Studies on Terpenoids and Steroids. Part 1. Structures of Six Novel 27-Hydroxy and 6β-Hydroxy Di- and Tri-oxygenated D : A-*friedo*-Oleanane Triterpenes from *Kokoona zeylanica* †

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The benzene extract of the inner stem bark of *Kokoona zeylanica* Thwaites (Celastraceae) contains twelve D : A-*friedo*-oleananes of which nine are new. The new triterpenes have been classified under three series; kokoonol (3,27-dioxy and 3,21,27-trioxy), zeylanol (3,6-dioxy and 3,6,21-trioxy), and kokzeylanol (3,6,27-trioxy and 3,6,21,27-tetraoxy). Six of these triterpenes belonging to the kokoonol and zeylanol series have been identified as 27-hydroxy-D : A-*friedo*-oleanan-3-one (4) (kokoonol), 27-hydroxy-D : A-*friedo*-oleanane-3,21-dione (5) (kokocnonol), 21α,27-dihydroxy-D : A-*friedo*-oleanan-3-one (6) (kokoondiol), 6β-hydroxy-D : A-*friedo*-oleanan-3-one (21) (zeylanol), 6β-hydroxy-D : A-*friedo*-oleanane-3,21-dione (22) (zeylanonol) and 6β,21β-dihydroxy-D : A-*friedo*-oleanan-3-one (23) (zeylandiol), by spectroscopic methods and chemical interconversions. The biosynthetic significance of 6-hydroxy-D : A-*friedo*-oleananes is discussed.

Claims to the effect that antimicrobial- and antitumour-active polyoxygenated terpenes and quinone-methide triterpenes occurred in the Celastraceae [1] prompted us to initiate an investigation of Sri Lankan plants belonging to this family. In this and following papers we present our results on the isolation and characterisation of several novel D : A-*friedo*-oleanane triterpenes from *Kokoona zeylanica* Thwaites., a plant with reputed medicinal properties [2] and having restricted distribution in Sri Lanka and South India.

Detailed investigation of the hot benzene extract of the inner stem bark of *K. zeylanica* indicated the presence of at least twelve D : A-*friedo*-oleananes belonging to eight structural types based on their oxygenation patterns; namely, 3-monooxy, 3,21-dioxy, 3,6-dioxy, 3,27-dioxy, 3,6,21-trioxy, 3,6,27-trioxy, 3,21,27-trioxy, and 3,6,21,27-tetraoxy derivatives. Of these, the last six types are new and have been classified into three series; kokoonol(3,27-dioxy and 3,21,27-trioxy), zeylanol(3,6-dioxy and 3,6,21-trioxy), and kokzeylanol(3,6,27-trioxy and 3,6,21,27-tetraoxy). We have previously shown the occurrence of friedelin (1), D : A-*friedo*-oleanane-3,21-dione (2), and 21α-hydroxy-D : A-*friedo*-oleanan-3-one (3) in *K. zeylanica*.[3] Here we report the isolation of the nine last-named novel D : A-*friedo*-oleananes and the structural assignment of six of them to the kokoonol and zeylanol series.

The occurrence of D : A-*friedo*-oleananes bearing a C-27 hydroxy substituent is significant, since of the eight methyl groups in this skeleton it is the only one which was not encountered previously in nature in an oxidised state. 6-Hydroxy-D : A-*friedo*-oleananes could be implicated as possible biosynthetic precursors of the quinone-methide triterpenes peculiar to Celastraceae.[4]

Results and Discussion

The pale yellow inner stem bark of *K. zeylanica* was separated from the brilliant yellow outer bark and the former was extracted successively and exhaustively with hot light petroleum, hot benzene, and hot methanol. The hot benzene extract on concentration yielded a solid which was dissolved in the minimum amount of chloroform. Addition of light petroleum to this precipitated a white solid. This was separated into twelve crystalline compounds by combined column and thin-layer chromatography. Liebermann-Burchard colour tests along with i.r. and mass spectra suggested all these compounds to be derivatives of friedelin (1). The names proposed for these triterpenes and some of their physical data are depicted in Table 1.

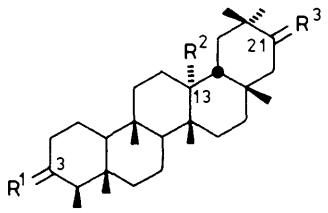
The three low polar triterpenes eluted from the column with 50% benzene in light petroleum and pure benzene were identified as friedelin (1), D : A-*friedo*-oleanane-3,21-dione (2) and 21α-hydroxy-D : A-*friedo*-oleanan-3-one (3).[3]

Kokoonol Series.—The minor triterpene, kokoonol, eluted with 10% chloroform in benzene was identified as 27-hydroxy-D:A-*friedo*-oleanan-3-one (4) from the evidence presented below. The i.r. spectrum indicated it to be an oxo-alcohol and the ^{1}H n.m.r. and mass spectra (see Experimental section and Scheme 3) indicated the presence of a CH_2OH attached to a quaternary centre. This was further supported by the presence of only seven methyl signals in the ^{1}H n.m.r. spectrum, one of which appeared as a doublet (J 8 Hz) and was assigned to the 4-Me group. Kokoonol afforded a monoacetate (7), m.p. 211—213 °C, $[\alpha]_D$ −25.0°, whose ^{1}H n.m.r. spectrum showed a clear double doublet (J 12 Hz) at δ 4.40 and 4.63 which may be due to the prochiral nature of the CH_2OAc group.

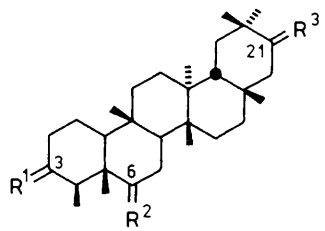
With ethane-1,2-diol, kokoonol gave the monoacetal (8). Jones oxidation of (8) afforded the aldehyde (9), Huang-Minlon reduction of which yielded a less polar product. Deacetalisation of this gave friedelin (1) (see Scheme 1), thus confirming the presence of 3-oxo function in kokoonol. Therefore, it remained to determine the attachment of the CH_2OH group.

Jones oxidation of kokoonol gave the oxo-aldehyde (10), (m.p. 282—284 °C, $[\alpha]_D$ −2.3°). Attachment of the CHO group to C-17 and C-14 of the D : A-*friedo*-oleanane skeleton was ruled out by direct comparison of this oxo-aldehyde with canophyllal (42) [5] and trichadonal (43),[6] respectively. The physical data (m.p., $[\alpha]_D$, and mass spectral fragmentation) of the above oxo-aldehyde also differed from those of D : A-*friedo*-24-formyloleanan-3-one (40),[7] thus ruling out the attachment of the CHO function to C-5. Attachment of the CHO group to C-4 was also ruled out as the aldehyde proton appeared as a singlet in the ^{1}H n.m.r. spectrum at δ 10.30. Oxidation ($KMnO_4$, acetone) of the oxo-aldehyde derived from kokoonol afforded the corresponding carboxylic acid

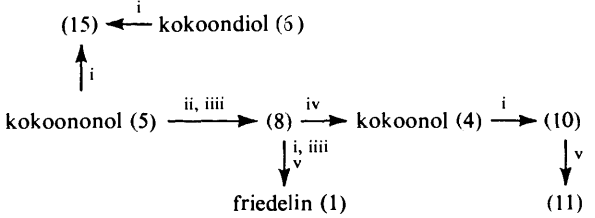
† Preliminary communications, A. A. L. Gunatilaka, N. P. D. Nanayakkara, and M. U. S. Sultanbawa, *J. Chem. Soc., Chem. Commun.*, 1979, 434; *Tetrahedron Lett.*, 1979, 1727.



(1) $R^1 = O, R^2 = Me, R^3 = H_2$
(2) $R^1 = R^3 = O, R^2 = Me$
(3) $R^1 = O, R^2 = Me, R^3 = \alpha\text{-}OH, \beta\text{-}H$
(4) $R^1 = O, R^2 = CH_2OH, R^3 = H_2$
(5) $R^1 = R^3 = O, R^2 = CH_2OH$
(6) $R^1 = O, R^2 = CH_2OH, R^3 = \alpha\text{-}OH, \beta\text{-}H$
(7) $R^1 = O, R^2 = CH_2OAc, R^3 = H_2$
(8) $R^1 = [CH_2]_2O_2, R^2 = CH_2OH, R^3 = H_2$
(9) $R^1 = [CH_2]_2O_2, R^2 = CHO, R^3 = H_2$
(10) $R^1 = O, R^2 = CHO, R^3 = H_2$
(11) $R^1 = O, R^2 = CO_2H, R^3 = H_2$
(12) $R^1 = \beta\text{-}OH, \alpha\text{-}H, R^2 = CH_2OH, R^3 = O$
(13) $R^1 = R^3 = O, R^2 = CH_2OAc$
(14) $R^1 = O, R^2 = CH_2OAc, R^3 = \alpha\text{-}OAc, \beta\text{-}H$
(15) $R^1 = R^3 = O, R^2 = CHO$
(16) $R^1 = [CH_2]_2O_2, R^2 = CH_2OH, R^3 = O$
(17) $R^1 = [CH_2]_2O_2, R^2 = CH_2OH, R^3 = \alpha\text{-}OH, \beta\text{-}H$
(18) $R^1 = \beta\text{-}OH, \alpha\text{-}H, R^2 = CH_2OH, R^3 = O$
(19) $R^1 = \beta\text{-}OH, \alpha\text{-}H, R^2 = CH_2OH, R^3 = \alpha\text{-}OH, \beta\text{-}H$
(20) $R^1 = \beta\text{-}OH, \alpha\text{-}H, R^2 = Me, R^3 = O$



(21) $R^1 = O, R^2 = \beta\text{-}OH, \alpha\text{-}H, R^3 = H_2$
(22) $R^1 = R^3 = O, R^2 = \beta\text{-}OH, \alpha\text{-}H$
(23) $R^1 = O, R^2 = R^3 = \beta\text{-}OH, \alpha\text{-}H$
(24) $R^1 = O, R^2 = \beta\text{-}OAc, \alpha\text{-}H, R^3 = H_2$
(25) $R^1 = R^3 = O, R^2 = \beta\text{-}OAc, \alpha\text{-}H$
(26) $R^1 = O, R^2 = R^3 = \beta\text{-}OAc, \alpha\text{-}H$
(27) $R^1 = O, R^2 = \beta\text{-}OC(=S)C_6H_5, \alpha\text{-}H, R^3 = H_2$
(28) $R^1 = R^3 = O, R^2 = \beta\text{-}OC(=S)C_6H_5, \alpha\text{-}H$
(29) $R^1 = O, R^2 = R^3 = \beta\text{-}OC(=S)C_6H_5, \alpha\text{-}H$
(30) $R^1 = [CH_2]_2O_2, R^2 = \beta\text{-}OH, \alpha\text{-}H, R^3 = H_2$
(31) $R^1 = [CH_2]_2O_2, R^2 = \beta\text{-}OH, \alpha\text{-}H, R^3 = O$
(32) $R^1 = R^2 = O, R^3 = H_2$
(33) $R^1 = R^2 = R^3 = O$
(34) $R^1 = R^2 = [CH_2]_2O_2, R^3 = H_2$
(35) $R^1 = R^2 = \beta\text{-}OH, \alpha\text{-}H, R^3 = H_2$
(36) $R^1 = R^2 = H_2, R^2 = \beta\text{-}OH, \alpha\text{-}H$
(37) $R^1 = R^3 = H_2, R^2 = \beta\text{-}OAc, \alpha\text{-}H$
(38) $R^2 = O, R^1 = R^3 = H_2$
(39) $R^1 = R^2 = \beta\text{-}OH, \alpha\text{-}H, R^3 = O$



