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Studies on Terpenoids and Steroids. Part 27.[1] Structure of a D:A-*Friedo*-oleanane Triterpenoid from *Salacia reticulata* and Revision of the Structures of Kokoonol and Kokzeylanol Series of Triterpenoids[a]

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***Abstract*:** The structure of *epi*-kokoondiol isolated from the outer root bark of *Salacia reticulata* var. β-diandra has been elucidated as 21α,26-dihydroxy-D:A-*friedo*-oleanan-3-one (1) by the application of 2D and NOE difference NMR spectroscopy. Reinvestigation of some *Kokoona* triterpenoids by NOE difference spectroscopy led to the revision of the structures of kokoondiol, kokoononol, kokzeylanol, kokoonol, and kokzeylanonol as 21β,26-dihydroxy-D:A-*friedo*-oleanan-3-one (2), 26-hydroxy-D:A-*friedo*-oleanane-3,21-dione (3), 6β,26-dihydroxy-D:A-*friedo*-oleanan-3-one (4) 26-hydroxy-D:A-*friedo*-oleanan-3-one (5), and 6β,26-dihydroxy-D:A-*friedo*-oleanane-3,21-dione (6), respectively.

As a part of our continuing studies on triterpenoids of Sri Lankan Celastraceae and Hippocrateaceae, we have investigated the triterpenoid constituents of *Salacia reticulata* Wight var. ß-diandra (Hippocrateaceae) and in this paper we report the application of two dimensional and NOE difference NMR spectroscopy for the structure elucidation of a D:A-*friedo*-oleanane triterpenoid encountered in the outer root bark of this species. The close resemblance of the NMR spectral data of this triterpenoid with those reported for kokoondiol[2] and subsequent revision of the structures of the triterpenoids with which the comparisons were made during the structure elucidation of *Kokoona* triterpenoids prompted us to submit three of the available kokoonol and kokzeylanol series of triterpenoids to a complete NMR spectral analysis which resulted in a revision of the structures previously proposed[2,3] for these two series of triterpenoids.

RESULTS AND DISCUSSION

Repeated chromatography of the benzene extract of the outer root bark of *S. reticulata* afforded *epi*-kokoondiol (1) (0.006%), $C_{30}H_{50}O_3$, m.p. 269-270°C, $[\alpha]_D$ -28.° The IR and MS were superimposable with those of kokoondiol.[2] Chemical interconversions and comparison with the literature data were not attempted as

[a] Dedicated with great admiration and affection to Professor Sir Derek Barton on the occasion of his 75th Birthday.
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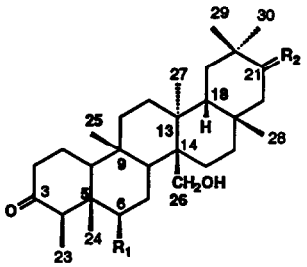
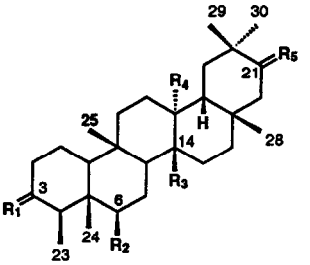
these in methyl oxygenated D:A-*friedo*-oleanane triterpenoids have led to some confusion (see later). The structure elucidation was therefore undertaken with the aid of ^{1}H, ^{13}C, ^{1}H-^{1}H and ^{1}H-^{13}C COSY, ^{1}H-^{13}C long-range COSY and difference NOE spectroscopy.





