mixture was then evapd to dryness, silylated with bis(trimethylsilyl)trifluoroacetamide (BSTFA) in pyridine at 90° for 30 min, concd to dryness, dissolved in $CHCl_3$ and analysed by GC [6].

NMR spectroscopy. 2-D DQF H, H-COSY experiments were performed at 400 MHz. A digital resolution of 4.3 Hz in both dimensions were used and the FID's were multiplied by a non-shifted sine-square function before Fourier transformation. NOE-difference experiments [9, 10] were performed with a JEOL pulse-sequence available in the GSX software.

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REFERENCES

1. Chopra, R. M., Handa, K. L., Kapur, L. D. and Chopra, I. C. (1956) *Indigenous Drugs of India* 2nd Edn, p. 507.
2. Chopra, N., Nayar, S. L. and Chopra, I. C. (1956) *Glossary of Indian Medicinal Plants*, p. 116.
3. Rahman, A. and Ansari, A. A. (1982) *Heterocycles* **19**, 217.
4. Rahman, A. and Ansari, A. A. and Kenne, L. (1984) *J. Nat. Prod.* **47**, 187.
5. Ansari, A. A., Kenne, L. and Rahman, A. (1987) *Phytochemistry* **26**, 1487.
6. Gerwig, G. J., Kamerling, J. P. and Vliegenthart, J. F. G. (1978) *Carbohydr. Res.* **62**, 349.
7. Bendall, M. R., Pegg, D. T., Dodrell, D. M. and Williams, D. H. (1982) *J. Org. Chem.* **47**, 3023.
8. Schneider, H. J., Buchheit, B., Becker, N., Schmidt, G. and Siehl, U. (1985) *J. Am. Chem. Soc.* **107**, 7027.
9. Richarz, R. and Wüthrich, K. (1978) *J. Magn. Res.* **30**, 147.
10. Sanders, J. K. M. and Mersh, J. D. (1982) *Progr. NMR Spectroscopy*, **15**, 353.
11. Tori, K., Komeno, T., Sangaré, M., Septe, B., Delpech, B., Ahond, A. and Lukacs, G. (1974) *Tetrahedron Letters* **13**, 1157.

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LYCOPERSICONOL, A PREGNANE DERIVATIVE FROM TOMATO STOCK ROOTS

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Key Word Index—*Lycopersicon esculentum* × *L. hirsutum*; Solanaceae; tomato stock; lycopersiconol; 3β,16β-dihydroxy-5α-pregnan-20-one.

Abstract—Lycopersiconol was isolated from tomato stock roots and characterized as 3β, 16β-dihydroxy-5α-pregnan-20-one.

INTRODUCTION

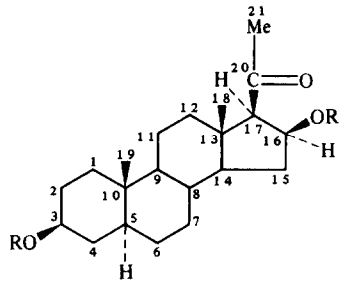
In a previous communication [1], a steroid lactone, lycopersiconolide (**3**), was reported as a constituent of roots of a tomato stock (Taibyo shinko No. 1; *Lycopersicon esculentum* × *L. hirsutum*, hybrid, Takii Co. Ltd). A further study of the plant material has now allowed the isolation of a new pregnane derivative, lycopersiconol (**1**).

RESULTS AND DISCUSSION

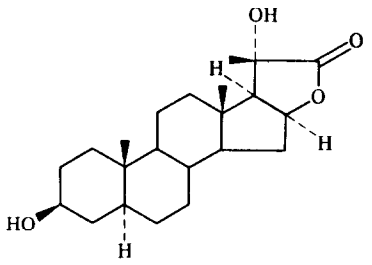
Lycopersiconol (**1**) was obtained as a crystalline compound; mp 202–204°; IR ν_{max}^{KBr} cm^{-1}: 3380 and 3290 (OH), 1670 (C=O); HRMS: 334.2511 ($C_{21}H_{34}O_3$). The ^{13}C NMR spectrum (Table 1) exhibited 21 signals; three methyls, eight methylenes, seven methines and three quaternary carbons. The chemical shift values of the carbon atoms of rings A, B and C of **1** were found to be very similar to those of **3**, whereas those of ring D showed some differences. The remaining two signals at δ31.7 (Me) and 213.0 (quaternary) arose from the methyl ketone, which was attached to ring D rather than from a γ-lactone ring as found in compound **3**. Compound **1** was acetylated with acetic anhydride–pyridine to yield the diacetate **2**, whose mass spectrum exhibited an ion at *m/z* 419 [M + H]$^+$ and the ^1H NMR spectrum showed two acetyl

Table 1. ^{13}C NMR chemical shifts of lycopersiconol (1) and lycopersiconolide (3) [67.8 MHz, CD_3OD–$CDCl_3$ (1:1), TMS as internal standard]