Scheme 1. *Reagents:* CrO_3, pyridine, 25 °C; ii, $(CH_2OH)_2$, *p*-$MeC_6H_4SO_3H$, C_6H_6, reflux, 8 h; iii, $NH_2NH_2{\cdot}H_2O$ (98—100%), $(CH_2OH)_2$, 150—160 °C for 5 h, 220 °C for 10 h; iv, *p*-$MeC_6H_4SO_3H$, acetone, reflux, 12 h; v, $KMnO_4$, acetone, reflux, 2 h

(11), m.p. 210—212 °C, which differed (mixed m.p., i.r., and co-t.l.c.) from octandronic acid [8] (44),* polpunonic acid (45),[9] and roxburghonic acid (41),[10] thus ruling out the attachment of the COO_2H to C-20β, C-20α, and C-9, respectively. Therefore, kokoonol should be 27-hydroxy-D : A-*friedo*-oleanan-3-3-one (4) where the attachment of the CH_2OH is to C-13. This location to the CH_2OH function was further confirmed by the irradiation of 3β,27-dihydroxy-D : A-*friedo*-oleanan-21-one (12) derived from kokoononol isolated from the same extract (see later).

Elution of the column with 20 and 50% chloroform in benzene gave two new D:A-*friedo*-oleananes, zeylanol and zeylanonol. Elution of the column with pure chloroform gave kokoononol whereas 5% methanol in chloroform eluted two further trioxygenated triterpenes, zeylandiol and kokoondiol, Structure elucidation of the triterpenes belonging to the zeylanol series is presented elsewhere in this paper.

Out of the trioxygenated compounds, two were found to contain a CH_2OH group as in kokoonol (4). The less polar of these, *viz.* kokoononol, was found to contain an additional carbonyl function. An i.r. spectrum of kokoononol (5) showed the presence of a OH and two carbonyl functions ($\nu_{max.}$ 3 480, 1 710, and 1 700 cm^{-1}). The ^1H n.m.r. spectrum showed the presence of a CH_2OH group attached to a quaternary centre, six tertiary CH_3 groups, and a secondary CH_3 group. The more

* It has been suggested recently that the structure of octandrolic acid should be revised and it may be identical with canophyllic acid (see ref. 11).

Table 1. Names and some physical data of D : A-*friedo*-oleanane triterpenes from *K. zeylanica*

Type	Name (structure) [a]	M.p. (°C)	$[\alpha]_D$°	Molecular weight [b]	Molecular formula [c]	Functional group(s) [d] No. of >C=O; >CH–OH; CH_2OH		
Mono-oxygenated	Friedelin (1)	265	−22.4	426	$C_{30}H_{50}O$	1	—	—
Dioxygenated	D : A-*friedo*-Oleane-3,21-dione (2)	248—250	+110.5	440	$C_{30}H_{48}O_2$	2	—	—
	21α-Hydroxy-D : A-*friedo*-olean-3-one (3)	266—268	−13.8	442	$C_{30}H_{50}O_2$	1	1	—
	Kokoonol (4)	272	−28.5	442	$C_{30}H_{50}O_2$	1	—	1
	Zeylanol (21)	274—276	−0.95	442	$C_{30}H_{50}O_2$	1	1	—
Trioxygenated	Zeylanonol (22)	271—272	+118.0	456	$C_{30}H_{48}O_3$	2	1	—
	Kokoononol (5)	>325	+100.0	456	$C_{30}H_{48}O_3$	2	—	1
	Zeylandiol (23)	270—272	+80.0	458	$C_{30}N_{50}O_3$	1	2	—
	Kokoondiol (6)	298—300	−9.2	458	$C_{30}H_{50}O_3$	1	1	1
	Kokzeylanol [e]	274—276	−0.8	458	$C_{30}H_{50}O_3$	1	1	1
Tetraoxygenated	Kokoona triterpene A [f]	273—275	+30.0	472	$C_{30}H_{48}O_4$	2	2	—
	Kokzeylanonol [e]	276—278	+86.8	472	$C_{30}H_{48}O_4$	2	2	1

[a] Arranged in the order of increasing polarity. [b] By high resolution mass spec. [c] By high resolution mass spec. and/or by combustion analysis. [d] By i.r. and ^{1}H n.m.r. spectroscopy. [e] For details see A. A. L. Gunatilaka, N. P. D. Nanayakkara, and M. U. S. Sultanbawa, *Tetrahedron Lett.*, 1981, **22**, 1425. [f] Unidentified.

Table 2. ^{1}H N.m.r. data ($CDCl_3$, 60 MHz) (*J*/Hz or $W_{\frac{1}{2}}$/Hz in parentheses) of photoirradiation products

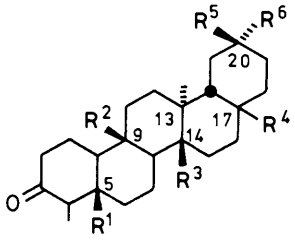
	Compound (47)	(48)	(49) *	(50)
3α-H	3.76 (m, $W_{\frac{1}{2}}$ 8)	3.70 (m, $W_{\frac{1}{2}}$ 8)	3.73 (m, $W_{\frac{1}{2}}$ 8)	3.70 (m, $W_{\frac{1}{2}}$ 6)
6α-H	—	—	—	3.40 (m, $W_{\frac{1}{2}}$ 18)
16-H	—	5.50 (m)	5.33 (m)	5.33 (m)
18-H	2.29 (d, *J* 10)	2.75 (dm, *J* 10)	2.70 (dm, *J* 10)	2.47 (dm, *J* 10)
19-H	5.12 (dm, *J* 10)	4.97 (dm, *J* 10)	5.04 (dm, *J* 10)	5.03 (dm, *J* 10)
22-H_2	2.53 (d, *J* 4)	—	—	—
CHO	9.83 (t, *J* 4)	—	—	—
CH_2OH	4.23 (br s)	3.83 (s)	—	—
Allylic	1.77 (d, *J* 1)	1.73 (d, *J* 1)	1.76 (d, *J* 1)	1.80 (d, *J* 1)
(28-, 29- or 30-) methyls	1.63 (d, *J* 1)	1.62 (d, *J* 1)	1.63 (d, *J* 1)	1.56 (d, *J* 1)
		1.53 (d, *J* 1)	1.53 (d, *J* 1)	1.53 (d, *J* 1)
Other methyls	1.00—1.15 (5 × Me)	0.80—1.10 (4 × Me)	0.94—1.03 (5 × Me)	0.86—1.30 (5 × Me)

* Ref. 3.

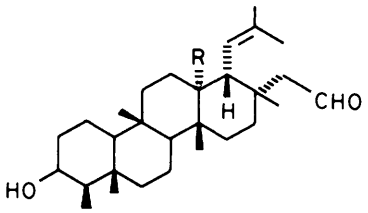
polar trioxygenated triterpene, kokoondiol (6), had two hydroxy groups, one primary [δ 4.13br (2 H, s)] and the other secondary [δ 3.80 (1 H, m, $W_{\frac{1}{2}}$ 14 Hz)], as indicated by its ^{1}H n.m.r. spectra. On acetylation kokoononol yielded a monoacetate (13) and kokoondiol a diacetate (14).

The three triterpenes were interrelated by the following sequence of reactions (see Scheme 1). Jones oxidation of both kokoononol and kokoondiol afforded the same diketo-aldehyde (15) (m.p. 258—260 °C) confirming that both natural products have the same oxygenation pattern and that kokoondiol is a reduced product of kokoononol. Kokoononol gave a monoethylene acetal (16) (m.p. 301—302 °C) whose i.r. spectrum showed the presence of hydroxy and carbonyl groups ($\nu_{max.}$ 3 480 and 1 702 cm^{-1}). Huang-Minlon reduction product of this monoacetal (16) afforded a less polar product (m.p. 297 °C) which on deacetalisation gave kokoonol (4) (m.p., mixed m.p., $[\alpha]_D$, and co-t.l.c.). Lithium aluminium hydride reduction of kokoononol monoacetal resulted in a more polar product (m.p. 301—303 °C) which on deacetalisation afforded kokoondiol (6) (m.p., mixed m.p., $[\alpha]_D$, and co-t.l.c.) as the major product. Sodium borohydride reduction of kokoononol yielded a keto-diol (18) ($C_{30}H_{50}O_3$, m.p. 278—280 °C, $[\alpha]_D$ +140.3°, $\nu_{max.}$ 3 500—3 400 and 1 712 cm^{-1}) which was different from kokoondiol. $LiAlH_4$ reduction of kokoononol however, gave the corresponding triol (19) ($C_{30}H_{52}O_3$, m.p. 300 °C, $[\alpha]_D$ +27.7°). The foregoing evidence suggested that kokoononol and kokoondiol are derivatives of kokoonol (4) where a methylene group of kokoonol is oxidized to a CO and CHOH, respectively, and that the CO group in kokoononol is located at a sterically hindered environment. The comparable reactivities of this carbonyl group to the 21-oxo group in D : A-*friedo*-oleanane-3,21-dione (2) suggested the possible location of the second oxo group of kokoononol at C-21. Irradiation of the above $NaBH_4$ reduction product of kokoononol proved this to be so.