1 $R_1 = H$; $R_2 = \alpha$-OH,β-H

2 $R_1 = H$; $R_2 = \beta$-OH,α-H

3 $R_1 = H$; $R_2 = O$

4 $R_1 = OH$; $R_2 = H_2$

5 $R_1 = H$; $R_2 = H_2$

6 $R_1 = OH$; $R_2 = O$

7 $R_1 = O$; $R_2 = H$; $R_3 = CHO$; $R_4 = Me$; $R_5 = H_2$

8 $R_1 = \beta$-OH,α-H ; $R_2 = H$; $R^3 = Me$; $R_4 = CO_2H$; $R^5 = H_2$

9 $R_1 = O$; $R_2 = H$; $R_3 = Me$; $R_4 = CH_2OH$; $R_5 = \alpha$-OH,β-H

10 $R_1 = O$; $R_2 = H$; $R_3 = Me$; $R_4 = CHO$; $R_5 = H_2$

11 $R_1 = R_5 = O$; $R_2 = H$; $R_3 = Me$; $R_4 = CH_2OH$; $R^5 = H_2$

12 $R_1 = O$; $R_2 = OH$; $R_3 = Me$; $R_4 = CH_2OH$; $R_5 = H_2$

In the ^{1}H NMR spectrum, **1** had signals due to six tertiary methyls (δ 0.74, 1.17, 1.25, 1.27, 1.28 and 1.33), a secondary methyl (δ 0.96, d, J= 7 Hz), a hydroxymethine (δ 4.00, dd, J=12 and 5 Hz), a hydroxymethylene (δ 4.16 and 4.24, each d, J= 12 Hz) in addition to a complex pattern in the region δ 1.00-2.40 due to methylene and methine protons (Table 1). The ^{13}C NMR spectrum of **1** showed signals due to carbons of CO (δ 211.8, s), CH_2OH (δ 61.9, t), CHOH (δ 73.2, d) together with those of seven methyls, ten methylenes, four methines and six quaternary carbons (Table 2). These data suggested that **1** is a D:A-*friedo*-oleanane-type triterpene carrying CO, CH_2OH and CHOH groups. The 1H quartet at δ 2.22 in the ^{1}H NMR spectrum was placed at C-4 initially on the assumption that the CO group in **1** is located at the biogenetically favorable C-3. Careful analysis of the ^{1}H and ^{13}C NMR spectra with the aid of ^{1}H-^{1}H (COSY-45) and ^{1}H-^{13}C COSY (HETCOR) spectra suggested the presence of partial structures depicted in Figure 1. In the long-range ^{1}H-^{13}C COSY spectrum of **1**, the methyl signal at δ 0.74 showed long-range correlation with the carbon signals at δ 57.9, 42.4, 42.6 and 59.9. This methyl signal was readily assigned to Me-24, since the C-4 signal (δ 57.9) was unambiguously assigned by correlation with H-4 (δ 2.22, q) observed in the ^{1}H-^{13}C COSY spectrum. Thus, the carbon signals at δ 42.4, 42.6 and 59.9 were assigned to C-5, C-6 and C-10, respectively. The methyl signal at δ 1.17 showed a long-range correlation with C-10 (δ 59.9) and with the carbon signals at δ 36.2 (C-11), 37.8 (C-9) and 52.1 (C-8). This observation led to the assignment of this signal to Me-25, and further established the assignment of the C-11, C-9 and C-8 signals. These and other significant long-range ^{1}H-^{13}C correlations observed are given in Table 3.

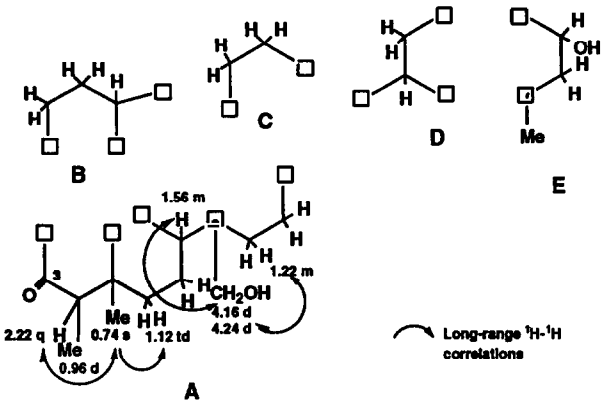
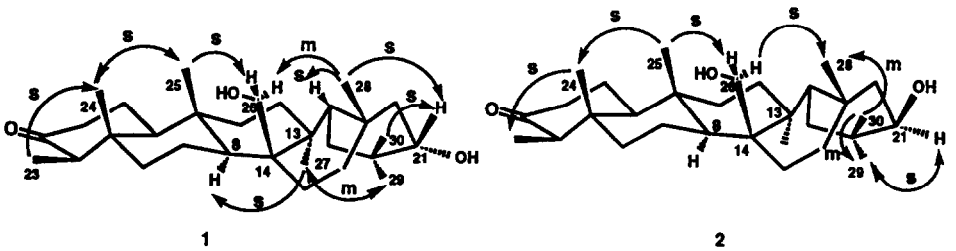


Figure 1. Partial Structures of 1 Deduced from ^1H-^1H and ^1H-^{13}C COSY and Long-range Correlations Observed in ^1H-^1H COSY.

