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# 21α,30-DIHYDROXY-D:A-FRIEDOOLEANAN-3-ONE FROM *SALACIA RETICULATA* VAR. *β-DIANDRA* STEM BARK

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**Key Word Index**—*Salacia reticulata* var. *β-diandra*, Celastraceae, 21α,30-dihydroxy-D A-friedooleanan-3-one, D.A-friedooleananes

**Abstract**—*Salacia reticulata* var *β-diandra* stem bark contained 21α,30-dihydroxy-D A-friedooleanan-3-one and eight other D:A-friedooleananes.

## INTRODUCTION

*Salacia reticulata* Wight var *β-diandra* is a woody climber growing in the low country rain forests of south western Sri Lanka. We have previously reported the presence of iquesterin, pristimerin and 21α,26-dihydroxy-D A-friedooleanan-3-one in the stem bark of *Salacia reticulata* var *β-diandra* [1]. Gutta, long chain hydrocarbon oils, sitosterol and mangiferin have been reported from the roots of *Salacia reticulata* itself [2, 3]. We now report the isolation of 21α,30-dihydroxy-D A-friedooleanan-3-one and eight other friedooleananes from *Salacia reticulata* var. *β-diandra* bark

## RESULTS AND DISCUSSION

The methanol insoluble fraction of the benzene extract of *Salacia reticulata* var. *β-diandra* stem bark contained the triterpenoids, D.A-friedooleanan-3-one, 28-hydroxy-D A-friedooleanan-3-one, 3-oxo-D·A-friedooleanan-28-al, 3-oxo-D.A-friedooleanan-30-al, D A-friedooleanan-3, 21-dione, 30-hydroxy-D:A-friedooleanan-3-one, 21α-hydroxy-D·A-friedooleanan-3-one, 3-oxo-D:A-friedooleanan-30-oic acid, pristimerin and a new polar diol (**1**)

The diol **1** gave a diacetate **2** whose $^1$H NMR spectrum, together with its mass spectral fragmentation pattern, was strongly suggestive of a D·A-friedooleanane structure. The $^1$H NMR spectrum of the diacetate **2** showed a two proton singlet at $\delta$3.92 for a $CH_2OH$ group and a double doublet at $\delta$5.18 ($J$=5 and 11 Hz) for a CHOH proton Intense peaks at $m/z$ 273 in the mass spectra of both diol **1** and diacetate **2** indicated that the carbonyl group resided in one of the rings A–C and that no other groups were present in these rings

Oxidation of diol **1** with chromium trioxide–pyridine gave an aldehyde **3**, which was reduced with borohydride to a different diol **4**. The spectral data of diol **4** suggested that like diol **1** it too was an oxo-D·A-friedooleananediol. However, the base peak at $m/z$ 275 in the mass spectrum of diol **4** suggested that the carbonyl group in rings A, B or C of diol **1** had been reduced to a hydroxyl group in **4**. Reduction of diol **4** under Huang–Minlon conditions gave D A-friedooleanane-3β,30-diol (**5**), identical with that prepared from 30-hydroxy-D.A-friedooleanan-3-one (**6**) confirming that C-30 in diol **1** was oxygenated and that the carbonyl group was at C-3

Reduction of diol **1** itself under similar conditions gave a less polar diol **7** with no carbonyl absorption in its IR spectrum Acetylation of diol **7** gave a diacetate **8**, whose reduction with lithium in ethylenediamine gave diol **7**, together with two alcohols, D A-friedooleanan-30-ol (**9**) [4] and D·A-friedooleanan-21α-ol (**10**) [4] The second hydroxyl group in diol **1** must be therefore at C-21 and the diol should be 21α,30-dihydroxy-D·A-friedooleanan-3-one

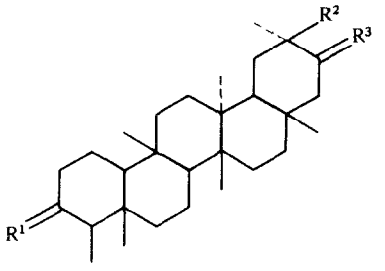
With benzaldehyde and zinc chloride, diol **1** gave a benzal derivative **11**, whose UV and IR spectra indicated that an aromatic ring had been incorporated. Its $^1$H NMR spectrum contained a singlet at $\delta$5.65 for the benzylic proton and a five proton aromatic multiplet at $\delta$7.40. The formation of a benzal derivative confirmed that the two hydroxyl groups in the diol **1** had a 1,3-relationship with each other.