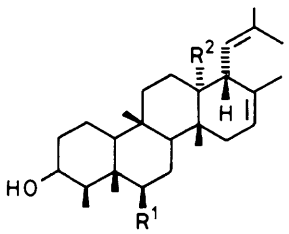
The major product of irradiation obtained in 60% yield was shown to be 3β,27-dihydroxy-E-secofriedel-19-ene-21-carbaldehyde (47) (m.p. 129—130 °C), by the following spectroscopic evidence. The i.r. spectrum was suggestive of the presence of hydroxy and carbonyl groups ($\nu_{max.}$ 3 500—3 400 and 1 710 cm^{-1}). In the ^{1}H n.m.r. spectrum (Table 2) the presence of a low field triplet (*J* 4 Hz) at δ 9.83 was indicative of an aldehyde group attached to a CH_2 moiety; it also had a signal at δ 5.12 due to an olefinic proton (two sets of multiplets separated by 10 Hz); a 2 H singlet at δ 4.23 and a 1 H multiplet at δ 3.76 were assigned to CH_2OH and $CHOH$, respectively. The ^{1}H n.m.r. spectrum also showed the presence of two methyl groups on double bonds at δ 1.77 and 1.63 exhibiting allylic coupling (*J* 1 Hz). Double irradiation studies showed that the olefinic proton at δ 5.12 is allylically

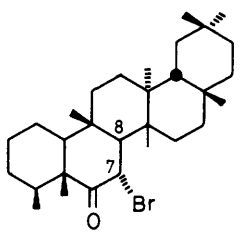


(40) R^1 = CHO, R^2 = R^3 = R^4 = R^5 = R^6 = Me
(41) R^2 = CO_2H, R^1 = R^3 = R^4 = R^5 = R^6 = Me
(42) R^4 = CHO, R^1 = R^2 = R^3 = R^5 = R^6 = Me
(43) R^3 = CHO, R^1 = R^2 = R^4 = R^5 = R^6 = Me
(44) R^5 = CO_2H, R^1 = R^2 = R^3 = R^4 = R^6 = Me
(45) R^6 = CO_2H, R^1 = R^2 = R^3 = R^4 = R^5 = Me



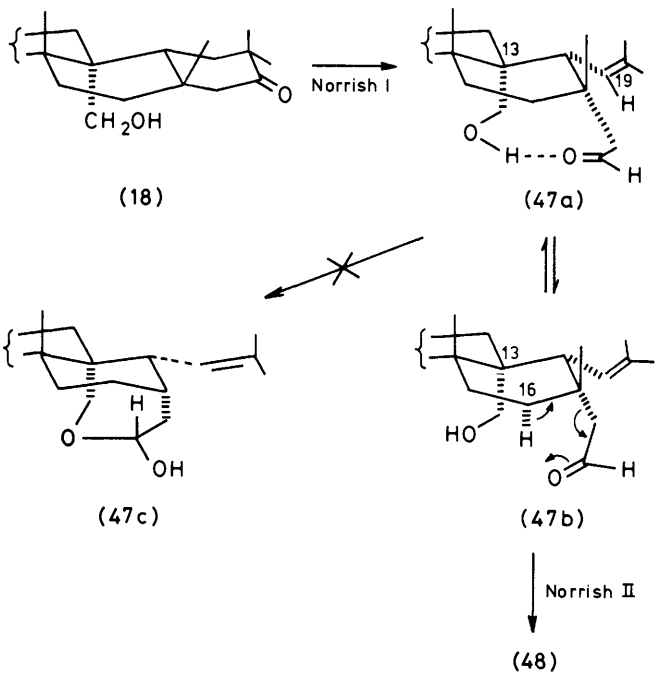
(46) R = Me
(47) R = CH_2OH





(48) R^1 = H, R^2 = CH_2OH
(49) R^1 = H, R^2 = Me
(50) R^1 = OH, R^2 = Me

(51)



Scheme 2.

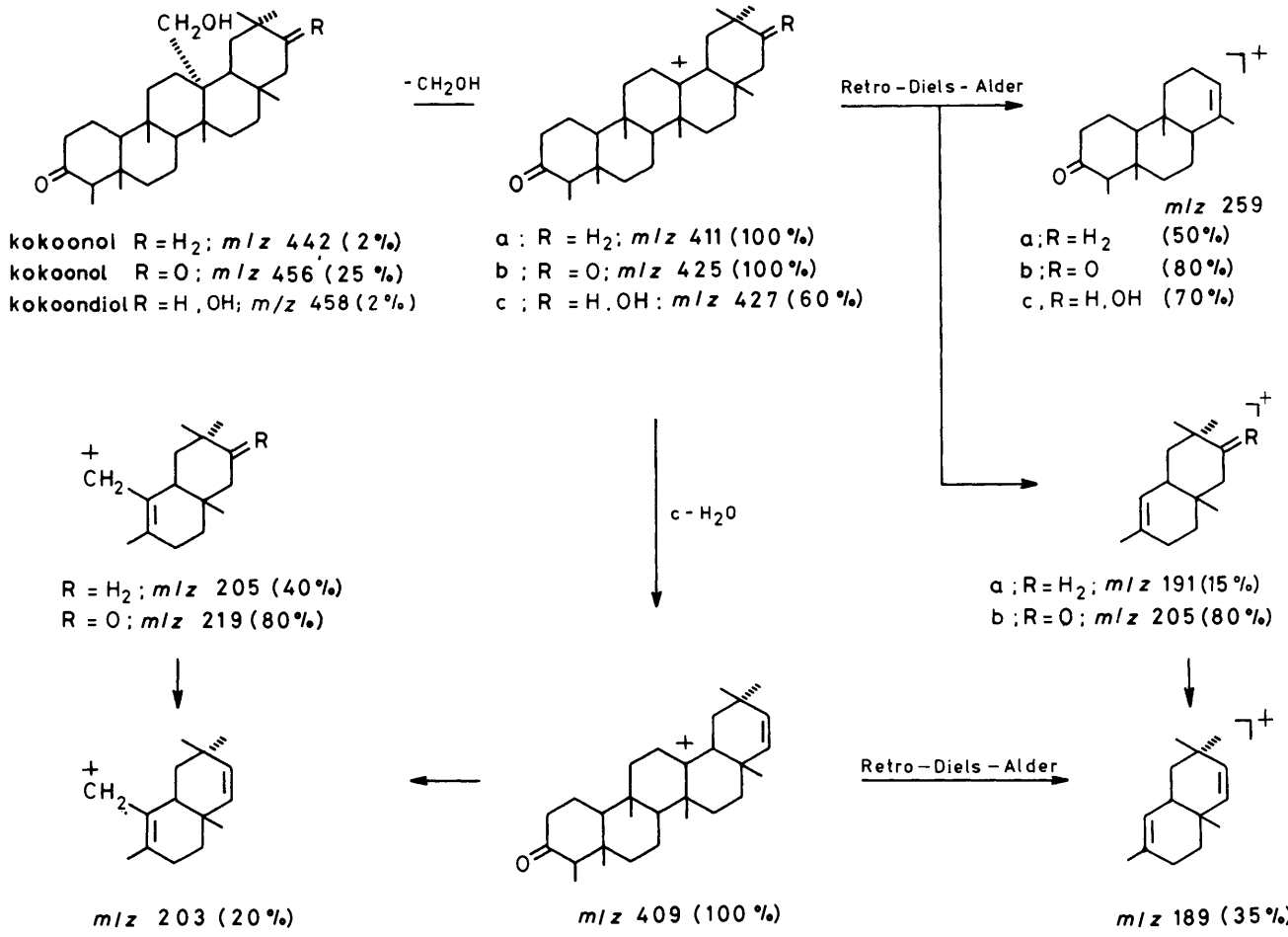
coupled to the two methyl groups at δ 1.77 and 1.63, which was also coupled to a proton which exhibited a doublet at δ 2.29 (*J* 10 Hz) indicative of the presence of a CH–CH=CMe_2 moiety. Decoupling studies further indicated that the CHO proton at δ 9.83 was coupled to a 2 H doublet at δ 2.53 suggesting the presence of a CH_2CHO group on a quaternary centre.

The minor product (30% yield) of irradiation was identified as 3β,27-dihydroxy-21,22-bisnor-*friedo*-E-seco-oleana-16,19-diene (48) (m.p. 112—114 °C) by the evidence presented below. The i.r. spectrum of it showed the presence of a OH and an unconjugated double bond ($\nu_{max.}$ 3 500 and 1 640 cm^{-1}). The ^1H n.m.r. spectrum (Table 2) had signals at δ 5.50 (1 H, m) and 4.97 (1 H, two sets of multiplets separated by 10 Hz), both due to olefinic protons; the doublets at δ 1.73, 1.62 and 1.53 (3 H each, *J* 1 Hz) exhibiting allylic coupling were assigned to the methyl groups on double bonds; a 1 H multiplet at δ 3.70 and a 2 H singlet at δ 3.83 were assigned to *CH*OH and *CH*$_2$OH, respectively. Double irradiation experiments showed that the olefinic proton at δ 5.50 was coupled to the methyl group at δ 1.53, and that the olefinic proton at δ 4.97 was coupled to the methyl groups at δ 1.73 and 1.62 and also to a proton which exhibited a doublet at δ 2.75. The latter must be doubly allylic. Thus the photo-irradiation product must have the partial structure, CH=C(Me)CHCH=CMe_2, which can arise as a result of a Norrish type II process (Scheme 2) on the major photo-irradiation product (47).

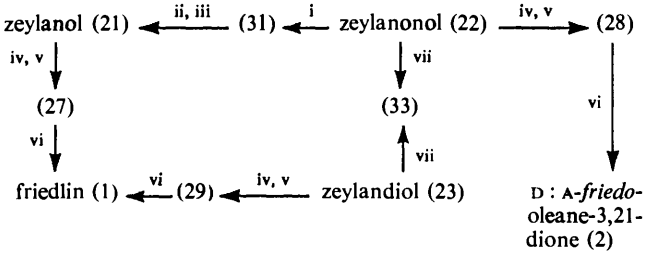
Failure to detect the intermediate carbaldehyde (46) during the irradiation of 3β-hydroxy-D : A-*friedo*-oleanan-21-one (20) [3,12] under identical conditions suggests a partial inhibition of a Norrish type II process on (47) which may be possible only if the hydroxymethyl group is present on C-13, thus avoiding the abstraction of the 16-H by the CH_2CHO group (see Scheme 2). The ^1H n.m.r. spectrum of 3β,27-dihydroxy-E-secofriedel-19-ene-21-carbaldehyde (47) showed the absence of the hemiacetal structure (47c). In (47a) the CHO and OH groups are not in close enough proximity to give rise to a hemiacetal. However, Drieding models indicate that the H-bonded structure (47a) is possible and this is confirmed by the ^1H n.m.r. spectrum of (47) which shows significant paramagnetic shifts of the protons (19-H, *CH*$_2$OH) in the vicinity of the carbonyl group (see Table 2).

The foregoing evidence was consistent with the identification of kokoononol as 27-hydroxy-D : A-*friedo*-oleanane-3,21-dione (5) and kokoondiol as 21α,27-dihydroxy-D : A-*friedo*-oleanan-3-one (6). The configuration of the hydroxy function at C-21 was evident from the half width value ($W_{\frac{1}{2}}$ 14 Hz) of the signal due to 21-H.[13] The mass spectra of kokoonol (4), kokoononol (5) and kokoondiol (6) were of some interest. Significant peaks were observed in their mass spectra due to the loss of the hydroxymethyl group followed by a retro-Diels–Alder type fragmentations of the resulting ions (see Scheme 3).

Zeylanol Series.—Spectroscopic evidence together with resistance towards catalytic hydrogenation and the absence of any olefinic signals in the ^1H n.m.r. spectra suggested that zeylanol was a keto-alcohol, zeylanonol a diketo-alcohol,



Scheme 3.



