Neben den Alkaloiden wurde Tyrosol isoliert, das bereits aus Blüten von *Osmanthus fragrans* var. *auranticus* [6] sowie Blättern von *Ligustrum ovalifolium* [7] (beide Oleaceae) erhalten wurde.

EXPERIMENTELLES

Pflanzenmaterial. Leg. et det. H. Ripperger, Mai 1977 in Halle (Saale); Vergleichsmaterial befindet sich im Besitz des Autors.

Tyrosol. Frische Blätter von *S. vulgaris* wurden mit MeOH bei Raumtemperatur extrahiert. Nach Einengen des Extrakts i. Vak. versetzte man den Rückstand mit 0.5 N HCl, reinigte durch Ausschütteln mit C_6H_6–Et_2O (1:1), versetzte mit NH_3 und extrahierte mit $CHCl_3$–EtOH (2:1). Nach SC an Si gel mit $CHCl_3$–MeOH (99:1) und Kristallisation aus Me_2CO–$CHCl_3$ wurde Tyrosol in 0.007 proz. Ausbeute erhalten; Schmp. 91–92.5° (Lit.[6]: 93°). ν_{max}^{Nujol} cm^{-1}: 3396, 3140 (OH), 3025, 1615, 1599, 1516, 822 (Aromat). λ_{max}^{EtOH} nm (log ε): 279 (3.23), 224 (3.89). PMR (60 MHz, Me_2CO-d_6, TMS: δ 2.72 (2 H, *t*, J = 7 Hz, $C_6H_5C\underline{H}_2$), 3.52 (1 H, *s*, $CH_2O\underline{H}$), 3.74 (2 H, *t*, *J* = 7 Hz, $C\underline{H}_2OH$), 6.76 (2 H, *d*, *J* = 8 Hz, m-H), 7.09 (2 H, *d*, *J* = 8 Hz, o-H), 8.41 ppm (1 H, *s*, phenolisches OH). MS 80 eV *m/e* (rel. Int.): 138 (M; 34), 120 (M − H_2O; 2), 107 (Tropyliumspaltung; 100).

Jasminin (**2**). Bei der oben beschriebenen SC an Si gel wurde mit $CHCl_3$–MeOH (49:1) **2** eluiert; aus $CHCl_3$–Et_2O Kristalle vom Schmp. 170–173° und $[\alpha]_D^{24}$ − 29.8° ($CHCl_3$; *c* 1.01) (Lit. [4]: Schmp. 174.5–176°, $[\alpha]_D$ − 37.5°, $CHCl_3$); Ausbeute 0.001%. ν_{max}^{KBr} cm^{-1}: 3190 (NH), 3065, 1580, 1480, 1209, 1048, 783 (Pyridinring), 1728, 1296, 1175 (CO_2Me), 1680 (NHCO). λ_{max}^{EtOH} nm (log ε): 270 (3.24), 214 (3.81). ORD (EtOH): $[\phi]_{274}$ − 610° (Tal), $[\phi]_{260}$ − 410° (Gipfel). PMR (100 MHz, $CDCl_3$, TMS): δ 1.56 (3 H, *d*, *J* = 7 Hz, 1-Me), 3.95 (3 H, *s*, CO_2Me), 4.05 (2 H, *m*, 4-H), 4.78 (1 H, *m*, nach Schütteln mit D_2O *q*, *J* = 7 Hz 1-H), 7.70 (1 H, breites Signal, verschwindet nach Schütteln mit D_2O, NH), 8.59 (1 H, *s*, 8-H), 9.04 ppm (1 H, *s*, 6-H). Elektronenanlagerungs-MS 2–4 eV *m/e* (rel. Int.): 220 (M; 100), 218 (99), 204 (94), 190 (39), 176 (28), 161 (M − CO_2Me; 39). Elektronenstoss-MS 70 eV *m/e* (rel. Int.): 220.0831 ($C_{11}H_{12}N_2O_3$, M; 1), 218.0680 (M − 2 H; 1), 205.0609 (M − Me; 100), 189.0685 (M − Me; 12), 173.0338 (M − MeOH − Me; 91), 161.0706 (M − CO_2Me; 4), 145.0419 (M − MeOCHO − Me; 19).

