suspension was allowed to warm to room temperature over a 5–10-min period, diluted with ether, and extracted once each with water, 10% sulfuric acid, saturated sodium bicarbonate, and saturated brine. The dried ($MgSO_4$) ethereal solution was evaporated, a 1.4-g crop of yellow crystals (from petroleum ether, bp 60–68°) was separated by filtration, and the concentrated filtrate was distilled under reduced pressure. *tert*-Butyl thiolbenzoate (8.7 g, 45%) was obtained as a water-white liquid: bp ~135–145°(15–25 mm) [lit.[41] bp 127° (11 mm)]; ir (all s) 687, 772, 908, 1060, 1205, 1655 cm^{-1} (C=O); nmr δ 1.55 (s, 9 H), 7.2–7.4 (m, 3 H), 7.7–7.9 (m, 2 H).

A solution of the thiolbenzoate (99 mg, 0.51 mmol) in ~30 ml 50% aqueous dioxane (v/v before mixing) was heated at 105° for 12 days in a sealed ampoule. The ester (83 mg, 84%), recovered by extraction with pentane, had unchanged ir and nmr spectra.

Acknowledgment.—We thank the National Institutes of Health for financial assistance and the National Science Foundation for funds used in the purchase of a Varian HR 220 nmr spectrometer.

(41) H. Reinholt, F. Mott, and E. Motzkers, *J. Prakt. Chem.*, **134**, 274 (1932).

Registry No.—**5**-OH, 40599-63-1; **5**-OMs, 40599-64-2; **5**-d_3-OMs, 40625-59-0; **6** (R = H), 40599-65-3; **6** (R = H) *p*-nitrobenzoate, 40599-66-4; **6**-d_3 (R = H) (R*), 40599-67-5; **6**-d_3 (R = H) (S*), 40625-60-3; **6** (R = Ac), 40599-68-6; **6** (X = N_3), 40625-61-4; *cis*-**7**, 32166-40-8; *trans*-**7**, 21370-71-8; *cis*-**8a** (X = OH), 40599-69-7; *trans*-**8a** (X = OH), 40599-70-0; *cis*-**8b** (X = S-*n*-Bu), 40599-71-1; *trans*-**8b** (X = S-*n*-Bu), 40599-72-2; **9**, 40599-73-3; **9**-d_3, 40625-62-5; **10**, 40599-74-4; **10**-d_3, 40625-63-6; **11**, 40599-75-5; **12**, 40724-84-3; **13**, 40599-77-7; **14a**, 40599-78-8; **14b**, 40599-79-9; **15**, 40599-80-2; **16**, 40599-81-3; **17b**, 40599-82-4; **18**, 40599-83-5; **19**, 40599-84-6; **20**, 40599-85-7; **23**, 60-12-8; **24**, 40625-64-7; **26a**, 40599-86-8; **26b**, 40599-87-9; **27a**, 40599-88-0; **27b**, 40599-89-1; **28a**, 40599-90-4; **28b**, 40599-91-5; **29a**, 40599-92-6; **29b**, 40599-93-7; **30a**, 40599-94-8; **30b**, 40599-95-9; **31a**, 40599-96-0; **31b**, 40599-97-1; *n*-butanethiol, 109-79-5; methanesulfonyl chloride, 124-63-0; 4α,β-methyl-3,4,4aβ,5,6,7,8,8aα-octahydronaphthalen-2(1*H*)-one, 938-07-8; sodium azide, 12136-89-9; *p*-nitrophenol, 100-02-7.

Triterpenes of *Datura innoxia* Mill. Structure of Daturadiol and Daturaolone

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Two new pentacyclic triterpenes, daturadiol and daturaolone, have been isolated from *Datura innoxia* Mill. seeds (Solanaceae). The structures—3β,6β-dihydroxyolean-12-ene and 3-oxo-6β-hydroxyolean-12-ene—were established by chemical degradation and supported by the spectral properties.

Two new pentacyclic triterpenes have been isolated from *Datura innoxia* Mill. (Solanaceae), a known source of tropane alkaloids.[1] A mixture of these two compounds crystallized from the oil extracted from the seeds.[2] The determination of their structure is presented below.