Evidence for the placement of the hydroxy functions in the D:A-*friedo*-oleanane framework was sought by 2D NMR experiments and difference NOE spectroscopy. As shown in the partial structure A (Figure 1), in the ^1H-^1H COSY spectrum, one of the hydroxymethylene protons (δ 4.16 d, *J*= 12 Hz) showed long-range correlation with the signal at δ 1.56 (m) [which has already been assigned to H-8 with the aid of ^1H-^{13}C COSY and long-range ^1H-^{13}C COSY] suggesting the attachment of the CH_2OH to C-14. The other hydroxymethylene proton (δ 4.24, d, *J*=12) showed a long-range correlation with a proton at δ 1.22 (m) in the ^1H-^1H COSY and this was assigned to H-15. The placement of the CH_2OH group at C-14 was further supported by the difference NOE spectroscopy. Thus irradiation of Me-23 (δ 0.96) caused a NOE enhancement of the 3H signal at δ 0.74 (Me-24) and irradiation of the latter signal resulted in a NOE enhancement of the Me signal at δ 1.17 (Me-25). Irradiation of the signal at δ 1.17 caused an enhancement of the signals at δ 0.74 (Me-24) and the methylene signal at δ 4.24 confirming the attachment of the CH_2OH group to C-14. Further, the irradiation of the 3H singlet at δ 1.28 (Me-28) caused enhancements of the other methylene proton of the CH_2OH at δ 4.16 along with the signals at δ 1.81(H-16β), 1.56 (H-18) and 4.00 (H-21). These NOE enhancement data also suggested that D ring in **1** is in boat conformation which is in agreement with the earlier observations.[4] The placement of the second OH group at C-21 and its α configuration was also supported by difference NOE spectra. Thus the irradiation of the signals at δ 1.28 (Me-28) and 1.27 caused an enhancement of the signal at δ 4.00 (dd, *J*= 12,5 Hz) due to H-21, while no enhancement of this signal was observed on irradiation of the methyl signal at δ 1.33. Thus, they were assigned to Me-30 (δ 1.27) and Me-29 (δ 1.33), and the configuration of H-21 was confirmed to be β. The results of these NOE difference spectroscopic studies are summarized in Figure 2. The foregoing suggested the structure of **1** to be 21α,26-dihydroxy-D:A-*friedo*-oleanan-3-one. The structure proposed for **1** was also supported by major mass spectral fragmentation pathways which are depicted in Figure 3.

The isolation of 21α,26-dihydroxy-D:A-*friedo*-oleanan-3-one (**1**) from *S.reticulata* has previously been reported by Kumar *et al.*[5] and its structure elucidation was based mainly on ^{13}C NMR data and chemical transformation into trichadonal [3-oxo-D:A-*friedo*-oleanan-26-al (**7**)]. Trichadonal has been isolated from *Trichadenia zeylanica* along with trichadenic acid B (3β-hydroxy-D:A-*friedo*-oleanan-26-oic acid).[6]



1 2

Figure 2. Schematic Representation of the Results of NOE Difference Spectroscopy of *Epi*-kokoondiol (1) and Kokoondiol (2) [Extent of signal intensity enhancements are indicated above arrows: s=strong (>10%); m=medium (5-10%); weak enhancements are not indicated].

