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TRITERPENOID SAPOGENOLS FROM *ANDROSACE SAXIFRAGIFOLIA*: THE STRUCTURE OF ANDROSACENOL

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Key Word Index—*Androsace saxifragifolia*, Primulaceae, androsacenol, cyclamiretin A, cyclamiretin D

Abstract—Acid hydrolysis of the saponin mixture isolated from the aerial part of *Androsace saxifragifolia* afforded a mixture of triterpenoid sapogenols which on chromatographic separation yielded a new triterpenoid designated androsacenol together with cyclamiretin A and cyclamiretin D The structure of androsacenol was established as 3β,16α-dihydroxyolean-13,28-epoxy-22β-acetoxy-30-al

INTRODUCTION

Androsace saxifragifolia (Syn *Androsace rotundifolia*) is a small herb occurring wild in many parts of India Surina *et al* reported [1] that the extract of *Androsace septentrionalis* retarded maturation of the sexual organs in female rats without causing any degeneration of the organs This observation, in conjunction with the reputation of *A saxifragifolia* as an abortifacient agent, prompted us to take up detailed chemical investigation of the plant Recently primulagenin A, a known triterpenoid sapogenol, was isolated from this plant [2] This paper is concerned with the isolation and characterization of a new triterpenoid sapogenol, androsacenol (**1**), along with cyclamiretin A (**2**) and cyclamiretin D (**3**)

RESULTS AND DISCUSSION

The ethanol extract of the plant on chromatographic purification over silica gel afforded a mixture of triterpenoid saponins which on acid hydrolysis [3] yielded a mixture of three triterpenoid sapogenols which were separated by silica gel CC into the new triterpenoid, androsacenol (**1**) and compounds **2** and **3** Compound **2**, $C_{30}H_{48}O_4$ (M^+ at *m/z* 472), mp 200–202°, was found to be identical with cyclamiretin A [4] by comparison with an authentic sample

Compound **3**, $C_{30}H_{48}O_4$ (M^+ at *m/z* 472), mp 245–247°, was obtained as a major product It was eventually characterized as cyclamiretin D [4] by comparison of its IR, ^1H NMR and mass spectrum with those of an authentic sample Its ^{13}C NMR spectrum was determined and ^{13}C signals were assigned (Table 1) from their chemical shifts [5–7], off-resonance studies and comparison of the shift data with those of compounds having a similar carbon skeleton Treatment of **3** in chloroform solution with conc H_2SO_4 yielded compound **4**

Compound **1**, $C_{32}H_{50}O_6$ (M^+ at *m/z* 530), mp

Table 1 ^{13}C NMR chemical shifts δ_C (±0 1) of compounds **1** and **3**

Carbon no	1	3
1	38 0 *t*	38 9 *t*
2	28 3 *t*	27 5 *t*
3	78 2 *d*	77 8 *d*
4	39 6 *s*	38 9[a] *s*
5	55 8 *d*	55 4 *d*
6	18 3[c] *t*	18 3 *t*
7	32 7 *t*	32 8 *t*
8	42 9[f] *s*	39 6[a] *s*
9	47 6 *d*	47 0 *d*
10	37 3 *s*	36 8 *s*
11	19 2[c] *t*	23 4 *t*
12	31 8[b] *t*	122 5 *d*
13	86 1 *s*	144 0 *s*
14	44 6[f] *s*	41 4 *s*
15	34 4 *t*	34 3 *t*
16	73 2[d] *d*	73 3 *d*
17	46 5[e] *s*	40 0 *s*
18	50 6 *d*	43 2 *d*
19	36 8 *t*	30 2 *t*
20	47 6[e] *s*	46 7 *s*
21	30 1[b] *t*	29 5 *t*
22	74 1[d] *t*	27 5 *t*
23	28 8 *q*	28 3 *q*
24	16 6 *q*	15 4 *q*
25	16 4 *q*	16 1[b] *q*
26	18 7[a] *q*	16 6[b] *q*
27	20 1[a] *q*	27 2 *q*
28	70 3 *t*	69 7 *t*
29	24 2 *q*	23 8 *q*
30	205 3 *d*	207 6 *d*
22-OAc	169 8 *s*	
	20 9 *q*	

