13α*H*-Olean-18-ene Derivatives. Forced Wolff-Kishner Reduction Products of 19-Oxoolean-12-ene Derivatives[1]

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Methyl 2α,3β,23-triacetoxy-13α*H*-olean-18-en-28-oate (**4**) and methyl 2α,3β-diacetoxy-13α*H*-olean-18-en-28-oate (**7**) were obtained from methyl 2α,3β,23-triacetoxy-19-oxoolean-12-en-28-oate (**2**) and from methyl 2α,3β-diacetoxy-19-oxoolean-12-en-28-oate (**5**), respectively, by the forced Wolff-Kishner reduction and subsequent acetylation and methylation. Methyl 2α,3β-diacetoxy-13β*H*-olean-18-en-28-oate (**10**), prepared from methyl 2,3-di-*O*-acetylarjunate (**13**) *via* methyl 2α,3β-diacetoxy-19α-hydroxy-12-oxooleanan-28-oate (**18**) and methyl 2α,3β-diacetoxy-19α-hydroxyoleanan-28-oate (**19**), was shown to be not identical with **7**. This led to a 13α*H*-olean-18-ene structure for **7**.

It is well known that the reduction of sterically hindered ketones, such as 11-oxosteroids, is not easily effected using the usual Wolff-Kishner procedure, while modified procedures under forced reaction conditions developed by Barton[2] or Nagata[3] are successfully applied to the reduction of hindered or masked carbonyl groups.

In connection with the structure determination of arjungenin (**1**),[4] a new constituent of *Terminalia arjuna*, a forced Wolff-Kishner reduction of methyl 2α,3β,23-triacetoxy-19-oxoolean-12-en-28-oate (**2**)[4] derived from **1**, was attempted aiming at the conversion into the known compound, methyl 2,3,23-tri-*O*-acetylarjunolate (**3**).[5] The 19-oxoolean-12-ene derivative (**2**) was subjected to a forced Wolff-Kishner reduction modified by Nagata under conditions described as procedures "A" and "B",[3] followed by acetylation and methylation. However, the resulting products were so complex that no definite product could be separated. The reduction of **2** using Barton's procedure[2] and subsequent methylation and acetylation gave a trisubstituted olefin (**4**; yield 32 %) as a sole reaction product, which was found to be not identical with methyl 2,3,23-tri-*O*-acetylarjunolate (**3**).

In order to obtain information on the structure of the reduction product (**4**), a simpler model compound of **2**, methyl 2α,3β-diacetoxy-19-oxoolean-12-en-28-oate (**5**)[6] derived from arjunic acid (**6**),[6] was subjected to the Wolff-Kishner reduction by Barton's procedure.[2] The reduction product, after acetylation and methylation, was separated by column chromatography into an olefin (**7**; yield 46 %) and an α,β-unsaturated ketone (**8**; yield 20 %). This olefin (**7**), mp 224—225 °C, $[\alpha]_D$ +71°, was indicated to be a pentacyclic trisubstituted monoolefin having a methoxycarbonyl and two acetoxyl groups by IR (1740 and 1630 cm^{-1}), PMR [δ 1.98, 2.05 (each 3H, s; 2×CH_3COO–), 3.64 (3H, s; –$COOCH_3$), and 5.30 (1H, sharp singlet)], and mass spectrum ($C_{35}H_{54}O_6$), but was shown not to be an expected deoxygenated product, methyl 2,3-di-*O*-acetylmasulinate (**9**; =methyl 2α,3β-diacetoxyolean-12-en-28-oate, mp 184—186 °C, $[\alpha]_D$ +33.5°, IR 1730, 1720, 1659, and 819 cm^{-1})[7] by comparison with their melting points and spectral data. Although the mass spectrum of **7** showed peaks at *m/e* 249, 248, and 189, characteristic for Δ^{18}-oleanene derivatives,[8] this olefin (**7**) was found to be not identical with methyl 2α,3β-diacetoxyolean-18-en-28-oate (**10**) as described below. The olefin (**7**), therefore, was inferred to be methyl 2α,3β-diacetoxy-13α*H*-olean-18-en-28-oate, and the proposed structure was supported by the following transformation and evidence.