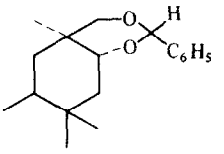
Jones oxidation [5] of diol **1** gave 3,21-dioxo-D·A-friedooleanan-30-oic acid (**12**), which although a β-keto acid, did not readily decarboxylate on heating This behaviour is not unexpected as substitution at C-20 prevents the formation of the enol intermediate required for ionic decarboxylation [6]

## EXPERIMENTAL

Mps uncorr, UV EtOH, IR KBr, $^1$H NMR 60 MHz, $CDCl_3$ using $SiMe_4$ as int standard, Optical rotations $CHCl_3$ at 25°, Prep TLC Merck silica gel $PF_{254+366}$ Petrol 40–60°. Identities of compounds were established by mmp, IR and $^1$H NMR comparisons, unless otherwise stated

*Extraction of plant material* The outer stem bark of *Salacia reticulata* Wight var, *β-diandra* was collected from Kanneliya in southwest Sri Lanka, and the dried, ground material (100 g) was extracted with $C_6H_6$ The $C_6H_6$ extract (30 g) was dissolved in $CHCl_3$ and MeOH added The cream powder (12 g) which pptd was filtered





**11** $R^1$ = O

**1** $R^1$ = O, $R^2$ = $CH_2OH$, $R^3$ = αOH, βH
**2** $R^1$ = O, $R^2$ = $CH_2OAc$, $R^3$ = αOAc, βH
**3** $R^1$ = O, $R^2$ = CHO, $R^3$ = O
**4** $R^1$ = αH, βOH, $R^2$ = $CH_2OH$, $R^3$ = O
**5** $R^1$ = αH, βOH, $R^2$ = $CH_2OH$, $R^3$ = $H_2$
**6** $R^1$ = O, $R^2$ = $CH_2OH$, $R^3$ = $H_2$
**7** $R^1$ = $H_2$, $R^2$ = $CH_2OH$, $R^3$ = αOH, βH
**8** $R^1$ = $H_2$, $R^2$ = $CH_2OAc$, $R^3$ = αOAc, βH
**9** $R^1$ = $H_2$, $R^2$ = $CH_2OH$, $R^3$ = $H_2$
**10** $R^1$ = $H_2$, $R^2$ = Me, $R^3$ = αOH, βH
**12** $R^1$ = O, $R^2$ = COOH, $R^3$ = O

*Chromatography of the extract* The cream powder (12 g) was chromatographed on silica gel (250 g) Elution with petrol–$CHCl_3$ mixtures gave as colourless needles from $CHCl_3$–MeOH D A-friedooleanan-3-one (80 mg), mp 262–264°, $[\alpha]_D$ −22° (lit [7] mp 264°, $[\alpha]_D$ −22°), 3-oxo-D A-friedooleanan-28-al (20 mg), mp 267–268°, $[\alpha]_D$ −16°, (lit [8] mp 268–270°, $[\alpha]_D$ −18°), 28-hydroxy-D A-friedooleanan-3-one (80 mg) on further purification on prep TLC ($CH_2Cl_2$), mp 276–277°, $[\alpha]_D$ −21° (lit [8] mp 278–280°, $[\alpha]_D$ −23°), 3-oxo-D A-friedooleanan-30-al (210 mg), mp 214–215°, $[\alpha]_D$ −16° (lit [9] mp 215–216°, $[\alpha]_D$ −13°) and D A-friedooleanan-3,21-dione (130 mg), mp 248–250°, $[\alpha]_D$ +118° (lit [7] mp 248–250°, $[\alpha]_D$ +115°), identical with authentic samples