a, b, c, d, e and f may be reversed on each vertical column

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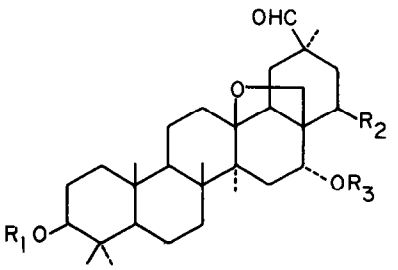
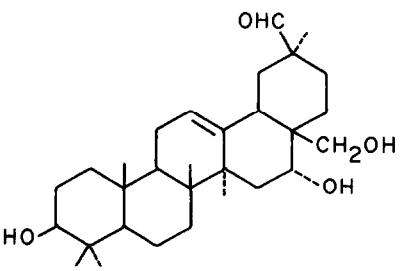


1 R_1 = H, R_2 = OAc, R_3 = H

2 R_1 = H, R_2 = H, R_3 = H

5 R_1 = Ac, R_2 = OAc, R_3 = Ac

6 R_1 = H, R_2 = OH, R_3 = H



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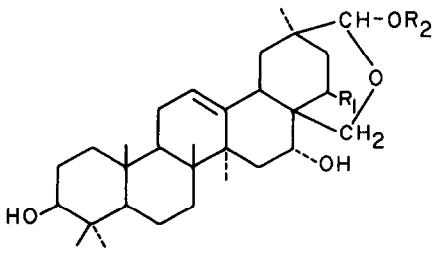
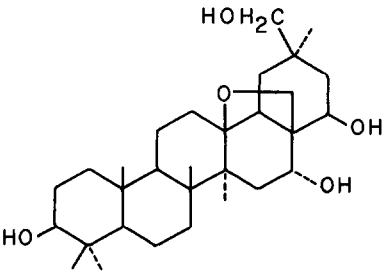


4 R_1 = H, R_2 = H

10 R_1 = OH, R_2 = CH_3



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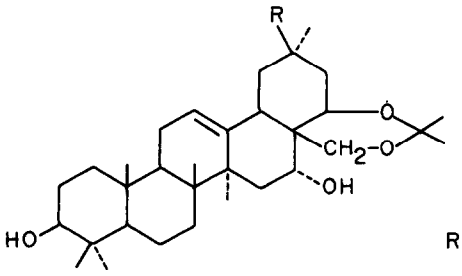
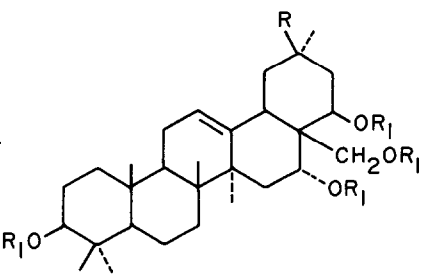


7 R = CHO

9 R = CH_2OH



11 R = CHO, R_1 = H

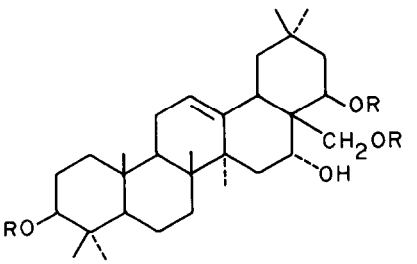
12 R = CH_2OH, R_1 = H

13 R = CHO, R_1 = Ac

14 R = CH_2OAc, R_1 = Ac

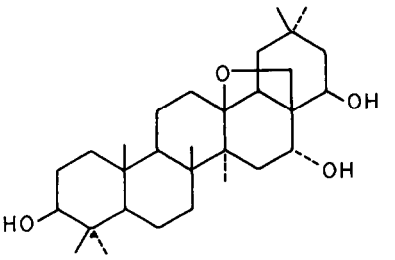
262–265°, was obtained in lower yield in comparison to 3 The IR spectrum showed absorption bands at 3400 (br), 2675 and 1720, 1730 and 1240 cm^{-1} assigned to hydroxyl, aldehyde and acetate functions respectively Moreover, the sharp bands between 1120 and 880 cm^{-1} indicated the presence of an ether linkage On acetylation compound 1 yielded 5 containing three acetoxy groups

