

Derivatives of pyrroline in *Lilium candidum* L.

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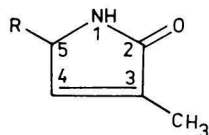
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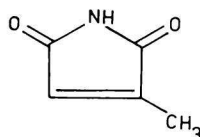
Dedicated to Professor J. Tomko, DrSc., in honour of his 70th birthday

Ethyljatropham, jatropham, and citraconimide were isolated from *Lilium candidum* L.; they were identified by spectral methods.

In our previous papers on constituents from petals of *Lilium candidum* L. we reported the presence of succinic, itaconic, and fumaric acids, methyl *R*-(+)-succinate, a mixture of C₂₀—C₃₀ fatty acids [1, 2], a flavone alkaloid lilaline [3], jatropham [4], substituted dimeric γ -lactams 1-(3'-methyl-2'-oxo-5'-pyrrolidinyl)-3-methyl-3-pyrrolin-2-one, 1-(2'-oxo-5'-pyrrolidinyl)-3-methyl-3-pyrrolin-2-one, and 1-(3'-methyl-2'-oxo-5'-pyrrolidinyl)-5-hydroxy-3-methyl-3-pyrrolin-2-one [5], kaempferol, 8-(3-methylsuccinyl)kaempferol [6], 2-phenylethyl α -L-arabinopyranosyl-(1 \rightarrow 6)- β -D-glucopyranoside and 2-phenylethyl palmitate [7]. Now, we wish to report on isolation and identification of ethyljatropham (*I*) from petals and jatropham (*II*) and citraconimide (*III*) from bulbs of *Lilium candidum*. The plant material was exhaustively extracted by dilute ethanol and worked up as detailed in Experimental.



I R = OC₂H₅
II R = OH



III

Compound *I* of molecular formula C₇H₁₁NO₂ revealed in its infrared spectrum a band corresponding to a carbonyl group; the ¹H NMR spectrum showed additional signals for a C₂H₅O grouping when contrasted with that of jatropham.

pham (*II*) [4]. In ^{13}C NMR spectrum of *II* the C-5 signal appeared [4] at $\delta = 79.2$, whilst that for compound *I* was shifted to $\delta = 85.5$ thus confirming the presence of an ethoxy group at C-5.

Compound *II* ($\text{C}_5\text{H}_7\text{NO}_2$) was found to be identical with jatropham (5-hydroxy-3-methyl-3-pyrrolin-2-one) isolated previously from petals; its occurrence in bulbs has not been described as yet.

Compound *III* ($\text{C}_5\text{H}_5\text{NO}_2$) disclosed in its mass spectrum peaks indicating an elimination of CO and CONH from the molecular radical ion at $m/z = 83$ and 68, respectively. Fragment $m/z = 68$ lost another molecule of CO to produce species $\text{C}_3\text{H}_4^{+\bullet}$ ($m/z = 40$). A molecule of water was split off of the molecular radical ion (enol form) to give the little intense peak of an ion at $m/z = 93$. The ultraviolet spectrum ($\lambda = 280$ and 310 nm) indicates the presence of conjugated carbonyl groups. These findings are in agreement for the structure of citraconimide.

Experimental

The melting points were determined with a Kofler micro-hot stage, the ultraviolet spectra were measured with a spectrophotometer UV—VIS (Zeiss, Jena), the infrared spectra with a model 477 (Perkin—Elmer) in KBr pellets. The mass and NMR spectra were recorded with spectrometers MS 100 D (Jeol), ZAB-EQ (VG Analytical, Manchester) at 70 eV ionization energy and AM-300 (Bruker); in deuteroacetone with tetramethylsilane as an internal standard, respectively. Silica gel No. 3 and 4 (Silpearl, Kavalier, Votice) conditioned according to [8] were employed for column chromatography, Kieselgel G, type 60 according to Stahl and Silufol UV254 and UV366 for thin-layer chromatography.

