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LYCOPERSICONOLIDE, A STEROID LACTONE FROM TOMATO ROOTS

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Key Word Index—*Lycopersicon* sp.; Solanaceae; roots; steroid lactone; lycopersiconolide; ^{1}H NMR; ^{13}C NMR.

Abstract—Lycopersiconolide has been characterized as (20*S*)-3β,16β,20-trihydroxy-5α-pregnane-20-carboxylic acid 22,16-lactone.

INTRODUCTION

From roots of the tomato Taibyo Shinko No. 1 (*Lycopersicon esculentum* × *L. hirsutum*, hybrid, Takii Co. Ltd.) a new steroid lactone, lycopersiconolide (**1**), was isolated as colourless needles.

RESULTS AND DISCUSSION

The ^{13}C NMR spectrum of **1** contained signals for three methyls, eight methylenes, seven methines and four quaternary carbons. The chemical shift values of the carbon atoms of rings A, B and C of compound **1** (Table 1) and tomatidine (**4**) [1] agreed very well, whereas those of ring D showed some differences. By comparison with the ^{13}C NMR values of several other steroids [2, 3] it was presumed that **1** possessed a 3β-hydroxy-5α-androstane ring system. The rest of the ^{13}C NMR signals [δ74.9 (quaternary), 19.1 (Me), and 179.6 (quaternary)] and the IR spectrum indicated the presence of two hydroxy groups (3500, 3300 cm^{-1}) and a γ-lactone group (1780, 1750 cm^{-1}) and suggested that a α-hydroxy-α-methyl-γ-lactone moiety was bound to ring D. The molecular formula expected from these data was $C_{22}H_{34}O_4$ and in agreement with this the FDMS of **1** exhibited the molecular ion peak at *m/z* 362. The location of the lactone was evident from the ^{1}H NMR spectrum in which the signals at δ1.52 (3H, *s*, –Me), 2.06 (1H, *d*, J = 5.9 Hz, HC–), and 5.09 (1H, *ddd*, J = 7.8, 6.2, 3.9 Hz, HC–O) were assigned to the protons of the γ-lactone moiety. These data support the structure of 3β,16,20-trihydroxy-5α-pregnane-20-carboxylic acid 22,16-lactone for **1**.

In order to determine the configuration of C-20 and of the D–E ring junction, NOE difference spectra were measured. A strong NOE was observed between 21-Me (1.52 ppm) and 18-Me (0.80 ppm). The irradiations, however, had no effect on H-16 and H-17. This indicated that the H-atoms at C-16 and C-17 were in the α-configuration, and that C-20 had *S*-configuration.

Acetylation of **1** with acetic anhydride/pyridine at room temperature afforded a monoacetate (**2**) and a diacetate (**3**). The spectral and physicochemical data of **2** and **3** completely agree with those of the mono and diacetate derived from (20*S*)-hydroxytigogenin acetate with concentrated HNO_3 [4]. Hence, **1** was confirmed to be (20*S*)-3β,16β,20-trihydroxy-5α-pregnane-20-carboxylic acid 22,16-lactone.

The occurrence of three other lactones of this type has been reported in *Solanum* species; solanolide (**5**) from *S. hispidum* [5], vespertilin (**6**) [6] and 20*S*-hydroxyvespertilin (**7**) [4] from *S. vespertilio*.

Table 1. ^{13}C NMR chemical shifts of lycopersiconolide (**1**) (67.8 MHz, CD_3OD–$CDCl_3$ (1:1), TMS as internal standard)

Carbon No.	Chemical shift, **1**
1	37.6
2	31.4
3	71.2
4	38.1
5	45.4
6	29.1
7	32.2
8	35.2
9	54.7
10	36.1
11	20.8
12	39.3
13	41.1
14	56.4
15	32.5
16	83.5
17	64.2
18	14.0
19	12.6
20	74.9
21	19.1
22	179.6

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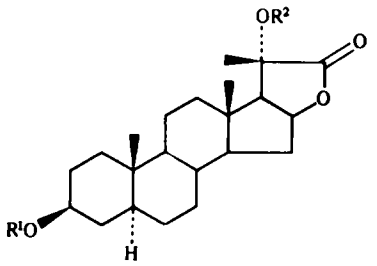
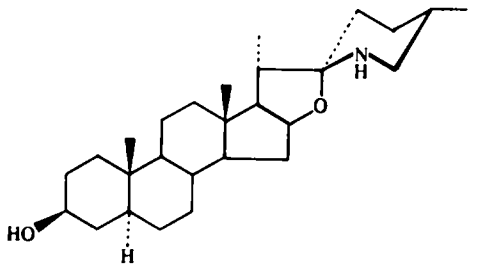


1 $R^1 = R^2 = H$
2 $R^1 = Ac$, $R^2 = H$
3 $R^1 = R^2 = Ac$



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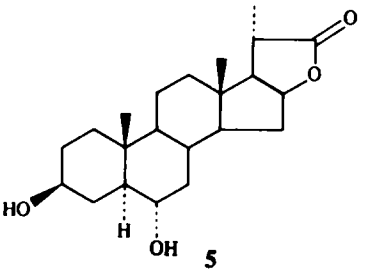

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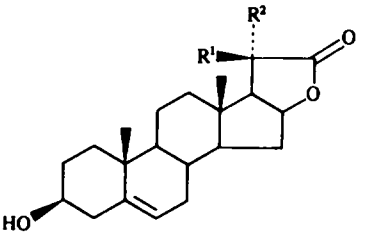