Table 1. ^{1}H NMR Spectral Data of 1 - 4 [in d_5-pyridine at 400 MHz; coupling constants (Hz) in parenthesis]

Proton	1[a]	2[b]	3[a]	4[a]
H-1α	1.94 m	1.92 m	1.91 ddd (14,7,2)	1.97 m
H-1β	1.67 m	1.68 m	1.67 qd (14,5)	1.80 qd (12,6)
H-2α	2.37 td (14,8)	2.36 td (13.5,7)	2.36 td (14,7)	2.40 td (12,6)
H-2β	2.47 m	2.46 ddd (13.5,4.5,1.5)	2.47 ddd (14,5,2)	2.50 ddd (12,6,2)
H-4	2.22[c] q (7)	2.26 q (7)	2.27[c] q (7)	2.58[c] q (7)
H-6α	1.12[c] td (14,4)	1.13 m	1.13[c] td (14,3)	3.75 dd (12,4)
H-6β	1.69 m	1.71 m	1.71 dt (14,3)	-
H-7α	1.89 m	1.87 m	1.81 br d (14)	2.33 br dd (12,4)
H-7β	2.16 q (12)	2.22 m	2.18 qd (14,3)	2.58 qd (12,6)
H-8	1.56[h] m	1.58 m	1.56 br d (14)	1.74[e] br d (12)
H-10	1.58 m	1.44 dd (9,3)	1.59 br d (14)	1.66 m
H-11α	1.37 m	1.41 m	1.37[e] m	1.36 m
H-11β	1.51 m	1.53 m	1.54 m	1.53 m
H-12α	1.37 m	1.41 m	1.33 m	1.37 m
H-12β	1.41 m	1.53 m	1.51[f] m	1.43 m
H-15α	1.22[h] m	1.25 m	1.23 m	1.22 m
H-15β	2.42 m	2.65 dt (14.5,9)	2.61 dt (14,10)	2.62 dt (14,6)
H-16α	1.67 m	1.54 m	1.39 td (14,10)	1.49 m
H-16β	1.81 dt (14,8)	1.72 m	1.83 dt (14,10)	1.66 m
H-18	1.56 m	not identified	1.86 dd (12,5)	1.61 m
H-19α	1.54 m	1.64 m	1.95[g] t (12)	1.22 m
H-19β	1.74 dd (12,3)	1.87 dd (14,5)	1.61 dd (12,5)	1.43 m
H-21α	-	4.09 br d (4.5)	-	1.29 br d (14)
H-21β	4.00 dd (12,5)	-	-	1.47 m
H-22α	2.11[d] t (12)	1.87[d] dd (14,5)	2.75[d] d (14)	1.57 m
H-22β	1.47 dd (12,5)	1.64 m	1.90 d (14)	0.94 br d (14)
H_3-23	0.96 d (7)	0.97 d (7)	0.97 d (7)	1 61 d (7)
H_3-24	0.74 s	0.76 s	0.75 s	1 05 s
H_3-25	1.17 s	1.21 s	1.18 s	1.21 s
H_2-26	4.16 d (12)	4.29 d (11.5)	4.17 d (12)	4 21 d (12)
	4.24 d (12)	4.39 d (11.5)	4.24 d (12)	4.26 d (12)
H_3-27	1.25 s	1.18 s	1.23 s	1.16 s
H_3-28	1.28 s	1.74 s	1 21 s	1.22 s
H_3-29	1.33 s	1.20 s	1.16 s	1.02 s
H_3-30	1.27 s	1.37 s	1.23 s	1.03 s

[a]Assignments based on ^{1}H-^{1}H and ^{1}H-^{13}C COSY spectra.

[b]Assignments based on ^{1}H-^{1}H COSY spectrum.

[c,d,e,f,g]Long-range coupling was observed with H_3-24, H_3-28, H_3-25 and H_3-30, respectively.

[h]Long-range coupling was observed with H-26.