Jasminidin (**1**). Bei der oben beschriebenen SC an Si gel wurde mit $CHCl_3$–MeOH (97:3) **1** eluiert und erneut an Al_2O_3 (Akt. III) mit $CHCl_3$ chromatographiert; aus $CHCl_3$–Et_2O Kristalle vom Schmp. 190–194° (Zers., Sublimation bei 145°) und $[\alpha]_D^{27}$ − 3·2° ($CHCl_3$; *c* 0.35); Ausbeute 0.0001%. ν_{max}^{KBr} cm^{-1}: 3227 (NH), 3060, 1604, 1488, 1058, 769 (Pyridinring), 1682 (NHCO). λ_{max}^{EtOH} nm (log ε): 266 (3.22), 259 (3.31). ORD (EtOH): $[\phi]_{268}$ − 470° (Tal), $[\phi]_{245}$ + 620° (Gipfel). PMR (80 MHz, $CDCl_3$, TMS): δ 1.58 (3 H, *d*, *J* = 6.7 Hz, 1-Me), 3.58 (2 H, *s*, 4-H), 4.72 (1 H, *q*, *J* = 7 Hz, 1-H), 7.07 (1 H, *d*, *J* = 4.9 Hz, 5-H), 7.60 (1 H, breites Signal, NH), 8.45 ppm (2 H, *m*, 6-H und 8-H). Elektronenanlagerungs-MS 2–4 eV *m/e* (rel. Int.): 161 (M − H; 100); 146 (161 − Me; 26), 133 (161 − CO; 30). Elektronenstoss-MS 70 eV *m/e* (rel. Int.): 162.0806 ($C_9H_{10}N_2O$, M; 12), 161.0702 (M − H; 12), 147.0553 (M − Me; 100), 119.0616 (M − Me − CO; 65), 92.0492 (119 − HCN; 33).

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A NEW STEROIDAL ALKALOID FROM *SOLANUM HAINANENSE**

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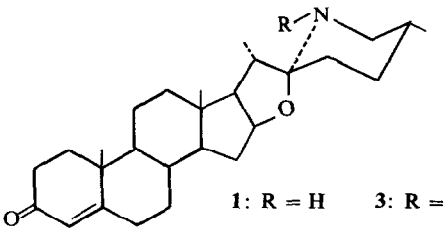
Key Word Index—*Solanum hainanense*; Solanaceae; steroidal alkaloids; spirosolanes; solasodenone.

As a part of our studies on Vietnamese plants of biological and medical interest, we have investigated *Solanum hainanense* Hance, used in Vietnamese folk medicine as an antiphlogistic. We now wish to report the isolation and structure of the new steroidal alkaloid solasodenone (**1**) from this plant.

Al_2O_3 chromatography of the chloroform extracts of dried roots or leaves yielded 0.03% of the new alkaloid $C_{27}H_{41}NO_2$ (M^+ 411.3131), mp 178°, showing the presence of a spiroaminoketal system [1] (883, 913, 965, 978 cm^{-1}) as well as an α,β-unsaturated ketone (1621, 1680 cm^{-1}) in its IR spectrum. The UV data with λ_{max} (ε) at 242 (15000) and 310 (138) indicated also an enone chromophore. The measured ORD curve was in agreement with the Cotton effect, well known for Δ^4-3-keto steroids ($\Delta\varepsilon_{315}$ −1.1) [2]. The 100 MHz ^1H NMR spectrum gave signals at $\delta_{TMS}^{CDCl_3}$ 0.83 (*d*, *J* = 6 Hz, 27-H_3) [3], 0.86 (*s*, 18-H_3), 0.94 (*d*, *J* = 7 Hz, 21-H_3) [3], 1.20 (*s*, 19-H_3), 2.63 (*m*, 26-H_2), 4.30 (*dd*, *J* = 14 Hz, *J'* = 7 Hz, 16α-H), 5.74 (*s*, 4-H). Mass fragmentation pattern indicates that **1** is a steroidal alkaloid having spirosolane