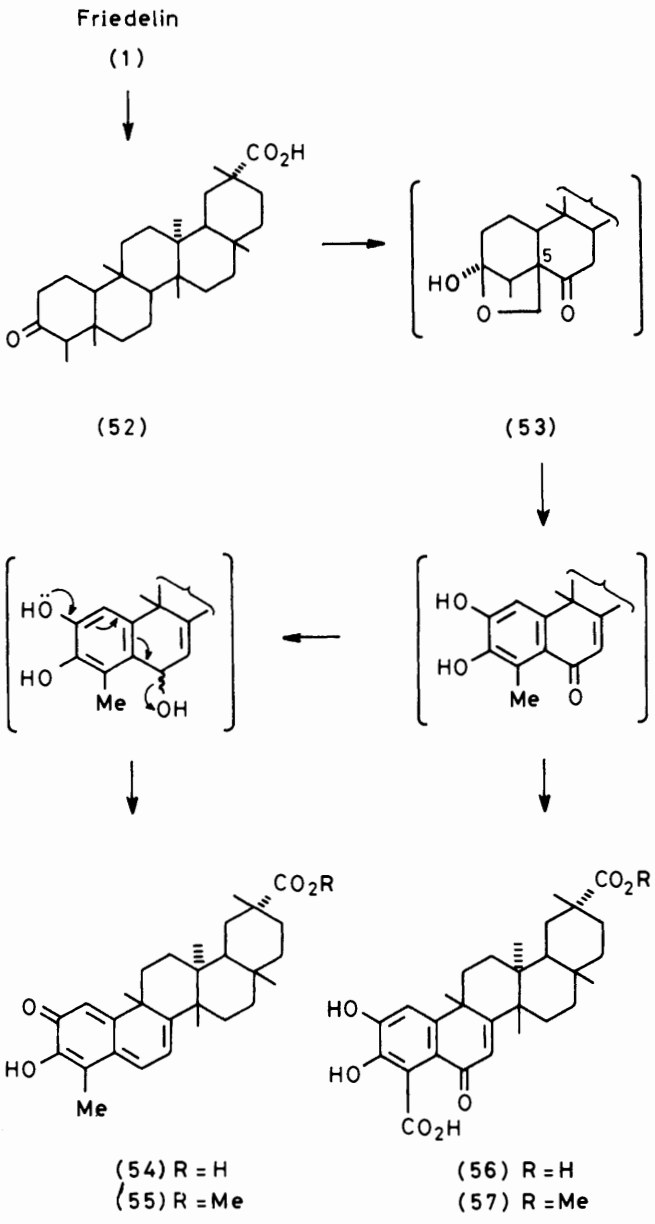
Scheme 4. *Reagents:* i, $(CH_2OH)_2$, *p*-$MeC_6H_4SO_3H$, C_6H_6, reflux, 8 h; ii, $NH_2NH_2 \cdot H_2O$ (98—100%), $(CH_2OH)_2$, 150—160 °C for 5 h and 220 °C for 10 h; iii, *p*-$MeC_6H_4SO_3H$, acetone, reflux, 12 h; iv, $PhC(Cl)=\overset{+}{N}Me_2Cl^-$, CH_2Cl_2, THF; v, H_2S, pyridine; vi, Ph_3SnH, PhMe, N_2, reflux, 2 h; vii, CrO_3, pyridine, 25 °C

and zeylandiol a keto-diol. On acetylation, zeylanol and zeylanonol yielded their corresponding mono-acetates (24) and (25), respectively whereas zeylandiol afforded the di-acetate (26) (see Experimental section).

The three triterpenes were interrelated by the sequence of reactions depicted in Scheme 4. The presence of a 3-oxo function in zeylanol (21) was shown by conversion of it into the corresponding thiobenzoate (27) which on reduction with triphenyltin hydride afforded friedelin (1). Zeylanonol (22) yielded the monoethylene acetal (31) (m.p. 231—235 °C, $\nu_{max.}$ 3 480, 1 712, and 1 060 cm^{-1}) on acetalisation with ethane-1,2-diol. Huang-Minlon reduction of (31) afforded a less polar product (m.p. 268—270 °C, $\nu_{max.}$ 3 480 and 1 060 cm^{-1}) which on subsequent deacetalisation gave zeylanol (21) (m.p., mixed m.p., i.r., and co-t.l.c.), suggesting that zeylanonol is a derivative of zeylanol where a methylene group of the latter is oxidized to a carbonyl. Oxidation of both zeylanonol (22) and zeylandiol (23) afforded the same triketone (33), $C_{30}H_{46}O_3$, m.p. 335—337 °C, $[\alpha]_D$ +152°, whose i.r. spectrum indicated the presence of three carbonyl groups ($\nu_{max.}$ 1 700, 1 710, and 1 720 cm^{-1}). Thus it was inferred that both zeylanonol and zeylandiol have an identical oxygenation pattern.

Deoxygenation of zeylandiol (23) by reduction with triphenyltin hydride of the derived dithiobenzoate (29) gave friedelin (1) whereas similar treatment of zeylanonol (22) afforded D : A-*friedo*-oleanane-3,31-dione (2). This recent deoxygenation method of Barton and McCombie [14] employing triphenyltin hydride was found to be superior to other conventional methods such as Huang-Minlon reduction of the derived carbonyl compounds [15] and $LiAlH_4$ reduction of the tosyl esters,[5] and has been applied for the first time to deoxygenate triterpene alcohols. More significantly, the method was successful in removing two oxygen atoms in one reaction as exemplified by the conversion of zeylandiol (23) into friedelin *via* its dithiobenzoate (29).

From the foregoing it is evident that both zeylanonol and zeylandiol have the same oxygenation pattern with a 3-oxo function in zeylandiol and 3,21-dioxo substituents in zeylanonol. Thus, zeylandiol should have a hydroxy group at C-21 with a β-configuration ($W_{\frac{1}{2}}$ 2 Hz).[6] The presence of



Scheme 5.

21-oxo group in zeylanonol was also shown by the following evidence. Sodium borohydride reduction of zeylanonol gave a keto-diol (39) (m.p. 280—282 °C) which was shown to be different from zeylandiol (23), thus indicating that the reduction of the 3-oxo group had occurred and that the remaining carbonyl is located in a sterically hindered environment (see discussion on kokoononol).

Irradiation of the foregoing keto-diol (39) afforded the non-conjugated diene (50) (m.p. 135—138 °C) suggesting [3,12] the presence of 21-oxo group in zeylanonol. In the i.r. spectrum, the above diene (50) had a band at $\nu_{max.}$ 3 500 cm^{-1}. The ^1H n.m.r. spectrum (see Table 2) was almost superimposable on that of (49) [3] except for the presence of an additional 1 H multiplet at δ 3.40 due to a second *CH*OH group. ^1H N.m.r. double irradiation studies further supported structure (50), indicating that the additional OH group in zeylanonol cannot be in the rings D or E of the D : A-*friedo*-oleanane nucleus.

Zeylanol on oxidation afforded the diketone (32) (m.p. 305—306 °C). The i.r. spectrum ($\nu_{max.}$ 1 714 and 1 700 cm^{-1}) of this diketone ruled out the presence of a α-diketo system.[16] The ^1H n.m.r. spectrum was devoid of any signals above δ 3.00 suggesting the absence of β-diketo structure.[7] Thus the OH group in zeylanol cannot be in ring A. The possible location of the OH group in zeylanol in an unhindered environment was indicated by the ready formation of the ethylene diacetal (34) (m.p. 270—272 °C), and easy reduction ($NaBH_4$, CH_3OH, room temperature) of the above diketone (32) to the diol (35) (m.p. 286—288 °C).

Huang-Minlon reduction of zeylanol afforded (36) (m.p. 248—250 °C) whose i.r. spectrum indicated the absence of carbonyl group. On acetylation, (36) gave the monoacetate (37) (m.p. 282—284 °C). Oxidation of (36) gave the monoketone (38) (m.p. 276—278 °C, $\nu_{max.}$ 1 693 cm^{-1}). The ^1H n.m.r. spectrum of this monoketone showed a clear AMX pattern [13] due to 7-H_2 and 8-H [δ 2.73 and 2.03 (7-H), and 1.63 (8-H); J_{AM} 14 Hz, J_{MX} 12 Hz and J_{AX} 4 Hz]. Addition of $Eu(fod)_3$ caused a lowfield shift of the signals due to these protons. This AMX pattern in the ^1H n.m.r. spectrum could arise only if the keto group is located at C-6 in ring B of the D : A-*friedo*-oleanane skeleton. The treatment of the above monoketone (38) with pyridine hydrobromide perbromide in acetic acid afforded a crystalline monobromo ketone (51) (m.p. 218—220 °C). The ^1H n.m.r. spectrum of this compound showed among other signals a double doublet (*J* 6 Hz) at δ 4.10 and 2.67 due to 7-H and 8-H, respectively. The ^{13}C n.m.r. spectra [17] of D : A-*friedo*-oleanan-6-one (38), D : A-*friedo*-oleanane-3,6-dione (32) and D : A-*friedo*-oleanane-3,6,21-trione (33), all derived from natural compounds further supported the 6-keto assignment. The ^1H n.m.r. spectra of all three natural products were in agreement with a β-configuration ($W_{\frac{1}{2}}$ 18 Hz) [6] for the hydroxy group at C-6.

Biogenetic Aspects.—Two biogenetic pathways have been proposed for the origin of natural triterpene quinone-methides which implicate polpunonic acid (52) as the precursor.[18,19] Conversion of (52) into the quinone-methides would involve oxidation of the A,B rings with concurrent demethylation at C-5. Thus, the natural occurrence of 6β-hydroxy-D : A-*friedo*-oleananes [(21), (22), and (23)] is significant. Further, the co-occurrence of these with the quinone-methides [celastrol (54),[20] pristimerin (55) [21]] and the phenols [desmethylzeylasterone (56),[20] zeylasterone (57) [21]] in *K. zeylanica* suggests a possible biosynthetic relationship between these and 6-oxo-D : A-*friedo*-oleananes [*e.g.* a 6-oxo-salaspermic acid (53) [22] type intermediate] (Scheme 5).

Experimental

General Procedures.—T.l.c. involved silica gel G: visualisation was by spraying with acidified anisaldehyde followed by charring with heat. Preparative separations (p.l.c.) used 1.0 mm layers of silica $PF_{254-366}$. Column chromatography involved silica gel of mesh 30—70. Light petroleum used had b.p. 60—80 °C. M.p.s were determined using a Kofler hot-stage apparatus and are uncorrected. Rotations were measured in chloroform solution at 27 °C with a Perkin-Elmer 241 polarimeter. The microanalytical results were obtained from the CSIRO, Microanalytical Service, Melbourne, Australia. I.r. spectra were recorded in KBr discs with a Perkin-Elmer model 257 grating i.r. spectrometer and ^1H n.m.r. spectra were recorded using a Varian T 60A spectrometer in $CDCl_3$ solution unless otherwise stated. Mass spectra were obtained from the University of Aberdeen (Scotland) and Imperial College (London).

All room temperature reactions were at 27 °C. Acetylations were carried out by heating the compound with acetic

anhydride in dry pyridine on a boiling water-bath for 2 h and leaving the mixture overnight at room temperature. Chromium trioxide (CrO_3) oxidations were carried out by adding the compound dissolved in pyridine to a well stirred ice-cold suspension of pyridine–CrO_3 complex and leaving the mixture overnight at room temperature. 'Work-up' refers to dilution of the reaction mixture with water, extraction with ether, and washing of the ether layer with water. Organic solutions were dried over magnesium sulphate, and evaporated from thin films under reduced pressure. Substances stated to be identical were compared by mixed m.p. determination, i.r. spectroscopy, and t.l.c.