Trichadenic acid B has recently been encountered in *Phyllanthus flexuosus* by Tanaka *et al.* and its structure revised as 3β-hydroxy-D:A-*friedo*-oleanan-27-oic acid (**8**) based on X-ray crystallographic analysis.[7] During the structure elucidation of their triterpenoid, Kumar *et al.* located the hydroxy group at C-26 based on the comparison made with the material derived from trichadenic acid B.[5] Therefore, Tanaka *et al.* suggested that the structure of the triterpenoid reported by Kumar *et al.* should be revised to 21α,27-dihydroxy-D:A-*friedo*-oleanan-3-one (**9**).[7] Although an authentic sample of the triterpenoid isolated by Kumar *et al.* was not available the close resemblance of the data [^{13}C NMR (Table 2), mp and $(\alpha)_D$] for our compound with those reported[5] for the previously isolated triterpene from the same source suggests in fact the structure **1** proposed by Kumar *et al.* to be correct; it is possible that a mistake was made in comparing its derivative with trichadonal (see above). The present work further suggests that the ^{13}C NMR assignments previously made[5] for C-12 and C-15 of **1** should be reversed.

Table 2. ^{13}C NMR Spectral Data of 1 - 4 [in d_5-pyridine at 100 MHz]

Carbon	1[a,b]		2[a]		3[c]		4[a,b]	
1	22.7	t	22.7	t	22.7	t	22.4	t
2	41.7	t	41.7	t	41.7	t	41.8	t
3	211.8	s	211.8	s	211.8	s	212.5	s
4	57.9[e,f]	d	58.0	d	57.9	d	58.7	d
5	42.4[f]	s	42.5	s	42.4	s	48.4[f]	s
6	42.6[f]	t	42.7	t	42.5	t	80.3	d
7	21.2	t	21.2	t	21.0	t	32.4	t
8	52.1[g]	d	53.9	d	54.0	d	50.2	d
9	37.8[g]	s	37.7	s	37.7	s	37.8[g]	s
10	59.9[f,g]	d	59.9	d	59.8	d	59.1	d
11	36.2[g]	t	36.7	t	36.4	t	36.4	t
12	30.4[h]	t	30.8	t	30.6	t	30.5	t
13	39.8[d,h]	s	40.3[d]	s	40.2[d]	s	40.1[d,h]	s
14	43.0[d,h]	s	42.6[d]	s	43.0[d]	s	42.3[d]	s
15	24.2	t	24.95	t	24.9	t	24.5	t
16	36.8[i]	t	36.8	t	35.2	t	36.0	t
17	33.0[j]	s	30.5	s	33.8	s	30.6[i]	s
18	45.2[h,i]	d	43.7	d	42.7	d	43.7	d
19	36.9[j,k]	t	37.3	t	37.4	t	35.8	t
20	35.2[j,k]	s	34.5	s	42.4	s	28.5[j]	s
21	73.2	d	74.5	d	217.5	s	33.2	t
22	48.0[i]	t	49.3	t	55.2	t	39.5	t
23	7.2	q	7.2	q	7.2	q	11.3	q
24	14.6	q	14.6	q	14.5	q	9.8	q
25	18.1	q	17.7	q	17.5	q	17.6	q
26	61.9	t	63.4	t	63.2	t	62.6	t
27	20.4	q	20.0	q	19.5	q	19.8	q
28	33.1[l]	q	34.5	q	33.1	q	31.8	q
29	26.1	q	35.1	q	28.7	q	34.6	q
30	32.5	q	25.03	q	24.8	q	32.0	q

[a]Assignment based on ^{1}H-^{13}C COSY (HETCOR) data.
[b]Assignment based on long-range ^{1}H-^{13}C COSY (long-range HETCOR) data.
[c]Assignments by comparison with **1**,**2** and **4**
[d]Assignments in any one column may be interchanged
[e,f,g,h,i,j,k,l]Long-range correlations were observed respectively with H_3-23, H_3-24, H_3-25, H_3-27, H_3-28, H_3-29, H_3-30 and H-22, in the long-range ^{1}H-^{13}C COSY spectrum.