Elution with $CHCl_3$ gave a mixture, which was treated with $Ac_2O$–pyridine for 24 hr Work-up followed by crystallization from petrol gave 21α-acetoxy-D A-friedooleanan-3-one (2 21 g) as needles, mp 235–236°, $[\alpha]_D$ −36° (lit [10] mp 236–240°, $[\alpha]_D$ −40°), while the mother liquors on prep TLC ($C_6H_6$, 2 developments) gave 30-acetoxy-D A-friedooleanan-3-one (800 mg), needles from MeOH, mp 195–196°, $[\alpha]_D$ −12° (lit [9] mp 188–190°, $[\alpha]_D$ −10°) Refluxing the acetates for 4 hr with 5% methanolic KOH gave 21α-hydroxy-D A-friedooleanan-3-one, needles from petrol, mp 268–270°, $[\alpha]_D$ −31° (lit [10] mp 264–268°, $[\alpha]_D$ −32°) and 30-hydroxy-D A-friedooleanan-3-one, needles from petrol, mp 265–267°, $[\alpha]_D$ −12° (lit [9] mp 268–269°, $[\alpha]_D$ −15°), respectively

Elution with $CHCl_3$–MeOH mixtures gave on purification by prep TLC ($CHCl_3$–MeOH, 49 1), 3-oxo-D A-friedooleanan-30-oic acid (55 mg), needles from petrol, mp 260–261°, $[\alpha]_D$ +2° (lit [9] mp 262°, $[\alpha]_D$ 0°), identical with that prepared by Jones oxidation [5] of 30-hydroxy-D A-friedooleanan-3-one, pristimerin (85 mg), orange needles from MeOH, mp 210–212°, $[\alpha]_D$ −165° (lit [1] mp 213–214°, $[\alpha]_D$ −162°), identical with authentic sample, and 21α,30-dihydroxy-D A-friedooleanan-3-one (**1**) (480 mg), which was sparingly soluble in most organic solvents Acetylation of diol **1** with $Ac_2O$–pyridine (1 1, 6 ml) at 50° for 24 hr gave 3-oxo-D A-friedooleanane-21α,30-diol, diacetate (**2**) (420 mg), plates from petrol, mp 175–177°, $[\alpha]_D$ −26°, (Found. C, 75 4, H, 9 9 $C_{34}H_{54}O_5$ requires C, 75 2, H, 10 0%), (HRMS 542 3979 $[M]^+$, Calc for $C_{34}H_{54}O_5$ 542 3971), IR $\nu_{max}$ $cm^{-1}$ 1735 and 1700, $^1H$ NMR δ0 88 (3H, *d*, *J* = 7 Hz, 4-Me), 0 73, 0 89, 0 95, 1 03, 1 13 and 1 30 (each 3H, *s*, Me), 2 02 and 2 07 (each 3H, *s*, OAc), 3 92 (2H, *br s*, $W_{1/2}$ = 2 5 Hz, 30-H) and 5 10 (1H, *dd*, *J* = 5 and 12 Hz, 21-H), MS *m/z* (rel int) 542 $[M]^+$ (18), 482 (55), 422 (100), 406 (35), 355 (26), 273 (55) and 231 (35)

21α,30-*Dihydroxy*-D A-*friedooleanan*-3-*one* (**1**) The diacetate (**2**) (400 mg) was refluxed with 5% methanolic KOH for 2 hr Work-up gave diol **1** (382 mg), mp 280–282°, $[\alpha]_D$ −40°, (Found C, 78 8, H, 10 9 $C_{30}H_{50}O_3$ requires C, 78 6, H, 11 0%), IR $\nu_{max}$ $cm^{-1}$ 3500–3300 and 1700, MS *m/z* (rel int) 458 $[M]^+$ (6), 440 (56), 427 (56), 409 (46), 353 (15), 342 (47) and (100)