The pmr spectrum of the more polar *Datura* triterpene—daturadiol **1a**—shows the presence of two secondary hydroxyl groups and a trisubstituted double bond (Table I). The spectrum shows also the presence of eight tertiary methyl groups. The latter observation, combined with the shape and position of the olefinic proton signal [triplet δ 5.22 (J = 3 Hz)], suggested that the compound was most probably a diol of the β-amyrin type. Acetylation at room temperature gave the monoacetate **1d**; its pmr spectrum (Table I) showed that only the triplet-like signal, ascribed to the 3α-H, was shifted downfield with a slight change in shape. The molecular rotation change caused by the acetylation ($\Delta[M]_D$ = −57°) is consistent with similar values for 3β-hydroxytriterpenes (*e.g.*, β-amyrin −33°, α-amyrin, −29°, lupeol −69°, taraxasterol −67°, and ψ-taraxasterol −53°).

The low reactivity of the second secondary hydroxyl group, and the shape of the signal corresponding to the HCOH [broad singlet at δ 4.54 ($W_{1/2}$ = 10 Hz)] indicated that it was axially oriented. Prolonged reaction time at boiling temperature with pyridine–acetic anhydride or acetic anhydride–boron trifluoride etherate at room temperature led to daturadiol diacetate **1c**.

This diacetate, when oxidized with a stoichiometric amount of selenium dioxide, gave a derivative typical for a β-amyrin, that is the 11,13(18)-diene[3] **2**, with characteristic uv absorption. Prolonged oxidation with an excess of selenium dioxide led to a second characteristic product[4] **3**, showing typical uv and ir absorption.

To assure the presence of the β-amyrin skeleton the axial hydroxyl group was removed by the following series of reactions. The monoacetate **1d** was oxidized with Jones reagent to the keto acetate **1e**. The latter underwent Wolff–Kishner reduction only under drastic conditions (anhydrous hydrazine, sodium in ethylene glycol), yielding β-amyrin in 25% yield.

Evidence for the location of the second hydroxyl group is provided by the pmr spectrum of keto acetate **1e** (Table I). The broad singlet of the equatorial proton was replaced by a slightly broadened doublet at δ 2.51 (J = 12.5 Hz) and a singlet at δ 2.23. Thus the fragment $\gtrless CCHCOCH_2C \lessgtr$ should be present in the keto acetate. In β-amyrin there is only one such possible location for a carbonyl group, *i.e.*, position 6.

The second new triterpene, daturaolone **1b**, was less polar than daturadiol. Its ir spectrum showed the presence of hydroxyl and carbonyl groups. As in the case of daturadiol, an olefinic proton signal and a broad singlet of 6α-H are present (Table I), as well as a one-proton multiplet (doublet of triplets) at 2.76 ppm. In addition, eight tertiary methyl group signals are

(1) H. G. Boit, "Ergebnisse der Alkaloid Chemie bis 1960," 1961.
(2) C. K. Atal, *et al.*, Indian Pharmaceutical Congress, Hajderabad, 1967.
(3) "Elsevier Encyclopedia," 14th Suppl., 1952, pp 945–1064.
(4) H. Budzikiewicx, J. M. Wilson, and C. Djerassi, *J. Amer. Chem. Soc.*, **85**, 3688 (1963).

TABLE I

100-MHz SPECTRAL DATA OF *Datura* TRITERPENES AND THEIR DERIVATIVES[a]

Compd	2β-H	3α-H	5α-H	6α-H	7α-H	12-H	23	24	25	26	27	28	29,30	CH_3COO-
							Methyl group signals, the most probable assignment[b]							
1a		3.15 t (7.5)		4.54 b s		5.21 t (3)	1.08	1.18	1.32	1.27	1.10	0.84	0.88	
1b	2.76 m			4.48 b s		5.23	1.17	1.42	1.51	1.33	1.10	0.85	0.88	
1c		4.44 q (10, 7)		5.55 b s		5.23 t (3)	0.93	1.03	1.33	1.14	1.10	0.81	0.87	2.03 (two)
1d		4.45 q (10, 6)		4.45 b s		5.23 t (3)	0.95	1.26	1.35	1.26	1.10	0.83	0.87	2.04
1e		4.41 q	2.21 s		2.51 d (12.5)	5.23 t (3)	1.01	1.31	0.98	0.94	1.26	0.81	0.88	2.04
1g			2.12		2.52 d (12.2)	5.20 t (3)	1.00	1.27	0.93	0.93	1.27	0.81	0.88	
5α-1h	2.79 m		2.47 s		2.52 d (12)	5.24 t (3)	1.25	1.52	1.12	1.08	1.25	0.82	0.88	
5β-1h			2.40 s		2.50 d (12)	5.27 t	(1.23,	1.20,	1.16,	1.13,	1.04)	0.82	0.88	
4				5.58 t, 4.2		5.24 t (3)	(1.27,	1.24,	1.13,	1.04,	0.93)	0.85	0.88	

[a] In $CDCl_3$, δ values (*J* in hertz). [b] The following values of the "6-substitution effect" (close to those given in ref 4) were used.

