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STEROIDAL ALKALOIDS FROM ROOTS OF *SOLANUM SPIRALE**

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Key Word Index—*Solanum spirale*; Solanaceae; steroid alkaloids; solaspiralidine; etioline; 3-*O*-(β-D-glucopyranosyl)etioline.

Abstract—In addition to etioline two new alkaloids, solaspiralidine and a glycoside, were isolated from roots of *Solanum spirale*. Their structures were elucidated as (20*R*,25ξ)-23,26-epimino-3β,16α-dihydroxycholesta-5,23(*N*)-dien-22-one and 3-*O*-(β-D-glucopyranosyl)etioline [(25*S*)-22,26-epimino-3β-(β-D-glucopyranosyloxy)cholesta-5,22(*N*)-dien-16α-ol]. Copyright © 1996 Published by Elsevier Science Ltd

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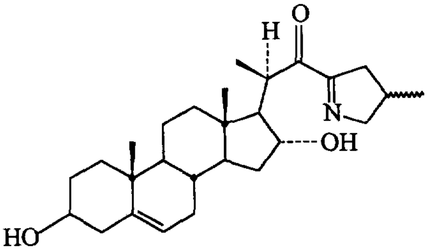
INTRODUCTION

Tomatidenol, 15α-hydroxytomatidenol and yamogenin were isolated from the leaves and etioline from the roots of *Solanum spirale* Roxb. [2]. In the present study, in addition to etioline (**2**), two new compounds, solaspiralidine and a glycoside, were obtained from the roots. Their structures were elucidated as (20*R*,25ξ)-23,26-epimino-3β,16α-dihydroxycholesta-5,23(*N*)-dien-22-one (**1**) and 3-*O*-(β-D-glucopyranosyl)etioline [(25*S*)-22,26-epimino-3β-(β-D-glucopyranosyloxy)cholesta-5,22(*N*)-dien-16α-ol, **3**], as outlined below.

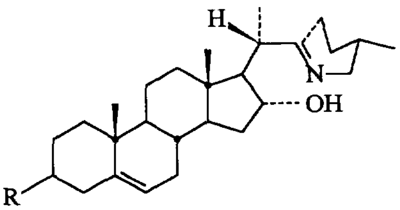
RESULTS AND DISCUSSION

The elemental composition of solaspiralidine was shown to be $C_{27}H_{41}NO_3$ by high resolution mass spectrometry. Diagnostic peaks at *m/z* 140 and 111 indicated a structure of the tomatillidine type [23,26-epiminocholest-23(*N*)-en-22-one] [3 4].

The ^{13}C NMR signals of etioline (**2**) (Table 1) were assigned by comparison with the spectra of solafloridine, 20-isosolafloridine and 20,25-bisisoetioline [1], the ^{13}C NMR signals of solaspiralidine (**1**) by comparison with the values of etioline (Table 1) (C-1–C-19) and of (20*R*,25*R*)-23,26-epimino-3β-hydroxy-5α-cholest-23(*N*)-ene-6,22-dione [5] (C-20–C-27). All ^{13}C assignments in this paper were supported by APT measurements. The ^{1}H NMR signals of **1** were assigned by HMQC, ^{1}H–^{1}H DQF COSY and NOESY measurements. The spectra indicated 3β- and 16-hydroxy groups as well as a Δ^5-double bond. A NOE between H-16 and H_3-18 was in agreement with a 16α-hydroxy group of **1** (Fig. 1), between H_3-18 and H-20 indicated a 17β-side chain. NOEs between H-20 on the one hand, and H-16 and H_3-18 on the other, as well as a missing effect between H-17 and H-20 displayed, at least approximately, antiperiplanar positions of H-17



1



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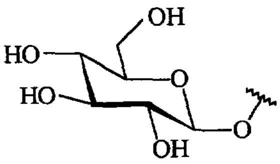
3 R =



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*Part 137 in the series '*Solanum* Alkaloids'. For part 136 see ref. [1].

