Phytochemistry, 1977, Vol. 16, pp. 1723-1726. Pergamon Press. Printed in England.

TRITERPENE ALCOHOLS IN THE SEEDS OF SOLANACEAE

T. ITOH, T. TAMURA and T. MATSUMOTO

College of Science and Technology, Nihon University, 8, Kanda Surugadai, 1-chome, Chiyoda-ku, Tokyo, 101 Japan

(*Received* 30 *April* 1977)

Key Word Index—Solanaceae; triterpene alcohols; lanost-8-en-3β-ol; lanosterol; 24-methylenelanost-8-en-3β-ol; seeds.

Abstract—Lanost-8-en-3β-ol, lanosterol and 24-methylenelanost-8-en-3β-ol in addition to cycloartanol, cycloartenol, 24-methylenecycloartanol, lupeol, β-amyrin, daturaolone and daturadiol were identified in the seeds of Solanaceae plants. The distribution of the first eight triterpene alcohols in the seeds of eleven plants belonging to seven genera of Solanaceae family was determined.

INTRODUCTION

In a recent paper [1] we reported the tentative identification of lanost-8-en-3β-ol (**1**) besides cycloartanol (**4**), cycloartenol (**5**), 24-methylenecycloartanol (**6**) and lupeol (**7**) in the seeds of *Capsicum annuum* (Solanaceae). More recently, lanosterol (**2**) in addition to **1** was isolated from these seeds by way of its epoxide [2]. This paper describes the isolation and identification of three Δ^8-lanostane triterpenes, **1**, **2** and 24-methylenelanost-8-en-3β-ol (**3**), besides the corresponding 9β,19-cyclopropyl isomers, **4**, **5** and **6**, and four pentacyclic triterpenes, **7**, β-amyrin (**8**), daturaolone (**9**) and daturadiol (**10**), from some solanaceous seeds. The distribution of the first eight triterpenes in the seeds of eleven Solanaceae plants also is determined. Triterpene 3β-monols, **5** [3–6], **6** [4, 5], **7** [7] and **8** [4], were identified previously in some Solanaceae plants.

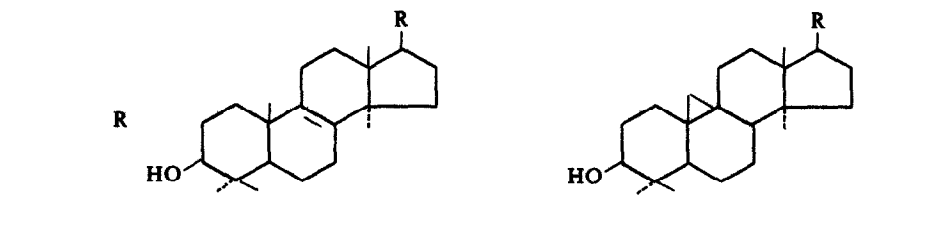
RESULTS AND DISCUSSION

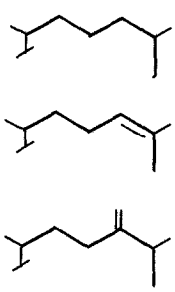
4,4-Dimethylsterol (triterpene 3β-monol) fractions separated from the solanaceous seeds listed in Table 1 were acetylated. The following triterpenes as their acetates were separated by $AgNO_3$–Si gel PLC of the acetylated fractions and identified: lanost-8-en-3β-ol (**1**), 24-methylenelanost-8-en-3β-ol (**3**), cycloartanol (**4**), cycloartenol (**5**) and 24-methylenecycloartanol (**6**) from *Physalis alkekengi* var. *francheti*; **1**, lanosterol (**2**), **4**, **5**, **6** and lupeol (**7**) from *Capsicum annuum* (California chili); and **5** and β-amyrin (**8**) from *Datura stramonium*. Furthermore, two triterpenes isolated from the other fractions of the unsaponifiable matter of *D. stramonium* were identified as daturaolone (**9**) and daturadiol (**10**), respectively.

