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TRITERPENES IN ORGAN PIPE CACTUS*

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Key Word Index *Stenocereus thurberi*; Cactaceae; organ pipe cactus; pentacyclic triterpenes; lipids; triterpene glycosides; betulinic aldehyde; oleanolic aldehyde.

Abstract—Twelve triterpenes in the lup-20(29)-ene and olean-12-ene series have been isolated from the triterpene glycoside and lipid fractions of organ pipe cactus. Physical properties and chromatographic mobilities of these compounds and some of their derivatives are given and they are arranged in a biosynthetic scheme based on degree of oxidation. Betulinic and oleanolic aldehydes, two of the cactus triterpenes, were also synthesized and fully characterized.

INTRODUCTION

Organ pipe is a large columnar cactus which grows in southwestern Arizona and northwestern Mexico. Its necrotic tissue is a specific host for *Drosophila mojavensis* [1] and it has recently been reclassified from *Lemaireocereus thurberi* to *Stenocereus thurberi* (Engelm.) Buxb. [2]. The plant is rich in lipids and triterpene glycosides [3, 4]; the former constitute 8–12% of the dry wt and exist at higher concentrations in the outer tissues of mature stems. Oleanolic acid [4], thurberogenin [4–6] and queretaroic acid [3] are components of the glycoside fraction and betulin [6] and calenduladiol [6, 7] were isolated from the lipids. Our interest in organ pipe is based on its relationship to the *Drosophila* [1, 8] and yeast [9, 10] ecologies of the Sonoran Desert.

RESULTS AND DISCUSSION

Lipids extracted from outer tissues of fresh mature stems of organ pipe cactus were hydrolysed with alcoholic NaOH. The non-sap fraction, $2\frac{1}{2}$ times as large as the fatty acid fraction, was separated into its components by crystallization, chromatography on large Si gel columns and by fractional crystallization of acetates.

Lupeol was the first triterpene to emerge from the columns. β-Amyrin, maniladiol and erythrodiol, presumed precursors to the oleanene series of compounds, were not detected in either the lipid or triterpene glycoside fractions.

The next material to elute was a mixture that gave a single spot by TLC and a single peak by GLC, either as the free hydroxy or TMSi derivative. Acetylation of a small portion and TLC on $AgNO_3$-Si gel plates revealed four components. The original mixture was partly separated by rechromatography on Si gel columns into a less polar and more polar fraction. After acetylation the former gave the two lower spots and the latter the two upper ones. The two acetylated mixtures were fractionally crystallized so that from each an acetoxy aldehyde and an acetoxy methyl ester were isolated. The two esters were shown to be methyl betulinate acetate and methyl oleanolate acetate by their physical and spectroscopic properties and by conversion to the respective methyl esters, acids and acetylated acids. The two acetoxy aldehydes were shown to be betulinic and oleanolic aldehyde acetates. Since the mps of these compounds and their derivatives were a function of how they were taken and were at variance with those recorded in the literature, the two aldehydes were synthesized. The physical and spectroscopic properties of the synthetic derivatives corresponded exactly to those of the cactus-derived compounds (see Experimental).

Betulinic aldehyde was isolated from six plants [11–16] and has been synthesized by oxidation of betulin 3-THP ether [16] or betulin 3-acetate [17–19]. Oleanolic aldehyde was isolated from a different cactus [20] and 8 other plants [21–28] and has been synthesized on three different occasions by the Rosenmund reduction of acetyl oleanolyl chloride [26, 29–31]. The physical constants of the two aldehydes isolated from organ pipe cactus and their derivatives are given in Tables 1 and 2 where they are compared to the literature values.

After a very small phytosterol fraction, betulin and calenduladiol, the most abundant triterpenes in the lipids of the cactus, eluted from the Si gel columns. The next component was longispinogenin, a triol present in several related cacti [32], and after this, lup-20(29)-en-3β,16β,28-triol, a triterpene isolated only once before from a *Euphorbia* species [33]. The last material to elute from the columns was a mixture of 3β,6α-sterol diols. The composition of this mixture as well as that of the phytosterol and fatty acid fractions is currently being investigated.