6β-OH	0.08	0.39	0.40	0.27	−0.03	0	0
6β-OAc	0.07	0.17	0.37	0.18	−0.03	−0.01	0.01
6-Oxo	0.14	0.45	0.03	−0.02	0.12	−0.03	0.01

clearly visible. Oxidation of daturaolone with Jones reagent led to the same diketone **1h** as obtained from daturadiol. Therefore daturaolone must have the structure **1b** (3-oxo-6β-hydroxyolean-12-ene). The one-proton multiplet in the pmr spectrum of daturaolone is ascribed to the 2β(axial)-H. It is also visible at the same position in the spectrum of daturadione **1h**, which in addition shows the signals of the 5α and 7α protons. The 5α-H signals in the spectra of **2e** and **1h** are shifted downfield by 0.09 and 0.35 ppm, respectively, compared with the position in the spectrum of the 6-oxo compound **1h** described below, an observation which provides additional evidence for the close vicinity of both oxygen functions.

Daturadione **1h**, when refluxed with base, underwent epimerization to the more polar 5β epimer to the extent of approximately 10%. The mass spectrum of the latter was very similar to that of the 5α epimer (Table II), but its pmr spectrum, with shifted methyl and 2-, 5-, and 7-H signals, reflected the change in configuration (Table I). When the epimerization was carried out with D_2O and NaOD in monoglyme, five deuterium atoms were incorporated, as shown by the change in the molecular ion from *m/e* 438 to 443 (Table II).

TABLE II

MASS SPECTRAL DATA OF *Datura* TRITERPENES

Compd	Molecular ion *m/e*	Molecular ion %	189,[a] %	203,[a] %	218, %	258, %
1a	442	3.2	14	38	100	4.8
1b	440	4.1	11	37	100	4.2
1c	526	1.3	6	34	100	15
1d	484	2.6	7	18	100	4.6
1e	482	5.1	7	30	100	3.9
1f	426	5.0	16	51	100	8.1
1g	424	2.1	7	21	100	5.1
5α-1h	438	9.5	12	51	100	3.1
5β-1h	438	12	10	63	100	5.5
1h-d_5	443	3.4	9	48	100	3.3
	442	1.9				
	441	0.3				
	422	27	24	52	100	18

[a] Ions *m/e* 189 and 203 are formed from the ion *m/e* 218 by elimination of *m/e* 15 and 29: K. Takahashi, K. Kanayama, Y. Tanabe, and M. Takani, *Chem. Pharm. Bull.*, **20**, 2106 (1972).

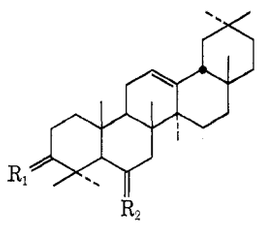
The mass spectra of all compounds are fully consistent with 3,6 substitution of the oleane skeleton. For Δ^{12} compounds the dominating fragmentation process is the formation of the ion 218 in the retrodiene reaction which represents the base peak in all compounds and is derived from ring D and E.[4] A second retrodiene reaction starting with the formation of the 5(6) double bond is also present[5,6] (ion *m/e* 258 for **1** and **4**, shifted to 256 for **2**). This process is more pronounced in the spectra of daturadiol diacetate **1c** and anhydrodaturaolone **4** (Table II).