The plant material was collected from Kanneliya rain forest. Yields of the pure material isolated are expressed as % of the dry weight of the plant material used.

Inner Bark Extractives.—The bark of *K. zeylanica* was separated into inner and outer bark. The dried and powdered inner bark (5.50 kg) was successively and exhaustively extracted with hot light petroleum, hot benzene, and hot methanol. All three extracts on concentration yielded off-white solids [light petroleum, 34 g (0.62%); benzene, 48 g (0.87%); methanol, 48 g (0.87%)] and yellow-brown solutions which were separated by filtration. The filtrates were evaporated under reduced pressure to yield brown oils [light petroleum 60 g (1.1%); benzene 85 g (1.5%), methanol 225 g (4.1%)].

The above off-white solid obtained from hot benzene extract (48 g) was dissolved in chloroform (200 ml) and re-precipitated with light petroleum (300 ml). The solid thus obtained was filtered and washed several times with light petroleum to yield a white powder (35 g); 20.0 g of this were chromatographed on a column of silica gel (400 g) made up in light petroleum.

Isolation of Friedelin (1), D:A-friedo-*Oleanane*-3,21-*dione* (2), *and* 21α-*Hydroxy*-D : A-friedo-*oleanan*-3-*one* (3).—Elution of the column with 10% benzene in light petroleum, 50% benzene in light petroleum, and pure benzene gave (1), (2), and (3) in the yields of 1.8×10^{-4}, 2.7×10^{-4}, and 1.4×10^{-4} %, respectively.[3]

Isolation of Kokoonol (4).—Elution of the column with 10% chloroform in benzene gave a white solid which on crystallisation from chloroform–light petroleum gave *kokoonol* (4) as white needles (150 mg, 0.5×10^{-4} %), m.p. 272 °C, $[\alpha]_D$ −28.5°; $\nu_{max.}$ 3 520(OH) and 1 700 cm^{-1} (C=O); δ 4.10br (2 H, s, CH_2OH), 2.50—1.20 (CH_2), 1.60 (3 H, s, Me), 1.10 (3 H, s, Me), 1.05 (3 H, s, Me), 0.96 (6 H, s, 2 × Me), 0.73 (3 H, s, Me), and 0.86 (3 H, d, *J* 7 Hz, 4-Me); *m/z* 442 (M^+, 2%), 424(9), 411(100), 259(50), 245(45), 233(15), 205(40), 191(15), 179(25), 151(15), 137(35), 123(35), 109(50), 81(45), and 69(50) (Found: C, 81.25; H, 11.3. $C_{30}H_{50}O_2$ requires C, 81.4; H, 11.3%).

Isolation of Zeylanol (21).—Elution of the column with 25% chloroform in benzene afforded *zeylanol* (1.2 g, 4.3×10^{-4} %) as white needles (from chloroform–light petroleum), m.p. 276—278 °C, $[\alpha]_D$ −0.95°; $\nu_{max.}$ 3 490 (OH) and 1 715 cm^{-1} (C=O); δ 2.66br (1 H, m, $W_{\frac{1}{2}}$ 20 Hz, C*H*OH), 2.56—1.20 (CH_2), 1.16 (6 H, s, 2 × Me), 1.03 (3 H, s, Me), 1.00 (6 H, s, 2 × Me), 0.86 (3 H, s, Me), 0.73 (3 H, s, Me), and 1.00 (3 H, d, *J* 6 Hz, 4-Me); *m/z* 442 (M^+, 40%), 437(15), 434(18), 409(8), 399(8), 370(30), 327(15), 318(35), 292(20), 273(40), 205(40), 179(30), 139(30), 121(70), 95(90), and 69(100) (Found: C, 81.65; H, 11.3. $C_{30}H_{50}O_2$ requires C, 81.4; H, 11.3%).

Isolation of Zeylanonol (22).—Elution of the column with 50% chloroform in benzene gave *zeylanonol* (0.8 g, 2.9×10^{-4} %) as white needles (from chloroform–light petroleum), m.p. 272—274 °C, $[\alpha]_D$ +11.8°; $\nu_{max.}$ 3 480 (OH) and 1 715 cm^{-1} (C=O); δ 3.66br (1 H, m, $W_{\frac{1}{2}}$ 18 Hz, C*H*OH), 2.80—1.30 (CH_2), 1.16 (9 H, s, 3 × Me), 1.06 (6 H, s, 2 × Me), 0.86 (3 H, s, Me), 0.76 (3 H, s, Me), and 1.10 (3 H, d, *J* 6 Hz, 4-Me); *m/z* 456 (M^+, 60%), 438(20), 384(60), 341(55), 287(100), 219(25), 137(65), 121(70), 109(95), and 95(100) (Found: C, 78.6; H, 10.5. $C_{30}H_{48}O_3$ requires C, 78.8; H, 10.65%).

Isolation of Kokoononol (5).—Elution of the column with pure chloroform afforded *kokoononol* (4.7 g, 1.7×10^{-3} %) as white plates (from chloroform–methanol), m.p. >325 °C, $[\alpha]_D$ +100.0°; $\nu_{max.}$ 3 480 (OH), 1 710 and 1 700 cm^{-1} (C=O); δ 4.03br (2 H, s, CH_2OH), 2.80—1.30 (CH_2), 1.20 (3 H, s, Me), 1.13 (6 H, s, 2 × Me), 1.10 (6 H, s, 2 × Me), 0.73 (3 H, s, Me), and 0.85 (3 H, d, *J* 6 Hz, 4-Me); *m/z* 456 (M^+, 25%), 438(25), 425(100), 407(90), 353(55), 339(60), 299(40), 285(50), 273(55), 259(80), 245(65), 219(80), and 205(80) (Found: C, 78.9; H, 10.6. $C_{30}H_{48}O_3$ requires C, 78.8; H, 10.65%).

Isolation of Zeylandiol (23).—Elution of the column with 5% methanol in chloroform gave *zeylandiol* (0.5 g, 1.8×10^{-4} %), as colourless crystalline solid (from chloroform–light petroleum), m.p. 272—274 °C, $[\alpha]_D$ +11.5°; $\nu_{max.}$ 3 490 (OH) and 1 715 cm^{-1} (C=O); δ[$(CD_3)_2CO$–$CDCl_3$] 3.73br (1 H, m, $W_{\frac{1}{2}}$ 18 Hz, C*H*OH), 3.30br (1 H, s, $W_{\frac{1}{2}}$ 2 Hz, C*H*OH), 2.50—1.50 (CH_2), 1.06 (1 H, s, 4 × Me), 1.03 (3 H, s, Me), 0.90 (3 H, s, Me), 0.76 (3 H, s, Me), and 0.80 (3 H, d, *J* 7 Hz, 4-Me); *m/z* 458 (M^+, 35%), 434(40), 415(40), 409(40), 386(50), 355(20), 343(40), 308(50), 303(30), 289(70), 273(55), 271(55), 231(60), 207(65), 203(70), 177(75), 135(80), 123(100), and 109(95) (Found: C, 78.2; H, 10.9. $C_{30}H_{50}O_3$ requires C, 78.6; H, 10.9%).

Isolation of Kokoondiol (6).—Further elution of the column with 5% methanol in chloroform afforded *kokoondiol* (0.6 g, 2.2×10^{-4} %) as white needles (from chloroform–light petroleum), m.p. 298—300 °C, $[\alpha]_D$ +18.0°; $\nu_{max.}$ 3 490(OH) and 1 705 cm^{-1} (C=O); δ 4.13br (2 H, s, CH_2OH), 3.80br (1 H, m, $W_{\frac{1}{2}}$ 14 Hz, C*H*OH), 2.50—1.20 (CH_2), 1.60 (15 H, s, 5 × Me), 0.73 (3 H, s, Me), and 0.86 (3 H, d, *J* 6 Hz, 4-Me); *m/z* 458 (M^+, 2%), 456(4), 440(10), 427(60), 409(100), 339(5), 299(5), 287(7), 273(10), 259(70), 245(50), 233(18), 231(20), 205(30), 203(35), 201(20), 189(25), and 167(25) (Found: C, 78.1; H, 11.2. $C_{30}H_{50}O_3$ requires C, 78.6; H, 10.9%).

Isolation of Kokoona Triterpene A.—Elution of the column with 10% methanol in chloroform yielded a white solid (0.1 g, 0.3×10^{-4} %) which on recrystallisation from chloroform–methanol afforded white needles of kookona triterpene A, m.p. 273—275 °C, $[\alpha]_D$ −0.8°; $\nu_{max.}$ 3 500(OH), 1 720, and 1 710 cm^{-1} (C=O); δ[$(CD_3)_2SO$] 4.40br (1 H, t, $W_{\frac{1}{2}}$ 12 Hz, C*H*OH), 4.20br (1 H, s, $W_{\frac{1}{2}}$ 22 Hz, C*H*OH), 1.90(CH_2), 1.05 (3 H, s, Me), 0.97 (3 H, s, Me), 0.92 (3 H, s, Me), 0.88 (3 H, s, Me), 0.76 (3 H, s, Me), 0.58 (3 H, s, Me), and 0.80 (3 H, d, *J* 8 Hz, 4-Me); *m/z* 472 (M^+, 5%), 454(15), 442(18), 427(65), 409(70), 370(25), 291(60), 289(29), 271(70), 247(66), 165(50), 163(65), 149(65), 137(100), and 123(90) (Found: M^+, 472.412. $C_{30}H_{48}O_4$ requires *M*, 472.418).

Isolation of Kokzeylanol.—Further elution of the column with 10% methanol in chloroform gave *kokzeylanol* (0.6 g, 2.1×10^{-4} %) as white needles (from chloroform–light petroleum), m.p. 274—276 °C, $[\alpha]_D$ +75°; $\nu_{max.}$ 3 500(OH) and 1 720 cm^{-1} (C=O); δ 4.08br (2 H, s, CH_2OH), 3.50br (1 H, m, $W_{\frac{1}{2}}$ 18 Hz, C*H*OH), 2.50—1.20 (CH_2), 1.13 (3 H, s,

Me), 1.06 (3 H, s, Me), 1.05 (3 H, s, Me), 0.96 (6 H, s, 2 × Me), 0.76 (3 H, s, Me), and 1.08 (3 H, d, *J* 8 Hz, 4-Me); *m/z* 458 (M^+, 5%), 440(20), 427(100), 409(75), 386(5), 343(5), 317(5), 299(10), 275(50), 261(40), 257(50), 249(25), 245(35), 243(35), 231(30), and 205(50) (Found: C, 78.5; H, 10.8. $C_{30}H_{50}O_3$ requires C, 78.6; H, 10.9%).