Table 1 shows the distribution of the triterpenes in the 4,4-dimethylsterol fractions from the seeds of eleven plants belonging to seven genera of the Solanaceae family. The most significant feature of the solanaceous triterpenes is the occurrence of the three Δ^8-lanostane triterpenes, lanost-8-en-3β-ol (**1**), lanosterol (**2**) and 24-methylenelanost-8-en-3β-ol (**3**), in all of the seeds investigated with one exception, *Nicotiana tabacum* seeds which contain only a trace amount of **1**. The co-occurrence in these solanaceous seeds of the Δ^8-triterpenes with the larger amounts of the corresponding 9β,19-cyclopropyl isomers, cycloartanol (**4**), cycloartenol (**5**) and 24-methylenecycloartanol (**6**), suggests that the enzymatic opening of the 9β,19-cyclopropane ring may occur at the 4,4-dimethylsterol level in these plants. Other than these solanaceous seeds, the materials from higher plants which hitherto have been demonstrated to contain the Δ^8-triterpenes are the latex of some species of Euphorbiaceae [8–11] and the seeds of *Brassica napus* (Cruciferae) [12]. The presence of the $\Delta^{9(11)}$-isomers of **5** and **6**, parkeol [13, 14] and 24-methylenelanost-9(11)-en-3β-ol [15] respectively, has been reported in shea butter from the kernals of *Butyrospermum parkii* (Sapotaceae).

Table 1. Approximate composition (%) of triterpene 3β-monols in solanaceous seeds

Solanaceous seeds	1	2	3	4	5	6	7	8	Others
Capsicum annuum L. (California chili)	16	3	tr	22	50	2	2	tr	5
C. annuum L. (Takanotsumetougarashi)	3	7	tr	18	46	4	16	tr	6
C. annuum L. var. *fasciculatum* Irish (Yatsubusa)	4	tr	tr	26	49	3	15	2	1
C. annuum L. var. *cerasiforme* Irish (Goshikitougarashi)	20	14	1	14	47	2	tr	tr	2
C. annuum L. var. *angulosum* Mill.	10	tr	tr	21	33	3	7	20	6
Nicotiana tabacum L. (MC-1)	tr			4	87	5		tr	4
Datura stramonium L.	2	tr	tr	tr	34	7	2	53	2
Lycopersicon esculentum Mill.	5	tr	tr	55	38	1	tr	tr	1
Solanum melongena L. (Shinkuro)	15	tr	tr	69	7	tr	tr	tr	9
Physalis alkekengi L. var. *francheti* Hort.	24	tr	3	35	27	11			
Lycium chinense Mill.	tr	tr	tr	13	49	38	tr	tr	

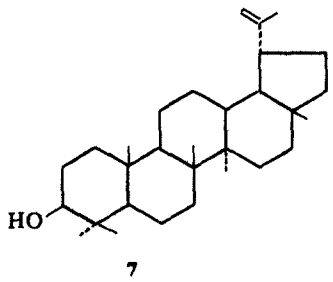




1 4

2 5

3 6



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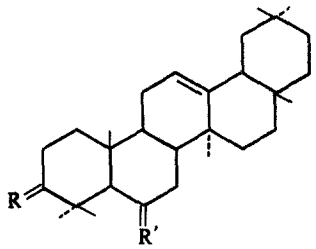

8 R = β-OH, α-H; R′ = H_2
9 R = O; R′ = β-OH, α-H
10 R,R′ = β-OH, α-H

The other noteworthy observation is that most of the 4,4-dimethylsterol fractions of the seeds examined contained significant amounts of the lanostane triterpenes possessing an unalkylated (C_8) side chain. A similar compositional pattern of triterpenes was observed also on some Liliaceae [16]. *D. stramonium* contained an exceptionally high proportion of β-amyrin (**8**) in the 4,4-dimethylsterol fraction. β-Amyrin represents the parent compound of the other two oleanane type triterpenes, daturaolone (**9**) and daturadiol (**10**), isolated together from *D. stramonium* seeds. The latter two triterpenes were identified first in the seeds of *D. innoxia* Mill. [17].

EXPERIMENTAL

Recrystallizations were performed in Me_2CO–MeOH unless otherwise stated. Mp's are uncorr. and IR spectra were recorded in KBr. PMR spectra were measured on a 100 MHz FT-instrument in $CDCl_3$ with TMS as int. ref. MS (70 eV) taken with a probe injection indicated the ions over *m/e* 200 unless otherwise mentioned. GLC were carried out on OV-17 SCOT glass capillary column (30m × 0.3mm, 260°, split ratio 50:1, sample vol. 1–2 μl) and $AgNO_3$–Si gel (1:4) PLC (0.5 mm) were developed 4×–6× with CH_2Cl_2–CCl_4 (1:5). The R_f's on the GLC and the relative R_f's on the PLC of the acetates of standard samples were: cholesterol, R_f 1.0 (relative R_f 1.0); lanost-8-en-3β-ol, 1.31 (1.58); lanosterol, 1.57 (0.63); 24-methylenelanost-8-en-3β-ol, 1.76 (0.27); cycloartanol, 1.56 (1.40); cycloartenol, 1.87 (0.55); 24-methylenecycloartanol, 2.09 (0.24); lupeol, 1.94 (0.30); β-amyrin, 1.66 (1.52). For each of the eleven seed samples, the oil extracted from the ground and dried seeds was saponified and the 4,4-dimethylsterol fraction was separated by Si gel PLC of the unsaponifiable matter as described previously [1]. The 4,4-dimethylsterol fraction, after acetylation by Ac_2O–Py, was further fractionated by $AgNO_3$–Si gel PLC. Identification of the compounds not isolated was based upon the comparison of GLC and argentation PLC data with those of authentic samples. Isolated compounds were identified by argentation PLC, GLC, mp, and IR, MS and PMR spectral comparisons with authentic samples unless otherwise specified. Approximate composition of the triterpenes determined in Table 1 was based upon GLC and argentation PLC data.

