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STUDIES ON TERPENOIDS AND STEROIDS—2[1]

STRUCTURES OF TWO NEW TRI- AND TETRA-OXYGENATED D:A-FRIEDO-OLEANAN TRITERPENES FROM *KOKOONA ZEYLANICA*[2]†

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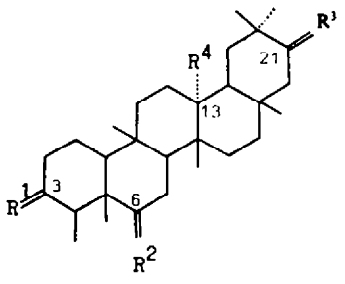
Abstract—The two D:A-friedo-oleanane triterpenes kokzeylanol and kokzeylanonol isolated from the inner bark of *Kokoona zeylanica* have been characterized as 6β,27-dihydroxy-D:A-friedo-olean-3-one and 6β,27-dihydroxy-D:A-friedo-olean-3,21-dione, respectively, by the deoxygenation of their 27-acetoxy derivatives using lithium–ethylenediamine reduction coupled with spectroscopic and irradiation methods. Kokzeylanonol represents the first tetra-oxygenated D:A-friedo-oleanane triterpene obtained from a nautral source. Significance of some of these D:A-friedo-oleananes in the biosynthesis of quinonoid triterpenes in Celastraceae is discussed.

Kokoona zeylanica Thwaites is a plant with reputed medicinal properties[4] and having restricted distribution in Sri Lanka and South India.[5] Twelve D:A-friedo-oleanane triterpenes have been isolated from the hot benzene extract of the inner stem bark of this plant[1] and we have already reported the characterization of friedelin (**1**), D:A-friedo-olean-3,21-dione (**2**), 21α-hydroxy-D:A-friedo-olean-3-one (**3**),[6] kokoonol (27-hydroxy-D:A-friedo-olean-3-one; **4**), kokoononol (27-hydroxy-D:A-friedo-olean-3,21-dione; **5**), kokoondiol (21α,27-dihydroxy-D:A-friedo-olean-3-one; **6**),[1,7] zeylanol (6β-hydroxy-D:A-friedo-olean-3-one; **7**), zeylanonol (6β-hydroxy-D:A-friedo-olean-3,21-dione; **8**), and zeylandiol (6β,21β-dihydroxy-D:A-friedo-olean-olean-3-one; **9**).[1,8]

The present paper deals with the characterization of two novel 27-hydroxy-D:A-friedo-oleananes named kokzeylanol and kokzeylanonol from *K. zeylanica* and establishment of their structures as 6β,27-dihydroxy-D:A-friedo-olean-3-one (**11**) and 6β,27-dihydroxy-D:A--friedo-olean-3,21-dione (**12**), respectively. Kokzeylanonol is the first example of a natural tetraoxygenated D:A-friedo-oleanane and is significant as polyoxygenated triterpenes are reported to exhibit antitumor activity.[9]

RESULTS AND DISCUSSION

The triterpene mixture obtained from the hot benzene extract of the inner stem bark of *K. zeylanica* has been separated into twelve constituent crystalline compounds by combined column and TLC.[1] Characterization of nine of these D:A-friedo-oleanane triterpenes have been reported earlier[6-9] (see above). The two most polar compounds eluted from the column with 10% methanol in chloroform were found to have 3,6,27-trioxy and 3,6,21,27-tetraoxy D:A-friedo-oleanane systems[1] and were named as kokzeylanol and kokzeylanonol, respectively.