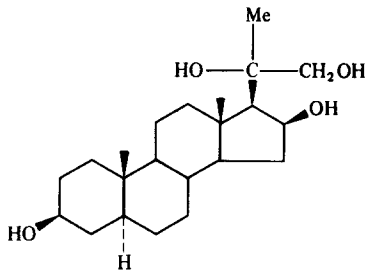
C	Chemical shift 1	3
1	37.5 *t*	37.6 *t*
2	31.4 *t*	31.4 *t*
3	71.2 *d*	71.2 *d*
4	38.1 *t*	38.1 *t*
5	45.5 *d*	45.4 *d*
6	29.1 *t*	29.1 *t*
7	32.5 *t*	32.2 *t*
8	35.5 *d*	35.2 *d*
9	54.5 *d*	54.7 *d*
10	36.1 *s*	36.1 *s*
11	21.3 *t*	20.8 *t*
12	39.4 *t*	39.3 *t*
13	43.7 *s*	41.1 *s*
14	55.0 *d*	56.4 *d*
15	37.4 *t*	32.5 *t*
16	72.6 *d*	83.5 *d*
17	67.9 *d*	64.2 *d*
18	14.7 *q*	14.0 *q*
19	12.6 *q*	12.6 *q*
20	213.0 *s*	74.9 *s*
21	31.7 *q*	19.1 *q*
22	—	179.6 *s*



1 R = H
2 R = Ac



3



4

signals at δ2.01 and 2.02. This indicated that another substituent on ring D was a hydroxy group. The positions of the methyl ketone and the hydroxy groups on ring D were evident from ^1H NMR COSY spectrum in which the unit ■–C(H)–C(H)(OH)–CH_2–C(H)(■)–R was revealed. These data suggested that compound **1** was 3β,16-hydroxy-5α-pregnan-20-one.

The configurations of C-16 and C-17 were determined by preparing compound **1** from lycopersiconolide (**3**) whose stereochemistry had been established previously. Reduction of **3** with lithium aluminium hydride afforded tetraol **4**; EIMS *m/z* 335 $[M-CH_2OH]^+$ and ^1H NMR δ1.42 (H_3-21). Oxidation of compound **4** with sodium iodate yielded **1**, the spectral data of which agreed closely with those of the isolated compound. Furthermore, the melting point and the specific rotation of diacetate **2** agreed with those of 16β-hydroxy synthetic compounds [2, 3]. In addition, a clear NOE was observed between 18-Me and 21-Me. This suggests that the methyl ketone group at C-17 is *cis* with respect to the neighbouring 18-Me. Considering all the above evidence lycopersiconol was determined to be 3β,16β-dihydroxy-5α-pregnan-20-one (**1**). This is the first report of the natural occurrence of **1**, whereas the epimer with a 16α-hydroxy group has been isolated as a urinary steroid in pregnancy [4] and a bioconversion product by newborn rat adrenal cells [5].

EXPERIMENTAL

Isolation of compound **1**. For general experimental details see ref. [1]. Chromatography of this tomato root extract was described previously. The 6th fraction eluted with $CHCl_3$ was further chromatographed on a silica gel column with EtOAc–*n*-hexane (2:8). Compound **1** (83 mg) was obtained as colourless needles from MeOH–$CHCl_3$. Mp 202–204°; $[\alpha]_D^{20}$ +69.8° ($CHCl_3$, *c* 0.754). FDMS *m/z* (rel. int.): 335 $[M+H]^+$ (100), 334 $[M]^+$ (72), 317 $[M+H-H_2O]^+$ (33); EIMS *m/z* (rel. int.); 334 $[M]^+$ (1), 316 $[M-H_2O]^+$ (29), 301 $[316-Me]^+$ (7), 273 $[316-MeCO]^+$ (17), 255 $[273-H_2O]^+$ (13). Mass measurements 334.2511 ($C_{21}H_{34}O_3$ = 334.2508), 316.2410 ($C_{21}H_{32}O_2$ = 316.2402); IR ν_{max}^{KBr} cm^{-1}: 3380, 3290, 1670, 1080; ^1H NMR (270 MHz, CD_3OD, TMS): 0.85 (3H, *s*, H_3-19), 1.03 (3H, *s*, H_3-18), 2.16 (3H, *s*, H_3-21), 2.26 (1H, *ddd*, *J* = 6.9, 8.1, 13.2 Hz, H-15a), 2.35 (1H, *d*, *J* = 7.3 Hz, H-17), 3.50 (1H, *m*, H-3), 4.65 (1H, *ddd*, *J* = 4.4, 7.3, 8.1 Hz, H-16).