Plant material. The following seeds were courteously supplied: *Capsicum annuum* L. (Takanotsume-tougarashi) and *Datura stramonium* L. from Dr. M. Takido of this university; *C. annuum* L. (California chili) from Dr. Y. Koyama, Aichi Food Research Institute, Nagoya; *Lycopersicon esculentum* Mill. from Kagome Co., Tochigi Test Farm, Tochigi; and *Nicotiana tabacum* L. (MC-1) from Japan Monopoly Corp. Chiba Office, Chiba. The followings were purchased: seeds of *C. annuum* L. var. *cerasiforme* Irish (Goshikitougarashi), *C. annum* L. var. *angulosum* Mill. and *Solanum melongena* L. (Shinkuro) from Sakata Seeds Co., Yokohama; seeds of *C. annuum* L. var.

fasciculatum Irish (Yatsubusa) and berries of *Physalis alkekengi* L. var. *francheti* Hort., from which seeds were obtained, from Hirata Seeds Co., Narashino, Chiba, and dried berries of *Lycium chinense* Mill. (a crude drug), from which seeds were obtained, from Kinokuniya Kan-Yaku Kyoku Co., Tokyo.

Triterpenes of P. alkekengi *var.* francheti *seeds.* The acetylated 4,4-dimethylsterol fraction (191 mg) from the seeds (225 g) was fractionated into four major zones on argentation PLC. The least polar zone gave 1-acetate (30 mg): mp 118–120°. IR ν_{max} cm^{-1}: 1730, 1245 (OAc). PMR: δ 0.69 (3H, *s*, C-18), 0.88 (9H, *s*, C-30, C-31, C-32), 1.00 (3H, *s*, C-19), 2.05 (3H, *s*, C-3β-OAc), 0.86 (6H, *d*, C-26, C-27, J = 6.1 Hz), 4.50 (1H, *m*, C-3α, $W_{1/2}$ = 15.2 Hz). MS *m/e* (rel. int.): 470 (M^+, 40), 455 (100), 410 (1), 395 (60), 357 (1), 315 (1), 301 (3), 297 (9), 296 (12). The second zone from the solvent front gave 4-acetate (35 mg): mp 134–136°. IR ν_{max} cm^{-1}: 3050 (cyclopropyl); 1736, 1239 (OAc). PMR: δ 0.90 (9H, *s*, C-30, C-31, C-32) [18], 0.96 (3H, *s*, C-18) [15], 2.05 (3H, *s*, C-3β-OAc), 0.34, 0.56 (each 1H, *d*, C-19, J = 4 Hz), 0.87 (6H, *d*, C-26, C-27, J = 5.7 Hz), 4.55 (1H, *m*, C-3α, $W_{1/2}$ = 15.9 Hz). MS *m/e* (rel. int.): 470 (M^+, 24), 455 (23), 410 (100), 395 (72), 367 (30), 357 (10), 341 (24), 297 (28), 288 (49), 203 (28). The third zone gave 5-acetate accompanied with 2-acetate (traces) (19 mg): mp 123–124°. IR ν_{max} cm^{-1}: 3050 (cyclopropyl); 840, 816 (>C=CH—); 1732, 1240 (OAc). PMR: δ 0.89 (9H, *s*, C-30, C-31, C-32), 0.96 (3H, *s*, C-18), 1.63 (3H, *bs*, C-26, [19], 1.69 (3H, *bs*, C-27) [19], 2.05 (3H, *s*, C-3β-OAc), 0.34, 0.57 (each 1H, *d*, C-19, J = 4 Hz), 5.10 (1H, *t*, C-24, J = 7.2 Hz), 4.58 (1H, *m*, C-3α, $W_{1/2}$ = 13.3 Hz). MS *m/e* (rel. int.): 468 (M^+, 20), 453 (13), 408 (100), 393 (52), 357 (2), 339 (30), 297 (21), 286 (45), 271 (25), 255 (15). The fraction (22 mg) from the most polar zone was a mixture of the acetates of **3** (25%) and **6** (75%). Repeated argentation PLC of the upper part of the zone gave **3**-acetate ($\simeq$1 mg, 86% pure on GLC): mp 133–137° (because of the insufficiency of the available material it could not be obtained in a high purity). IR ν_{max} cm^{-1}: 3060, 1630, 882 (>C=CH_2), 1730, 1238 (OAc). PMR: δ 0.69 (3H, *s*, C-18), 0.88 (9H, *s*, C-30, C-31, C-32), 1.00 (3H, *s*, C-19), 2.05 (3H, *s*, C-3β-OAc), 1.03 (6H, *d*, C-26, C-27, J = 6.4 Hz), 4.69 (2H, *bd*, C-28, J = 4.4 Hz), 4.50 (1H, *m*, C-3α, $W_{1/2}$ = 15.7 Hz). MS *m/e* (rel. int.): 482 (M^+, 64), 467 (100), 439 (5), 422 (3), 407 (57), 301 (13), 297 (3), 283 (8), 241 (14). The acetate of authentic **3** prepared from **2**-acetate [20] showed mp 145–146° (lit. [21] mp 147–150°). The lower part of the most polar zone gave **6**-acetate (8 mg) after repeated argentation PLC: mp 116–118°. IR ν_{max} cm^{-1}: 3080, 1640, 885 (>C=CH_2); 3040 (cyclopropyl); 1734, 1245 (OAc). PMR: δ 0.90 (9H, *s*, C-30, C-31, C-32), 0.97 (3H, *s*, C-18, 2.05 (3H, *s*, C-3β-OAc), 0.34, 0.58 (each 1H, *d*, C-19, J = 4.4 Hz), 1.03 (6H, *d*, C-26, C-27, J = 6.8 Hz), 4.69 (2H, *bd*, C-28, J = 4.4 Hz), 4.58 (1H, *m*, C-3α, $W_{1/2}$ = 21 Hz). MS *m/e* (rel. int.): 482 (M^+, 16), 467 (14), 422 (100), 407 (84), 379 (36), 357 (7), 353 (17), 301 (14), 300 (36), 297 (34), 285 (15).