1: R¹ = 0; R² = R³ = H₂; R⁴ = Me
2: R¹ = R³ = 0; R² = H₂; R⁴ = Me
3: R¹ = 0; R² = H₂; R³ = α-OH, β-H; R⁴ = Me
4: R¹ = 0; R² = R³ = H₂; R⁴ = CH_2OH
5: R¹ = R³ = 0; R² = H₂; R⁴ = CH_2OH
6: R¹ = 0; R² = H₂; R³ = α-OH, β-H; R⁴ = CH_2OH
7: R¹ = 0; R² = β-OH, α-H; R³ = H₂; R⁴ = Me
8: R¹ = R³ = 0; R² = β-OH, α-H; R⁴ = Me
9: R¹ = 0; R² = R³ = β-OH, α-H; R⁴ = Me
10: R¹ = 0; R² = β-OAc, α-H; R³ = H₂; R⁴ = Me
11: R¹ = 0; R² = β-OH, α-H; R³ = H₂; R⁴ = CH_2OH
12: R¹ = R³ = 0; R² = β-OH, α-H; R⁴ = CH_2OH
13: R¹ = 0, R² = β-OAc, α-H; R³ = H₂; R⁴ = CH_2OAc
14: R¹ = R³ = 0; R² = β-oAc, α-H; R⁴ = CH_2OAc
15: R¹ = R² = R³ = H₂; R⁴ = CH_2OH
16: R¹ = R² = R³ = H₂; R⁴ = $CH_2OC(=S)Ph$
17: R¹ = R² = R³ = H₂; R⁴ = CH_2OCH_2Ph
18: R¹ = R² = R³ = H₂; R⁴ = CH_2OAc
19: R¹ = R³ = H₂; R² = β-OH, α-H; R⁴ = CH_2OH
20: R¹ = R² = 0; R³ = H₂; R⁴ = CHO
21: R¹ = R² = OH, H; R³ = H₂; R⁴ = CHO
22: R¹ = R² = 0; R³ = H₂; R⁴ = Me
23: R¹ = R² = β-OH, α-H; R³ = O; R⁴ = CH_2OH
24: R¹ = R² = β-OH, α-H; R³ = O; R⁴ = Me

The IR spectrum of kokzeylanol, $C_{30}H_{50}O_3$, m.p. 274–276°, was indicative of the presence of hydroxyl (3490 cm^{-1}) and carbonyl (1740 cm^{-1}) functions. Examination of the ^1H NMR spectrum revealed the presence of six tertiary CMe, one secondary CMe, two protons appearing as a broad singlet at δ4.08 assigned to a CH_2OH on a quarternary carbon atom, and one proton appearing as a multiplet at 3.05

†Dedicated to Prof. Carl Djerassi with great admiration for the appearence of his one thousandth paper and in appreciation to his contribution in the fields of triterpenoids and steroids.

($W_{1/2}$ = 18 Hz) assigned to a CHOH in a ring system. Kokzeylanol, $C_{30}H_{48}O_4$, m.p. 295–297°, had in its IR spectrum strong bands at 3490, 1722 and 1714 cm^{-1} indicating the presence of hydroxy and carbonyl groups. In the ^1H NMR spectrum it had signals due to six tertiary CMe, one secondary CMe, two protons appearing as a broad singlet at δ4.10 assigned to a CH_2OH on a quarternary carbon atom, and one proton appearing as a multiplet at 3.50 ($W_{1/2}$ = 18Hz) assigned to a CHOH in a ring system. On acetylation both kokzeylanol (**11**) and kokzeylanonol (**12**) afforded their corresponding diacetates **13** and **14**, respectively. The prochiral nature of the CH_2OAc group in **13** and **14** was apparent from their ^1H NMR spectra where each proton of the CH_2 group appeared as a doublet (J = 12Hz) (see Experimental).

In order to relate kokzeylanol (**11**) and kokzeylanonol (**12**) to known D:A-friedo-oleananes, a deoxygenation method applicable to both primary and secondary alcohol functions was required. Presence of oxo groups ruled out the possible use of conventional Huang-Minlon reduction.[10]

Triphenyltin hydride reduction previously employed by us to deoxygenate 6β-hydroxy and 21β-hydroxy-D:A-friedo-oleananes[9] having a secondary alcohol group, when attempted on the model compound, 27-thiobenzoyloxy-D:A-friedo-oleanane (**16**), afforded 27-benzyloxy-D:A-friedo-oleanane (**17**) and not the deoxygenated product (friedelan). However, reduction of the derived acetate (**18**) by Barton's recent procedure,[11] but employing lithium and ethylenediamine proved to be the method of choice as exemplified by successful deoxygenation of several triterpene acetates bearing both primary and secondary alcohol functions (see Table 1).

