JATROPHAM 5-*O*-β-D-GLUCOPYRANOSIDE FROM *Lilium candidum* L.

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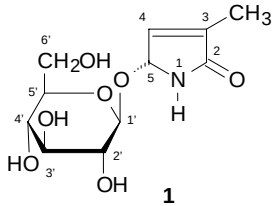
Jatropham 5-*O*-β-D-glucopyranoside [(3-methyl-2-oxo-3-pyrroline-5-yl)-β-D-glucopyranoside] was isolated from the ethanolic extract of the petals of *Lilium candidum* L.
Key words: *Lilium candidum* L.; *Liliaceae*; Jatropham 5-*O*-β-D-glucopyranoside.

From the petals and the bulbs of *Lilium candidum* L. we have isolated pyrroline compounds jatropham, ethyljatropham and citraconic acid imide[1,2] and in previous works we also described isolation of new dimeric pyrroline and pyrroline-pyrrolidine types of alkaloids from this plant species[3–5]. Now, we report the isolation of monomeric pyrroline glycoside – jatropham 5-*O*-β-D-glucopyranoside **1**, from the petals of *Lilium candidum* L.

EI mass spectrum does not show any molecular ion and a base peak is formed by the



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very stable jatropham ring at *m/z* 97. Other intensive ions at *m/z* 31, 43, 60 and 73 are typical for sugars decomposed under EI. In FAB mass spectrum there is an $[M + H]^+$ ion at *m/z* 276 accompanied by $[M + Na]^+$ at *m/z* 298. Protonized aglycone forms the most intensive peak of the spectrum followed by aglycone ion at *m/z* 115 and 114, respectively.

^1H and ^{13}C NMR spectra in CD_3OD indicate glycoside structure containing one hexose unit and heterocyclic aglycone. Detailed analysis of the proton and ^{13}C NMR

spectra proved the presence of β-glucopyranose ring and jatropham structure for aglycone. Jatropham 5-*O*-β-D-glucopyranoside **1** was isolated earlier from the bulbs of *Lilium hansonii*[6] and *Lilium medeoloides*[7]. The additional ^{1}H NMR measurement of our compound in C_5D_5N – for direct comparison purpose with literature NMR data[6] proved the structure identity.

EXPERIMENTAL

The melting point was measured on a Kofler micro hot-stage. The UV and IR spectra were recorded with the respective Specord UV VIS (Zeiss, Jena), and Perkin–Elmer, model 477 spectrophotometers. Mass spectra were measured on the ZAB-EQ mass (VG Organic, Manchester, U.K.) using both electron impact (EI) and fast atom bombardment (FAB) with a glycerol matrix. EI high resolution spectrum was obtained at a resolving power 10 000.

NMR spectra were measured on NMR spectrometer Varian UNITY-500 (^{1}H at 500 MHz, ^{13}C at 125.7 MHz). Chemical shifts are given in ppm (δ-scale), coupling constants (*J*) in Hz. Proton 2D-COSY spectrum was used for the assignment of spin-coupled protons. The APT ^{13}C NMR spectrum allowed to distinguish carbon signals according to the number of directly bonded protons.

For TLC Silufol UV 254, 366 silica gel plates were used. Silica gel No. 4 (Silpearl, Kavalier Votice, Czech Republic) modified according to ref.[8] were used for CC.

Isolation of Jatropham 5-*O*-β-D-Glucopyranoside

Petals from *Lilium candidum* L. (6.8 kg) were extracted with ethanol. After removal of solvent under reduced pressure, the dark residue was divided between butyl alcohol and water (1 : 1). Butanolic layer was evaporated under reduced pressure and the residue (60 g) was separated on silica gel column. Fractions (150 ml) were controlled by TLC. Total 480 fractions were collected.