Triterpenes of C. annuum (*California chili*) *seeds.* The acetylated 4,4-dimethylsterol fraction (808 mg) from the seeds (1000 g) was separated into five major zones on argentation PLC. The zone nearest to the solvent front gave **1**-acetate accompanied with **8**-acetate (traces) (126 mg): mp 118–119°, and the second zone afforded **4**-acetate (159 mg): mp 134–135°. The third zone gave a mixture (293 mg) of the acetates of **2** (17%) and **5** (83%). Repeated argentation PLC of the upper part of the zone gave **2**-acetate (3 mg, 81% pure on GLC): mp 132–134°. IR ν_{max} cm^{-1}: 814 (>C=CH—); 1732, 1240 (OAc). PMR: δ 0.69 (3H, *s*, C-18), 0.88 (9H, *s*, C-30, C-31, C-32), 1.00 (3H, *s*, C-19), 1.61 (3H, *s*, C-26), 1.69 (3H, *s*, C-27), 2.05 (3H, *s*, C-3β-OAc), 5.09 (1H, *t*, C-24, J = 7.1 Hz), 4.51 (1H, *m*, C-3α, $W_{1/2}$ = 16 Hz). MS *m/e* (rel. int.): 468 (M^+, 79), 453 (100), 408 (10), 393 (62), 315 (5), 301 (13), 297 (5), 255 (11), 241 (14), 229 (10). The lower part of the zone gave **5**-acetate (150 mg) after repeated argentation PLC: mp 122–124°.

The fourth zone from the solvent front gave **7**-acetate (16 mg): mp 216–218°. IR ν_{max} cm^{-1}: 3080, 1640, 878 (>C=CH_2); 1730, 1245 (OAc). PMR [22]: δ 0.78 (3H, *s*, C-28), 0.84 (9H, *s*, C-23, C-24, C-25), 0.94 (3H, *s*, C-27), 1.03 (3H, *s*, C-26), 1.68 (3H, *s*, C-30), 2.04 (3H, *s*, C-3β-OAc), 4.57, 4.67 (each 1H, *bs*, C-29, $W_{1/2}$ = 5 Hz), 4.48 (1H, *m*, C-3α, $W_{1/2}$ = 16 Hz). MS *m/e* (>150, rel. int.): 468 (M^+, 66), 453 (14), 408 (9), 393 (9), 357 (14), 299 (11), 289 (9), 276 (19), 249 (24), 218 (35), 203 (43), 189 (100). The most polar zone gave **6**-acetate accompanied with **3**-acetate (traces) (24 mg): mp 116–117°.