As expected, lithium-ethylenediamine reduction of 27-acetoxy-D:A-friedo oleanane (**18**) yielded the deoxygenation product, friedelan (65%). The product due to hydrolysis, 27-hydroxy-D:A-friedo-oleanane (**15**) (30%) was also formed. When kokzeylanol diacetate (**13**) was subjected to similar treatment, a mixture of products was obtained. However, on oxidation (CrO_3/pyridine), this mixture afforded friedlin (**1**) as the major product (64%), thus confirming that kokzeylanol is a derivative of friedelin (see Scheme 1).

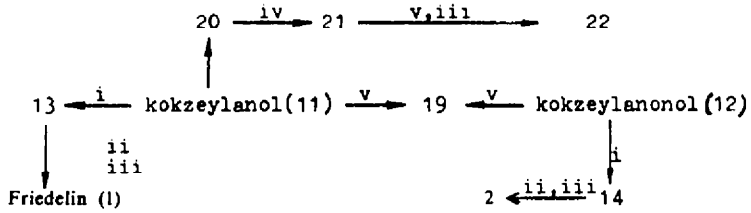
Lithium–ethylenediamine reduction of kokzeylanonol diacetate (**14**) yielded a mixture of products which on subsequent oxidation as above afforded D:A-friedo-olean-3,21-dione (**2**) as the major product (40%). Thus, kokzeylanonol should be a derivative of **2**.

It remained then to locate positions of the hydroxyl groups in kokzeylanol and kokzeylanonol. Huang–Minlon reduction of both natural products gave the same diol **19**, $C_{30}H_{52}O_2$, m.p. 278–280°. Oxidation (CrO_3/pyridine) of kokzeylanol (**11**) yielded the diketo-aldehyde **20**, m.p. 298–300°. Sodium borohydride reduction of **20** gave a product, $C_{30}H_{50}O_3$, m.p. 266–268°, whose spectral data indicated it to be a aldehyde-diol **21**. Huang–Minlon reduction of this aldehyde-diol **21** followed by oxidation afforded a diketone, m.p. 304–306°, which was identified as D:A-friedo-olean-3,6-dione (**22**).[8] Thus, the secondary hydroxy function in kokzeylanol and kokzeylanonol should be with a β-configuration ($W_{1/2}$ = 18Hz).[8]

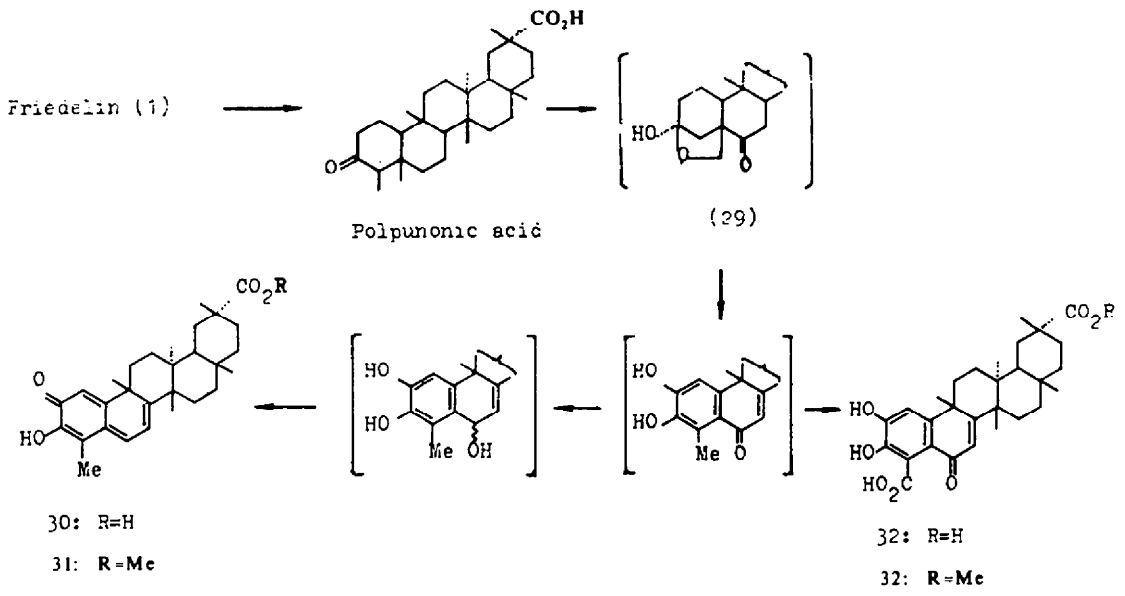
By analogy with kokoonol, the hydroxy methylene group in both kokzeylanol and kokzeylanonol was placed at C-13. In order to confirm this, photolysis of the 21-keto group previously used by us in the structure elucidation of kokoonol and kokoononol[1,7] was employed. Sodium borohydride reduction of kokzeylanonol (**12**) afforded **23**, m.p. 336–338°, photolysis of which gave two products. IR, ^1H NMR and spin-spin decoupling experiments[1,12] suggested the major (58%) product to be 3β,6β,27-trihydroxy-*E*-seco-D:A-friedo-olean-19-ene-21-carboxaldehyde (**25**), m.p. 130–132°, and the minor (32%) product to be 3β,6β,27-trihydroxy-21,22-bisnor-*E*-seco-D:A-friedo-olean-16,19-diene (**27**), m.p. 98–100°, formed due to a Norrish type II process on the major product **25**. Failure to detect the intermediate carboxaldehyde **26** during the irradiation of 3β,6β-dihydroxy-D:A-friedo-olean-21-one (**24**) under identical conditions suggests a partial inhibition of Norrish type II process on **25** which may only be possible if the hydroxymethylene group is present on C-13 avoiding the abstraction of the 16-H by the CH_2CHO group.[1,7] Since Huang–Minlon reduction of both kokzeylanol (**11**) and kokzeylanonol (**12**) gave the same diol **19**, kokzeylanol should also have the hydroxymethylene function at C-13.

