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N^1,N^{10}-Ditigloylspermidine, a novel alkaloid from the seeds of *Ipomoea nil**

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A novel spermidine alkaloid, *N*^{1},*N*^{10}-ditigloylspermidine (**1**), has been isolated from the seeds of *Ipomoea nil* (L.) Roth (Convolvulaceae). Structural elucidation was achieved by EIMS, HRMS, ^{1}H NMR, and ^{13}C NMR spectroscopy.

Ipomoea nil (L.) Roth [syn.: *Pharbitis nil* (L.) Choisy], a herbaceous climber of putative neotropical origin but of pantropical distribution (Austin et al. 2001) is one of the famous and often cultivated ornamental Morning Glories (Convolvulaceae). The occurrence of resin glycosides in the seeds of this species is well documented (Kawasaki et al. 1971 and literature therein). However, to date no reports on alkaloids have been published.

In our present study, the alkaloid fraction obtained from the seeds of *I. nil* collected in Tanzania contained one major compound. Structural elucidation of **1** was achieved by EIMS, HRMS, ^{1}H NMR, and ^{13}C NMR spectroscopy. The EIMS displayed a molecular ion peak at m/z 309, corresponding to a molecular formula of $C_{17}H_{31}N_3O_2$ (HRMS). Characteristic fragments at m/z 83 (base peak), 197, 183, 169, and 140 in the EIMS suggested the compound to be a derivative of spermidine substituted by angelic or tiglic acid.

Table: ^{1}H and ^{13}C NMR data of compound 1 (CD_3OD, ppm)

Carbon	δ_H (Hz)	δ_C
2	3.28 t (6.0)	38.5
3	1.73 quint (6.0)	30.2
4	2.61 br s	48.8
6	2.61 br s	50.3
7	1.55 m	28.3
8	1.55 m	27.9
9	3.24 t (6.0)	40.5
1′		172.5
2′		133.1^a
3′	6.37 qq (1.3, 5.4)	131.6^b
4′	1.75 d (7.0)	12.5
5′	1.82 s	13.9
1″		172.5
2″		133.2^a
3″	6.37 qq (1.3, 5.4)	131.8^b
4″	1.75 d (7.0)	12.5
5″	1.82 s	13.9

$^{a, b}$ interchangeable

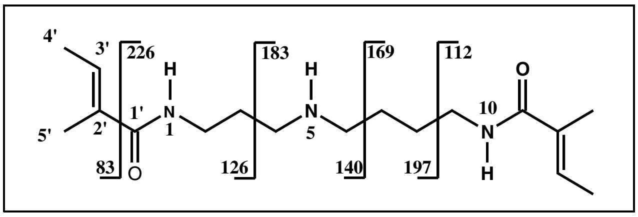

Fig.: Mass fragmentation pattern of compound **1**

The ester side chain was assigned on the basis of diagnostic ^{1}H NMR signals (Table): a quartet of quartets at δ 6.37 (J = 1.3, 5.4 Hz), and a pair of methyl signals at δ 1.75 (d, J = 7.0 Hz) and δ 1.82 (s), together with the strong mass spectral peak at m/z 83. With regard to the intensity of the signals in the ^{1}H NMR spectrum, the acyl residue had to be present twice in the molecule. The remaining ^{1}H NMR signals turned out to be in accordance with the signals derived from the spermidine moiety of *N*^{1},*N*^{10}-bis(dihydrocaffeoyl)spermidine isolated from *Iochroma cyaneum* (Lindl.) M. L. Green, Solanaceae (Sattar et al. 1990).

Additional support for the proposed structure of **1** was contributed by ^{13}C NMR measurements. The ^{13}C NMR spectrum (Table) displayed signals at δ 172.5 (carbonyl moiety), δ 133.1 and δ 133.2 (quaternary olefinic carbons, C-2′/C-2″), respectively, as well as δ 131.6 and δ 131.8 (C-3′/C-3″), respectively. The ^{13}C NMR shifts of the methyl groups at δ 12.5 and 13.9 are diagnostic for tiglic acid, whereas the isomeric angelic acid is characterized by values at δ 15 and 20, respectively (Röder et al. 1991, Mao et al. 2005). Subsequently, **1** should be *N*^{1},*N*^{10}-ditigloylspermidine.