Triterpenes of D. stramonium *seeds.* Unsaponifiable matter (1.92 g) from the seeds (500 g) was separated into five major zones on Si gel PLC. The 4,4-dimethylsterol fraction (181 mg) from the second zone (R_f 0.46) from the solvent front was further fractionated, after acetylation (190 mg), into four major zones on argentation PLC. The least polar zone gave **8**-acetate accompanied with minor quantities of the acetates of **1** and **4**, which on further purification afforded **8**-acetate (80 mg): mp 245–247°. IR ν_{max} cm^{-1}: 810 (>C=CH—); 1731, 1240 (OAc). PMR [23]: δ 0.83 (3H, *s*, C-28), 0.87 (12H, *s*, C-23, C-24, C-29, C-30), 0.97 (3H, *s*, C-26), 1.13 (3H, *s*, C-25), 1.26 (3H, *s*, C-27), 2.04 (3H, *s*, C-3β-OAc), 5.18 (1H, *t*, C-12, J = 3 Hz), 4.52 (1H, *m*, C-3α, $W_{1/2}$ = 16 Hz). MS *m/e* (rel. int.): 468 (M^+, 3), 453 (1), 408 (2), 218 (100), 207 (37). The second zone from the solvent front gave **5**-acetate accompanied with **2**-acetate (traces) (51 mg): mp 122–123°. The third zone afforded **7**-acetate (3 mg): mp 217–219°, and the most polar zone gave a mixture of the acetates of **3**, **6** and other unidentified compounds (11 mg). The least polar zone (R_f 0.52) on the Si gel PLC of the unsaponifiable matter gave a pentacyclic keto alcohol (R_t 2.6 on GLC, 150 mg): mp 285–286° (from C_6H_6). IR ν_{max} cm^{-1}: 3500 (OH); 1688 (C=O); 810 (>C=CH—). PMR [17]: δ 0.85 (3H, *s*, C-28), 0.88 (6H, *s*, C-29, C-30), 1.11 (3H, *s*, C-27), 1.17 (3H, *s*, C-23), 1.34 (3H, *s*, C-26), 1.42 (3H, *s*, C-24), 1.52 (3H, *s*, C-25), 4.52 (1H, *bs*, C-6α, $W_{1/2}$ = 6.9 Hz), 5.26 (1H, *t*, C-12, J = 3.4 Hz), 2.78 (1H, *m*, C-2β). MS *m/e* (rel. int.): 440 (M^+, 29, found 440.3648, $C_{30}H_{48}O_2$, required 440.3651), 425 (8), 407 (3), 258 (13), 218 (100), 203 (78). These spectral data were identical with those reported for daturaolone (**9**, lit. mp 276–279°) [17]. Therefore, the triterpene is considered to have the structure **9**. The most polar zone (R_f 0.23) on the Si gel PLC of the unsaponifiable matter afforded a pentacyclic triterpene diol (R_t 2.8 on GLC, 220 mg): mp 261–265°. IR ν_{max} cm^{-1}: 3500 (OH); 818 (>C=CH—). PMR [17]: δ 0.84 (3H, *s*, C-28), 0.88 (6H, *s*, C-29, C-30), 1.08 (3H, *s*, C-23), 1.11 (3H, *s*, C-27), 1.18 (3H, *s*, C-24), 1.27 (3H, *s*, C-26), 1.33 (3H, *s*, C-25), 4.59 (1H, *bs*, C-6α, $W_{1/2}$ = 6.9 Hz), 3.15 (1H, *t*, C-3α, J = 7.7 Hz), 5.27 (1H, *t*, C-12, J = 3 Hz). MS *m/e* (rel. int.): 442 (M^+, 8, found 442.3789, $C_{30}H_{50}O_2$, required 442.3807), 427 (2), 409 (2), 258 (5), 218 (100), 203 (27). Since these spectral data were identical with those reported for daturadiol (**10**, lit. mp 260–261°) [17], the triterpene diol isolated is regarded as **10**.

Acknowledgements—We thank Dr. M. Takido, Dr. Y. Koyama, Kagome Co. and Japan Monopoly Corp. for generous gifts of the seed samples. Our thanks are also due to Dr. Y. Toyama for valuable comments and advice.

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