We have previously reported a series of 27-hydroxy-D:A-*friedo*-oleananes from *Kokoona zeylanica*.[2,3] The structures proposed were based mainly on chemical interconversions and the direct comparison of their derivatives with previously reported D:A-*friedo*-oleananes. The locations of the oxygen functions in the main D:A-*friedo*-oleanane framework of these *Kokoona* triterpenoids have been established beyond any doubt to be at C-3 and C-21.[2,3] However, the hydroxymethylene group was placed at C-13 by the direct comparison of the corresponding derivatives with canophyllal,[8] trichadonal,[6] octandronic acid[9] and polpunonic acid.[10] Since then it has been suggested that the structures of trichadonal and octandronic acid should be revised to D:A-*friedo*-oleanan-3-on-27-al (**10**)[7] and D:A-*friedo*-oleanan-3-on-28-oic acid (canophyllic acid),[11] respectively. This prompted us to reinvestigate the structures of the available triterpenoids from *K. zeylanica* , *viz.* kokoondiol, kokoononol, and kokzeylanol by the application of 2D NMR and difference NOE techniques.

Table 3. Long-range ^{1}H-^{13}C Correlations (Long-range HETCOR) of 1 (in d_5-pyridine at 400 MHz)

Carbon	Observed long-range correlation	Carbon	Observed long-range correlation
4	H-23, H-24	14	H-27
5	H-24	16	H-28
6	H-24	17	H-28
8	H-25	18	H-27, H-28
9	H-25	19	H-29, H-30
10	H-24, H-25	20	H-29, H-30
11	H-25	22	H-28
12	H-27	29	H-30
13	H-27	30	H-29

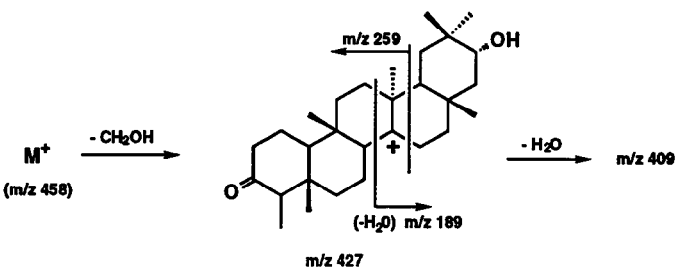


Figure 3. Major MS Fragmentations of 1.

The ^{1}H and ^{13}C NMR assignments for kokoononol, kokoondiol and kokzeylanonol were made by the application of ^{1}H-^{1}H and ^{1}H-^{13}C shift correlations and the long-range ^{1}H-^{13}C COSY experiments and by comparison with the assignments already made above for 21α,26-dihydroxy-D:A-*friedo*-oleanan-3-one (**1**). The ^{1}H and ^{13}C NMR assignments for these triterpenoids are given in Tables 1 and 2, respectively. Since the presence of D:A-*friedo*-oleanane skeleton and oxygenations at C-3, C-6 and C-21 have already been established (see above and refs. 1 and 2), it was only necessary to locate the hydroxymethylene function (in all three triterpenoids) and determine the stereochemical disposition of the hydroxy groups at C-6 (in kokzeylanonol) and at C-21 (in kokoondiol), and these were done by the application of difference NOE spectra as discussed below.

The ^{1}H NMR signals for the methyl groups of kokoondiol was found to occur at δ 0.76 (s), 0.97 (d, *J*=7), 1.18(s), 1.21(s), 1.37(s) and 1.74(s). Of these, the doublet at δ 0.97 (due to Me-23) and the singlet at δ 1.21 showed enhancements on irradiation of the methyl singlet at δ 0.76. Thus the singlets at δ 0.76 and 1.21 may be assigned to Me-24 and Me-25, respectively. Irradiation of the singlet at δ 1.21 (Me-25) in addition to enhancing the singlet at δ 0.76 showed an NOE enhancement of one of the hydroxymethylene protons (δ 4.29, d, *J*=11.5 Hz). This is possible only if the CH_2OH group is located at C-14. On the other hand, irradiation of the counterpart signal of the CH_2OH group (δ 4.39, d, *J*=11.5 Hz) caused an enhancement of the methyl singlet at δ 1.74 suggesting that the latter signal was due to Me-28. Further the irradiation of the signal at δ 1.74 caused an enhancement of the methyl singlet at δ 1.37 and the irradiation of this signal caused an NOE enhancement of the signal due to Me-28 (δ 1.74) and the signal at δ 1.20 (s). Therefore, the signals at δ 1.37 and 1.20 may be assigned to Me-30 and Me-29, respectively. Irradiation of the signal at δ 1.20 (Me-29) caused an NOE enhancement of the br. d at δ 4.09 (21-H) and vice versa, suggesting the configuration of this proton to be α. These diagnostic enhancements observed are depicted in Figure 2.