The ^1H NMR spectrum of 1 showed, besides five singlets assignable to six tertiary methyls, a three-proton singlet at δ 2.04 assigned to an acetoxy methyl group but did not show any signal attributable to any olefinic proton The mass spectrum of 1 displayed RDA-fragmentation typical of a Δ^{12}-oleanene or ursene [8] Consequently, it could be inferred that 1 might contain an oxide ring involving C-28 and C-13 as in 2 which readily opens up to yield the Δ^{12}-derivative with subsequent generation of the RDA-fragments 18 and 19 appearing at *m/z* 322 and 207, respectively Furthermore, formation of these fragments suggested that the aldehyde group, a hydroxyl group and the acetoxy group are present in rings D/E whereas one hydroxyl group is present in rings A/B The presence of the latter hydroxyl group at C-3 was assumed from biogenetic considerations The orientation of the C-3 hydroxyl group was indicated to be equatorial



15 R = H

17 R = Ac



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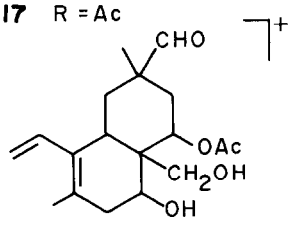

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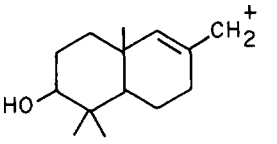

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(β) from the ^{1}H NMR characteristics of its geminal proton The C-27 methyl of **1** resonated at δ1 32, i e downfield from its usual position [9], indicating the presence of a C-16α hydroxyl group which was further supported by the ^{13}C NMR spectrum (Table 1) considering a hydroxyl substituent effect on C-16 [10] The ^{1}H NMR spectrum of **1** displayed a signal at δ5 2 (1H, *t*, J = 4 Hz) assigned to the proton geminal to the acetoxy group and the lower coupling constant indicated an axial configuration of the acetoxy group and it could be placed either at C-21 or C-22 Hydrolysis of **1** afforded a triol (**6**) which formed an acetonide (**7**) The ^{1}H NMR spectrum of **7**, besides showing the absorption of the gem dimethyl of the acetonide moiety, exhibited the olefinic proton signal (1H, *t*-like) at δ5 52 Lithium aluminium hydride reduction of **1** yielded a tetrol (**8**) which formed an acetonide (**9**) with dry acetone–conc H_2SO_4 The C-16α hydroxyl group does not normally form an acetonide with the C-28 hydroxyl group and Dreiding model inspection revealed that acetonide formation between the C-28 and C-21α (axial) hydroxyl groups is unlikely However, acetonide formation between the C-22β (axial) and C-28 hydroxyl groups is quite feasible The results clearly demonstrated the presence of the C-22β acetoxy function in **1** Mild acid treatment of **7** and **9** yielded **11** and **12**, respectively On acetylation with acetic anhydride and pyridine at 100° compounds **11** and **12** yielded **13** and **14**, respectively

The presence of a methyl signal at δ1 32 indicated that the formyl group might be attached to C-20 Furthermore, when the solution of **1** in methanol was treated with a drop of conc H_2SO_4 it was converted to the acetal (**10**) whose ^{1}H NMR spectrum did not show the formyl proton signal but showed the signals at δ3 44 (3H, *s*), 4 68 (1H, *s*), 3 40 and 3 62 (2H, AB*q*, J = 8 Hz) assignable to OMe, –O–CH–O and $\geqslant$C–CH$_2$–O– systems, respectively Acetal formation demonstrated the presence of the C-30β aldehyde Finally the structure and stereochemistry of **1** were ascertained by its chemical correlation with the 22-epimer of dihydropriverogenin A (**15**) Huang-Minlon reduction of **6** afforded **16** which on treatment in methanol solution with a drop of conc H_2SO_4 yielded **15** Acetylation of **15** yielded **17** identical with an authentic sample of the triacetate of the 22-epimer of dihydropriverogenin A [11]