*Part 106 of the series 'Solanum Alkaloids'. For part 105 see: Ripperger, H. (1978) *Pharmazie* in press.

skeleton [4, 5], high resolution diagnostic ion fragments being discernible at *m/e* 396 ($C_{26}H_{38}NO_2$, 6%), 383 ($C_{26}H_{39}O_2$, 9%), 298 ($C_{21}H_{30}O$, 11%), 269 ($C_{19}H_{25}O$, 10%), 138 ($C_9H_{16}N$, 100%), 125 ($C_8H_{15}N$, 10%), 114 (C_6H_2NO, 78%) and 98 ($C_6H_{12}N$, 5%). The alkaloid was characterized by the *N*-acetyl derivative **2**, M^+ 453, mp 124°, *N*-chloroamine **3**, mp 168–170° (dec.), and *N*-nitrosamino compound **4**, mp 159°, whose molecular rotation differences ($\Delta[M]_D$ **1** → **2** = +59°, **1** → **3** = −186°, **1** → **4** = +13°) are in good agreement with a (22*R*:25*R*) spirominoketal side chain stereochemistry [6]. All these data suggested solasodenone as (22*R*:25*R*)-spirosol-4-en-3-one (**1**); this structure was



1: R = H **3**: R = Cl

2: R = Ac **4**: R = NO

finally confirmed by a partial synthesis of **1** via Oppenauer oxidation of solasodine [6] leading to a product identical in all respects with solasodenone (**1**) isolated from *S. hainanense*. Solasodenone (**1**) may be a suitable starting material for pharmaceutically interesting pregnane derivatives of the progesterone type.

EXPERIMENTAL

Mps are corr. Specific rotations in $CHCl_3$; UV in ORD in MeOH; NMR in $CDCl_3$ with TMS as int. stand.

Isolation. Dried and powdered leaves or roots (100 g), collected near Hanoi, were extracted exhaustively with $CHCl_3$ in a Soxhlet. $CHCl_3$ soln was concd to 1/3 and extracted ×3 with petrol to remove pigments and lipids. Evapn of the $CHCl_3$ phase gave a residue which was chromatographed over Al_2O_3 (Woelm. neutral, grade I). The progress of the separation was followed by TLC on SiO_2 (Merck) ($CHCl_3$–EtOH, 9:1) Elution with $CHCl_3$–EtOH (7:3) yielded solasodenone (**1**). Needles (Me_2CO–H_2O), mp 178°, $[\alpha]_D^{26}$ + 28.0° (*c* = 0.4). Spectral data is in the text.

N-*Acetate* **2**. (mp 124° (Et_2O), $[\alpha]_D^{25}$ + 40.1° (*c* = 0.513); ν_{max}^{Nujol} cm^{-1}; 870, 924, 965, 1623, 1685. NMR; 0.88 (*d*, *J* = 6 Hz), 0.92 (*d*, *J* = 6 Hz) (21- and 27-H_3), 0.90 (*s*, 18-H_3) 1.12 (*s*, 19-H_3), 2.14 (*s*, *N*-acetyl-H_3), 4.15 (*dd*, *J* = 15 Hz, *J'* = 7 Hz, 16α-H), 5.69 (s, 4-H).

N-*Chloroamine* **3**. Obtained from **1** and NCS in CH_2Cl_2 at −5° crystallized in needles, mp 168–170° (dec., Me_2CO), $[\alpha]_D^{25}$ −16.0° (*c* = 0.312). The *N*-nitroso derivative **4**, mp 159° (MeOH), $[\alpha]_D^{25}$ +29.0° (*c* = 0.450).

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