Biosynthetic considerations

It is interesting to note that *K. zeylanica* contains a variety of oxygenated D:A-friedo-oleanane triterpenes. This may be attributed to the presence of oxidase enzyme(s) in this plant. The co-occurence of 6β-hydroxy-D:A-friedo-oleananes, desmethyl zeylasterone (**32**), zeylasterone (**33**), celastrol (**30**) and pristimerin (**31**)[13] in *K. zeylanica* suggests the possible biosynthetic relationship between 6-oxo-D:A-friedo-oleananes (e.g. 6-oxo-salaspermic acid (**29**)[14] type intermediate) and the quinonoid triterpenes peculiar to Celastraceous plants (Scheme 2).



Scheme 1. Reagents: i. Ac_2O, pyridine; ii. Li–$(CH_2NH_2)_2$, reflux, 30 min; iii. CrO_3, pyridine, 25°C; iv. $NaBH_4$, $[CH_2OH]_2$, 25°, 10 min; v. $NH_2NH_2{\cdot}H_2O$ (98–100%), $(CH_2OH)_2$, KOH, 150–160° for 3 h and 210° for 4 h.

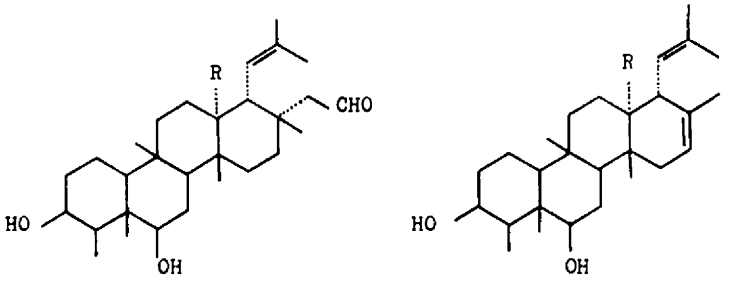


Scheme 2. Possible biosynthetic relationship between 6-oxo-D:A-friedo-oleananes and quinonoid triterpenes in celastraceae.

Table 1. Results of lithium ethylenediamine reduction of some triterpene acetates

Triterpene acetate	Product(s)	% yield
27-Acetoxy-D:A-friedo-oleanane (**18**)	friedelan	65
	27-hydroxy-D:A-friedo-oleanane (**15**)	30
6-Acetoxy-D:A-friedo-olean-3-one (zeylanol acetate) (**10**)	friedelin (**1**)[a]	75
Kokzeylanol diacetate (**13**)	friedelin (**1**)[a]	60
Kokzeylanonol diacetate (**14**)	D:A-friedo-olean-3,21-dione (**2**)[a]	40