Isolation of Kokzeylanonol.—Further elution of the column with 10% methanol in chloroform gave *kokzeylanonol* (0.2 g, 0.7 × 10^{-4} %) as white needles, m.p. 276—278 °C (from chloroform–light petroleum), $[\alpha]_D$ +86.8°; $\nu_{max.}$ 1 718 and 1 710 cm^{-1} (C=O); δ 4.10 (2 H, s, CH_2OH), 3.50 (1 H, m, $W_{\frac{1}{2}}$ 18 Hz, CHOH), 2.80—1.30 (CH_2), 1.20 (3 H, s, Me), 1.13 (6 H, s, 2 × Me), 1.06 (9 H, s, 3 × Me), 0.76 (3 H, s, Me), and 1.16 (3 H, d, *J* 6 Hz, 4-Me); *m/z* 472 (M^+, 10%), 441(45), 423(100), 407(17), 405(15), 357(15), 285(10), 273(10), 257(25), 245(15), 231(15), 219(20), and 203(15) (Found: C, 76.1; H, 10.1. $C_{30}H_{48}O_4$ requires C, 76.2; H, 10.2%).

Acetylation of Kokoonol (4).—Acetylation of kokoonol (50 mg) with acetic anhydride (1 ml) in pyridine (5 ml), followed by the customary work-up and crystallisation from methanol afforded *kokoonol acetate* (7) as white needles (40 mg, 72%), m.p. 211—213 °C, $[\alpha]_D$ −25.0°; $\nu_{max.}$ 1 740 (ester C=O), 1 715 (ring C=O) and 1 220 cm^{-1} (ester C–O); δ 4.63 and 4.40 (2 H, dd, *J* 10 Hz, CH_2OAc), 2.06 (3 H, s, $OCOCH_3$), 2.50—1.30 (CH_2) and 1.10—0.70 (8 × Me) (Found: C, 79.25; H, 10.8. $C_{32}H_{52}O_2$ requires C, 79.35; H, 10.74%).

Acetalisation of Kokoonol (4).—A solution of kokoonol (200 mg) and ethane-1,2-diol (0.5 ml) in benzene (25 ml) containing toluene-*p*-sulphonic acid (25 mg) was refluxed for 8 h using a Dean-Stark water separator. The benzene solution was washed with aqueous Na_2CO_3 and water and then dried and evaporated. The product on crystallisation from chloroform–methanol gave *kokoonol ethylene acetal* (8) as white needles (160 mg, 72%), m.p. 295—297 °C; $\nu_{max.}$ 3 500—3 400 (OH) and 1 070 cm^{-1} (acetal) (Found: C, 79.05; H, 10.95. $C_{32}H_{54}O_3$ requires C, 78.96; H, 11.30%).

CrO_3 *Oxidation of the Acetal* (8).—Oxidation of kokoonol ethylene acetal (100 mg) with CrO_3 (50 mg) in pyridine (5 ml), followed by the customary work-up and crystallisation from methanol afforded 3,3-*ethylenedioxy*-D:A-friedo-*oleanane*-27-*carbaldehyde* (9) as white needles (88 mg, 89%), m.p. 307 °C; $\nu_{max.}$ 1 710 (CHO) and 1 070 cm^{-1} (acetal) (Found: C, 79.15; H, 10.85. $C_{32}H_{52}O_3$ requires C, 79.28; H, 10.81%).

Huang-Minlon Reduction of the Aldehyde (9).—A mixture of the above acetal aldehyde (8) (60 mg), diethylene glycol (5 ml), hydrazine hydrate (100%, 1 ml), and sodium hydroxide (100 mg) was refluxed at 140 °C for 5 h, after which the solvent was allowed to evaporate until the temperature rose to 210 °C. The reaction mixture was refluxed at this temperature for further 5 h. The customary work-up and crystallisation from methanol yielded 3,3-ethylenedioxyfriedelin (30 mg, 54%) as white plates, m.p. 306—308 °C; $\nu_{max.}$ 1 070 cm^{-1} (acetal) (Found: C, 81.3; H, 11.3. $C_{32}H_{54}O_2$ requires C, 81.64; H, 11.56%).

Deacetalisation of 3,3-*Ethylenedioxyfriedelin.*—A solution of the above ethylene acetal (25 mg) and toluene-*p*-sulphonic acid (25 mg) in acetone (20 ml) was refluxed for 12 h, evaporated under reduced pressure, digested with aqueous Na_2CO_3, and extracted with chloroform. The chloroform solution was washed with water, dried, and evaporated to yield friedelin (1) (10 mg, 60%) as white needles, m.p. 263—265 °C (from methanol), $[\alpha]_D$ −22.6° (lit.,[3] m.p. 264 °C, $[\alpha]_D$ −22.1°); $\nu_{max.}$ 1 713 cm^{-1} (C=O), identical with an authentic sample.

CrO_3 *Oxidation of Kokoonol* (4).—Oxidation of kokoonol (200 mg) with CrO_3 (100 mg) in pyridine (10 ml), followed by the customary work-up and crystallisation of the product from methanol gave D:A-friedo-3-*oxo-oleanane*-27-*carbaldehyde* (10) as white needles (180 mg, 90%), m.p. 282—284 °C, $[\alpha]_D$ − 2.3°; $\nu_{max.}$ 1 711 (ring C=O) and 1 705 cm^{-1} (CHO); δ 10.30 (1 H, s, CHO), 2.60—1.20 (CH_2), 1.20—0.73 (18 H, 6 × Me), and 0.86 (3 H, d, *J* 6 Hz, 4-Me) (Found: C, 81.6; H, 10.95. $C_{30}H_{48}O_2$ requires C, 81.7; H, 11.0%).

$KMnO_4$ *Oxidation of* D:A-friedo-3-*oxo-oleanane*-27-*carbaldehyde* (10).—A solution of the aldehyde (10) (150 mg) in acetone (25 ml) was refluxed with $KMnO_4$ (400 mg) for 2 h. Solvent was evaporated under reduced pressure and the residue treated with dilute sulphuric acid and sodium bisulphite and then extracted with chloroform. The organic extract was washed with water, dried, and evaporated. Purification of the crude product thus obtained by preparative t.l.c. [eluant: 10% methanol in chloroform] afforded D:A-friedo-3-*oxo-oleanane*-27-*carboxylic acid* (11) (95 mg, 60%) as white crystals, m.p. 210—211 °C; $\nu_{max.}$ 1 715 (C=O) and 1 690 cm^{-1} (CO_2H) (Found: M^+, 456.3599. $C_{30}H_{48}O_3$ requires *M*, 456.3603); *m/z* 456 (M^+, 100%), 438(35), 423(20), 411(15), 395(15), 383(30), 371(45), 306(70), 259(25), 237(40), 219(40), and 205(35).

Acetylation of Kokoononol (5).—Acetylation of kokoononol (5) (100 mg) with acetic anhydride (2 ml) in pyridine (5 ml) followed by the customary work-up and crystallisation from methanol gave *kokoononol acetate* (13) as white plates (90 mg, 82%), m.p. 254 °C, $[\alpha]_D$ +92.2°; $\nu_{max.}$ 1 740 (ester C=O), 1 710 (C=O), and 1 220 cm^{-1} (ester C–O); δ 4.63, 4.24 (2 H, dd, *J* 13 Hz, CH_2OAc), 2.50—1.25 (CH_2), 2.03 (3 H, s, $OCOCH_3$), 1.20—0.75 (6 × Me), and 0.80 (3 H, d, *J* 8 Hz, 4-Me) (Found: C, 77.1; H, 9.85. $C_{32}H_{50}O_4$ requires C, 77.12; H, 10.0%).

Acetylation of Kokoondiol (6).—Acetylation of kokoondiol (100 mg) as above yielded *kokoondiol diacetate* (14) as white needles (87 mg, 82%), m.p. 292—294 °C (from methanol), $[\alpha]_D$ −11.1°; $\nu_{max.}$ 1 740 (ester C=O) and 1 720 cm^{-1} (C=O); δ 5.49 (1 H, m, $W_{\frac{1}{2}}$ 12 Hz, CHOAc), 4.80, 4.30 (2 H, dd, *J* 10 Hz, CH_2OAc), 2.50—1.30 (CH_2), 2.06 (3 H, s, $OCOCH_3$), 2.00 (3 H, s, $OCOCH_3$), 1.26—0.70 (6 × Me), and 0.83 (3 H, d, *J* 8 Hz, 4-Me) (Found: C, 75.5; H, 10.5. $C_{34}H_{54}O_5$ requires C, 75.3; H, 9.9%).

CrO_3 *Oxidation of Kokoononol* (5).—Oxidation of kokoononol (50 mg) with CrO_3 (50 mg) in pyridine (5 ml) followed by the customary work-up and crystallisation from methanol afforded D:A-friedo-3,21-*dioxo-oleanane*-27-*carbaldehyde* (15) as white needles (45 mg, 93%), m.p. 258—260 °C, $[\alpha]_D$ +64.3°; $\nu_{max.}$ 1 715 (C=O) and 1 720 cm^{-1} (CHO); δ 10.60 (1 H, s, CHO), 2.60—1.60 (CH_2), 1.60—0.63 (6 × Me), and 0.90 (3 H, d, *J* 6 Hz, 4-Me) (Found: C, 79.05; H, 10.2. $C_{30}H_{46}O_3$ requires C, 79.25; H, 10.2%).

CrO_3 *Oxidation of Kokoondiol* (6).—Oxidation of kokoondiol (50 mg) with CrO_3 as above yielded (15) (40 mg, 83%) identical {m.p., mixed m.p., $[\alpha]_D$, i.r. and *co-* t.l.c.} with the sample obtained above.

Preparation of Kokoononol 3-*Ethylene Acetal* (16).—A solution of kokoononol (1.0 g) and ethane-1,2-diol (2 ml) in

benzene (100 ml) containing toluene-*p*-sulphonic acid (100 mg) was refluxed for 8 h using a Dean-Stark water separator. The benzene solution was washed with aqueous Na_2CO_3 and water, dried, and evaporated. The residue crystallised from methanol to give (16) as white needles (950 mg, 90%), m.p. 296—298 °C; $\nu_{max.}$ 3 480 (OH), 1 703 (C=O) and 1 070 cm^{-1} (acetal) (Found: C, 76.5; H, 10.55. $C_{32}H_{54}O_4$ requires C, 76.75; H, 10.47%).

Huang-Minlon Reduction of (16).—A mixture of kokoononol 3-ethylene acetal (16) (400 mg), ethane-1,2-diol (8 ml), hydrazine hydrate (100%, 2 ml), and sodium hydroxide (500 mg) were refluxed for 150—160 °C for 5 h, after which the solvent was evaporated until the temperature rose to 210 °C; the mixture was then refluxed for a further 5 h at this temperature. The customary work-up and crystallisation from methanol yielded kokoonol 3-ethylene acetal (8) (300 mg, 70%), m.p. 295—297 °C, identical with the sample obtained above.

Deacetalisation of (8).—A solution of (8) (200 mg) and toluene-*p*-sulphonic acid (200 mg) in acetone (150 ml) was refluxed for 12 h. Work-up as described earlier afforded kokoonol (4) (120 mg, 85%) as white needles, m.p. 272 °C (from chloroform–light petroleum), identical with the natural product.

