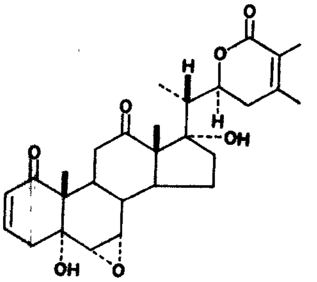
1700 (saturated six membered-ring ketone) and at 3526, 3510 cm^{-1} (two -OH groups). The compound remained unchanged upon attempted acetylation under mild conditions (Ac_2O–C_5H_5N at room temp.) indicating the tertiary nature of both –OH groups.

The NMR (100 MHz, $CDCl_3$) gave bands at δ: 5·85*d* (10, showing a weak allylic coupling with C-4 hydrogens), 2-H; 6·60 *dq* (10:4·5:3), 3-H; 3·08*d*(4), 6-H; 3·42*d* 4:1), 7-H; 4·55*m*, 22-H; and methyl group signals for 18 H, 19 H, 21 H, 27 H and 28 H at 1·1*s*, 1·26*s*, 0·9*d* (7), 1·52*s* and 1·58*s*, respectively (coupling constants are in Hz and given in brackets).

Most of the NMR signals of (1) are similar to the corresponding signals of the withanolides[2]. However, a significant difference between the positions of the 27 and 28 methyl signals, which appear very much upfield in the present compound is observed. This can be explained if the stereochemistry of C-22, unlike that of the other withanolides, is S. In this case the plane of the lactone ring lies at about 90° with respect to C(20)-C(22) bond, with the result that 27 and 28 methyls face[3] the rest of the molecule and in NMR, therefore, appear in the upfield. This, however, requires confirmation by CD studies.



(1)

MS of the compound shows trivial fragments at *m/e* 471 (M^+-15) 466 (M^+-18) and 448 (M^+-2 × 18). Cleavage of the C(20)-C(22) bond common to all withanolides gives rise to base peak at *m/e* 125.

Upon catalytic hydrogenation the compound quickly absorbed one mole of hydrogen giving rise to a dihydroderivative, mp 278–80°, λ_{max} (MeOH) at 227 nm and a low intensity band between 320–260 nm. There is a significant lowering in the intensity of the UV obsorption band in the dihydroderivative This shows that the double bond of the $\alpha\beta$-unsaturated carbonyl chromophore only has been hydrogenated. MS of this compound shows M^+ at 486 and other fragments at *m/e* 468, 450, 129, 125, 109, 105, 98, 97, 93, 81 etc. From the above data the compound can be assigned the structure as 5α, 17α-dihydroxy-1,12-dioxo-6α,7α-epoxy-22 *S*, witha-2, 24-dienolide. The compound was found identical with the product obtained by oxidation of daturalactone [1].

EXPERIMENTAL

Isolation Crushed fresh leaves of *D. quercifolia* were extracted with cold C_6H_6. The extract on concentration deposited a pale green crystalline substance which was chromatographed over a column of Si gel and eluted with C_6H_6–EtOAc (5:1). TLC (Si gel) R_f: 0·35 (C_6H_6–EtOAc, 1:1), (Found: C, 67·1:H, 7·51. Calculated for $C_{28}H_{36}O_7$:C, 67·35; H, 7·43%).

Hydrogenation Compound was hydrogenated (1 mol H_2) over 10% Pd–C in EtOAc. The hydrogenated product was crystallized from C_6H_6–EtOAc into microcrystalline needles, TLC, R_f; 0·45 (C_6H_6–EtOAc, 1:1), (Found: C, 66·88; H, 7·72. Calculated for $C_{28}H_{38}O_7$: C, 67·07; H, 7·81%).

Acknowledgements—Our thanks are due to Dr. C. K. Atal, Director, for his keen interest in this work and Mr. E. A. Underwood, Exeter University, for the spectral data. One of the authors AKK thanks C.S.I.R., New Delhi, for Senior Research Fellowship.