The triterpenes in organ pipe cactus are formed by oxidative processes either preceded or followed by esterification or glycosidation, which places them into two categories independent of skeletal type, lupene or oleanene. Oleanolic acid, queretaroic acid and the lactone, thurberogenin, are present only as water-soluble tetrasaccharides of glucose and rhamnose [3]. The neutral triterpenes on the other hand, the diols, triols, hydroxyaldehydes and methyl esters of betulinic and oleanolic acids, are found only in the water-insoluble lipid

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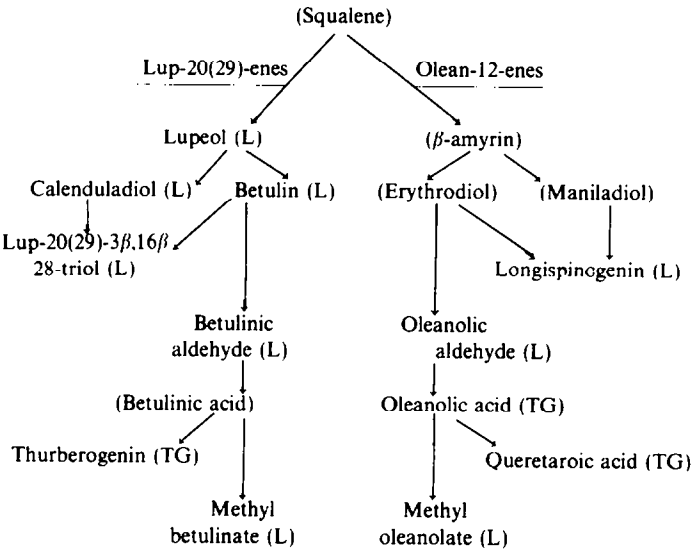


Scheme 1. Biochemical pathways for triterpenes in organ pipe cactus. Compounds in parentheses were not found. L = occurs in lipids. TG = occurs in glycoside fraction.

fraction of the cactus where they exist mainly as fatty acid esters with only small amounts also occurring unesterified (unpublished observations) (Scheme 1).

Of the 12 triterpenes in organ pipe, calenduladiol, betulinic aldehyde, methyl betulinate, methyl oleanolate and lup-20(29)-en-3β,16β,28-triol have not been isolated from other cacti. Oleanolic acid, queretaroic acid, thurberogenin and betulin occur in other *Lemaireocereus* species, longispinogenin was also found in these as well as in *Escontria chiotilla* and three *Myrtillo cactus* species, lupeol occurs in *Lophocereus schotti* [32] and oleanolic aldehyde in *Heliobrava chende* [20].

A list of structural formulae, mps, $[\alpha]_D$s and chromatographic mobilities of the various compounds isolated and prepared here and in a previous study [3] is given in Tables 1 (lupenes) and 2 (oleanenes).

EXPERIMENTAL

Mps in capillary tubes, air or *vacuo*, corr. IR (cm^{-1}) in CS_2, 0.5 mm NaCl cells. ^1H NMR (δ, 60 MHz, TMS) in CCl_4. MS direct inlet, fragments a, g, oo, etc. refer to Djerassi *et al.* [37, 38]. $[\alpha]_D^{24}$ *c*3, $CHCl_3$ unless stated otherwise. TLC on Si gel (Merck aluminum sheets), hexane–EtOAc (6:4, solvent A), hexane Et_2O–HOAc (80:20:1, solvent B), or 3 developments with CH_2Cl_2–$CHCl_3$ (1:1, solvent C) on Si gel sheets dipped in 10% $AgNO_3$ in 80% EtOH and activated 20 min at 110° before use. Mallinkrodt 100 mesh Si gel was mixed 2:1 with Celite for CC. GLC of TMSi ethers (BSA), 2 m silanized stainless steel column, 4 mm i.d. 5% OV-101, 245°, Ar at 750 ml/min, ^{90}Sr detector, RR_t TMSi lupeol (13 min = 1.00).