Based on the above evidence, the structure of kokoondiol should also be revised from 21α,27-dihydroxy-D:A-*friedo*-oleanan-3-one (**9**) to 21β,26-dihydroxy-D:A-*friedo*-oleanan-3-one (**2**). Similar NOE enhancement studies on kokoononol and kokzeylanol suggested that their structures should be revised from 27-hydroxy-D:A-*friedo*-oleanane-3,21-dione (**11**) to 26-hydroxy-D:A-*friedo*-oleanane-3,21-dione (**3**) and 6β,27-dihydroxy-D:A-*friedo*-oleanan-3-one (**12**) to 6β,26-dihydroxy-D:A-*friedo*-oleanan-3-one (**4**). Since kokoonol and kokzeylanonol were related to kokoondiol (**2**) and kokzeylanol (**4**),[1,2] the structures of the former two triterpenoids should also be revised to 26-hydroxy-D:A-*friedo*-oleanan-3-one (**5**) and 6β,26-dihydroxy-D:A-*friedo*-oleanane-3,21-dione (**6**), respectively.

EXPERIMENTAL

General Experimental Procedures. TLC involved Si gel GF; visualization was by spraying with acidified anisaldehyde followed by charring with heat; Prep. TLC used 1.0 mm layers of Si gel $PF_{254-366}$. Flash chromatography involved Si gel of mesh 30-70; Mp was determined on a Koffler hot-stage apparatus and is uncorrected; Optical rotation determined on a Perkin-Elmer 241 polarimeter; IR spectrum was recorded for KBr disc with a Shimadzu IR-408 spectrometer; MS was recorded on a JEOL JMS-D300 with a direct inlet system; NMR spectra were measured on a JEOL JNM-GX 400 spectrometer in d_5-pyridine with TMS as an internal standard. Mutiplicities of carbon signals were determined by means of DEPT. 2D NMR spectra were measured with the same instrument by the use of the JEOL standard pulse sequences (VCOSYN, VBDCHSHF, and VCHSHF) and collected data were treated by the JEOL standard software. Difference NOE spectra were taken with a JEOL JNM-GX 400 spectrometer in d_5-pyridine by the use of the JEOL standard pulse sequence (DIFNOE 2) at 25°C with 5 s irradiation. The collected data were treated by the JEOL standard software.

Plant Material. The root bark of *S. reticulata* var. β-diandra was collected at Sinharaja forest in Sri Lanka under the auspices of late Prof. S. Balasubramaniam, Department of Botany, University of Peradeniya, Sri Lanka, where voucher specimens are maintained.

Extraction and Isolation. The coloured outer root bark was separated from the inner root bark, dried and powdered. The processed outer root bark (375 g) was successively and exhaustively extracted with hexanes and benzene. Evaporation yielded the hexanes (35 g) and benzene (65 g) extracts as bright red solids. The benzene extract (35 g) was subjected to flash chromatography and eluted with various mixtures of hexane, EtOAc and MeOH in increasing polarity to yield a total of 100 x 50 ml fractions. Further purification of the combined column fractions 32-37 (3.8 g) by flash chromatography followed by prep. TLC afforded *epi*-kokoondiol (23 mg, 0.006%) as a colourless crystalline solid.

Epi-kokoondiol (1). Mp 269-70°; $[\alpha]_D^{25}$ -28° (c 1.1 in $CHCl_3$) (lit.[5] mp 271-73°, $[\alpha]_D$ -29°); IR υ_{max} 3490 (OH) and 1705 cm^{-1} (C=O); EIMS m/z (%): 458 (2), 440 (9), 427 (50), 409 (100), 339 (4), 299 (3), 287 (5), 273 (10), 259 (65), 245 (48), 233 (15), 231 (18), 205 (29), 203 (30), 201 (20), 189 (29), and 167 (25); ^1H NMR (see Table 1); ^{13}C NMR (see Table 2).

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