Fractions 216–227 afforded 650 mg (0.01% calculated according to initial quantity of material) of jatropham glucoside **1**, m.p. 183–185 °C ($CHCl_3$–MeOH), $[\alpha]_D$ –22° (methanol, c 0.25). UV spectrum (methanol): 240 nm, shoulder. IR spectrum (KBr): 3 400, 2 930, 2 895, 1 690, 1 650, 1 430, 1 370, 1 345, 1 240, 1 170, 1 130, 1 070, 1 030, 980, 950, 900, 825 cm^{-1}. EI mass spectrum, *m/z* (%): 97 (100%, C_5H_7NO, found 97.0491, calculated 97.0528), 73 (48), 60 (38), 43 (27), 31 (27). FAB mass spectrum, *m/z* (%): 276 (30) $[M + H]^+$, 298 (60) $[M + Na]^+$, 115 (100) $[aglycone + H]^+$, 114 (64) $[aglycone]^+$. ^{1}H NMR spectrum (C_5D_5N): 9.26 b, 1 H (NH); 6.76 m, 1 H, *J*(4,5) = *J*(4,CH_3) = *J*(4,NH) = 1.5 (H-4); 5.89 m, 1 H, *J*(5,4) = *J*(5,CH_3) = *J*(5,NH) = 1.5 (H-5); 1.84 t, 3 H, *J*(CH_3,4) = *J*(5,CH_3) = 1.5 (CH_3); 5.12 d, 1 H, *J*(1′,2′) = 7.8 (H-1′); 4.16 dd, 1 H, *J*(2′,1′) = 7.8, *J*(2′,3′) = 8.9 (H-2′;); 4.25 dd, 1 H, *J*(3′,2′) = 8.9, *J*(3′,4′) = 8.9 (H-3′); 4.16 dd, 1 H, *J*(4′,3′) = 8.9, *J*(4′,5′) = 9.6 (H-4′); 3.96 ddd, 1 H, *J*(5′,4′) = 9.6, *J*(5′,6a′) = 2.4, *J*(5′,6b′) = 6.1 (H-5′); 4.53 dd, 1 H, *J*(6a′,5′) = 2.4, *J*(6a′,6b′) = 11.9 (H-6a′); 3.55 dd, 1 H, *J*(6b′,5′) = 6.1, *J*(6b′,6a′) = 11.9 (H-6b′). ^{1}H NMR spectrum (CD_3OD): 6.66 p, 1 H, *J*(4,5) = *J*(4,CH_3) = 1.5 (H-4); 5.43 p, 1 H, *J*(5,4) = *J*(5,CH_3) = 1.5 (H-5); 1.74 t, 3 H, *J*(CH_3,4) = *J*(5,CH_3) = 1.5 (CH_3); 4.36 d, 1 H, *J*(1′,2′) = 7.8 (H-1′); 3.09 dd, 1 H, *J*(2′,1′) = 7.8, *J*(2′,3′) = 9.2 (H-2′); 3.25 dd, 1 H, *J*(3′,2′) = 9.2, *J*(3′,4′) = 8.8 (H-3′); 3.13 dd, 1 H, *J*(4′,3′) = 8.8, *J*(4′,5′) = 9.7 (H-4′); 3.20 ddd, 1 H, *J*(5′,4′) = 9.7, *J*(5′,6a′) = 2.2, *J*(5′,6b′) = 6.3 (H-5′); 3.80 dd, 1 H, *J*(6a′, 5′) = 2.2, *J*(6a′,6b′) = 12.0 (H-6a′); 3.55 dd, 1 H, *J*(6b′,5′) = 6.3, *J*(6b′,6a′) = 12 (H-6b′). ^{13}C NMR spectrum (CD_3OD): 172.5 (C-2), 137.47 (C-3), 140.61 (C-4), 86.56 (C-5), 10.36 (CH_3), 103.41 (C-1′), 74.83 (C-2′), 77.93 (C-3′), 71.51 (C-4′), 78.38 (C-5′), 62.71 (C-6′).

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