Thus the structure of androsacenol was established as 3β,16α-dihydroxy-olean-13,28-epoxy-22β-acetoxy-30-al (**1**)

EXPERIMENTAL

The plant material was collected from Muzaffarpur area, North Bihar and was identified by Mr U Bhattacharya, Indian Botanic Garden, Howrah A voucher specimen has been deposited at the herbarium of IICB Mps are uncorr ^{1}H NMR spectra were recorded at 100 MHz in $CDCl_3$ soln with TMS as internal standard The ^{13}C NMR spectrum was recorded in C_5D_5N at 25 15 MHz in the Fourier transform mode Mass spectra were determined at 70 eV using a direct inlet system and IR spectra were taken in Nujol HPLC was done in a Spectra-Physics model 8000B instrument

Isolation of the triterpenoid saponins Finely ground aerial parts of *A saxifragifolia* (1 kg) were defatted with petrol and extracted successively with $CHCl_3$ and EtOH The EtOH extract (20 g) was chromatographed over silica gel and elution with $CHCl_3$–MeOH (4 3) afforded a mixture of saponins (2 5 g) The saponin mixture was hydrolysed with 2 N HCl for 6 hr at 100° The mixture of aglycones (0 8 g) was chromatographed on silica gel to give **1** and compounds **2** and **3**

Cyclamiretin A (**2**) Compound **2** was crystallized from EtOAc as needles, mp 200–202°, IR ν_{max}^{Nujol} cm^{-1} 3450, 2670, 1720, ^{1}H NMR ($CDCl_3$) δ0 76 (3H, *s*), 0 88 (3H, *s*), 1 00 (3H, *s*), 1 02 (3H, *s*), 1 12 (3H, *s*), 1 24 (3H, *s*), 3 06 (1H, *d*, J = 8 Hz, H-28), 3 20 (1H, *t*, J = 8 Hz, H-3), 3 48 (1H, *d*, J = 8 Hz, H-28), 4 06 (1H, *m*, H-16), 9 44 (1H, *s*, H-30)

Cyclamiretin D (**3**) Compound **3** was crystallized from EtOAc as needles, mp 245–247° IR ν_{max}^{Nujol} cm^{-1} 3470, 2680, 1720, ^{1}H NMR ($CDCl_3$) δ0 80 (3H, *s*), 0 92 (3H, *s*), 0 96 (3H, *s*), 1 02 (6H, *s*), 1 35 (3H, *s*), 3 16 (1H, *d*, J = 8 Hz, H-28), 3 24 (1H, *m*, H-3), 3.28 (1H, *d*, J = 8 Hz, H-28), 4 08 (1H, *m*, H-16), 5 36 (1H, *m*, H-12), 9 48 (1H, *s*, H-30)

Compound **4** Compound **3** (40 mg) in dry $CHCl_3$ (3 ml) was treated with 0 1 ml conc H_2SO_4, worked up in the usual way and compound **4** (32 mg) obtained was crystallized from EtOAc as needles, mp 238–240°, IR ν_{max}^{Nujol} cm^{-1} 3450, 870, ^1H NMR ($CDCl_3$) δ 0 78 (3H, *s*), 0 90 (3H, *s*), 0 93 (3H, *s*), 0 95 (3H, *s*), 1 20 (3H, *s*), 1 22 (3H, *s*), 3 16 (1H, *d*, *J* = 8 Hz, H-28), 3 20 (1H, *m*, H-3), 3 26 (1H, *d*, *J* = 8 Hz, H-28), 4 12 (1H, *m*, H-16), 4 78 (1H, *s*, H-30), 5 36 (1H, *m*, H-12)