21α,30-*Benzaldioxy*-D A-*friedooleanan*-3-*one* (**11**). Diol **1** was stirred with $C_6H_5CHO$ (5 ml) and dry $ZnCl_2$ for 7 days in the dark Work-up followed by prep TLC ($CH_2Cl_2$) gave the benzal derivative **11** (106 mg), colourless plates from $C_6H_6$, mp 265–266°, $[\alpha]_D$ −7° (Found C, 81 5, H, 10 2 $C_{37}H_{54}O_3$ requires C, 81 3, H, 10 0%), UV $\lambda_{max}$ nm 252, 258 and 263, IR $\nu_{max}$ $cm^{-1}$ 1700 and 1600; $^1H$ NMR δ0 89 (3H, *d*, *J* = 7 Hz, 4-Me), 0 73, 0 89, 0 89, 1 23, 1 26 and 1 26 (each 3H, *s*, Me), 3 40–3 85 (2H, AB *dd*, *J* = 10 Hz, 30-H), 3 90 (1H, *dd*, *J* = 4 and 8 Hz, 21-H), 5 65 (1H, *s*, Ar-CH) and 7 25–7 75 (5H, *m*, Ar-H), MS *m/z* (rel int) 546 $[M]^+$ (26), 440 (6), 423 (10), 410 (21), 342 (100), 327 (18) and 273 (34)

3,21-*Dioxo*-D A-*friedooleanan*-30-*al* (**3**) Diol **1** (200 mg) with $CrO_3$ (100 mg) in pyridine (5 ml) for 24 hr at 27° gave the aldehyde **3** (112 mg), colourless needles from MeOH, mp 274–276°, $[\alpha]_D$ −36° (HRMS 454 3459 $[M]^+$, Calc for $C_{30}H_{46}O_3$ 454 3447), IR $\nu_{max}$ $cm^{-1}$ 1715–1700, $^1H$ NMR δ0 84 (3H, *d*, *J* = 7 Hz, 4-Me), 0 68, 0 84, 0 87, 0 94, 1 09 and 1 20 (each 3H, *s*, Me) and 9 61 (1H, *s*, CHO), MS *m/z* (rel int) 454 $[M]^+$ (6), 439 (8), 426 (100), 411 (72), 369 (28), 341 (55), 273 (72) and 231 (52)

3β,30-*Dihydroxy*-D A-*friedooleanan*-21-*one* (**4**) Aldehyde **3** (40 mg) and $NaBH_4$ (100 mg) in MeOH (10 ml) were stirred for 0 5 hr at 27° Prep TLC ($CHCl_3$–MeOH, 99 1) after work-up gave diol **4** (28 mg), mp 269–270°, $[\alpha]_D$ −2°, IR $\nu_{max}$ $cm^{-1}$ 1700, MS *m/z* (rel int) 458 $[M]^+$ (8), 442 (52), 434 (25), 412 (18), 358 (20), 275 (100) and 259 (46)

D A-*Friedooleanane*-3β,30-*diol* (**5**) (i) Diol **4** (24 mg) was reduced under Huang-Minlon conditions [diethylene glycol

(10 ml), $N_2H_4$ $H_2O$ (0 1 g), KOH (50 mg), reflux 3 hr, distil to 200° and heat at 200° for 3 hr] Work-up followed by prep. TLC ($CHCl_3$–MeOH, 99:1) gave diol **5** (18 mg), colourless needles from $CHCl_3$–petrol, mp 280–281°, $[\alpha]_D$ −29°, (HRMS 444.3971 $[M]^+$, Calc for $C_{30}H_{52}O_2$ 444 3968), IR $\nu_{max}$ $cm^{-1}$ 3500–3350, MS *m/z* (rel. int ): 444 $[M]^+$ (40), 426 (50), 411 (16), 394 (15), 304 (35), 275 (100) and 248 (52)

(ii) 30-*Hydroxy*-D:A-*friedooleanan*-3-*one* (**6**) (25 mg) and $NaBH_4$ (50 mg) in MeOH (25 ml) were stirred for 0.5 hr at 27° Work-up followed by crystallization gave diol **5** (22 mg), mp 280–281°, $[\alpha]_D$ −30°, identical with that obtained above