Petals of *Lilium candidum* L. dried at room temperature (3500 g) were exhaustively macerated with 70 % ethanol, the extract was concentrated under reduced pressure to dryness. The residue (1370 g) was dissolved in 5 % hydrochloric acid and the solution was successively extracted with petroleum ether, ether, and chloroform. The acid layer alkalinized with 10 % KOH and 10 % NaHCO_3 ($\phi_r = 1:1$) to pH 11 was extracted with chloroform and chloroform—ethanol ($\phi_r = 2:1$).

The chloroform extract from the alkaline medium (2 g) was crystallized to give a colourless substance (m.p. = $47\text{--}49^\circ\text{C}$, 2.75 mg) identified as ethyljatropham from the following spectral data: Mass spectrum, m/z : $\text{M}^{+\bullet}$ 141.0803, M_r calc. for $\text{C}_7\text{H}_{11}\text{NO}_2$ 141.0789. ^1H NMR spectrum, δ : 6.65 (dq, 1H, H-4, $J_{4,5} = 1.8$ Hz, $J_{\text{CH}_3,4} = 1.7$ Hz), 5.35 (dq, 1H, H-5, $J_{\text{CH}_3,5} = 1.4$ Hz), 3.55 (m, 2H, CH_2), 1.84 (dd, 3H, $\text{CH}_3\text{—C-3}$), 1.18 (t, 3H, $J_{\text{CH}_3\text{CH}_2} = 7.1$ Hz). ^{13}C NMR spectrum, δ : 175.7 (C-2), 141.1 (C-4), 138.0 (C-3), 85.5 (C-5), 63.4 (CH_2), 15.7 (CH_3CH_2), 10.5 ($\text{CH}_3\text{—C-3}$).

Bulbs of *Lilium candidum* L. (20 kg) were macerated stepwise with 96 and 70 % ethanol ($3 \times 80 \text{ dm}^3$) and the extracts concentrated under reduced pressure to 5 dm^3 were freeze-dried at -40°C . The dry extract (1042 g) dissolved in 5 % hydrochloric acid and

extracted successively with petroleum ether, ether, and chloroform was then made alkaline with 10 % KOH and 10 % NaHCO_3 ($\varphi_r = 1:1$) to pH 11 and extracted with chloroform and chloroform—ethanol ($\varphi_r = 2:1$).

The chloroform layer obtained after alkalization (5.64 g) was chromatographed over silica gel No. 3 (150 g) with chloroform—methanol ($\varphi_r = 9.9:0.1, 9.5:0.5, 9:1$, and $1:1$) and finally with methanol. 112 Fractions (150 cm^3 each) were collected, their content was monitored by thin-layer chromatography (solvent systems chloroform—methanol, $\varphi_r = 9:1, 8:2$) and detected by UV_{254} light.

Fraction 7 afforded a compound (6 mg) identical with ethyljatropham. Fractions 29—35 gave after a work-up a crystalline compound (25 mg), which was proved to be identical with jatropham.

The mixture of compounds present in the ethereal extract (40.2 g) was chromatographed over silica gel (550 g) with benzene—acetone ($\varphi_r = 9:1$). The fractions (150 cm^3 each) were monitored by thin-layer chromatography in benzene—acetone ($\varphi_r = 9:1, 8:2, 6:4$, and $1:1$) and chloroform—methanol ($\varphi_r = 9:1$), detection with UV_{254} light after spraying with concentrated sulfuric acid in ether. Totally 347 fractions were collected, which were combined according to their R_f values.

Rechromatography of fractions 231—347 afforded a substance (8 mg) with m.p. = $105\text{--}106^\circ\text{C}$ identified according to the following spectral data as citraconimide. UV spectrum, $\lambda_{\text{max}}/\text{nm}$ (MeOH): 228, 280, 310. Mass spectrum, m/z ($I_r/\%$): M^{++} 111.0320, M_r calc. for $\text{C}_5\text{H}_5\text{NO}_2$ 111.0320 (100), $\text{M} - 18, 93$ (3), $\text{M} - \text{CO}, 83$ (13), $\text{M} - \text{CONH}, 68$ (55), $68 - \text{CO}, 40$ (72).

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