[a]Product obtained after oxidation with CrO_3-pyridine



EXPERIMENTAL

General methods. M.ps were determined on a Kofler hot-stage melting point apparatus and are uncorrected. IR spectra were determined in KBr discs with a Perkin–Elmer model 257 grating spectrophotometer. Nuclear magnetic resonance spectra were determined in deuterio-chloroform, unless otherwise noted, on a Varian T 60 A or FT-80 spectrometer with tetramethylsilane as an internal standard. Mass spectra were obtained from University of Aberdeen, Scotland, and microanalyses were performed by the CSIRO Microanalytical Service, Melbourne, Australia. Optical rotations were determined on a Perkin–Elmer 241 automatic polarimeter. Thin-layer chromatography (TLC) was carried out on silica gel (E. Marck) plates (0.1 mm), and visualization was effected with acidified anisaldehyde spray. Preparative-layer chromatography (PLC) was carried out on silica gel $PF_{254-366}$ (Merck) plates (1.0 mm). Column chromatography was carried out on silica gel (30–70 mesh, Merck).

The plant material was collected from Kanneliya rain

forest, Sri Lanka and the authenticity of material was confirmed by Prof. S. Balasubramaniam, Dept of Botany, University of Peradeniya, Sri Lanka. Processing of plant material, isolation and physical data of kokzeylanol (**11**) and kokzeylanonol (**12**) have been reported in Part 1 of this series.[1]

Acetylation of kokzeylanol (**11**). Acetylation of (**11**) (100 mg) with Ac_2O (2 ml) in pyridine (5 ml), usual work up and crystallization yielded kokzeylanol diacetate (**13**) as white needles (95 mg, 87%); m.p. 250–252°; $[\alpha]_D^{27}$ –19.5° ($CHCl_3$); IR (KBr) 1740, 1722 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.70 (1H, m, CHOAc, $W_{1/2}$ = 18Hz), 4.66 and 4.35 (2H, dd, J = 13Hz, CH_2OAc), 2.06 and 2.03 (6H, s, 2 × $OCOCH_3$), 2.73–1.40 (CH_2) and 1.30–0.80 (7 × Me). Found C, 75.30; H, 9.80. Calc for $C_{34}H_{54}O_5$: C, 75.21: H, 10.04%.

Acetylation of kokzeylanonol (**12**). Acetylation of kokzeylanonol (100 mg) with Ac_2O (2 ml) in pyridine (5 ml) usual work up and crystallization from methanol afforded kokzeylanonol diacetate (**14**) as white needles (95 mg, 90%); m.p. 270–272° $[\alpha]_D^{27}$ + 64.5° ($CHCl_3$); IR (KBr) 1740, 1710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.70 (1H, m, $W_{1/2}$ = 18Hz, CHOAc), 4.66 and 4.35 (2H, dd, J = 13Hz, CH_2OAc), 2.06 (3H, s, $OCOCH_3$), 2.03 (3H, s, $OCOCH_3$), 2.73–1.10 (CH_2) and 1.30–0.80 (7 × Me). Found: C, 73.32; H, 9.40. Calc for $C_{34}H_{52}O_6$: C, 73.33; H, 9.43%.

Preparation of 27-hydroxy-D:A-friedo-oleanane (**15**). A mixture of kokoononol (**5**) (500 mg), ethane-1,2-diol (15 ml), hydrazine hydrate (99–100%, 5 ml), and potassium hydroxide (500 mg) was heated under reflux (160–170°) for 4 hr. The condenser was removed and the solvent distilled off until the temperature rose to 210°, after which the condenser was replaced and the mixture refluxed for 4 h. The reaction mixture was cooled to room temp and worked up in the usual manner to obtain **15** as white needles (400 mg, 86%); m.p. 225–227°; $[\alpha]_D^{27}$ + 9.0° ($CHCl_3$); IR (KBr) 3490 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.13 (2H, br, s, CH_2OH), 1.80–1.30 (CH_2) and 1.20–0.83 (21H, 7 × Me). Found: C, 84.30; H, 12.21. Calc for $C_{30}H_{52}O$: C, 84.00; H, 12.30%.