Androsacenol (**1**) Compound **1** was crystallized repeatedly from EtOAc to give plates, mp 262–264°, $[\alpha]_D^{25}$ + 23° ($CHCl_3$), IR ν_{max}^{Nujol} cm^{-1} 3400, 2675, 1730, 1720, 1240, 1050, 1030, 980, ^1H NMR ($CDCl_3$) δ 0 84 (3H, *s*), 0 95 (3H, *s*), 1 04 (6H, *s*), 1 20 (3H, *s*), 1 32 (3H, *s*), 2 04 (3H, *s*, 22 – OAc), 3 24 (1H, *m*, H-3), 3 32 (2H, *s*, H-28), 4 12 (1H, *m*, H-16), 5 2 (1H, *t*, *J* = 4 Hz, H-22), 9 44 (1H, *s*, H-30) MS *m/z* (rel int) 530 $[M]^+$ (7), 512 $[M-H_2O]^+$ (13), 501 $[M-CHO]^+$ (10), 470 $[M-AcOH]^+$ (18), 452 $[M-H_2O-AcOH]^+$ (19), 442 (24), 421 (12), 322 [**18**] (12), 293 [**18** $-CHO]^+$ (7), 262 [**18** $-AcOH]^+$ (14), 232 (30), 220 (65), 214 (72), 207 [**19**] (100), 203 (60), 189 [**19** $-H_2O]^+$ (7) (Found C, 72 40; H, 9 48 $C_{32}H_{50}O_6$ requires C, 72 41, H, 9 50%)

The triacetate (**5**) Compound **1** (10 mg) furnished the triacetate (**5**) with Ac_2O (1 ml) and pyridine (1 ml) at 100° for 4 hr It was crystallized from EtOAc, mp 230–232°, IR ν_{max}^{Nujol} cm^{-1} 1730, 1720, 1240, 1040, 975 (Found C, 70 31, H, 8 90 $C_{36}H_{54}O_8$ requires C, 70 33, H, 8 85%)

Hydrolysis of androsacenol (**1**) *to triol* (**6**) Compound **1** (20 mg) was refluxed with 2% KOH in *t*-BuOH (5 ml) for 1 hr The product was poured into ice-water, worked up as usual and purified by silica gel CC eluting with petrol–EtOAc (7 3) The product was crystallized from EtOAc as needles (16 mg), mp 304–306°, IR ν_{max}^{Nujol} cm^{-1} 3500, 2675, 1715, 1030, 980, ^1H NMR ($CDCl_3$) δ 0 80 (3H, *s*), 0 88 (3H, *s*), 1 00 (3H, *s*), 1 12 (3H, *s*), 1 20 (3H, *s*), 1 24 (3H, *s*), 3 28 (1H, *m*, H-3), 3 35 (1H, *d*, *J* = 8 Hz, H-28), 3 98 (1H, *d*, *J* = 8 Hz, H-28), 4 02 (2H, *m*, H-16 and H-22), 9 40 (1H, *s*, H-30), MS *m/z* (rel int) 488 $[M]^+$ (2), 470 $[M-H_2O]^+$ (8), 452 $[M-2H_2O]^+$ (10), 279 (15), 251 (18), 232 (36), 220 (42), 214 (45), 207 (85), 189 (100), 185 (80) (Found C, 73 75, H, 9 85 $C_{30}H_{48}O_5$ requires C, 73 73, H, 9 90%)

Acetonide derivative (**7**) *of triol* (**6**) Triol **6** (10 mg) was stirred in dry Me_2CO (5 ml) and one drop of conc H_2SO_4 at room temp for 6 hr Work up as usual and crystallization of the product from EtOAc afforded colorless crystals of **7** (4 5 mg), mp 278–280°, $[\alpha]_D$ + 14° ($CHCl_3$), IR ν_{max}^{Nujol} cm^{-1} 3500, 2670, 1720, 1050, 850, ^1H NMR ($CDCl_3$) δ 0 80 (3H, *s*), 0 92 (3H, *s*), 0 96 (3H, *s*), 1 00 (3H, *s*) 1 28 (3H, *s*), 1 32 (3H, *s*), 1 36 (3H, *s*), 1 48 (3H, *s*), 3 24 (1H, *m*, H-3), 3 36 (1H, *d*, *J* = 8 Hz, H-28), 3 98 (1H, *d*, *J* = 8 Hz, H-28), 4 04 (2H, *t*, *J* = 4 Hz, H-16 and H-22), 5 64 (1H, *t*, *J* = 4 Hz, H-12), 9 44 (1H, *s*, H-30), MS *m/z* (rel int) 528 $[M]^+$ (2), 513 $[M-Me]^+$ (2), 470 $[M-MeCOMe]^+$ (24), 452 (5), 424 (4), 265 (19), 262 (15), 234 (35), 218 (37), 207 (84), 185 (100) (Found C, 74 93, H, 9 89 $C_{33}H_{52}O_5$ requires C, 74 96, H, 9 91%)