The GC-MS of the crude alkaloid fractions of the seeds, immature fruits, and stems displayed apart of **1** (m/z 309, RI 2612) altogether seven minor congeners. Most of them are isomers of **1** (m/z 309, RI 2564, 2589, 2622, 2685, 2688). In one compound (m/z 311, RI 2586) one angeloyl or tigloyl moiety might be replaced by 2-methylbutyric acid, whereas the last compound (m/z 323, RI 2650) according to its GC-MS fragmentation pattern should be a homologous spermidine derivative identical with the *N*^{1},*N*^{11}-disubstituted *sym*-homospermidine.

Amides of the polyamine spermidine bearing aliphatic or aromatic-aliphatic acyl residues are widely distributed in the plant kingdom (Bienz et al. 2002). In most cases the acyl moieties represent hydroxycinnamic acids. Nevertheless, **1**, as a novel natural compound, displayed individual structural features not being observed so far. Finally, it should be pointed out that **1,** as well as any of the other above-mentioned related compounds, could not be detected in the herbal material of *I. nil* from Ecuador. Unfortunately, seeds from this neotropical provenance were not available for investigation.

Experimental

1. Equipment

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker AC 400 NMR spectrometer with TMS as internal standard. EIMS and HRMS spectra were obtained using Varian MAT CH_7A, or Finnigan MAT 711 mass spectrometer, respectively.

2. Plant material

The seeds of *Ipomoea nil* (L.) Roth were collected on the island of Zanzibar, Republic of Tanzania, Africa, in 1990. The epigeal vegetative parts from Ecuador have been collected in the wild near Guayaquil in 1991. Voucher specimens are deposited at the Institut für Pharmazie, Pharmazeutische Biologie, Freie Universität Berlin.

3. Extraction and isolation

Ground seeds of *Ipomoea nil* (50 g) were extracted with MeOH (70%). After evaporation, the extract was acidified (2% aq. tartaric acid) and partitioned between H_2O and organic solvents (petrol, CH_2Cl_2, EtOAc). The aq. phase was then made alkaline (10% aq. NH_3) and extracted with $CHCl_3$−i-PrOH (3 : 1; v/v) to yield 10 mg of pure **1**.

N^1,N^{10}-Ditigloylspermidine (**1**)

Colorless gum. EIMS m/z (%): 309 $[M]^+$ (5), 282 (1), 226 (1); 197 (18), 183 (48), 169 (95), 140 (60), 83 (100), 55 (42); HRMS m/z: 309.24153 ($C_{17}H_{31}N_3O_2$, 309.24163 of calcd), 197.16549 ($C_{11}H_{21}N_2O$, 197.16539 of calcd), 183.14911 ($C_{10}H_{19}N_2O$, 183,14974 of calcd), 169.13416 ($C_9H_{17}N_2O$, 169.13409 of calcd), 140.10749 ($C_8H_{14}NO$ 140.10754 of calcd), 83.049691 (C_5H_7O 83.04969 of calcd); ^{1}H NMR and ^{13}C NMR data: Table.

4. GC-MS-Analysis

Extracts have been prepared as described above. The GC-MS system consisted of a Carlo Erba 5160 GC equipped with a 30 m × 0.32 mm fused silica capillary column coated with the methyl silicone stationary phase DB 1 (J & W Scientific, California). Helium was used as carrier gas. Conditions during split injection: injector 250 °C, split 1 : 20, temperature program 70−300 °C, 6 °C/min. The capillary column was directly coupled to the quadrupole mass spectrometer Finnigan MAT 4515. Retention indices (RI) have been calculated according to Kováts (1958).

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[*] Part 19 in the series "Phytochemistry and Chemotaxonomy of the Convolvulaceae". For part 18 see Jenett-Siems et al. [Phytochemistry, 66: 1448−1464].

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