Preparation of 27-thiobenzoyloxy-D:A-friedo-oleanane (**16**). A mixture of *N,N*-dimethyl benzamide (150 mg) and phosgene (150 mg) in benzene (2 ml) was kept for 18 h with stirring under N_2. The solvent was evaporated and the residue taken up in dichloromethane (3 ml) and added to a solution of **15** (250 mg) in THF (5 ml) with stirring. This was kept for 30 min and was converted into the thiobenzoate **16** by the addition of pyridine (0.25 ml) followed by the treatment with hydrogen sulphide for 10 min. Usual work up gave the crude product which on purification by PLC (eluant–benzene) and recrystallization from methanol afforded pure **16** as yellow needles (200 mg, 66%); m.p. 194–196°; $[\alpha]_D^{27}$ + 56.0° ($CHCl_3$); IR (KBr) 1235 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.30–8.06 and 7.53–7.30 (5H, m, ArH), 5.00 (2H, s, CH_2OCSPh), 2.00–1.30 (CH_2) and 1.16–0.66 (21H, 7 × Me). Found: C, 79.09; H, 9.80; S, 5.75. Calc for $C_{37}H_{54}O_2S$: C, 78.90; H, 9.70; S, 5.70%.

Triphenyltin hydride reduction of (**16**). 27-Triobenzoyloxy-D:A-friedo-oleanane (100 mg) in toluene (8 ml) was added during 15 min to a solution of triphenyltin hydride (100 mg) in toluene (7 ml) with refluxing under dry N_2. After the disappearance of the yellow colour (2 h), the solvent was removed *in vacuo* and the residue was purified by TLC (eluant:benzene) and recrystallized from methanol to obtain 27-benzyloxy-D:A-friedo-oleanane (**17**) as colourless crystals (68 mg, 76%); m.p. 115–116°; $[\alpha]_D^{27}$ + 3.6° ($CHCl_3$); IR (KBr) 1110 cm^{-1}; ^1H NMR (CCl_4) δ 7.23 (5H, m, ArH), 4.40 (2H, br, s, $PhCH_2O$), 3.70 (2H, br, s, CH_2OCH_2Ph), 2.00–1.10 (CH_2), 1.00–0.76 (21H, 7 × Me).

Acidic cleavage of (**17**). A mixture of the above benzyl ether (30 mg), conc HCl (1 ml) and absolute ethanol (5 ml) was refluxed for 24 h. The solvents were evaporated *in vacuo* and the product purified by TLC (eluant:chloroform) and crystallized from methanol to give 27-hydroxy-D: A-friedo–oleanane (**15**; 12 mg, 52%); m.p. and mixed m.p. 225–227°; identical with an authentic sample.

Acetylation of 27-hydroxy-D:A-friedo-oleanane (**15**). Acetylation of **15** (125 mg) with Ac_2O (2 ml) in pyridine (5 ml) and usual work up and recrystallization from methanol afforded 27-acetoxy-D:A-friedo-oleanane (**18**) as white needles (115 mg, 82%); m.p. 163–165°; $[\alpha]_D^{27}$ + 9.2° ($CHCl_3$); IR (KBr) 1738, 1250 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.60, 4.40 (2H, dd, J = 10Hz, CH_2OAc), 2.06 (3H, s, $OCOCH_3$), 2.50–1.30 (CH_2) and 1.00–0.73 (21H, 7 × Me).

Lithium–ethylenediamine reduction of (**18**). A mixture of **18** (100 mg), anhydrous ethylenediamine (10 ml) and lithium (100 mg) was stirred under dry N_2 until blue colour appeared. After 20 min (TLC control), the reaction mixture was cooled, excess lithium destroyed with t-butanol and worked up in the usual manner to yield a mixture of two products. This mixture was separated by PLC (eluant:chloroform) to give (in order of increasing polarity) friedelan (56 mg, 65%); m.p. 246–247°, $[\alpha]_D^{27}$ + 18.7° ($CHCl_3$); identical with an authentic sample, and the hydrolysis product, 27-hydroxy-D:A-friedo-oleanane (**15**) (26 mg, 30%); identical with an authentic sample.

Lithium–ethylenediamine reduction of kokzeylanol diacetate (**13**). 50 mg of **13** was reduced with ethylenediamine (10 ml) and lithium (100 mg) as above to obtain a product mixture (40 mg) which was oxidized with CrO_3 (25 mg) in pyridine (5 ml) for 1 h. Usual work up and purification by PLC (eluant:benzene) afforded friedelin (**1**) (27 mg, 64%); m.p. 265°C, $[\alpha]_D^{27}$–22.1° ($CHCl_3$); identical with an authentic sample.

