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NIC-1-LACTONE, A MINOR STEROIDAL CONSTITUENT OF *NICANDRA PHYSALOIDES* (SOLANACEAE)

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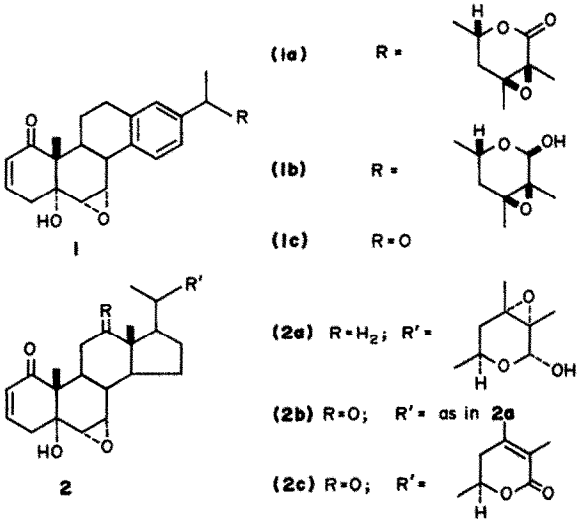
Key Word Index—*Nicandra physaloides*; Solanaceae; aromatic rang D; steroid; withanolides; Nic-1-lactone.

We wish to report on the isolation and characterization of Nic-1-lactone $C_{28}H_{32}O_6$, **1a**, mp 230–232°, a minor steroidal constituent of *Nicandra physaloides* (Solanaceae), the only plant known [1, 2] to contain steroids with an aromatic D ring. The compound was found to be identical with 6α,7α:24,25-diepoxy-5-hydroxy-17(13→18)abeo-5α-ergosta-2,13,15,17-tetraen-1-one-26,22-lactone, obtained [3] by oxidation with chromium trioxide of the lactolic C-26 hydroxyl group in Nic-1 (**1b**), the major steroidal component of *N. physaloides*.

The Nic constituents may be divided into two groups: (a) those with the usual steroid skeleton as encountered in Nic-3 (**2a**), Nic-7 (**2b**) [1] and withanicandrin (**2c**) [4]; (b) those with a rearranged skeleton, as found in Nic-1 (**1b**) [1, 2], obtained by expansion of ring D through inclusion of the C-13 methyl and subsequent aromatization. Most Nic constituents characterized so far possess an ergostane type side chain which has undergone oxidative processes leading to the closure of a six membered epoxy-lactol. In several compounds this side chain has gradually lost most of its carbon atoms, until a two carbon fragment remains as present in Nic-10 (**1c**) [1]. The usual unsaturated six membered ring lactone, characteristic for the majority of the withanolides [4], is found in only one compound withanicandrin (**2c**), occurring in this plant [4].

In our opinion, the epoxy-lactol system present in Nic-1-lactone (**1a**) is formed in Nature by oxidation of the lactolic hydroxyl group present in Nic-1 (**1b**) and not by epoxidation of the Δ^{24} double bond of an unsaturated lactone such as that present in the side chain of withanicandrin (**2c**). This assumption is based on the fact that all the solanaceous plants which produce withanolides, Nic-derivatives and physalins, possess enzymes which can catalyse the epoxidation of isolated double bonds, or double bonds in allylic systems, but which cannot epoxidize double bonds in α,β-unsaturated carbonyl systems.



EXPERIMENTAL

N. physaloides was raised in the nursery of the Volcani Center, Bet Dagon, Israel (introduction No. 20-707), from seeds received from Pretoria, South Africa (No. M-71-384). It is interesting to note that populations of plants raised from seeds received from India (Pondicherry) did not contain compound **1a**.

The isolation was done according to the described procedure [4]. The first fractions containing Nic-1, obtained by chromatography on a column of Si gel H, were contaminated by a product possessing a slightly higher R_f value. Separation was achieved by PLC on Si gel PF_{254}, 1 mm thickness, 40 cm length, developed with C_6H_6–EtOAc (1:4). The product possessing the higher R_f value (accounting for only 5% of the total amount of Nic-1) crystallised from Me_2CO–hexane, mp 230–232°, undepressed on admixture with 6α,7α:24,25-diepoxy-5-hydroxy-17(13→18)abeo-5α-ergosta-2,13,15,17-tetraen-1-one-26,22-lactone [3]. All physical constants and spectral data were superimposable.