$LiAlH_4$ *Reduction of Kokoononol 3-Ethylene Acetal* (16).—Lithium aluminium hydride (300 mg) was added portionwise to an ice-cold solution of (16) (200 mg) in anhydrous THF (30 ml) and the mixture refluxed for 6 h. The customary work-up afforded *kokoondiol 3-ethylene acetal* (17) as white needles (150 mg, 50%), m.p. 303—305 °C; $\nu_{max.}$ 3 400 (OH) and 1 070 cm^{-1} (acetal) (Found: C, 76.0; H, 10.6. $C_{32}H_{54}O_4$ requires C, 76.4; H, 10.45%).

Deacetalisation of (17).—Kokoondiol 3-ethylene acetal (60 mg) was refluxed with acetone (50 ml) containing toluene-*p*-sulphonic acid (60 mg) for 12 h. The mixture was evaporated under reduced pressure and worked up to give a white solid (25 mg, 46%) which was recrystallised from chloroform–light petroleum to afford white needles of kokoondiol (6), identical with the natural triterpene.

$LiAlH_4$ *Reduction of Kokoononol* (5).—Kokoononol (100 mg) was reduced with $LiAlH_4$ (50 mg) in THF (20 ml) as described earlier. Recrystallisation from chloroform–light petroleum gave D : A-friedo-*oleanane*-3β,21α,27-*triol* (19) as white needles (78 mg, 76%), m.p. 300 °C, $[\alpha]_D$ +27.7°; $\nu_{max.}$ 3 600—3 400 cm^{-1} (OH) (Found: C, 77.85; H, 11.25. $C_{30}H_{52}O_3$ requires C, 78.2; H, 11.4%).

$NaBH_4$ *Reduction of Kokoononol* (5).—Kokoononol (200 mg) in methanol (20 ml) was treated with $NaBH_4$ (30 mg) in methanol (10 ml) at room temperature for 12 h. The solvent was evaporated under reduced pressure, excess dilute acetic acid was added and the mixture extracted with chloroform. The chloroform extract was washed with water, dried, and evaporated and the product purified by preparative t.l.c. (eluant: 2% methanol in chloroform, two developments) and crystallised from chloroform–light petroleum to afford 3β,27-*dihydroxy*-D : A-friedo-*oleanan*-21-*one* (18) (120 mg, 58%), m.p. 278—280 °C, $[\alpha]_D$ +140.3°; $\nu_{max.}$ 3 450, 3 500 (OH) and 1 712 cm^{-1} (C=O); δ 4.10br (2 H, s, CH_2OH), 3.76 (1 H, m, $W_{\frac{1}{2}}$ 8 Hz, C*H*OH), 2.90—1.30 (CH_2), and 1.30—0.96 (8 × Me) (Found: C, 78.7; H, 10.85. $C_{30}H_{50}O_3$ requires C, 78.6; H, 10.7%).

Photolysis of 3β,27-*Dihydroxy*-D : A-friedo-*oleanan*-21-*one* (18).—A solution of (18) (80 mg) in dry dioxan (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 under reduced pressure and the product mixture separated by preparative t.l.c. (2% methanol in chloroform, two developments) to give (in order of increasing polarity) 3β,27-*dihydroxy*-21,22-*bisnor*-friedo-E-*seco*-*oleana*-16,19-*diene* (48) (22 mg, 30%), m.p. 112—114 °C, $[\alpha]_D$ +28°; $\nu_{max.}$ 3 400—3 500 (OH) and 1 640 cm^{-1} (C=C); for ^1H n.m.r. data, see Table 2; *m/z* 414 (M^+, 25%), 396(10), 356(90), 247(55), and 218(100) (Found: M^+, 414.3245. $C_{28}H_{46}O_2$ requires *M*, 414.3238); and 3β,27-*dihydroxy*-friedo-E-*seco*-*olean*-19-*ene*-21-*carbaldehyde* (47) (48 mg, 60%), m.p. 128—130 °C, $[\alpha]_D$ +22°; $\nu_{max.}$ 3 400—3 500 (OH) and 1 710 cm^{-1} (CHO); for ^1H n.m.r. data, see Table 2; *m/z* 458 (M^+, 2%), 440(12), 427(35), 409(100), 391(25) and 257(90) (Found: M^+, 458.3452. $C_{30}H_{50}O_3$ requires *M*, 458.3448).

Acetylation of Zeylanol (21).—Acetylation of zeylanol (50 mg) with Ac_2O (2 ml) and pyridine (5 ml), followed by work-up and crystallisation from chloroform–methanol afforded *zeylanol acetate* (24) (48 mg, 96%) as white needles, m.p. 248—250 °C, $[\alpha]_D$ −2.2°; $\nu_{max.}$ 1 740 (ester C=O), 1 725 (C=O) and 1 241 cm^{-1} (ester C–O); δ 4.93 (1 H, m, $W_{\frac{1}{2}}$ 20 Hz, C*H*–OAc), 2.03 (3 H, s, OCOCH_3), 2.60—1.30 (CH_2), and 1.20—0.86 (8 × Me) (Found: C, 79.25; H, 10.75. $C_{32}H_{52}O_5$ requires C, 79.35; H, 10.74%).

Acetylation of Zeylanonol (22).—Acetylation of zeylanonol (50 mg) as above gave *zeylanonol acetate* (25) (45 mg, 81%) as white needles, m.p. 233—236 °C (from methanol), $[\alpha]_D$ + 95.0°; $\nu_{max.}$ 1 740 (ester C=O), 1 720 and 1 710 (C=O), and 1 245 cm^{-1} (ester C–O); δ 4.96 (1 H, m, $W_{\frac{1}{2}}$ 20 Hz, C*H*OAc), 2.03 (3 H, s, OCOCH_3), 2.80—1.30 (CH_2), and 1.03—0.73 (8 × Me) (Found: C, 76.9; H, 9.9. $C_{32}H_{50}O_4$ requires C, 77.12; H, 10.0%).

Acetylation of Zeylandiol (23).—Acetylation of zeylandiol (50 mg) as above yielded *zeylandiol diacetate* (26) (42 mg, 70%) as white needles m.p. 282—285 °C (from methanol), $[\alpha]_D$ + 19.2°; $\nu_{max.}$ 1 740 (ester C=O), 1 718 (C=O), and 1 245 cm^{-1} (ester C–O); δ 4.80 (1 H, m, $W_{\frac{1}{2}}$ 18 Hz, C*H*OAc), 4.90br (1 H, s, $W_{\frac{1}{2}}$ 2 Hz, C*H*OAc), 2.03 and 2.00 (3 H each, s, 2 × OCOCH_3), 2.50—1.10 (CH_2), and 1.10—0.80 (8 × Me) (Found: C, 75.2; H, 9.8. $C_{34}H_{54}O_5$ requires C, 75.3; H, 9.9%).

Preparation of Zeylanol Thiobenzoate (27).—A mixture of *N*,*N*-dimethylbenzamide (250 mg) and phosgene (250 mg) in benzene (3 ml) was stirred for 18 h; the solvent was evaporated and the resulting residue in dichloromethane (3 ml) was added to a solution of zeylanol (450 mg) in THF (5 ml) with stirring. After 30 min, pyridine (0.35 ml) was added followed by the treatment with H_2S for 10 min. The crude product obtained on work-up was purified by preparative t.l.c. (benzene only) and recrystallised from methanol to afford *zeylanol thiobenzoate* (27) as yellow cubes (350 mg, 61%), m.p. 220—222 °C, $[\alpha]_D$ +41.8°; $\nu_{max.}$ 1 713 (C=O) and 1 240 cm^{-1} (C=S); δ 8.20—8.00 and 7.80—7.30 (5 H, m, ArH), 5.66 (1 H, m, C*H*OCSPh), 2.50—1.30 (CH_2), and 1.26—0.96 (8 × Me) (Found: C, 79.0; H, 9.9; S, 5.8. $C_{37}H_{54}O_2S$ requires C, 78.9; H, 9.7; S, 5.7%).

Triphenyltin Hydride Reduction of (27).—Zeylanol thiobenzoate (27) (100 mg) in toluene (8 ml) was added during 15 min to a solution of triphenyltin hydride (100 mg) in the same solvent (7 ml) with refluxing under N_2. After disappearance of the yellow colour (*ca.* 2 h), the solvent was

removed under reduced pressure and the product purified by preparative t.l.c. (benzene only) to give friedelin (1) (45 mg, 60%) as white needles (from chloroform–methanol), m.p. 263—265 °C, $[\alpha]_D$ −22.2°, which was identical with an authentic sample.

Preparation of Zeylanonol Monoethylene Acetal (31).—A mixture of zeylanonol (200 mg), toluene-*p*-sulphonic acid (25 mg), ethane-1,2-diol (0.5 ml), and benzene (25 ml) was refluxed for 8 h using a Dean-Stark water separator. It was washed with aqueous Na_2CO_3 and water, dried, and evaporated. The resulting residue on crystallisation from chloroform–methanol afforded (31) as white needles (165 mg, 75%), m.p. 231—235 °C; $\nu_{max.}$ 3 480 (OH), 1 712 (C=O), and 1 060 cm^{-1} (acetal) (Found: C, 76.65; H, 10.6. $C_{32}H_{52}O_4$ requires C, 76.75; H, 10.5%).

Huang-Minlon Reduction of (31).—A mixture of (31) (100 mg) ethane-1,2-diol (7 ml), hydrazine hydrate (100%; 1.5 ml), and potassium hydroxide (125 mg) was refluxed at 140 °C for 5 h. The solvent was evaporated until the temperature rose to 210 °C and the mixture was then refluxed for further 10 h. Work-up followed by the purification by preparative t.l.c. (chloroform) and crystallisation from methanol yielded *zeylanol ethylene acetal* (30) as white needles (65 mg, 72%), m.p. 268—270 °C; $\nu_{max.}$ 3 480 (OH) and 1 160 cm^{-1} (acetal) (Found: C, 79.25; H, 11.3. $C_{32}H_{54}O_3$ requires C, 78.96; H, 11.18%).

Deacetalisation of (30).—A solution of (30) (40 mg) and toluene-*p*-sulphonic acid (40 mg) in acetone (40 ml) was refluxed for 12 h. The solvent was evaporated and the residue digested with aqueous Na_2CO_3, extracted with chloroform, and the organic layer washed with water, dried, and evaporated. The solid thus obtained was crystallised from chloroform–light petroleum to afford zeylanol (21) (20 mg, 62%), m.p. 274—276 °C, $[\alpha]_D$ +0.95°, which was identical with an authentic sample.

CrO_3 *Oxidation of Zeylanonol* (22).—Oxidation of zeylanonol (50 mg) with CrO_3 (30 mg) in pyridine (5 ml), followed by work-up and crystallisation from chloroform–light petroleum gave D:A-friedo-*oleanane*-3,6,21-*trione* (33) as white needles (45 mg, 93%), m.p. 335—337 °C; $[\alpha]_D$ +152°; $\nu_{max.}$ 1720, 1710, and 1700 cm^{-1} (C=O); δ 3.00—1.30 (CH_2) and 1.60—1.00 (8 × Me) (Found: C, 79.15; H, 10.2. $C_{30}H_{46}O_3$ requires C, 79.25; H, 10.2%).