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4β-HYDROXYWITHANOLIDE E, A NEW NATURAL STEROID WITH A 17α-ORIENTED SIDE-CHAIN

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Key Word Index—*Physalis peruviana*; Solanaceae; steroidal lactones; withanolides; 4β-hydroxywithanolide E.

To the best of our knowledge the withanolides are the first group of naturally occurring steroids including members which possess the unusual 17α-oriented side-chain with all the carbon atoms present. Withanolides E (**1a**) and F (**1b**) [1] isolated from *Withania somnifera* chemotype III were recently followed by Nic-2 [2] and Nic-11 [3] from *Nicandra physaloides*[‖] and by withano-

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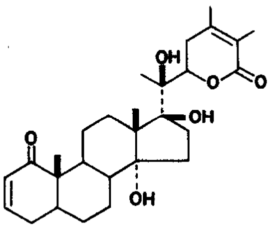
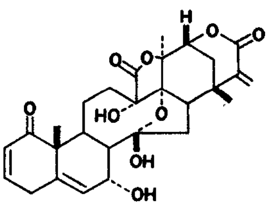
[‖] The steroids isolated from *N. physaloides* and designated as Nic 1 ... etc., are biogenetically related to the withanolides.

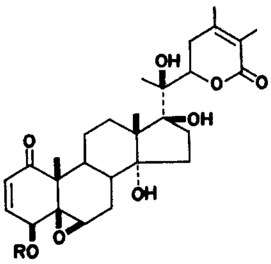
lide P (**1c**) [4] from *W. somnifera* chemotype I. The few previously known [5] 17α-alkyl steroids were pregnane derivatives.



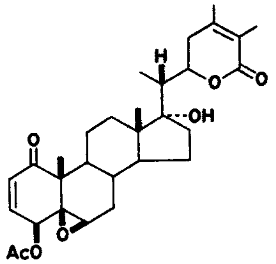
(**1a**) 5β,6β-epoxy
(**1b**) Δ^5
(**1c**) Δ^5, 20-desoxy



(**2**)



(**3a**) R = H
(**3b**) R = Ac



(**4**)

During an investigation of the constituents of *Physalis peruviana* (Solanaceae), a naturally growing perennial herb which is also cultivated in India for its edible fruit, four steroids have been isolated on silica gel by chromatography of the crude extract obtained from the leaves. They have been identified as physalin A (**2**) [6], withanolide E (**1a**), 2,3-dihydrowithanolide E and 4β-hydroxywithanolide E (**3a**). The structures of the first three compounds have been assigned by comparison with authentic samples, whereas the structure assigned to the latter is based on the analysis of its spectral data.

4β-Hydroxywithanolide E, $C_{28}H_{38}O_8$ (**3a**), ν_{max} 1710 and 1670 cm^{-1}, λ_{max} 215 nm (ε 17800) followed by end absorption (αβ-unsaturated ketone and αβ-unsaturated δ-lactone), c.d. (*c*, 0·24, ethanol) 340 nm (Δε + 1·42) (*cis* junction of rings A/B) and 252 nm (Δε + 4·25) (22 R). Acetylation afforded the non-crystalline mono-acetate (**3b**), the NMR spectrum (in $CHCl_3$) of which was compared with the spectra of (**4**) [4] and of (**1a**), thus revealing the similarity between rings A/B in (**3b**) and (**4**) (signals of 2-, 3-, 4- and 6-H and of 19-Me) and the similarity between ring D and the side chain in (**3b**) and (**1a**) (signals of 22-H and of 18-, 21-, 27- and 28-Me) (Table 1).

