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SOLANOPUBAMIDES A AND B, TWO FURTHER STEROIDAL ALKALOIDS FROM *SOLANUM PUBESCENS*

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Key Word Index—*Solanum pubescens*; Solanaceae; aerial parts; 3β-formylamino-5α,22αH,25βH-solanidan-23β-ol; solanopubamide A; 3β-*N*-acetylamino-22αH,25βH-5α,22αH,25βH-solanidan-23β-ol; solanopubamide B.

Abstract—Two new steroidal alkaloids, solanopubamides A and B, were isolated from the aerial parts of *Solanum pubescens*. Their structures were elucidated as 3β-formylamino-5α,22αH,25βH-solanidan-23β-ol (solanopubamine A) and 3β-acetylamino-5α,22αH,25βH-solanidan-23β-ol (solanopunamide B) by spectral and chemical methods.

INTRODUCTION

In continuation of our former communication [1] regarding the isolation and structural elucidation of a new steroidal alkaloid solanopubamine 3β-amino-5α,22αH,25βH-solanidan-23β-ol (**1**) from the aerial parts of *Solanum pubescens*, we now report the characterization of two further new steroidal alkaloids solanopubamide A (**2**) and B (**3**) from the same plant.

RESULTS AND DISCUSSION

Solanopubamide A analysed for $C_{28}H_{46}N_2O_2$. The $[M]^+$ at m/z 442 is 28 mu larger than that of **1**. The base peak (m/z 166) and an other fragment ion at m/z 220 indicated a solanidane skeleton with a hydroxyl group (ν_{max}^{KBr} 3550 cm^{-1}) on ring F as in **1** [2]. Its IR spectrum also showed absorption bands ν_{max}^{KBr} 3275, 1660 and 1540 cm^{-1} characteristic of a monosubstituted primary amide group [3]. The two signals in the ^{1}H NMR spectrum of **2** at δ8.12 (*d*, 1H) and 3.85 ($W_{1/2}$ = 22 Hz, 1H) were assigned to the formyl proton and the proton on the carbon bearing the *N*-formyl group, respectively, by analogy with *N*-formyl concurchine [4]. The remaining lowfield signal at δ5.42 (*d*, 1H, J = 7 Hz) was assigned to H–C–NH– at position 3 as in solanopubamine diacetate **6**. [1]. Hence, **2** is the *N*-formyl derivative of **1**. The presence of a carbonyl band at ν_{max}^{KBr} 1660 cm^{-1} in its IR spectrum and the signal at δ8.12 in the ^{1}H NMR spectrum suggested the presence of an *N*-formyl group in **2**; acid hydrolysis afforded **1**, indicating hydrolysis of the formamido group in **2**. The presence of this group was further supported by the ^{13}C NMR data from the downfield signal at δ160.3 for the carbonyl group. Thus, the structure of **2** was shown to be 3β-*N*-formylamino-5α,22αH,25βH-23β-ol.

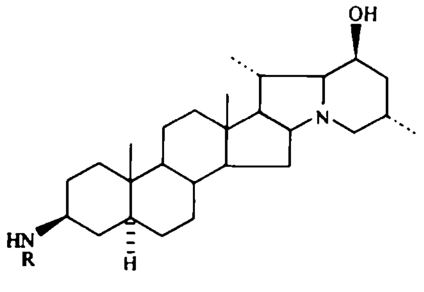
Solanopubamide B (**3**) analysed for $C_{29}H_{48}N_2O_2$. The $[M]^+$ at m/z 456 for **3** is 14 and 42 mu larger than that of **2** and **1** respectively. The base peak at m/z 166 and the fragment ions at m/z 220, 412 $[M-44]^+$ and 385 $[M-71]^+$ are similar to **1** and **2**. The ^{1}H NMR spectrum of **3** is similar to that of **2**. The absence of a signal at δ8.12 and the presence of an *N*-acetyl group, accounting for the monosubstituted amide frequencies in the IR spectrum (ν_{max}^{KBr} 3350, 1660 and 1550 cm^{-1}) and the difference in the M_r. That **3** was the *N*-acetyl derivative of **1** was also supported by acid hydrolysis of **3** when **1** was obtained; the identity of the product was confirmed by co-TLC and mmp. Thus the structure of **3** was shown to be 3β-*N*-acetylamino-5α,22αH,25βH-solanidan-23β-ol.