Tables I and II give properties of some other products derived from the new *Datura* triterpene. 6β-Hydroxy- and 6-oxoolean-12-ene (**1f** and **1g**) were obtained by Wolff–Kishner reduction of daturaolone and daturadiol, respectively. The latter reaction demonstrates the great steric hindrance of the 6-keto function, similar to the situation in the case of sumaresinolic acid[7] and astilbic acid.[8]

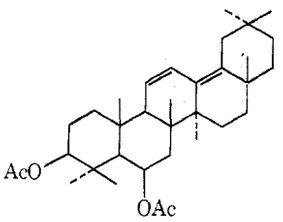
An independent proof of the daturaolone structure is the formation of the anhydro compound **4** from daturaolone by treatment with thionyl chloride in pyridine. The pmr spectrum of this product demonstrates the presence of only two olefinic proton signals, the triplet of H-12 at 5.24 (J = 3 Hz) and the triplet of H-6 at 5.58 ppm (J = 4.2 Hz).

Daturadiol and daturaolone are members of the rare class of 6β-hydroxylated β-amyrin derivatives.

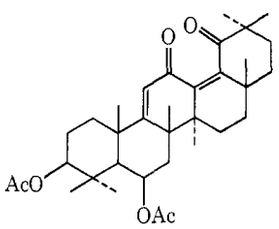
(5) I. Wahlberg and G. R. Enzell, *Acta Chem. Scand.*, **25**, 70 (1971).
(6) I. Kitagawa, A. Inada, I. Yosioka, R. Somanathan, and M. U. S. Sultanbawa, *Chem. Pharm. Bull.*, **20**, 633 (1972).
(7) C. Djerassi, G. N. Thomas, and O. Jeger, *Helv. Chim. Acta*, **38**, 1304 (1955).
(8) H. Hikino, S. Nabetani, and T. Takemoto, *Yakugaku Zasshi*, **92**, 891 (1972).



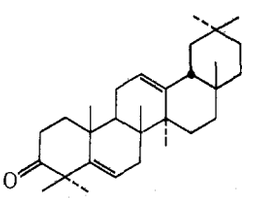
1	R_1	R_2
a	β-OH, α-H	β-OH, α-H
b	O	OH, H
c	β-OAc, α-H	β-OAc, α-H
d	β-OAc, α-H	β-OH, α-H
e	β-OAc, α-H	O
f	H_2	β-OH, α-H
g	H_2	O
h	O	O



2



3



4

The only other known examples are sumaresinolic acid,[7] its 3-keto derivative[5] (3β,6β-dihydroxy- and 3-oxo-6β-hydroxyolean-12-en-28-oic acid, respectively), and protobassic acid[6] (2β,3β,6β,23-tetrahydroxyolean-12-en-28-oic acid). Recently also 6β-hydroxylation of oleanolic acid by a soil bacterium[8] has been observed and the new acid astilbic acid[9] (3β,6β-dihydroxyolean-12-en-27-oic) has been described. The *Datura* triterpenes represent the parent compounds of the above group.

Experimental Section

Melting points were measured on a micro hot plate. Optical rotations were measured at 0.5% concentration in chloroform. Pmr spectra were determined with a Jeol 100-MHz spectrometer in $CDCl_3$ solution (accuracy of chemical shift measurements, ±0.5 Hz). Mass spectra were carried out on an LKB 9000 apparatus, ionization energy 70 eV.

Extraction and Purification of 1b and 1a.—Coarsely powdered *Datura innoxia* seeds (5 kg) were extracted with petroleum ether (bp 60–80°). The oil obtained (400 ml) was kept at 10° for 10 days, during which time a crystalline solid (4.5 g) separated. It was chromatographed on 150 g of alumina. Elution with benzene gave 3.5 g of daturaolone **1b**, which was crystallized from benzene and a mixture of chloroform and methanol: mp 276–279°; $[\alpha]_D$ +48.5°; ν_{max} (KBr) 3500, 1690 cm^{-1}.

Anal. Calcd for $C_{30}H_{48}O_2$: C, 81.76; H, 10.98. Found: C, 81.64; H, 10.72.

Subsequently 0.8 g of daturadiol **1a** was eluted with benzene–chloroform (9:1). It was recrystallized from benzene–chloroform and chloroform–methanol and had mp 260–261°, $[\alpha]_D$ +48.9°, ν_{max} (KBr) 3500 cm^{-1}.

Anal. Calcd for $C_{30}H_{50}O_2$: C, 81.39; H, 11.4. Found: C, 81.44; H, 11.31.