Table 1. NMR data (δ values) of compounds **1**–**3** (pyridine-d_5, 126 MHz for ^{13}C, 500 MHz for ^{1}H, TMS)

	1		**2**	**3** (aglycone portion)
Position	δ_C	δ_H (α, β or E/Z to C-27)	δ_C	δ_C
1	37.8	1.08, 1.80	37.7	37.4
2	32.6	2.06, 1.76	32.6	30.3
3	71.2	3.81, —	71.2	78.1[a]
4	43.5	2.60, 2.60	43.5	39.4
5	141.9	—	141.9	140.8
6	121.1	5.38	121.2	121.8
7	32.2	1.56, 1.95	32.3	32.2
8	31.7	—, 1.46	31.6	31.6
9	50.4	0.94, —	50.4	50.3
10	36.9	—	36.9	36.9
11	21.0	1.44, 1.30	21.2	21.1
12	39.6	1.30, 1.49	40.4	40.4
13	43.7	—	44.0	44.0
14	53.5	1.58, —	54.1	54.1
15	37.7	1.94, 1.80	36.5	36.5
16	75.1	—, 4.42[b]	76.1	76.1
17	62.5	2.42, —	64.2	64.2
18	14.8	0.83	13.8	13.8
19	19.6	1.02	19.6	19.45[c]
20	40.9	4.19[d]	45.5	45.5
21	17.8	1.60[e]	18.8	18.8
22	204.3	—	175.9	176.0
23	173.8	—	28.2[f]	28.2[g]
24	42.0	3.01[h], 2.46	28.7[f]	28.6[g]
25	31.3	2.32	27.8	27.8
26	70.1	4.26[i], 3.73[j]	56.7	56.6
27	20.1	0.89[k]	19.4	19.44[c]

[a] May be exchanged with the signal for C-5′.
[b] *t*, $J = 6.9$ Hz.
[c,f,g] May be exchanged.
[d] *dq*, $J = 10.7, 7.0$ Hz.
[e] *d*, $J = 6.7$ Hz.
[h] *dd*, $J = 17.5, 9.0$ Hz.
[i] *dd*, $J = 17.2, 7.5$ Hz.
[j] *d*, $J = 17.4$ Hz.
[k] *d*, $J = 7.0$ Hz.

and H-20. The coupling constant $^{3}J_{17,20} = 10.7$ Hz was in accord with this assumption. An NOE between H-16 and H_3-21 indicated the (20*R*)-configuration. The configuration at C-25 was not established.

The glycoside **3** had the empirical formula $C_{33}H_{53}NO_7$ according to high resolution mass spectrometry. Its characteristic fragment at *m*/*z* 125 was in accordance with a 22(*N*)-unsaturated 22,26-epiminocholestane structure [6]. The $[M - C_6H_{11}O_6]^+$ ion indicated the presence of a hexose.

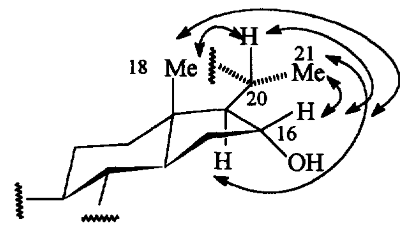

Fig. 1. NOEs of **1**.

Structure **3** was proved by comparison with the NMR data (C-1–C-10, C-1′–C-6′) of its known 16-*O*-acetyl derivative, which was unequivocally elucidated under the name havanine [7], and with the values of etioline (**2**) (C-11–C-27, Table 1). The ^{1}H NMR signals of the sugar portion were assigned by ^{1}H–^{1}H DQF COSY measurements. The coupling constants were in agreement with a glucopyranose moiety (see Experimental). Alkaloid **3** is possibly identical with deacetylveralosine [8], the aglycone of which, veralosidine, corresponded to etioline in nearly all properties [6]. The hexopyranose structure of deacetylveralosine was not proved [8].

EXPERIMENTAL

Roots of *Solanum spirale* were collected in December near Dalat City, High Plateau of Central

Vietnam, heated to 110° for 10 min and dried at 50–60°.

Isolation of alkaloids. Ground roots were extracted with 80% EtOH in a Soxhlet apparatus. Evaporation of the solvents *in vacuo* gave a residue which was partioned between 10% HOAc and C_6H_6–Et_2O (1 : 1). After addition of NH_3 to the aq. layer, the latter was extracted with $CHCl_3$–EtOH (2 : 1). After evaporation of the organic solvents *in vacuo*, the residue was chromatographed over silica gel. $CHCl_3$–MeOH (99 : 1) eluted solaspiralidine (**1**), $CHCl_3$–MeOH (49 : 1) eluted etioline (**2**) and $CHCl_3$–MeOH (23 : 2) eluted 3-*O*-(*β*-D-glucopyranosyl)etioline (**3**). After IR spectroscopy had indicated that **3** did not contain acyl groups, it was rechromatographed over silica gel with $CHCl_3$, shaken with an equal quantity of concd NH_3–MeOH (4 : 1).