According to the X-ray analysis of (**1a**) [1], the 14α and 20-OH groups are held together on the α face of the molecule by hydrogen bonding, thus decreasing at minimum the distances 17β-OH–18-Me and 17β-OH–22-H, while increasing at maximum the distance between 20-OH and 18-Me. These structural subtleties are reflected in the pyridine spectrum of (**1a**) (strong negative solvent shifts for 18-Me, 21-Me and 22-H). Since the β orientation of the 17-OH in (**1a**) is beyond any doubt, the similarity of the $CDCl_3$–C_5D_5N shifts in (**1a**) and (**3b**) strongly supports the structure assigned to the latter. Furthermore, the 18-Me signals in the pyridine spectra of (**3b**) and (**4**) (downfield shift of 0·36 ppm in the former) are in good agreement with the values recorded [2] in Nic-2 and Nic-3 (downfield shift of 0·50 ppm in the former). The smaller shift in the pair (**3b**):(**4**) is due to the influence of the 20-OH. In the absence of this group, the deshielding of the 18-Me due to the proximity of the 17β-OH is stronger. The comparison was done between the 18-Me signals in withanolide P (**1c**) [4] and in 17α-hydroxy-1-oxo-witha-5,24-dienolide (compound (25) in ref. [7]), the downfield shift recorded in the former being of 0·62 ppm. The structure assigned to (**3a**) is supported by its fragmentation under electron impact, which follows the same pattern as that of (**1a**). Both mass spectra are dominated by the cleavage of the C_{20}-C_{22} (*m/e* 125) and of the C_{17}-C_{20} bonds (*m/e* 169 and 170). The alternative fragments appear at *m/e* values

Table 1. NMR Data for *Physalis withanolides*

						Methyl groups			
Cpd	2-H	3-H	4-H	6-H	22-H	19-H	18-H	21-H	27 & 28-H
1a	6·03 *dq* (10)	6·87 *dq*		3·20 [3·18]	4·88 *m* [5·16]	1·25 *s* [1·30]	1·10 *s* [1·37]	1·42 *s* [1·76]	1·93; 1·88 [1·92; 1·68]
3a	[6·50 *d*] (10)	[7·33 *dd*] (10; 6)	[4·08 *d*] (6)	[3·42] (w½4)	[5·2 *m*]	[1·87]	[1·36]	[1·78]	[1·83; 1·95]
3b	6·30 *d* (10) [6·48]	7·08 *dd* (10; 6) [7·18]	4·66 *d* (6) [5·00]	3·31 (w½4) [3·47]	4·78 *dd* [5·15]	1·41 *s* [1·72]	1·08 *s* [1·32]	1·41 *s* [1·73]	1·89; 1·95 [1·82; 1·91]
4	6·27 *d* (10)	7·08 *dd* (10; 6)	4·68 *d* (6)	3·26 (w½ 4)	4·51 *dd* (14·5; 3·5) [4·84]	1·38 *s*	0·83 *s* [0·96]	1·25 *s* [1·43]	1·95

Spectra are recorded at 60 MHz in $CDCl_3$ soln. Chemical shifts are in δ units. Data for pyridine solutions are in brackets. Coupling constants (in Hz) are in parentheses.

corresponding to the gradual loss of up to 3 molecules of water in (**1a**) and up to 4 molecules in (**3a**).

EXPERIMENTAL

Optical rotations were recorded in MeOH. C.d. measurements were done by Mrs. B. Romano in EtOH. I.R. spectra were recorded on KBr pellets. NMR spectra were determined in $CDCl_3$ (or deuteriopyridine, as stated) containing tetramethylsilane as internal standard. TLC was carried on Si gel G (Merck) and spots were developed with iodine vapour. MS were taken under the direction of Dr. Z. Zaretskii. Analyses were performed under the direction of Mr. R. Heller.

Plant material. Physalis peruviana was collected (P.D.S. and S.S.S.) in India, the Ooty Hills, during the summer 1970 and then raised (A.A.) in our nursery at Bet Dagan, Israel, from seeds of the above specimens.

Isolation procedure. Crushed air-dried leaves (1 kg) were exhaustively extracted with MeOH; the extract was concentrated to a vol. of *ca* 2·5 l, a similar vol. of H_2O was added and the mixture was extracted with hexane to remove pigments. The residual sol was re-extracted with Et_2O; the ethereal extract was washed with H_2O, dried and the solvent removed to leave a green residue (*ca* 20 g) which was then chromatographed on Si gel H (1 kg); the column was eluted successively with C_6H_6–EtOAc (7:3) giving **2** (0·1 g), C_6H_6–EtOAc (1:1) giving 2,3-dihydro-**1a** (0·1 g) and **1a** (2 g), and then EtOAc–MeOH (49:1) giving **3a** (2 g). Physalin A (2) mp 263–265° (Me_2CO), withanolide E (**1a**), mp 167–168° (Me_2CO) and 2,3-dihydrowithanolide E, mp 273–275° (Me_2CO) were identified by direct comparison with authentic samples.