Daturadione 1h.—Oxidation of both of the above compounds with Jones reagent in acetone at room temperature for 5 min yielded the same compound **1h** (melting point, mixture melting point, ir, and R_f value) which was recrystallized from methanol–chloroform and had mp 198–201°, $[\alpha]_D$ +50.3°, ν_{max} (KBr) 1705 cm^{-1}.

Anal. Calcd for $C_{30}H_{46}O_2$: C, 82.13; H, 10.6. Found: C, 82.23; H, 10.45.

5-Epidaturadione.—Daturadione refluxed with 5% NaOH in ethylene glycol for 4 hr was transformed in about 10% yield to a more polar compound, which was separated by chromatography on silica gel with benzene as solvent and crystallized from dilute alcohol: mp 187–191°.

Deuteration of Daturadione.—Daturadione **1h** (25 mg) was refluxed for 1 hr with 5% NaOD in D_2O (2 ml) and 5 ml of monoglyme. When the hot solution was diluted with D_2O, 19 mg of a mixture of both epimers (9:1, tlc) separated and was purified by washing with D_2O: mp 168–182°; ν_{max} (KBr) 2250, 2140, 1705 cm^{-1}. Bands at 1440 and 1280 cm^{-1} in the spectrum of daturadione were no longer present.

Monoacetate of Daturadiol 1d.—**1a** (224 mg) was kept in 5 ml of pyridine and 1 ml of acetic anhydride for 4 days at room temperature. The usual work-up and chromatography on silica gel with benzene yielded pure monoacetate which was crystallized from dilute alcohol: 190 mg; mp 227–236°; ν_{max} (KBr) 3520, 1704, 1265 (C_2Cl_4), 3600, 1730, 1240 cm^{-1}.

Anal. Calcd for $C_{32}H_{52}O_3$: C, 79.28; H, 10.81. Found: C, 79.07; H, 10.82.

Daturadiol Diacetate 1c.—Daturadiol **1a** (142 mg) was refluxed in pyridine–acetic anhydride mixture for 4 hr. The two products formed were separated on a silica gel column with benzene as solvent. After the monoacetate **1d** (26 mg) was eluted, further elution gave the pure diacetate, which was crystallized from dilute alcohol: 54 mg; mp 141–144°; $[\alpha]_D$ +34.2°; ν_{max} (KBr) 1735, 1245 cm^{-1}.

Anal. Calcd for $C_{34}H_{54}O_4$: C, 77.52; H, 10.33. Found: C, 78.10; H, 10.23.

Acetylation of daturadiol with acetic anhydride in the presence of boron trifluoride etherate gave only the diacetate (same R_f value and melting point) accompanied by a small amount of nonpolar products.

3β,6β-Diacetoxyolean-11,13(18)-diene (2).—Daturadiol diacetate **1c** (66.5 mg) was refluxed with 20 mg of selenium dioxide in 5 ml of acetic acid for 3 hr. Chromatography of the products with benzene on a silica gel column yielded 40 mg of pure diene, which was crystallized from dilute methanol: yield 32 mg; mp 242°; ν_{max} (KBr) 1735, 1250, 1620 (w), 815 (w), 800 (w), 785 cm^{-1} (w); λ_{max} (ethanol) 242.5, 250.0, 260.0 nm (log ε 4.37, 4.40, 4.20); mass spectrum *m/e* (rel intensity) 524 (43, M^+), 509 (11), 464 (100), 449 (11), 404 (16), 389 (29), and 256 (21).

3β,6β-Acetoxy-12,19-dioxoolean-9(11),13(18)-diene (3).—Daturadiol diacetate **1c** (12 mg) was refluxed overnight with 100 mg of selenium dioxide in 5 ml of acetic acid. Chromatography of the products on a small silica gel column with benzene–ethyl acetate (9:1) gave the pure yellow product, which was crystallized from methanol: yield 7 mg; mp 252–256°; ν_{max} (KBr) 1730, 1685, 1610, 1590, 1240 cm^{-1}; λ_{max} (ethanol) 278 nm (log ε 3.96); mass spectrum *m/e* (rel intensity) 552 (100, M^+), 537 (5), 524 (4), 492 (13), 482 (79), 464 (6), 432 (5), 422 (25), 417 (8), 363 (31), 347 (12).