Solaspiralidine (**1**). Needles from Me_2CO; yield 0.06%. Mp 212–214°. $[\alpha]_D^{26}$ −63.1° ($CHCl_3$; *c* 0.86). R_f 0.66 [Merck TLC aluminium sheets silica gel 60 F_{254} with concentrating zone, $CHCl_3$–MeOH (7 : 3)]. CD: $\Delta\varepsilon_{364}$ +0.16, $\Delta\varepsilon_{271}$ +0.92 (MeOH; *c* 0.36). ^1H NMR: cf. Table 1. ^{13}C NMR: cf. Table 1. EI-MS (70 eV) *m/z* (rel. int.): 427.3068 $[M]^+$ ($C_{27}H_{41}NO_3$, calcd 427.3086) (100), 409 $[M-H_2O]^+$ (31), 399.3158 $[M-CO]^+$ ($C_{26}H_{41}NO_2$, calcd 399.3137) (33), 394 $[M-H_2O-Me]^+$ (42), 384 $[M-CO-Me]^+$ (28), 366 $[M-H_2O-CO-Me]^+$ (32), 152 (24), 140.1082 ($C_8H_{14}NO$, calcd 140.1075) (68), 124 (48), 111 (35).

Etioline (**2**). Needles from Me_2CO; yield 0.17%. Mp 150–153°, ref. [9]: 153–156°. $[\alpha]_D^{24}$ −1.2° ($CHCl_3$; *c* 0.72), ref. [9]: −4.2° ($CHCl_3$). R_f 0.39 (*vide supra*). ^1H NMR (500 MHz, pyridine-d_5, TMS): δ 0.75 (*s*, H_3-18), 0.79 (*d*, $J = 6.4$ Hz, H_3-27), 1.06 (*s*, H_3-19), 1.18 (*d*, $J = 6.7$ Hz, H_3-21), 2.56 (*dq*, $J = 11.0$, 6.7 Hz, H-20), 3.00 (*dd*, $J = 16.2$, 10.1 Hz, H-26a), 3.77 (*dd*, $J = 16.6$, 4.7 Hz, H-26e), 3.84 (*m*, H-3), 4.18 (*t*, $J = 5.8$ Hz, H-16), 5.40 (*d*, $J = 4.3$ Hz, H-6). ^{13}C NMR (126 MHz, pyridine-d_5, TMS): cf. Table 1. EI-MS (70 eV) *m/z* (rel. int.): 413 $[M]^+$ (12), 395 $[M-H_2O]^+$ (32), 380 $[M-H_2O-Me]^+$ (48), 162 (38), 138 (58), 125 (100), 98 (39).

3-O-(β-D-*Glucopyranosyl)etioline* (**3**). Needles from MeOH and a drop of conc NH_3, yield 0.045%. Mp 225–227° (dec.). $[\alpha]_D^{26}$ −78.8° (pyridine; *c* 0.72). R_f 0.19 (*vide supra*). ^1H NMR (500 MHz, pyridine-d_5, TMS): δ 0.73 (*s*, H_3-18), 0.79 (*d*, $J = 6.7$ Hz, H_3-27), 0.93 (*s*, H_3-19), 1.16 (*d*, $J = 7.0$ Hz, H_3-21), 2.57 (*dq*, $J = 11.0$, 7.0 Hz, H-20), 3.00 (*dd*, $J = 16.6$, 10.2 Hz, H-26a), 3.77 (*dd*, $J = 16.8$, 4.6 Hz, H-26e), 3.93 (*m*, H-3), 3.99 (*ddd*, $J = 9.2$, 5.2, 2.1 Hz, H-5′), 4.06 (*t*, $J = 8.1$ Hz, H-2′), 4.18 (*t*, $J = 6.0$ Hz, H-16), 4.29 (*t*, $J = 7.2$ Hz, H-4′), 4.30 (*t*, $J = 8.8$ Hz, H-3′), 4.42 (*dd*, $J = 11.9$, 5.2 Hz, H-6′), 4.57 (*dd*, $J = 11.7$, 2.3 Hz, H-6″), 5.05 (*d*, $J = 7.9$ Hz, H-1′), 5.31 (*d*, $J = 4.9$ Hz, H-6). ^{13}C NMR (126 MHz, pyridine-d_5, TMS): δ 62.9 (C-6′), 71.7 (C-4′), 75.4 (C-2′), 78.5[a] (C-5′), 78.6 (C-3′), 102.6 (C-1′), [a]may be exchanged with C-3 of the aglycone; signals of the aglycone see Table 1. EI-MS (70 eV) *m/z* (rel. int.): 575.3847 $[M]^+$ ($C_{33}H_{53}NO_7$, calcd 575.3822) (12), 557 $[M-H_2O]^+$ (52), 542 $[M-H_2O-Me]^+$ (67), 396 $[M-C_6H_{11}O_6]^+$ (26), 162 (37), 138 (48), 125 (100), 98 (32).

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