D:A-*Friedooleanane*-21α,30-*diol* (**7**) Diol **1** (100 mg) in diethylene glycol (10 ml) was reduced with $N_2H_4 \cdot H_2O$ (0 1 g), KOH (100 mg) under Huang–Minlon conditions Work-up followed by recrystallization from $CHCl_3$–petrol gave colourless needles of diol (**7**) (78 mg), mp 259–260°, $[\alpha]_D$ −14°, IR $\nu_{max}$ $cm^{-1}$: 3500–3300; MS *m/z* (rel int.) 444 $[M]^+$ (9), 429 (23), 426 (10), 413 (45), 395 (5), 279 (19) and 259 (100).

D A-*Friedooleanane*-21α,30-*diol, diacetate* (**8**) Diol 7 (75 mg) was stirred for 24 hr with $Ac_2O$–pyridine (1 1, 4 ml) at 27° Work-up followed by recrystallization from MeOH gave acetate **8** (72 mg) as colourless needles, mp 205–207°, $[\alpha]_D$ −30°, (HRMS 528.4177 $[M]^+$, Calc for $C_{34}H_{54}O_5$. 528.4180), IR $\nu_{max}$ $cm^{-1}$. 1735 and 1240; $^1H$ NMR δ0 76, 0.84, 0.94, 1.00, 1 09 and 1.29 (each 3H, *s*, Me), 0 76–0 90 (3H, overlapped, 4-Me), 2 00 and 2.06 (each 3H, *s*, OAc), 3 90 (2H, *s*, 30-H) and 5.06 (1H, *dd*, *J* = 5 and 12 Hz, 21-H); MS *m/z* (rel. int ). 528 $[M]^+$ (6), 513 (23), 468 (32) 453 (37), 408 (41), 393 (28), 259 (100), 217 (92) and 204 (72).

*Lithium ethylenediamine reduction of* D A-*friedooleanane*-21α,30-*diol, diacetate* (**8**) Acetate **8** in ethylenediamine (10 ml) was treated with Li (100 mg) under dry conditions until a blue colour appeared. The reaction mixture was cooled after 20 min and excess Li destroyed with *t*-BuOH Work-up followed by prep TLC ($C_6H_6$, 2 developments) gave D A-friedooleanan-30-ol (**9**), plates from MeOH, mp 230–232°, $[\alpha]_D$ +13° (lit [4], mp 230–232°, $[\alpha]_D$ +14°), the more polar D A-friedooleanan-21α-ol (**10**) (12 mg), needles from $CHCl_3$–MeOH, mp 260–262°, $[\alpha]_D$ +15°, (lit. [10], mp 261–264°, $[\alpha]_D$ +12°) and diol **7** (10 mg)

3,21-*Dioxo*-D:A-*friedooleanan*-30-*oic acid* (**12**) Jones reagent [5] (5 ml) was added to diol **1** (50 mg) in $Me_2CO$ (50 ml) at 0° and the mixture stirred for 2 hr at 27°. Work-up followed by prep TLC ($CHCl_3$–MeOH, 49 1, 2 developments) gave acid **12** (30 mg) as an amorphous powder, mp 278–281°, IR $\nu_{max}$ $cm^{-1}$ 3600–3100 and 1720–1700; $^1H$ NMR δ0.87 (3H, *d*, *J* = 7 Hz, 4-Me), 0.73, 0.87, 0.91, 0.95, 1.00, 1.03 and 1 26 (each 3H, *s*, Me) and 5 90 (1H, *br s*, COOH).

*Attempted decarboxylation of* 3,21-*dioxo*-D A-*friedooleanan*-30-*oic acid* (**12**) Acid **12** (10 mg) in (*a*) toluene (10 ml), (*b*) $C_6H_6$–$H_2O$ (1·1, 10 ml) and (*c*) diethylene glycol (5 ml) was refluxed for 5 hr Work-up gave only unreacted acid **12**

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