Extraction. Mature stems (2–3 m long, 15–24 cm dia) from several plants were collected along the road to Puerto Peñasco, Sonora, Mexico. The outer 2–4 cm of tissue was sliced from the stems, cut up and homogenized with an equal vol. MeOH the next day. The slurry was filtered through cheesecloth and the residue extracted by percolation with EtOH and then Me_2CO at room temp. The MeOH and EtOH extracts were evapd and the aq. residue extracted with Et_2O to leave a soln of H_2O sol. triterpene glycosides [3] (3070 g, 34.8%). The Et_2O soln was added to the Me_2CO extract and evapd to leave 1134 g (12.8%) lipids. The fibrous, insoluble residue weighed 4625 g (52.4% of the dry wt of the tissue). The lipids were saponified with 10% NaOH in 90% EtOH and fractionated with Et_2O to give 629 g non-saponifiable lipid (non-saps) and 312 g crude fatty acids. The non-saps were crystalized from 95% EtOH to ppt. 122 g betulin and calenduladiol and the remainder chromatographed on ten 1 kg Si gel–Celite columns with 25, 50, 75 and 100% Et_2O–petrol mixtures. Fractions were assayed by TLC (solvent A) and rechromatographed on Si gel columns with petrol and C_6H_6–petrol (1:4) (spots 1, 2, 3 on TLC), 25% Et_2O–petrol (spots 4, 5), 35% Et_2O–petrol (spots 6, 7) and 75% Et_2O–petrol (spot 8). The crude fatty acids were chromatographed on 1 kg Florosil; petrol eluted 260 g fatty acids and Et_2O 49 g sterol diols (spot 8).

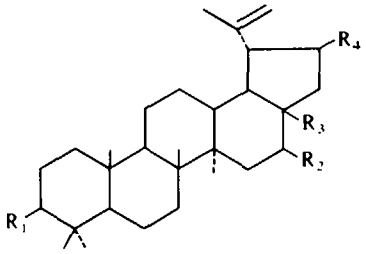
Identification of the triterpenes. Mps, $[\alpha]_D$s and chromatographic mobilities of the various compounds are given in Tables 1 and 2.

Lupeol, the first crystalline material to emerge from the columns after a small amount of wax, was converted (Ac_2O, 110°) to lupeyl acetate, IR ν_{max}^{CC} cm^{-1}: 1720, 1240 (OAc), 3080, 1640, 890 (CH_2=C); ^1H NMR: δ 0.80 (3H, *s*, C-28), 0.82 (9H, *s*, C-23, 24, 25), 0.93 (3H, *s*, C-27), 1.03 (3H, *s*, C-26), 1.70 (3H, *s*, C-30), 2.02 (3H, *s*, Me–CO), 4.63 (2H, *d*, CH_2=C); MS in accord with Djerassi [37, 38].

Separation of the components of spot 2. Fractions rich in spot 2 components (13 g) were rechromatographed on a 1 kg Si gel column with petrol. After elution of a small amount of lupeol, a mixture of betulin aldehyde and methyl betulinate emerged (fractions 6–10, 1–21) and after this C_6H_6–petrol (1:4) eluted a mixture of oleanolic aldehyde and methyl oleanolate (fractions 11–17). The aldehydes were not stable to air in non-hydroxylic solvents [39]. Each combined fraction was acetylated with Ac_2O–pyridine at room temp. and the products crystallized from MeOH. The acetoxy methyl esters were less soluble in MeOH–$CHCl_3$ than the acetoxy aldehydes; the latter were then crystallized from Me_2CO. The separation process was readily followed by TLC on Ag^+ plates (solvent C). Enough (200–1500 mg) of each component was isolated in a chromatographically pure, sharp melting state to enable identification.

Betulinic aldehyde acetate, plates from EtOH, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1720, 1245 (OAc), 2700, 2675, 1725 (CHO), 3080, 1640, 890