CrO_3 *Oxidation of Zeylandiol* (23).—Oxidation of zeylandiol (40 mg) as above afforded D:A-*friedo*-oleanane-3,6,21-trione (33) (32 mg, 94%), m.p. 333—335 °C, $[\alpha]_D$ +150°, which was shown to be identical with the above obtained sample.

Preparation of Zeylandiol Dithiobenzoate (29).—A mixture of *N*,*N*-dimethylbenzamide (300 mg) and phosgene (300 mg) in benzene (3.5 ml) was stirred for 18 h. The solvent was evaporated and the residue in dichloromethane (5 ml) was added to a solution of zeylandiol (300 mg) in THF (5 ml) with stirring. After 30 min, pyridine (5 ml) was added to the mixture and this was followed by treatment with H_2S for 10 min. The crude product obtained on work-up was purified by preparative t.l.c. (benzene only) and recrystallisation from methanol to afford yellow needles of *zeylandiol dithiobenzoate* (29) (125 mg, 27%), m.p. 235—237 °C; $\nu_{max.}$ 1 711 (C=O) and 1 238 cm^{-1} (C=S); δ 8.30—8.03 and 7.80—7.20 (10 H, m, ArH), 5.66 and 5.40 (2 H, m, 2 × C*H*OCSPh), 2.50—1.30 (CH_2), and 1.20—0.90 (8 × Me) (Found: M^+, 699.0736. $C_{44}H_{58}O_3S_2$ requires *M*, 699.0742).

Triphenyltin Hydride Reduction of (29).—Zeylandiol dithiobenzoate (125 mg) in toluene (7 ml) was added during 10 min to a solution of triphenyltin hydride (250 mg) in toluene (10 ml) with refluxing under N_2. After 1.5 h the solvent was removed and the product purified by preparative t.l.c. (benzene) and crystallisation from methanol to yield friedelin (1) (25 mg, 32%), m.p. 260—262 °C, $[\alpha]_D$ −22.1°, identical with an authentic sample.

Preparation of Zeylanonol Thiobenzoate (28).—Zeylanonol (440 mg) was converted into its thiobenzoate following the procedure described above. The product on crystallisation from methanol afforded yellow crystals of *zeylanonol thiobenzoate* (28) (310 mg, 56%), m.p. 215 °C; $\nu_{max.}$ 1 711 and 1 722 (C=O), and 1 238 cm^{-1} (C=S) (Found: M^+, 576.8689. $C_{32}H_{52}O_3S$ requires *M*, 576.8692).

Triphenyltin Hydride Reduction of (28).—Zeylanol thiobenzoate (100 mg) in toluene (7 ml) was added during 15 min to a solution of triphenyltin hydride (100 mg) in toluene (7 ml) with refluxing until the reaction mixture turned colourless (2 h). The solvent was evaporated under reduced pressure and the product purified by preparative t.l.c. (chloroform) and crystallisation from chloroform–light petroleum to give friedelane-3,21-dione (2) as white needles (25 mg, 32%), m.p. 248—250 °C, $[\alpha]_D$ +111.5°, $\nu_{max.}$ 1 712 and 1 722 cm^{-1} (C=O) which was identical with an authentic sample.

$NaBH_4$ *Reduction of Zeylanonol* (22).—Zeylanonol (125 mg) was dissolved in methanol (12 ml) and treated with $NaBH_4$ (25 mg). Work-up and purification by preparative t.l.c. (2% methanol in chloroform) afforded white needles of 3β,6β-*dihydroxy*-D : A-friedo-*oleanan*-21-*one* (39) (100 mg, 77%), m.p. 284—286 °C (chloroform–light petroleum), $[\alpha]_D$ +72°; $\nu_{max.}$ 3 600—3 400 (OH) and 1 703 cm^{-1} (C=O); δ 3.73 (1 H, m, $W_{\frac{1}{2}}$ 6 Hz, C*H*OH), 3.43 (1 H, *m*, $W_{\frac{1}{2}}$ 18 Hz, C*H*OH), 2.80—1.30 (CH_2), and 1.30—0.90 (8 × Me) (Found: C, 78.4; H, 10.85. $C_{30}H_{50}O_3$ requires C, 78.6; H, 10.9%).

Irradiation of 3β,6β-*Dihydroxy*-D : A-friedo-*oleanan*-21-*one* (39).—A solution of (39) (85 mg) in dioxan (20 ml) was refluxed for 18 h (t.l.c. control) whilst being irradiated with a high-pressure Hg lamp (125 W) under N_2. The solvent was evaporated under reduced pressure and the product purified by preparative t.l.c. (2% methanol in chloroform) to obtain 3β,6β-*dihydroxy*-21,22-*bisnor*-D : A-friedo-E-*seco*-*oleana*-16,19-*diene* (50) (31 mg, 40%), m.p. 135—136 °C, $[\alpha]_D$ +26.5°; $\nu_{max.}$ 3 500—3 300 (OH), 1 635 and 780 cm^{-1} (C=C); for ^1H n.m.r. data see Table 2; (Found: M^+, 414.6742. $C_{26}H_{46}O_2$ requires *M*, 414.6748).

CrO_3 *Oxidation of Zeylanol* (21).—Oxidation of zeylanol (300 mg) with CrO_3 (175 mg) in pyridine (10 ml), followed by work-up and crystallisation from chloroform–light petroleum afforded D : A-friedo-*oleanane*-3,6-*dione* (32) as white needles (275 mg, 94%), m.p. 305—306 °C, $[\alpha]_D$ +32.2°; $\nu_{max.}$ 1 714 and 1 700 cm^{-1} (C=O); δ 3.00—1.30 (CH_2) and 1.20—0.96 (8 × Me) (Found: C, 81.9; H, 11.0. $C_{30}H_{48}O_2$ requires C, 81.7; H, 11.0%).

Preparation of the Ethylene Diacetal of (32).—A mixture of (32) (100 mg), ethane-1,2-diol (0.5 ml), toluene-*p*-sulphonic acid (20 mg), in benzene (25 ml) was refluxed for 8 h using a Dean-Stark water separator. It was then washed with aqueous Na_2CO_3 and water, and then dried and evaporated; the product was crystallised from methanol to yield D : A-friedo-*oleanane*-3,6-*dione ethylene diacetal* (34) as white needles (80

mg, 66%), m.p. 270—272 °C, $\nu_{max.}$ 1 060 cm^{-1} (acetal) (Found: C, 77.35; H, 10.6. $C_{34}H_{56}O_4$ requires C, 77.29; H, 10.6%).

$NaBH_4$ *Reduction of* (32).—D : A-*friedo*-Oleanane-3,6-dione (32) (50 mg) in methanol (10 ml) was reduced with $NaBH_4$ (10 mg). Work-up followed by crystallisation from chloroform–light petroleum afforded 3β,6β-*dihydroxy*-D : A-friedo-*oleanane* (35) as white needles (42 mg, 76%), m.p. 286—288 °C, $[\alpha]_D$ −1.20°; $\nu_{max.}$ 3 490 cm^{-1} (OH); δ 3.86 (1 H, m, $W_{\frac{1}{2}}$ 6 Hz, C*H*OH), 3.66 (1 H, m, $W_{\frac{1}{2}}$ 6 Hz, C*H*OH), 2.00—1.20 (CH_2), and 1.20—0.90 (8 × Me) (Found: C, 81.2; H, 11.9. $C_{30}H_{52}O_2$ requires C, 81.0; H, 11.8%).

Huang-Minlon Reduction of Zeylanol (21).—A mixture of zeylanol (300 mg), ethane-1,2-diol (10 ml), hydrazine hydrate (2 ml), and NaOH (300 mg) was refluxed at 145—155 °C for 2 h. The solvent was evaporated until the temperature rose to 210 °C and was then refluxed at this temperature for a further 5 h. Work-up and purification by preparative t.l.c. (chloroform) gave 6β-*hydroxy*-D : A-friedo-*oleanane* (36) as white needles (175 mg, 63%), m.p. 250—252 °C (from methanol), $[\alpha]_D$ + 25.2°; $\nu_{max.}$ 3 490 cm^{-1} (OH); δ 3.40 (1 H, m, $W_{\frac{1}{2}}$ 18 Hz, C*H*OH), 2.00—1.10 (CH_2), and 1.00—0.80 (8 × Me) (Found: C, 83.8; H, 12.1. $C_{30}H_{52}O$ requires C, 84.0; H, 12.3%).

Acetylation of 6β-*Hydroxy*-D : A-friedo-*oleanane* (36).—Acetylation of (36) (40 mg) with Ac_2O (1.5 ml) in pyridine (5 ml), followed by work-up and crystallisation from chloroform–methanol afforded 6β-*acetoxy*-D : A-friedo-*oleanane* (37) as white needles (35 mg, 81%), m.p. 218—220 °C, $[\alpha]_D$ +0.15°; $\nu_{max.}$ 1 725 (ester C=O) and 1 240 cm^{-1} (ester C–O); δ 4.63 (1 H, m, $W_{\frac{1}{2}}$ 20 Hz, C*H*OAc), 2.00 (3 H, s, OCOC*H*$_3$), 1.80—1.10 (CH_2), and 1.00—0.85 (8 × Me) (Found: C, 81.5; H, 11.45. $C_{32}H_{54}O_2$ requires C, 81.7; H, 11.48%).

CrO_3 *Oxidation of* (36).—Oxidation of (36) (125 mg) with CrO_3 (80 mg) in pyridine (10 ml) followed by work-up gave D : A-friedo-*oleanan*-6-*one* (38) as white needles (110 mg, 91%), m.p. 276—278 °C (from methanol), $[\alpha]_D$ +78.7°; $\nu_{max.}$ 1 693 cm^{-1} (C=O); δ 2.73 (1 H, dd, *J* 14 and 4 Hz, 7-H), 2.03 (1 H, dd, *J* 14 and 2 Hz, 7-H), 1.30 (1 H, d, *J* 4 Hz, C*H*CH_2CO), 2.00—1.20 (CH_2), and 1.16—0.93 (8 × Me).

Preparation of 7α-*Bromo*-D : A-friedo-*oleanan*-6-*one* (51).—A mixture of (38) (80 mg), pyridine hydrobromide perbromide (80 mg), and acetic acid (5 ml) was heated on a boiling water-bath for 30 min. On cooling 7α-*bromo*-D : A-friedo-*oleanan*-6-*one* (51) was precipitated as white needles (45 mg, 46%), m.p. 218—220 °C, $[\alpha]_D$ + 28.0°; $\nu_{max.}$ 1 693 cm^{-1} (C=O); δ 4.10 (1 H, d, *J* 6 Hz, CH-C*H*BrCO), 2.67 (1 H, d, *J* 6 Hz, C*H*–CHBrCO), 2.00—1.20 (CH_2), and 1.16—0.70 (8 × Me) (Found: C, 71.4; H, 9.95; Br, 15.8. $C_{30}H_{49}BrO$ requires C, 71.25; H, 9.8; Br, 15.8%).

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