$LiAlH_4$ *reduction of androsacenol* (**1**) *yielding tetrol* (**8**) To a soln of **1** (8 mg) in dioxane (3 ml) was added $LiAlH_4$ (50 mg) and the mixture refluxed for 4 hr The reaction product was then treated with H_2O followed by crystallization from EtOAc to yield the tetrol (**8**) as flakes (6 mg), mp 298–299°, $[\alpha]_D$ + 13° ($CHCl_3$), IR ν_{max}^{Nujol} cm^{-1} 3450, 1040, 970, ^1H NMR (d_5-pyridine) δ 0 92 (3H, *s*), 1 02 (3H, *s*), 1 20 (3H, *s*), 1 24 (3H, *s*), 1 36 (3H, *s*), 1 56 (3H, *s*), 3 48 (1H, *t*-like, H-3), 3 56 (1H, *d*, *J* = 8 Hz, H-28), 3 72 (1H, *d*, *J* = 8 Hz, H-28), 3 90 (1H, *d*, *J* = 10 Hz, H-30), 4 16 (1H, *d*, *J* = 10 Hz, H-30), 4 40 (2H, *m*, H-16 and H-22), MS *m/z* (rel int) 490 $[M]^+$ (2), 472 $[M-H_2O]^+$ (4), 454 $[M-2H_2O]^+$ (5), 441 (9), 423 (9), 417 (10), 405 (7), 282 (8), 233 (21), 207 (42), 203 (45), 189 (46), 159 (64), 105 (100) (Found C, 73 40, H, 10 31 $C_{30}H_{50}O_5$ requires C, 73 43, H, 10 27%)

Acetonide derivative (**9**) *from tetrol* (**8**) Tetrol **8** (10 mg) was stirred with dry Me_2CO (5 ml) and one drop of conc H_2SO_4 at room temp for 5 hr The product after work up and crystallization from Me_2CO afforded acetonide (**9**, 6 mg), mp 260–262°, IR ν_{max}^{Nujol} cm^{-1} 3470, 1040, 850, ^1H NMR ($CDCl_3$) δ 0 84 (3H, *s*), 0 92 (6H, *s*), 0 96 (3H, *s*), 1 04 (3H, *s*), 1 28 (3H, *s*), 1 44 (3H, *s*), 1 48 (3H, *s*), 3 24 (1H, *m*, H-3), 3 32 (1H, *d*, *J* = 8 Hz, H-28), 3 40 (1H, *d*, *J* = 8 Hz, H-30), 3 42 (1H, *d*, *J* = 8 Hz, H-30), 3 96 (1H, *d*, *J* = 8 Hz, H-28), 4 02 (2H, *m*, H-16, H-22), 5 52 (1H, *t*, *J* = 4 Hz, H-12) (Found C, 74 65, H, 10 25 $C_{33}H_{54}O_5$ requires C, 74 67, H, 10 26%)

Deacetonidation of **7** *and* **9** *yielding* **11** *and* **12** (a) A soln of **7** (8 mg) in Me_2CO (1 5 ml), dioxane (1 ml) and 20% HCl–MeOH (0 5 ml) was left for 15 min at room temp and poured into H_2O Work up as usual was followed by crystallization from EtOAc to yield needles of **11** (6 mg), mp 208–210° (Found C, 73 79, H, 9 83 $C_{30}H_{48}O_5$ requires C, 73 73, H, 9 90%) (b) The product **9** (10 mg) was treated in the above manner and the needles of **12** (8 mg) were obtained, mp 270–272° (Found C, 73 40, H, 10 25 $C_{30}H_{50}O_5$ requires C, 73 43, H, 10 27%)