Table 1. Physical properties of derivatives of lup-20(29)-ene



Compound	Structures				Physical constants						Chromatographic mobilities			
					mps. °obs., corr.			$[\alpha]_D$			TLC. R_{Chol} s.			
	R_1	R_2	R_3	R_4	air	vac.	lit.	obs.	lit.	Ref	Si gel solv. A	Si gel solv. B	$AgNO_3$ Si gel solv. C 3X	GLC,TMSiderivs. *RR*, TMSi-lupeol
Lupeol	OH	H	Me	H	210–3	214–5	212 6	+23	+28	34	0.77	0 32	0.29	1.00
Lupeol acetate	OAc	H	Me	H	214·6	217·7.5	215 20	+43	+45	34	1.02	1 03	0.75	--
Betulin	OH	H	CH_2OH	H	250	257–8	260–1	+ 18	+15	34(a)	0.54	0.11	0.07	1 67
Betulin 3-acetate	OAc	H	CH_2OH	H	261–4	264–6	260–3	..	—	35	0 74	0.24	0 14	1 89
Betulin diacetate	OAc	H	CH_2OAc	H	218.5· 21	221–2	223–4	+21	+21	34(a)	0 94	0.72	0 50	--
Calenduladiol	OH	OH	Me	H	211–2 5	213–4	215–9	+16	+18	7	0.47	0 09	0 07	1 53
Calenduladiol diacetate	OAc	OAc	Me	H	194 4.6	195 6	195· 7	+34	+ 38	7	0 93	0 55	0 35	—
Betulinic aldehyde	OH	H	CHO	H	202–7	226–8	*	+16	*	*	0.70	0.24	0.27	1.56
Betulinic aldehyde acetate	OAc	H	CHO	H	172–6	228.5 9	†	+29	†	†	0 96	0.80	0.68	—
Betulinic aldehyde acetate semicarbazone	OAc	H	CH=N–NH / CO–NH_2	H	274·8d	267 72d	‡	+5		‡	0 09	0.07	0 01	—
Betulinic acid	OH	H	COOH	H	304–8	304–8	315· 21	+ 7 (Py)	+ 10 (Py)	34(b)	0 54	0 17	0.04	
Methyl betulinate	OH	H	COOMe	H	221–4	223 5· 5	221· 3	+4	+5	36	0 71	0.26	0 13	1.53
Betulinic acid acetate	OAc	H	COOH	H	287 91	291–6	287–95	+21	+22	34(b)	0 79	0.48	0.23	--
Methyl betulinate acetate	OAc	H	COOMe	H	196 8	198–9	201–4	+ 18	+ 19	36	0.96	0 86	0.61	
Thurberogenin	OH	H	–CO···O–		300 3	304 5	293 5	+ 0 3	+ 11	4	0.57	0 16	0.30	2 73
Thurberogenin diacetate	OAc	H	–CO···O–		249 52	251 2 5	249 51	+13	+22	34(c)	0.83	0 42	0.77	—
Lup-20(29)-en-3β,16β,28-triol (lupenetriol)	OH	OH	CH_2OH	H	308–10	310· 1 5	300·1	+9 +11 (Py)	+ 8	33	0 25	0 01	0	1.85
Lupenetriol triacetate	OAc	OAc	CH_2OAc	H	160–1 5	160 1 5		+4 3			0 80	0 28	0 26	—
Lupenetriol tribenzoate	OBz	OBz	CH_2OBz	H	197 242 6 5	198 200 § 246· 6 5 §	245 6	+33	+33	33	0 94	0.67	0 80	--
16β,28-Ethylidene lupenetriol	OH	–O–CH(Me)–O–CH_2–		H	262 5	subl	255·7	–10	–7	33	0 65	0 18	0.10	2 75
Lupan-3β,16β,28-triol	OH	OH	CH_2OH	H	314 6	subl	308·9		24	33	0 27	0 02	0 01	2.02

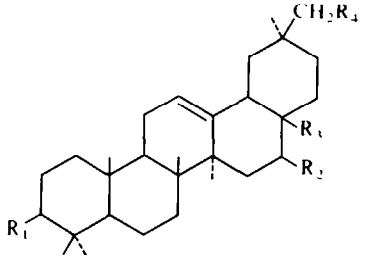
* Plant source (mp, $[\alpha]_D$, [ref.]): 192–4°, +19° [11]; 190–3° (vac.), +19° [12]; 190–2° [13]; 190°, +19° [14]; 199–200°, +28° [15]; 188 90° [16]. Synthetic: 188 90° [16]; 192–3° (vac.), +19° [18]; 195–8°, +17° [19].

† Plant source: 183–4° (vac.), +29° [11]; 173· 180° (vac.), +30° [12]; 199–200°, +28° [14]. Synthetic: 199–200° (vac.), +30° [17].

‡ Plant source: 264–6° [11]. Synthetic: 270· 80° [17].

§ Double fusion.