4β-Hydroxywithanolide E (**3a**), mp 197–198° (EtOAc). $[\alpha]_D$ +95·8° (*c* 0·5); *c.d.* λ_{max}/nm ($\Delta\epsilon$): 400 (0), 340 (+1·42), 304 (0), 294 (−0·32), 282 (0), 252 (+4·25), 217·5 (+13·91), strongly negative at shorter wavelengths. ν_{max} 1710 and 1670 cm^{-1}, λ_{max}^{EtOH} 215 nm (ϵ 17800) (Found: C, 66·80; H, 7·75; M^+ 502. $C_{28}H_{38}O_8$ requires C, 66·91; H, 7·62; M, 502·58). The acetate (**3b**), prepd. with Ac_2O–C_5H_5N, was purified by preparative TLC using C_6H_6–EtOAc (1:4). The compound could not be induced to crystallize. ν_{max} 1737, 1700 *sh* and 1677 cm^{-1}; λ_{max}^{EtOH} 218 nm (ϵ 17500). (Found: C, 65·92; H, 7·30; *m/e* 526 (M^+ − 18). $C_{30}H_{40}O_9$ requires C, 66·16; H, 7·40; M, 544·62).

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ISOLATION OF 2-(4-HYDROXYBENZYL)MALIC ACID FROM *LYCORIS RADIATA*

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Key Word Index—*Lycoris radiata*; Amaryllidaceae; auxin; 2-(4-hydroxybenzyl)-malic acid; phenolic compound.

Plant. Lycoris radiata Herb. is an infertile triploid plant. The clone used started from a single bulb cultivated in the medicinal herb garden of the Faculty of Pharmaceutical Sciences, University of Tokyo, at Kemigawa, Chiba Prefecture. *Previous work.* None on this species. The compound reported was isolated from *Petalostemon gattingeri* Heller, (Leguminosae) as a germination inhibitor of the seeds of *Arenaria patula* Michx. [1].

Plant part examined. L. radiata shows a peculiar growth pattern [2] in early August, scapes with flower buds grow out of the bulb, but without leaves, and elongate very rapidly, reaching a height of 40–50 cm within 10 days. Then the flowers come out, and the whole infloresence dies out before the leaves emerge around November. Scapes of 30–35 cm with buds were used.

Isolation and identification. The MeOH extract of the fresh material was concentrated *in vacuo*. The EtOAc soluble part was separated into acidic and non-acidic fractions. The acidic fraction was chromatographed over a mixture of active charcoal and Celite, and eluted with a mixture of H_2O and Me_2CO. The residue obtained from the 50–60% Me_2CO eluate gave a weak growth promotion in the *Avena* section test. The EtOAc soluble part of the residue was separated by adsorption column chromatography over silicic acid and eluted with C_6H_6–EtOAc with increasing amount of EtOAc. The C_6H_6–EtOAc (2:1) fraction yielded a crystalline product, which was further purified by silicic acid chromatography (C_6H_6–EtOAc). The colorless crystals were recrystallized twice from C_6H_6–MeOH to give needles, mp 178–180°. (*Anal.* Found: C, 56·23; H, 5·05. Calc. for $C_{11}H_{12}O_6 . 1/12$ C_6H_6: C, 56·00; H, 5·07%). MS (*m/e*); 240 (M^+), 222, 204, 150, 132, 131, 107, 94. $[\alpha]_D^{28}$ −19·9° (MeOH). IR ν_{max} (KBr) cm^{-1}: 3480–3100, 1725 (COOH). The 60 MHz NMR spectrum of the compound in $(CD_3)_2CO$ showed the presence of two methylene groups (2H, *s* at