Lithium–ethylenediamine reduction of kokzeylanonol diacetate (**14**). 50 mg of **14** was reduced with ethylenediamine (10 ml) and lithium (100 mg) as above to obtain a product mixture (42 mg) which was oxidized with CrO_3 (25 mg) in pyridine (5 ml) for 1 h. Usual work up and purification by PLC (eluant:chloroform) afforded D:A-friedo-oleanan-3,21-dione (**2**) (16 mg, 40%); m.p. 248–250°; $[\alpha]_D^{27}$ + 115.0° ($CHCl_3$); identical with an authentic sample.

Lithium–ethylenediamine reduction of zeylanol acetate (**10**). Reduction of 50 mg of **10**, followed by oxidation as above and purification by PLC (eluant:chloroform) afforded friedelin (**1**; 26 mg, 60%); identical with an authentic sample.

Huang-Minlon reduction of kokzeylanol (**11**). A mixture of kokzeylanol (60 mg), ethane-1,2-diol (5 ml), hydrazine hydrate (100%; 1 ml), potassium hydroxide (100 mg) was refluxed at 140° for 3 h. Then the solvent was distilled until the temperature rose to 210° and refluxed at this temperature for further 3 h. Usual work up and crystallization from methanol gave 6β,27-dihydroxy-D:A-friedo-oleanane (**19**) as white needles (40 mg, 80%); m.p. 278–280°; $[\alpha]_D^{27}$ + 1.0° ($CHCl_3$); IR (KBr) 3500–3480 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.00 (2H, br, s, $-CH_2OH$), 3.43 (1H, m, $W_{1/2}$ = 18Hz, CHOH), 2.20–1.20 (CH_2) and 1.30–0.80 (7 × Me). Found: C, 81.21; H, 11.78. Calc for $C_{30}H_{52}O_2$: C, 81.00; H, 11.80%.

Huang-Minlon reduction of kokzeylanonol (**12**). Reduction of **12** (50 mg) with ethane-1,2-diol (5 ml), hydrazine hydrate (100%; 1 ml) and potasium hydroxide (100 mg) at 140° for 5 h and then at 210° for 6 h. following the above procedure and purification of the product by PLC (eluant:chloroform) afforded 6β,27-dihydroxy-D:A-friedo-oleanane (**19**; 22 mg, 48%), which was identical with the above obtained sample.

CrO_3 oxidation of kokzeylanol (**11**). Kokzeylanol (150 mg) in pyridine (6 ml) was oxidized with CrO_3 (100 mg). Usual work up and crystallization from methanol yielded D:A-friedo-olean-3,6,17-trione (**20**) as white needles (130 mg, 79%); m.p. 298–300°; $[\alpha]_D^{27}$ + 38.3° ($CHCl_3$); IR (KBr) 1722, 1705 and 1695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 10.40 (1H, s, CHO), 2.96–1.20 (CH_2) and 1.20–0.86 (21H, 7 × Me). Found: C, 79.32; H, 10.17 Calc for $C_{30}H_{46}O_3$: C, 79.22; H, 10.22 %.

$NaBH_4$ reduction of D:A–friedo-olean-3,6,27-trione (**20**). D:A-friedo-olean-3,6,27-trione (100 mg) in methanol (10 ml) was reduced with $NaBH_4$ (30 mg) at 27°C for 10 min. Usual work up and purification by PLC (eluant: 5% methanol in chloroform) and recrystallization from methanol gave 3,6-dihydroxy-D:A-friedo-olean-27-one (**21**) as white plates (70 mg, 66%); m.p. 266–268°, $[\alpha]_D^{27}$ + 60.3° ($CHCl_3$); IR (KBr) 3540–3380, 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 10.00 (1H, s, CHO), 3.83 (1H, m, $W_{1/2}$ = 8Hz, CHOH), 3.63 (1H, m, $W_{1/2}$ = 18Hz, CHOH), 2.30–1.30 (CH_2) and 1.30–0.66 (21H, 7 × Me). Found: C, 78.70; H, 11.10. Calc for $C_{30}H_{50}O_3$: C, 78.53; H, 11.00%).