Table 2. Physical properties of derivatives of olean-12-ene



Compound	Structures				Physical constants: mps. °obs., corr			Physical constants: $[\alpha]_D$			Chromatographic mobilities: TLC, R_{Chol}			
	R_1	R_2	R_3	R_4	air	vac	lit	obs	lit	Ref.	Si gel solv. A	Si gel solv. B	$AgNO_3$ Si gel solv. C 3X	GLC, TMSi derivs *RR*, TMSi lupeol
Erythrodiol	OH	H	CH_2OH	H	231–2	234–5	229–37	+74	+77	34(c)	0.55	0.11	0.19	1.43
Erythrodiol diacetate	OAc	H	CH_2OAc	H	182–4	182–4.5	182–8	+58	+63	34(c)	0.94	0.72	0.95	-
Oleanolic aldehyde	OH	H	CHO	H	207–10	212.5–3	*	+66	*	*	0.67	0.22	0.40	1.46
Oleanolic aldehyde acetate	OAc	H	CHO	H	242–7	251–2	†	+64	†	†	0.96	0.83	1.00	
Oleanolic aldehyde acetate oxime	OAc	H	CH=NOH	H	202–6	217–7.5	‡	+67		‡	0.90	0.51	0.11	
Oleanolic acid	OH	H	COOH	H	300–5	300–2.5	308–10	+77 +67 (Py)	+78 +69 (Py)	4, 34(e)	0.49	0.14	0.07	
Methyl oleanolate	OH	H	COOMe	H	199–200	200.5–1	198–9	+64	+69	4	0.68	0.23	0.40	1.46
Oleanolic acid acetate	OAc	H	COOH	H	262–5	262–5	264–7	+72	+74	4, 34(e)	0.77	0.41	0.41	–
Methyl oleanolate acetate	OAc	H	COOMe	H	220.5–1.5	221.5–2	217–9	+68	+65	4	0.83	0.94	0.98	
Oleanolic acid acetate imidazolide	OAc	H	$CO-C_3H_3N_2$	H	184–6	186–7.5	—	+47(Py)	--	—	0.37	0.09	0.01	--
Queretaroic acid	OH	H	COOH	OH	345–8	345	318–23	+81(Py)	+78(Py)	3	0.08	0.01	0	–
Methyl queretaroate	OH	H	COOMe	OH	228–8.5	230.5–1	226–8	+70	+67	3	0.26	0.02	0.06	2.70
Queretaroic acid diacetate	OAc	H	COOH	OAc	297–300	302	295–9	+80	+82	3	0.43	0.12	0.09	
Methyl queretaroate diacetate	OAc	H	COOMe	OAc	234–5	234–5	211–2	+80	+72	3	0.81	0.27	0.43	
Queretarol	OH	H	CH_2OH	OH	283–5	285–6	275–6	+76 +88(Py)	+86(Py)	3	0.08	0.01	0	2.68
Queretarol triacetate	OAc	H	CH_2OAc	OAc	135–6	-	135–7	+73		3	0.56	0.06	0.01	
Longispinogenin	OH	OH	CH_2OH	H	247–50	249–51	243–52	+51	+53	34(d)	0.30	0.03	0.02	1.47
Longispinogenin triacetate	OAc	OAc	CH_2OAc	H	222–4	222–3.5	218–28	+69	+70	34(d)	0.86	0.40	0.68	
Longispinogenin triformate	OCHO	OCHO	CH_2OCHO	H	179–80	179–80.5	179–81	+85	+88	34(d)	0.85	0.54	0.89	-
16β,28-Ethylidene-longispinogenin	OH	$-O-\overset{Me}{\underset{\vert}{C}}-O-CH_2-$		H	amorphous			-			0.63	0.21	0.34	2.44

* Plant source (mp., $[\alpha]_D$, [ref.]): 112–186° [20]; 168–72°, +72° [23]; 182–9° [24]; 169–72°, +72° [25].

† Plant source: 225–8° [20]; 225–8° [21]; 225–6°, +57° [22]; 228°, −68° [26]; 226–8°, −61.5° [27]; 236–9°, +61.5° [28]. Synthetic: 227–9° [29, 30]; 222–6°, +67° [31].

‡ Plant source: 189–200° [20]. Synthetic: 190–200° [29, 30].