Diacetate **2** *from compound* **1**. A soln of **1** (14 mg) in Ac_2O (0.4 ml) and pyridine (0.4 ml) was kept at room temp. for 44 hr. The acetate was purified by prep. TLC [MeOH–$CHCl_3$ (1:19)]

to give the diacetate (**2**, 11.6 mg). Mp 188–193°, lit. 193–195° [2] 190–192° [3]; $[\alpha]_D^{20}$ +13.5 ($CHCl_3$, *c* 0.89), lit. 21.2° [MeOH–$CHCl_3$] (1:1), *c* 0.5] [3]; FDMS *m/z* (rel. int.): 419 $[M+H]^+$ (23), 358 $[M-AcOH]^+$ (100); EIMS *m/z* (rel. int.): 403 $[M-Me]^+$ (0.4), 358 (31), 300 (13), 255 (24), 43 (100); IR-ν_{max}^{KBr} cm^{-1}: 1740, 1720; ^1H NMR (270 MHz, $CDCl_3$: 0.83 (3H, *s*, H_3-19), 1.02 (3H, *s*, H_3-18), 2.01 (3H, *s*, Ac), 2.02 (3H, *s*, Ac), 2.07 (3H, *s*, H_3-21), 2.38 (1H, *d*, *J* = 7.5 Hz, H-17), 2.41 (1H, *ddd*, *J* = 7.5, 7.5, 13.5 Hz, H-15a), 4.68 (1H, *m*, H-3), 5.49 (1H, *ddd*, *J* = 4.4, 7.5, 7.5 Hz, H-16).

$LiAlH_4$ *reduction of* **3** *to yield compound* **4**. To a soln of **3** (8 mg) in THF (0.5 ml), $LiAlH_4$ (2 mg) was added and the soln was stirred for 3 hr at room temp. After extraction with Et_2O, the product was purified on a silica gel column [MeOH–$CHCl_3$ (3:97)] to give **4** as a solid (3 mg). EIMS *m/z* (rel. int.): 351 $[M-Me]^+$ (0.8), 335 $[M-CH_2OH]^+$ (27), 317 (14), 299 (26); ^1H NMR [270 MHz, CD_3OD–$CDCl_3$ (1:1), TMS]: 0.84 (3H, *s*, H_3-19), 1.09 (3H, *s*, H_3-18), 1.42 (3H, *s*, H_3-21), 2.22 (1H, *m*, H-15a), 3.45–3.80 (2H, *m*, H_2-22 and 1H, *m*, H-3).

$NaIO_4$ *oxidation of* **4** *to yield compound* **1**. To a soln of **4** (4 mg) in dioxane (0.8 ml), $NaIO_4$ (10 mg) in H_2O (0.1 ml) was added. The mixture was kept overnight at room temp. After extraction with EtOAc the product was purified on a silica gel column eluted with MeOH–$CHCl_3$ (1:19) affording an oxidation product which was shown to be identical with the isolated material **1** (mp, $[\alpha]_D$, TLC, ^1H NMR, EIMS).

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REFERENCES

1. Nagaoka, T., Yoshihara, T. and Sakamura, S. (1987) *Phytochemistry*, **26**, 2113.
2. Schreiber, K. and Adam, G. (1961) *Monatsh. Chem.*, **92**, 1093.
3. Nathansohn, G., Winters, G. and Vigevani, A. (1965) *Gazz. Chim. Ital.*, **95**, 1338; *Chem. Abst.*, **64**, 9791b (1966).
4. Haehnel, E., Wilkison, S. and Haehnel, R. (1985) *Clin. Chim. Acta* **151**, 259; *Chem. Abst.*, **103**, 172221J (1985).
5. Ramirez, L. C., Bournot, P., and Maume, B. F. (1986) *Biochim. Biophys. Acta*, **886**, 275.

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A GLYCOSIDE FROM DRIED ROOTS OF *CYNANCHUM PANICULATUM*

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Key Word Index—*Cynanchum paniculatum*; Asclepiadaceae; neocynpnoside A; 13,14:14,15 disecopregnane dilactone; deoxysugar.

Abstract—A new glycoside, neocynapanoside A, of disecopregnane with five-and nine-membered lactone rings was isolated from a Chinese herbal drug 'Xu-Chang-Qing' which is the dried roots of *Cynanchum paniculatum*. The structure of the aglycone was deduced to be 15,20α:18,20β-diepoxy-13,14:14,15-disecopregna-5,12-dien-14(16), 18(20β)dioic acid dilactone as found in neocynapanogenin A. The total structure of the new glycoside was established as neocynapanogenin A 3-α-L-cymaropyranosyl-(1 → 4)-β-D-digitoxopyranosyl-(1 → 4)-β-D-oleandropyranoside.

INTRODUCTION

The Chinese herbal drug 'Xu-Chaung-Qing' which is the dried root of *C. paniculatum* Kitagawa has been used as an anodyne and for the therapy of chronic tracheitis in northern China [1]. It possess a peculiar odour due to paeonol which is the odorous principle of this plant [2]. In our recent investigations, several disecopregnane glycosides (cynapanosides A, B, and C) have been isolated and their structures determined [3] in addition to the separation of known cynatratoside B [4] and 14β-hydroxy pregnenolone [5]. We wish to describe in this paper the isolation and structure determination of a new glycoside, neocynapanoside A (**1**) from a glycoside fraction of the drug.

*Part 69 in the series 'Studies on the Constituents of Asclepiadaceae Plants'. For part 68 see Hayashi, K., Iida, I., Nakao, Y. and Kaneko, K. (1988) *Phytochemistry* (in press).