Acetylation of **11** *and* **12** *yielding* **13** *and* **14** (a) Acetylation of **11** (5 mg) with pyridine (0 6 ml)–Ac_2O (1 ml) on a water bath for 3 hr and usual work up afforded colourless leaflets of **13** (4 mg), mp 185–187°, IR ν_{max}^{Nujol} cm^{-1} 1730, 1240, 1230, ^1H NMR ($CDCl_3$) δ 0 82 (3H, *s*), 0 86 (3H, *s*), 0 90 (3H, *s*), 0 96 (3H, *s*), 1 02 (3H, *s*), 1 28 (3H, *s*), 2 04–2 10 (12H, *s*, 4 × OAc), 4 0 (1H, *d*, *J* = 11 Hz, H-28), 4 25 (1H, *d*, *J* = 11 Hz, H-28), 4 50 (2H, *m*, H-3 and H-16), 5 20 (2H, *t*-like, H-12 and H-22), 9 48 (1H, *s*, H-30) (Found C, 69 42, H, 8 56 $C_{38}H_{56}O_9$ requires C, 69 48, H, 8 59%) (b) Acetylation of **12** (6 mg) as above afforded colourless needles of **14** (4 mg), mp 220–222°, IR ν_{max}^{Nujol} cm^{-1} 1736, 1244, 1235, ^1H NMR ($CDCl_3$) δ 0 88 (6H, *s*), 0 92 (3H, *s*), 0 98 (3H, *s*), 1 28 (6H, *s*), 1 96–2 12 (15H, all *s*, 5 × OAc), 3 60 (1H, *d*, *J* = 8 Hz, H-30), 3 80 (1H, *d*, *J* = 8 Hz, H-30), 3 92 (1H, *d*, *J* = 11 Hz, H-28), 4 08 (1H, *d*, *J* = 11 Hz, H-28), 4 52 (2H, *m*, H-3 and H-16), 5 18 (1H, *m*, H-22), 5 36 (1H, *m*, H-12) (Found C, 68 52, H, 8 61 $C_{40}H_{60}O_{10}$ requires C, 68 54, H, 8 63%)

Acetal derivative (**10**) *from androsacenol* (**1**) Compound **1** (10 mg) was stirred in MeOH with a drop of conc H_2SO_4 at room temp for 6 hr The reaction product after usual work up was purified by crystallization from EtOAc giving **10** (6 mg), mp 252°, IR ν_{max}^{Nujol} cm^{-1} 3500, 1010, 850, ^1H NMR ($CDCl_3$) δ 0 84 (3H, *s*), 0 92 (3H, *s*), 0 96 (3H, *s*), 1 02 (3H, *s*), 1 04 (3H, *s*), 1 36 (3H, *s*), 3 44 (3H, *s*, 30-OMe), 4 68 (1H, *s*, H-30), 3 28 (1H, *m*, H-3), 3 40 (1H, *d*, *J* = 8 Hz, H-28), 3 62 (1H, *d*, *J* = 8 Hz, H-28), 4 00 (2H, *m*, H-16, H-22), 5 44 (1H, *t*, *J* = 4 Hz, H-12), MS *m/z* (rel int) 484 $[M-H_2O]^+$ (5), 470 (3), 452 $[M-H_2O-MeOH]^+$ (7), 440 (14), 424 (5), 412 (26), 358 (18), 262 (17), 232 (72), 207 (81), 189 (70), 186 (100) (Found C, 74 10, H, 9 98 $C_{31}H_{50}O_5$ requires C, 74 06, H, 10 03%)

Conversion of **6** *to the triacetate* (**17**) Triol **6** (10 mg) in EtOH (1 ml), triethylene glycol (5 ml) and 80% hydrazine hydrate (1 ml) were refluxed for 3 hr KOH (250 mg) was added and the mixture refluxed further for 15 min The bath temp was then raised gradually with a downward condenser to remove low boiling components and finally heated at 230–240° for 4 hr and worked up as usual to yield the product **16** (8 mg) Compound **16** (7 mg) was stirred in MeOH with a drop of conc H_2SO_4 for 6 hr to afford **15** (6 mg) Acetylation of **15** (5 mg) with pyridine (0 5 ml) and Ac_2O (1 ml) at room temp overnight followed by usual work up and crystallization from MeOH yielded needles of **17** (4 mg), mp 239–241°

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