(CH_2=C) [11, 12, 14]; ^{1}H NMR: δ 0.83 (6H, *s*, C-23, 24), 0.87 (3H, *s*, C-25), 0.92 (3H, *s*, C-26), 0.95 (3H, *s*, C-27), 1.69 (3H, *s*, C-30), 2.00 (3H, *s*, MeCO), 4.67 (2H, *d*, CH_2=C), 9.57 (1H, *s*, CHO); MS *m/e* (rel. int.): 482 (M^+, 48), 454 (M^+ − CO, 61), 453 (M^+ − CHO, 32), 422 (M^+ − HOAc, 89), 408 (M^+ − 74, 31), 395 (M^+ − (C(Me)=CH_2 + 2H + CHO + Me) 32), 394 (M^+ − (HOAc + CO), 24), 380 (M^+ − (C(Me)=CH_2 + 2H + CHO + 2Me), 36), 262 (species oo, 11), 249 (species g, 15), 232 (species nn, 17), 204 (nn − CO, 33), 203 (nn − CHO, species mm, 37), 202 (oo − HOAc, 23), 201 (M^+ − 281, 26), 189 (g − HOAc, nn − (C(Me)=CH_2 + 2H), nn − (CO + Me), 100), 188 (nn − (CHO + Me), 30), 187 (oo − (HOAc + Me), 69), 175 (mm − CO, 27). Hydrolysed with alcoholic NaOH under N_2 [39] to betulinic aldehyde, needles from MeOH, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3630 (OH), 2700, 2675, 1725 (CHO), 3080, 1640, 890 (CH_2=C) [12, 14, 16], which was reduced with $NaBH_4$ in MeOH to betulin, mp, mmp, GLC, TLC. Betulinic aldehyde acetate semicarbazone, long plates from EtOH $CHCl_3$, was prepared [17].

Methyl betulinate acetate, prisms from MeOH–$CHCl_3$, ^{1}H NMR: δ 0.83 (6H, *s*, C-23, 24), 0.87 (3H, *s*, C-25), 0.92 (3H, *s*, C-26), 0.94 (3H, *s*, C-27), 1.69 (3H, *s*, C-30), 1.97 (3H, *s*, MeCO), 3.62 (3H, *s*, OMe) 4.67 (2H, *d*, CH_2=C). MS in accord with Djerassi [37, 38]. Hydrolysed with NaOH in refluxing EtOH to methyl betulinate and with NaOH in ethylene glycol at 200° to betulinic acid, which was acetylated (Ac_2O, 110°) to betulinic acid acetate.

Oleanolic aldehyde acetate, plates from EtOH–$CHCl_3$, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1720, 1245 (OAc), 2700, 2675, 1725 (CHO) [21, 22]; ^{1}H NMR: δ 0.72 (3H, *s*, C-26), 0.83 (3H, *s*, C-23), 0.85 (3H, *s*, C-24), 0.93 (9H, *s*, C-25, 29, 30), 1.10 (3H, *s*, C-27), 1.97 (3H, *s*, MeCO), 4.43 (1H, *dd*, CHOAc), 5.30 (1H, *t*, −CH=C), 9.25 (1H, *s*, CHO) [21, 22, 31]. Low ionization energy MS *m/e* (rel. int.): 482 (M^+, 100), 467 (M^+ − Me, 11), 454 (M^+ − CO, 17), 453 (M^+ − CHO, 55), 422 (M^+ − HOAc, 50), 407 (M^+ − (HOAc + Me), 38), 379 (M^+ − (HOAc + CO − Me), 21), 262 (species oo, 17). High intensity (70 eV) spectrum: 262 (oo, 1.7), 249 (species g, 5.6), 232 (species a, 41), 217 (species e, 3.4), 203 (species n, f, c, 100), 189 (g − HOAc, 24), 190 [23]. Hydrolysed with alcoholic NaOH under N_2 [39] to oleanolic aldehyde, stout needles from MeOH, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3630 (OH), 2700, 2675, 1725 (CHO) [23], which was reduced with $NaBH_4$ in MeOH to erythrodiol (GLC, TLC), acetylated to erythrodiol diacetate (TLC, $AgNO_3$ Si gel, solvent C).