6-Oxo-3β-acetoxyolean-12-ene (1e).—The monoacetate **1d** (85 mg) was oxidized with excess Jones reagent in acetone for 15 min, diluted with water, extracted into ether, and crystallized from dilute ethanol to give 78 mg of the pure keto acetate: mp 251°; $[\alpha]_D$ +62.5°; ν_{max} (KBr) 1730, 1700, 1245 cm^{-1}.

Anal. Calcd for $C_{32}H_{50}O_3$: C, 79.62; H, 10.44. Found: C, 79.53; H, 10.22.

Reduction of 1e to β-Amyrin.—The above keto acetate (53 mg) was refluxed at 135–140° for 2 days with 25 ml of ethylene glycol in which 1 g of sodium and 5 ml of anhydrous hydrazine were dissolved. Then the mixture was distilled until the temperature reached 200° and refluxed for an additional 6 hr; 10.7 mg of β-amyrin was obtained by chromatography of the products over silica gel with benzene as eluting solvent. The product was crystallized from dilute alcohol, melting point and mixture melting point identical with that of authentic β-amyrin, 196.5–198°. The ir spectra (KBr) were identical.

6β-Hydroxyolean-12-ene (1f).—Daturaolone **1b** (102 mg) was refluxed with 2.5 g of KOH, 2.0 ml of hydrazine hydrate, and 0.5 ml of hydrochloric acid in 12 ml of diethylene glycol for 4 hr; then the temperature of the mixture was adjusted to 210° by distillation of hydrazine and refluxed for an additional 4 hr.[10] The usual work-up and crystallization from dilute alcohol yielded

(9) K. Takahashi, K. Kanayama, Y. Tanabe, and M. Takani, *Chem. Pharm. Bull.*, **20**, 2106 (1972).

(10) W. Nagata and N. Itazaki, *Chem. Ind. (London)*, 1194 (1964).

82 mg of pure product: mp 178–182°; $[\alpha]_D$ +74°; ν_{max} (KBr) 3620 cm^{-1}.

Anal. Calcd for $C_{30}H_{50}O$: C, 84.44; H, 11.81. Found: C, 84.42; H, 11.75.

6-Oxoolean-12-ene (1g).—Daturadione **1h** (95 mg) was reduced in the same manner to give 69 mg of the product: mp 174–176°; $[\alpha]_D$ +88°; ν_{max} (KBr) 1705 cm^{-1}.

Anal. Calcd for $C_{30}H_{48}O$: C, 84.84; H, 11.4. Found: C, 84.74; H, 11.60.

Oxidation of the alcohol **1f** with Jones reagent yielded the same ketone, as proved by ir and mixture melting point.

3-Oxoolean-5,12-diene (4).—Daturaolone (205 mg) in 5 ml of pyridine was treated with 1 ml of thionyl chloride in an ice bath. The usual work-up and crystallization from dilute alcohol yielded 173 mg of pure product: mp 169–171°; ν_{max} (KBr) 1700, 1660, 840 cm^{-1}.

Anal. Calcd for $C_{30}H_{46}O$: C, 85.24; H, 11.0. Found: C, 85.16; H, 11.15.

Registry No.—**1a**, 41498-79-7; **1b**, 41498-80-0; **1c**, 41579-25-3; **1d**, 41498-81-1; **1e**, 41498-82-2; **1f**, 41498-83-3; **1g**, 41498-84-4; 5α-**1h**, 41498-85-5; 5β-**1h**, 41498-86-6; **1h**-d_5, 41499-07-4; **2**, 41498-87-7; **3**, 41498-88-8; **4**, 41498-89-9.

Cyclotrichosantol, a New C_{31} 31-Nortriterpene

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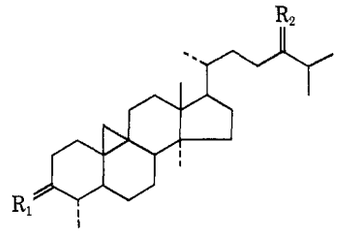
Isolation of cycloeucalenol **1a** and a novel methylsterol—cyclotrichosantol (**2a**, 4α,14α-dimethyl-24-ethyl-9:19-cyclocholest-25-en-3β-ol)—from the leaves of *Trichosantes palmata* L., Cucurbitaceae, is described. The structure was established on the basis of mass and nmr spectra with the use of $Eu(dpm)_3$. The probably biogenetic significance of cyclotrichosantol is discussed.