Huang–Minlon reduction of 3,6-dihydroxy-D:A-friedo-olean-27-one (**21**). 50 mg of **21** was subjected to Huang–Minlon reduction as in the case of kokzeylanol (see above) to obtain 42 mg of the crude product. This was oxidized with CrO_3 (30 mg) in pyridine (5 ml) and the crude product thus obtained was purified by PLC (eluant: chloroform) and recrystallized from chloroform-light petroleum giving D:A-friedo-olean-3,6-dione (**22**) as white needles (12 mg, 28%); m.p. 304–306°; $[\alpha]_D^{27}$ + 32.0° ($CHCl_3$); which was shown to be identical with an authentic sample.

$NaBH_4$ reduction of kokzeylanonol (**12**). Kokzeylanonol (200 mg) in methanol (15 ml) was reduced with $NaBH_4$ (60 mg) at 27°for 5 min. Usual work up and purification of the crude product by PLC (eluant: 10% methanol in chloroform) and recrystallization from chloroform-light petroleum gave 3β,6β,27-trihydroxy-D:A-friedo-olean-21-one (**23**) as white needles (165 mg, 80%); m.p. 336–338°; $[\alpha]_D^{27}$ + 124.5° ($CHCl_3$); IR (KBr) 3540–3380, 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.10 (2H, br, s, CH_2OH), 3.73 (1H, m, $W_{1/2}$ = 6Hz, CHOH), 3.23 (1H, m, $W_{1/2}$ = 18Hz, CHOH), 2.80–1.23 (CH_2) and 1.23–1.00 (21H, 7 × Me). Found: C, 75.75; H, 10.49. Calc for $C_{30}H_{50}O_4$: C, 75.95; H, 10.55%.

Photolysis of 3β,6β,27-trihydroxy-D:A-friedo-olean-21-one (**23**). A solution of **23** (100 mg) in dry dioxane (20 ml) was refluxed for 18 h under N_2 whilst being irradiated with a high pressure Hg lamp (125 W). The solvent was evaporated *in vacuo* and the product mixture separated by PLC (eluant: 5% methanol in chloroform) to give (in order of increasing polarity) 3β,6β,27-trihydroxy-21,22-bisnor-*E*-seco-D:A-friedo-olean-16,19-dione (**27**) (29 mg, 32%) and 3β,6β,27 - trihydroxy - *E* - seco - D: A - friedo - olean - 19 - one - 21 - carbaldehyde (**25**); 58 mg, 58%).

For **27**. m.p. 98–100°, $[\alpha]_D^{27}$ + 24.0° ($CHCl_3$); IR (KBr) 3480–3400 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.52 (1H, m, olefinic H), 5.03 (^1H, two *m* separated by 10Hz, olefinic H), 3.86 (2H, br, s, CH_2OH), 3.70 (1H, m, $W_{1/2}$ = 6Hz, CHOH), 3.30 (1H, m, $W_{1/2}$ = 18Hz, CHOH), 2.73 (1H, d, J = 10Hz, allylic H), 1.76, 1.56, 1.50 (3H each, d, J = 1Hz, allylic Me), 1.80–1.30 (CH_2) and 1.30–0.86 (12H, 4 × Me). Found: C, 79.80: H, 10.96. Calc for $C_{28}H_{46}O_3$: C, 80.00; H, 10.90%.

For **25**. m.p. 130–132°; $[\alpha]_D^{27}$ + 25.0° ($CHCl_3$); IR (KBr) 3450–3400, 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.53 (1H, m, olefinic H), 5.03 (1H, two *m* separated by 10Hz, olefinic H), 3.80 (2H, br, s, CH_2OH), 3.70 (1H, m, $W_{1/2}$ = 6Hz, CHOH), 3.30 (1H, m, $W_{1/2}$ = 18Hz, CHOH), 2.73 (1H, d, J = 10Hz, CH_2CHO), 1.76, 1.63 (6H, d, J = 1Hz, 2 × allylic Me), 1.80–1.30 (CH_2) and 1.30–0.86 (15H, 5 × Me). Found: C, 75.78; H, 10.59. Calc for $C_{20}H_{30}O_4$: C, 75.90: H, 10.60%.

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