Methyl oleanolate acetate, needles from acetone, ^{1}H NMR: δ 0.72 (3H, *s*, C-26), 0.83 (3H, *s*, C-23), 0.87 (3H, *s*, C-24), 0.92 (3H, *s*, C-25), 0.93 (6H, *s*, C-29, 30), 1.10 (3H, *s*, C-27), 1.95 (3H, *s*, MeCO), 3.55 (3H, *s*, OMe), 4.40 (1H, *m*, CHOAc), 5.23 (1H, *t*, −CH=C) [40]. MS in accord with Djerassi [37, 38]. Hydrolysed with alcoholic NaOH on the steam bath to methyl oleanolate and with NaOH in ethylene glycol at 200° to oleanolic acid which was acetylated to oleanolic acid acetate. The acetoxy methyl ester was reduced with $LiAlH_4$ in refluxing THF to erythrodiol from which erythrodiol diacetate was prepared (Ac_2O, 110°).

Phytosterol mixture. 6 g (0.07% of dry cactus, 0.9% of non-saps) were isolated by CC and MeOH crystallization and tentatively identified as 1:2:7 cholesterol–campesterol–sitosterol (GLC, TLC).

Betulin and calenduladiol were each converted to their acetates for mp, $[\alpha]_D$, TLC.

Longispinogenin, long prisms from Me_2CO, was converted (Ac_2O, 110°) to longispinogenin triacetate, needles from MeOH EtOH, with HCOOH in C_6H_6 to longispinogenin triformate, needles from Et_2O, and with HCl and paraldehyde in Et_2O [28] to amorphous 16β, 28-ethylidenelongispinogenin.

Lup-20(29)-*en*-3β,16β,28-*triol*, needles from dioxane, was acetylated (Ac_2O, 110°) to lupenetriol triacetate, tiny needles from petrol–Et_2O, not previously reported [28], difficult to crystallize. Lupenetriol tribenzoate needles from Me_2CO–C_6H_6. 16β,28-ethylidenelupenetriol, stout prisms from hexane and lupan-3β,16β,28-triol, needles from MeOH, were prepared as previously described [28].

Sterol diols. 228 g (2.6% of dry cactus, 33.5% of non-saps) of 3β,6α-sterol diols were isolated from the non-sap and crude fatty acid fractions of the cactus.

Synthesis of betulinic aldehyde. Betulin 3-acetate [41] (2.5 g) in 160 ml Me_2CO was oxidized at 25° with 0.95 ml Jones reagent [19] to yield betulin aldehyde acetate, plates from EtOH, mp and mmp 180–190° (air), 198–200° (vac.), 200–2° (evac. sealed tube, remelted 186–8°), $[\alpha]_D^{24}$ + 29°, IR superimposable on cactus derived material. Hydrolysed to betulinic aldehyde, mp and mmp 209–17° (air), 227° (vac.), 227.5 9° (evac. sealed tube), $[\alpha]_D^{24}$ + 16°. Betulinic aldehyde acetate semicarbazone mp and mmp 271.5–2.5° d (vac.), 274–9° d (evac. sealed tube).

Synthesis of oleanolic aldehyde. Oleanolic acid acetate (12 g) and 25 ml $SOCl_2$ were refluxed 3 hr in 125 ml dry C_6H_6. The soln was evaporated to dryness *in vacuo*, the residue dissolved in 125 ml fresh C_6H_6 and refluxed 1 hr with 25 g imidazole. The reaction mixture was evapd to dryness, the residue mixed with H_2O and filtered and the solid recrystallized from MeOH to give 8 g tiny prisms of oleanolic acid acetate imidazolide. The imidazolide in 120 ml refluxing THF was reduced by dropwise addition of LiAlH (O-t-Bu)$_3$ in 80 ml THF over 20 min [42]. After 20 min additional reflux the mixture was cooled, poured into 400 ml cold 1 N HCl and the crude product recrystallized from EtOH–$CHCl_3$ to give plates of oleanolic aldehyde acetate, mp 242–5° (air), 249–50° (vac.), $[\alpha]_D^{24}$ + 64°, mmp with cactus derived compound 242–7° (air), 251–2° (vac.), IRs superimposable. The acetate was hydrolysed to oleanolic aldehyde, mp and mmp 207–10° (air), 213–14.5° (vac.). Oleanolic aldehyde acetate oxime, tiny prisms from MeOH, was prepared with NH_2OH–HCl in EtOH pyridine [20].

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