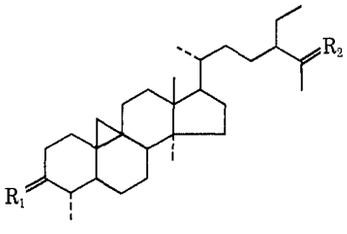
Although the biogenesis of C-29 plant sterols containing a 24-ethyl group by way of the precursors (24-methylenecycloartenol, cycloeucalenol, obtusifiol, and citrostadienol) has been well established,[1] it seems probable that this is not the only possible biogenetic pathway. It is also possible that certain minor Δ^{25} sterols, widely distributed in some plants,[2a] especially in those of the Cucurbitaceae family,[2b,c] are markers of an alternative pathway for the introduction of a 24-ethyl group, just as similarly 24-ethylidenesterols, *e.g.*, Δ^5 and Δ^7 avenasterols, are considered to be markers of such a pathway.

In the present paper we describe the structure elucidation of a new cyclopropane methylsterol, cyclotrichosantol **2a**, which was isolated from the leaves of *Trichosantes palmata* L. (Cucurbitaceae), an Indian medicinal plant, together with cycloeucalenol **1a**.

The so-called "methylsterol" fraction was isolated from the saponified petroleum ether (bp 30–60°) extract of the dry leaves by chromatography and crystallization subsequent to treatment of the whole saponified extract with urea to remove the aliphatic alcohols which mask the minute methylsterol fraction. Only two components were present as shown by tlc, and they were separated by preparative tlc, the less polar in 0.005 and the more polar in 0.009% yield based on the weight of dry leaves. The compound with lower R_f value was easily identified as cycloeucalenol **1a** on the basis of its properties (melting point, ir, mass spectrum, and pmr). This was confirmed by preparation of the acetate **1b**, the 3 ketone **1c**, and the 28 norketone **1d**, the properties of which were in good agreement with reported data.[3]



1



2

	R_1	R_2
a	β-OH, α-H	$=CH_2$
b	β-OAc, α-H	$=CH_2$
c	$=O$	$=CH_2$
d	β-OH, α-H	$=O$

The second compound—cyclotrichosantol—like cycloeucalenol **1a** exhibited the presence of cyclopropane and methylene groups in its ir and pmr spectra. Both compounds melted at nearly the same point (for cycloeucalenol mp 144–145°, for cyclotrichosantol mp 143–144°), and practically no depression was noted for the mixture, a circumstance which demonstrated the close relationship of the two compounds. Cyclotrichosantol gave an acetate **2b**, a 3 ketone **2c**, and a 26 norketone **2d**, the latter by oxidation with OsO_4–KIO_4.

Molecular ions in the mass spectra of all these compounds corresponded to the formula $C_{31}H_{52}O$ for the parent alcohol. The two previously known triterpenes having this composition, 24-methylenecycloartenol and cyclolaudenol, were excluded, as both melt at distinctly lower temperature (122 and 125°, respectively[4]).

Structure **2a** for cyclotrichosantol could, however,

(1) L. J. Goad in "Natural Substances Formed Biologically from Mevalonic Acid," T. W. Goodwin, Ed., Academic Press, New York, N. Y., 1970.

(2) (a) W. Sucrow, *Chem. Ber.*, **99**, 3559 (1966); M. Manzoor-i-Khuda, *Tetrahedron*, **22**, 2377 (1966); T. Sedane and T. Villacorta, *An. Real. Soc. Espan. Fis. Quim. Ser. B*, **66**, 1315 (1970); L. M. Belger, N. N. Rees, E. L. Ghisalberti, L. J. Goad, and T. W. Goodwin, *Tetrahedron Lett.*, 3043 (1970); S. C. Pakrashi and B. Achari, *ibid.*, 365 (1971). (b) R. R. Gonzales and F. M. Panizo, *An. Real. Soc. Espan. Fis. Quim. Ser. B*, **63**, 1123 (1967); W. Sucrow and A. Reimerdes, *Z. Naturforsch. B*, **23**, 42 (1968). (c) I. Belič, T. Čerin, and D. Stucin, *Vestn. Slov. Kem. Drûs.*, **18**, 1 (1971).

(3) J. S. C. Cox, F. F. King, and T. J. King, *J. Chem. Soc.*, 514 (1959).

(4) "Rodd's Chemistry of Carbon Compounds," Vol. IIC, 1969, p 423.