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NEUE INHALTSSTOFFE AUS *FELICIA*-ARTEN

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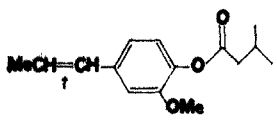
Key Word Index—*Felicia* species; Compositae; eugenol derivative; isocoumarin derivative; tetraenester.

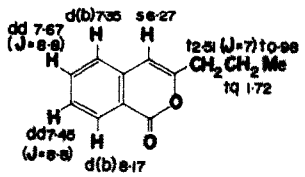
Pflanzen und Herkunft. Felicia wrightii Hilliard et Burtt, *F. uliginosa* (Wood et Evans) Gray, Prof. Dr. J. Grau, Botanisches Institut der Universität München, Herbarbelege ebenda.

Bisherige Untersuchungen. ca 10 andere *Felicia*-Arten ergaben Matricaria- und Lachnophyllumester bzw. keine Acetylenverbindungen [1].

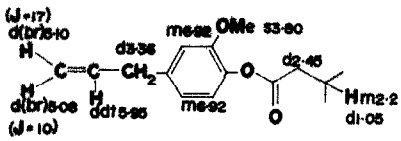
Ergebnisse. Die Wurzeln von *F. wrightii* enthalten das bereits bekannte Isoeugenolderivat (1) [2] und ein neues Isocumarinderivat, dem die Struktur (2) zukommt. Die oberirdischen Teile ergaben neben (1) den bisher nicht isolierten Ester (3):



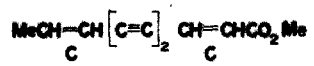
(1)



(2)



(3)



(4)

Die Wurzeln von *F. uliginosa* enthalten Matricariaester (4) und den bisher nicht bekannten Tetraenester (5), der den Acetylenverbindungen wahrscheinlich biogenetisch nahe steht:

$$\underset{t\ 1.01\ (J=7)}{H_3C}\underset{dq\ 2.13}{CH_2}[CH{=}CH]_4\underset{m\ 5.7-6.6}{CH_2}\underset{m\ 2.2}{CH_2}\underset{t\ 2.33\ (J=7)}{CH_2}\underset{(J=7.7)\quad tt\ 1.74}{CO_2Me}\quad\underset{s\ 3.90}{}\qquad (5)$$

Botanische Gesichtspunkte sprechen für eine Aufteilung der Gattung *Felicia* in eine basale Gruppe und mehrere abgeleitete Sektionen [3]. Die zur basalen Gruppe gehörenden Arten (*Felicia filifolia* Burtt. Davy = *Diplopappus filifolius* DC; *F. fruticosa* = *Diplopappus fructicosa*; *F. macrorhiza* = *Fresenia scaposa* DC; *F. tenella* Nees. *F. uliginosa* Gray) enthalten Acetylenverbindungen, während die abgeleiteten Arten (*F. ovata* (Thunb.) Compton, *F. echinata* Less., *F. aethiopica* (Burn.) Bol. et Wolley Dod; *F. amelloides* (L) Voss., *F. minima* = *F. bergeriana* O. Hoffm., *F. heterophylla* = *Charieis heterophylla*; *F. wrightii* Hilliard et Burtt.) keine Acetylenverbindungen enthalten. Man kann somit annehmen, dass letztere die Fähigkeit, derartige Verbindungen aufzubauen, verloren haben.

EXPERIMENTELLES

UV: in E_2O, Beckman DK 1; *IR*: in CCl_4, Beckman IR 9; NMR: in $CDCl_3$, Bruker WH 270; TMS als innerer Standard, δ-Werte; MS: Varian MAT 711 mit Datenverarbeitung. Die zerkleinerten Pflanzenteile extrahierte man bei RT mit Et_2O–Petroläther (=PÄ) 1:2, trennte die erhaltenen Extrakte durch