6 $R^1 = H$, $R^2 = Me$
7 $R^1 = Me$, $R^2 = OH$

EXPERIMENTAL

Isolation. Fresh roots (7.5 kg) taken from Taibyo Sinko No. 1 tomato plants grown at the Agricultural Experimental Farm of Hokkaido University, were finely cut and extracted with 70% EtOH (55 l). The extract was filtered and concentrated to 0.5 l under reduced pressure below 40°. The aq. residue was diluted with H_2O to 1 l and extracted with Et_2O (3 × 1 l). The Et_2O extracts were bulked, dried (Na_2SO_4), and the solvent removed *in vacuo*. The residue (10 g) was subjected to CC on silica gel and eluted with $CHCl_3$, $CHCl_3$–MeOH (19:1), (9:1), (4:1), (7:3) and MeOH to yield 13 fractions [monitoring with UV (280 nm)]. The 7th fraction eluted with $CHCl_3$–MeOH (19:1) was further chromatographed on a silica gel column with $CHCl_3$–MeOH (99:1). Compound **1** (50 mg) was obtained as colourless needles from $CHCl_3$–MeOH. Mp 295–297°; $[\alpha]_D^{20} - 48°$ (MeOH; *c* 0.088); FDMS *m/z* (rel. int.): 362 $[M]^+$ (5), 361 $[M-H]^+$ (9), 360 $[M-2H]^+$ (14), 346 (15), 318 (100); EIMS *m/z* (rel. int.): 360 $[M-2H]^+$ (0.4), 342 $[360-H_2O]^+$ (0.7), 329 (1), 318 $[M-CO_2]^+$ (3), 303 (41), 273 (4), 257 (6), 138 (11), 107 (61), 84 (100); IR ν_{max}^{KBr} cm^{-1}: 3500, 3300, 1780, 1750; ^1H NMR [500 MHz, CD_3OD–$CDCl_3$ (1:1), TMS]; δ0.80 (3H, *s*, H_3-18), 0.84 (3H, *s*, H_3-19), 1.52 (3H, *s*, H_3-21), 2.06 (1H, *d*, *J* = 5.9 Hz, H-17), 2.23 (1H, *m*, H-15α), 3.54 (1H, *m*, H-3), 5.09 (1H, *ddd*, *J* = 7.8, 6.2, 3.9 Hz, H-16).

Monoacetate (**2**) *and diacetate* (**3**) *of* **1**. A soln of **1** (18 mg) in Ac_2O (0.5 ml) and C_5H_5N (0.5 ml) was kept at room temp. for 12 hr. CC of the residue on silica gel developed with $CHCl_3$ gave a monoacetate (**2**, 15 mg) and a diacetate (**3**, 4 mg) *Monoacetate* (**2**), mp 280–282°, lit. 282–284° [4], needles ($CHCl_3$–*n*-Hexane); $[\alpha]_D^{20} - 58°$ ($CHCl_3$; *c* 0.24), lit. −54° ($CHCl_3$) [4]; FDMS *m/z* (rel. int.): 405 $[MH]^+$ (15), 360 (35), 344 (100); EIMS *m/z* (rel. int.): 404 $[M]^+$ (0.07), 386 $[M-H_2O]^+$ (0.9), 360 (2), 345 (28), 285 (6), 257 (6), 217 (11), 107 (29), 84 (100), 43 (94); IR ν_{max}^{KBr} cm^{-1}: 3450, 1780 (shoulder), 1760, 1740, 1240; ^1H NMR (270 MHz, $CDCl_3$, TMS): δ0.80 (3H, *s*, H_3-18), 0.83 (3H, *s*, H_3-19), 1.57 (3H, *s*, H_3-21), 2.02 (3H, *s*, H_3-Ac), 2.08 (1H, *d*, *J* = 6.2 Hz, H-17), 2.23 (1H, *m*, H-15α), 4.68 (1H, *m*, H-3), 5.07 (1H, *ddd*, *J* = 7.8, 6.2, 3.9 Hz, H-16). *Diacetate* (**3**), mp 270–272°, lit. 261–262° [4], needles ($CHCl_3$–*n*-Hexane); $[\alpha]_D^{20} - 27°$ ($CHCl_3$; *c* 0.11), lit. −26° ($CHCl_3$) [4]; FDMS *m/z* (rel. int.): 446 $[M]^+$ (22), 386 (100); EIMS *m/z* (rel. int.): 446 $[M]^+$ (0.1), 404 (0.5), 386 (23), 360 (22), 345 (65), 311 (8), 285 (10), 257 (13), 216 (19), 107 (31), 84 (32), 43 (100); IR ν_{max}^{KBr} cm^{-1}: 1790, 1740, 1730, 1250, 1220; ^1H NMR (270 MHz, $CDCl_3$): δ0.80 (3H, *s*, H_3-18), 0.83 (3H, *s*, H_3-19), 1.79 (3H, *s*, H_3-21), 2.02 (3H, *s*, H_3-Ac), 2.04 (3H, *s*, H_3-Ac), 2.23 (1H, *m*, H-15α), 2.70 (1H, *d*, *J* = 6.2 Hz, H-17), 4.68 (1H, *m*, H-3), 4.95 (1H. *ddd*, *J* = 7.8, 6.2, 3.9 Hz, H-16).

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