Only a few *N*-acetyl alkaloids have been isolated from nature. This is the first report of *N*-formyl and *N*-acetyl steroidal alkaloids from the genus *Solanum*. Alkaloid **3** was obtained in both methanol and acetic acid extracts and thus can be regarded as naturally occurring.

EXPERIMENTAL

All mps are uncorr. ^{13}C NMR were measured at 25.14 MHz, ^{1}H NMR at 270, 99.5, 199.5 and 100 MHz.

Extraction and isolation. Leaves and stems of *S. pubescens*



1 R = H
2 R = CHO
3 R = Ac

Willd. were collected at Nagarjuna Sagar in Andhra Pradesh, in February 1982. Air dried, powdered material (5 kg) was extracted with hexane and MeOH successively. The concd MeOH extract was separated into phenolic and non-phenolic parts with neutral $Pb(OAc)_2$. The non-phenolic part, after deleading, was refluxed with 10% HCl at 100° for 2 hr, cooled, basified with 10% NaOH soln to pH 8, filtered and washed with H_2O. The brown residue was chromatographed on silica gel using C_6H_6, C_6H_6–Me_2CO (9:1 and 17:3) to yield compounds **2** and **3**.

Compound **2** recrystallized from MeOH as white needles, mp 209–210°, yield 20 mg. (Found: C, 76.07; H, 10.34; N, 6.35; $C_{28}H_{46}N_2O_2$ requires C, 76.01; H, 10.39; N, 6.33%.) $[\alpha]_D = +26.1°$ ($CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3550 (w), 3275 (m), 2900 (s), 2850 (m), 2750 (m), 1660 (s), 1540 (m), 1440 (m), 1375 (s), 1335 (m), 1230 (w), 1180 (w), 1140 (w), 1115 (w), 1020 (w) and 820 (w). ^1H NMR ($CDCl_3$): δ0.80 (*s*, 3H), 0.86 (*s*, 3H), 0.96 (*d*, $J = 7$ Hz), 1.18 (*d*, $J = 7$ Hz, 3H), 2–2.3 (*m*), 2.70 (*d*, $J = 11$ Hz, 1H), 2.78 ($W_{1/2} = 18$ Hz, 1H), 3.77 ($W_{1/2} = 10$ Hz, 1H), 3.85 ($W_{1/2} = 22$ Hz, 1H), 5.42 (*d*, $J = 7$ Hz, NH), 8.12 (*d*, 1H). MS *m/z* (rel. int): 442 $[M]^+$ (23.8), 443 (7), 441 (6), 427 (4), 398 (4), 397 (3), 371 (5), 220 (20), 166 (100), 137 (7), 82 (6).

Compound 3 recrystallized from MeOH to yield white needles, mp 255–256°, yield 15 mg. (Found: C, 76.34; H, 10.54; N, 6.16; $C_{29}H_{48}N_2O_2$ requires C, 76.31; H, 10.52; N, 6.14%.) $[\alpha]_D^{CHCl_3}$ +40°; IR ν_{max}^{KBr} cm^{-1}: 3550 (w), 3350 (m), 2950 (s), 2850 (m), 1660 (s), 1550 (m), 1460 (m), 1380 (m), 1340 (w), 1029 (m), 820 (m). ^1H NMR ($CDCl_3$): δ0.79 (*s*, 3H), 2–2.3 (m), 2.71 (*d*, $J = 11$ Hz, 1H), 2.74 ($W_{1/2} = 18$ Hz, 1H), 3.83 (*m*, 2H), 5.33 (*d*, $J = 10$ Hz, NH). MS *m/z* (rel. int.): 456 $[M]^+$ (20.9), 455 (6), 457 (6), 412 (3), 385 (4), 397 (2), 220 (21), 166 (100), 82 (6), 56 (39).

Hydrolysis of 3. 3 (5 mg) was hydrolysed with 1 N HCl in MeOH. After work up, the product was isolated and identified as **1** [1].

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