unresolved multiplet at $\delta = 7.2$—7.3 ppm with an integral intensity corresponding to five protons, and a multiplet at $\delta = 2.89$ ppm (2H) in interaction with two magnetically nonequivalent methylene protons at $\delta = 4.12$ and 3.74 ppm are diagnostic of phenylethyl alcohol.

The ^{13}C NMR spectrum of *III* was in line with the deduced structure. Signals of the saccharide moiety of the molecule were assigned by analogy with the chemical shift values of peracetylated derivatives of β-D-glucopyranose and α-L-arabinopyranose [9]. The chemical shift values of the aglycone carbons were in accordance with those of 2-phenylethanol [10], and therefore compound *II* was ascribed the structure of 2-phenylethyl α-L-arabinopyranosyl-(1 → 6)-β-D--glucopyranoside.

Williams and coworkers reported [11] the isolation of an analogous glycoside from *Vitis vinifera* (*Vitaceae*). The difference between both glycosides was found in the saccharide moiety, where arabinofuranose was diagnosed. The same authors isolated further glycosides [12] having 6-*O*-α-L-arabinofuranosyl-β-D--glucopyranoside bound to various aglycones. The chemical shift values of C-2, C-3, and C-4 of arabinose in the ^{13}C NMR spectra of peracetylated derivatives of these substances were close to $\delta = 80$ ppm in contrast to compound *III*, where these values lied at about $\delta = 70$ ppm.

Experimental

The melting points were measured with a Kofler micro hot-stage. Optical rotation of methanolic solutions, IR spectra of substances in KBr pellets and UV spectra of methanolic solutions were taken with the respective Polamat A, Perkin—Elmer, model 477 and UV VIS (Zeiss, Jena) instruments. The electron impact mass spectra were recorded with a Jeol MS 100 S apparatus and the NMR spectra with an AM-300 Bruker spectrometer (at 30 °C, internal reference tetramethylsilane). The coupling constants and chemical shift values of compound *III* in the ^1H NMR spectrum were obtained employing the PANIC simulation program.

Silpearl (Kavalier, Votice) No. 3 and 4 adapted according to [13], silica gel G (according to Stahl, type 60), and Silufol UF 254 and 366 nm were used for column and thin-layer chromatography, respectively.

Isolation of products

Dried flowers (3500 g) were repeatedly macerated with 95 % and 70 % ethanol at room temperature. The macerate (1370 g) was evaporated to dryness, dissolved in 5 % hydrochloric acid, the filtered acid layer was extracted stepwise with petroleum ether, ether, and chloroform; finally, the solution was basified to pH = 11 and extracted with chloroform and chloroform—ethanol ($\varphi_r = 2:1$).

Compounds soluble in petroleum ether (27.5 g) were separated by column chromatography on silica gel No. 3 (900 g) by elution with petroleum ether—ether in various volume ratios (99 : 1, 95 : 5, 90 : 10, 80 : 20, 50 : 50) and with ether. Fractions (150 cm^3 each) were monitored by thin-layer chromatography on Silufol sheets in solvent system petroleum ether—ether ($\varphi_r = 99:1$, 95 : 5) and benzene—acetone ($\varphi_r = 9:1$), detection with sulfuric acid and UV light. Totally 253 fractions were collected. Combined fractions *21* and *22* gave after crystallization from chloroform white substance *I* (697 mg), m. p. = 29—31 °C. IR spectrum, $\tilde{\nu}/cm^{-1}$: 3420, 2920, 2845, 1730, 1170, 755. UV spectrum, λ_{max}/nm ($\log(\varepsilon/(m^2\,mol^{-1}))$): 260 (2.81). Mass spectrum, *m/z*: 256, 239, 104.

Compounds present in the chloroform—ethanol ($\varphi_r = 2:1$) macerate (8.6 g) were separated by column chromatography on silica gel No. 4 (280 g) by elution with benzene —acetone ($\varphi_r = 8.5:1.5$, 1 : 1), acetone, and methanol. Fractions (50 cm^3 each) were monitored by thin-layer chromatography. Totally 128 fractions were collected. Rechromatography of combined fractions *67—116* (3.2 g) on silica gel with chloroform—methanol ($\varphi_r = 8:2$) afforded a white crystalline product *II* (600 mg), m. p. = 185—

187 °C, $[\alpha]$(546 nm, 20 °C, $\varrho = 0.25$ g dm^{-3}, methanol) = −44°. IR spectrum, $\tilde{\nu}$/cm^{-1}: 3520, 3440, 1140, 1045, 1035, 1010, 910, 890, 855.

Peracetylated compound III

Compound *II* (50 mg) dissolved in acetic anhydride and pyridine (0.5 cm^3 each) was left standing for 24 h and the acetylation agent was removed under diminished pressure. The residue was purified by column chromatography on a silica gel No. 4 packed column by elution with chloroform—methanol ($\varphi_r = 9:1$). The crystalline product *III* (26 mg) had m. p. = 148—152 °C, $[\alpha]$(578 nm, 23 °C, $\varrho = 0.335$ g dm^{-3}, acetone) = −7.5°. IR spectrum, $\tilde{\nu}$/cm^{-1}: 3440, 1750, (1260), 1235. ^{1}H NMR spectrum, δ/ppm: 7.2—7.3 (m, 5H$_{arom}$), 5.22 (ddd, 1H, $J_{4',5'e} = 3.2$ Hz, $J_{4',5'a} = 1.7$ Hz, $J_{4',3'} = 3.5$ Hz, H-4′), 5.21 (dd, 1H, $J_{2,3} = 9.8$ Hz, $J_{3,4} = 9.5$ Hz, H-3) 5.11 (dd, 1H, $J_{1',2'} = 7.1$ Hz, $J_{2',3'} = 9.5$ Hz, H-2′), 5.05 (dd, 1H, H-3′), 4.94 (dd, 1H, $J_{4,5} = 10.1$ Hz, H-4), 4.88 (dd, 1H, $J_{1,2} = 8.1$ Hz, H-2), 4.73 (d, 1H, H-1), 4.63 (d, 1H, H-1′), 4.12 (dt, 1H, $J_{1''a,1''b} = 9.6$ Hz, $J_{1''a,2''} = 6.4$ Hz, H-1″a), 3.97 (dd, 1H, $J_{5'e,5'a} = 13.1$ Hz, H-5′e), 3.91 (dd, 1H, $J_{5,6a} = 2.3$ Hz, $J_{6a,6b} =$ = 11.3 Hz, H-6a), 3.86 (ddd, 1H, $J_{5,6b} = 5.9$ Hz, H-5), 3.79 (dd, 1H, H-5′a), 3.74 (dt, 1H, $J_{1''b,2''} = 7.0$ Hz, H-1″b), 3.62 (dd, 1H, H-6b), 2.89 (dd, 2H, H-2″). ^{13}C NMR spectrum, δ/ppm: 170.5, 170.3, 170.3, 170.0, 169.7, 169.5 (6 × $CH_3\underline{C}OO$), 139.8 (C-3″), 129.8 (C-4″, C-8″), 129.0 (C-5″, C-7″), 126.9 (C-6″), 101.8 (C-1 or C-1′), 101.0 (C-1 or C-1′), 73.9 (C-3 or C-5), 73.7 (C-3 or C-5), 72.0 (C-2), 71.1 (C-3′), 69.8 (C-4, C-2′), 70.1 (C-1″), 68.8 (C-4′), 68.2 (C-6), 63.9 (C-5′), 36.5 (C-2″), 20.8, 20.8, 20.7, 20.6, 20.6, 20.5 (6 × $\underline{C}H_3COO$).

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