On oxidation with selenium dioxide in acetic acid, the olefin (**7**) gave a known diene, methyl 2α,3β-diacetoxyoleana-12,18-dien-28-oate (**11**),[6] which was further converted into methyl 2α,3β-diacetoxyoleana-11,13(18)-dien-28-oate (**12**) by treatment with hydrochloric acid in chloroform. This diene (**12**) proved to be identical with the diene (**12**)[6] prepared by dehydration of methyl 2,3-di-*O*-acetylarjunate (**13**)[6] followed by isomerization according to the known procedures.[6]

Methyl *O*-acetylmorolate (**14**; =methyl 3β-acetoxyolean-18-en-28-oate) has been prepared from methyl 3-*O*-acetylsiaresinolate (**15**; =methyl 3β-acetoxy-19α-hydroxyolean-12-en-28-oate) *via* a 12-keto 19α-ol (**16**) and a 19α-ol (**17**) by Barton *et al.*[9] By the same procedures, methyl 2,3-di-*O*-acetylarjunate (**13**; =methyl 2α,3β-diacetoxy-19α-hydroxyolean-12-en-28-oate)[4,6] was converted into methyl 2α,3β-diacetoxyolean-18-en-28-oate (**10**). Arjunic acid (**6**), isolated from *Terminalia arjuna*,[4,6] was converted into methyl 2,3-di-*O*-acetylarjunate (**13**), which was treated with hydrogen peroxide in acetic acid to yield a 12-keto alcohol (**18**). The keto alcohol (**18**) showed IR absorption bands at 3500, 1750, 1730, 1720, and 1690 cm^{-1}. In the PMR spectrum of **18**, a signal due to $C_{(19\beta)}$–H appears at δ 4.55 as a triplet-like, which, on addition of D_2O, changes into a doublet (J=3.5 Hz). A doublet (J=7 Hz) due to $C_{(13\beta)}$–H was also observed at δ 3.10 and a double doublet (J=7 and J=3.5 Hz) due to $C_{(18\beta)}$–H at δ 2.90. The 13β*H*-configuration of **18** was suggested by the following attempted isomerization reaction. The ketone (**18**) was treated with potassium hydroxide in boiling ethanol and the reaction product was then acetylated to give the starting material in 50 % yield.

The ketone (**18**) was subjected to the Wolff-Kishner reduction and the product was then methylated and acetylated to give a mixture of deoxygenated alcohols (**19** and **20**), which was separated by silica gel column chromatography. An alcohol (**19**) showed a doublet (J=2 Hz) due to $C_{(19\beta)}$–H at δ 3.37, while a diastereomeric alcohol (**20**) at δ 3.40 as a doublet (J=5 Hz). The alcohols (**19** and **20**) were then oxidized with the Jones reagent to yield the corresponding ketones (**21** and **22**), respectively. In the PMR spectrum of **21**, a signal due to $C_{(18\beta)}$–H appeared at δ 3.15 as a doublet

($J_{13\beta,18\beta}$=4 Hz), while in **22** $C_{(18\beta)}$–H resonated at δ 3.28 as a doublet ($J_{13\alpha,18\beta}$=12 Hz). The CD values were $\Delta\varepsilon_{302}$=+1.60 and $\Delta\varepsilon_{302}$=−0.11 for **21** and **22**, respectively. The coupling constant, $J_{13,18}$ and CD values led to a 13β*H*- and a 13α*H*-configuration for **21** and **22**, respectively. Therefore a configuration at C-13 of the alcohol (**19**) was inferred to be 13β*H* (with an axial 19α-OH), and that of **20** 13α*H* (with an equatorial 19α-OH).

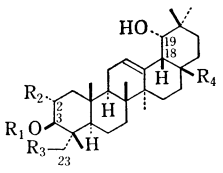
The alcohol (**19**) was treated with phosphoryl chloride in pyridine to afford an 18-ene (**10**), whose configuration at C-13 must be β*H*. The PMR spectrum of **10** showed a signal due to $C_{(19)}$–H at δ 5.10 as a singlet, and the mass spectrum gave fragment peaks characteristic for Δ^{18}-oleanene derivatives[8] at *m/e* 249 and 189, together with a molecular ion peak at *m/e* 570.3912 (M^+; *m/e* 570.3917 calcd for $C_{35}H_{54}O_6$). The isomeric alcohol (**20**), on dehydration under the same conditions, gave a 13(18)-ene (**23**), whose PMR spectrum showed no signal due to olefin proton. This olefin (**23**) was also obtainable by catalytic hydrogenation of the known methyl 2α,3β-diacetoxyoleana-11,13(18)-dien-28-oate (**12**).[6]

The 13β*H*-18-ene (**10**) thus prepared was found to be not identical with the olefin (**7**), obtained by the forced Wolff-Kishner reduction of methyl 2α,3β-diacetoxy-19-oxoolean-12-en-28-oate (**5**). The structure of the olefin (**7**) should therefore be formulated as methyl 2α,3β-diacetoxy-13α*H*-olean-18-en-28-oate.

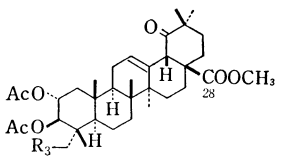
From this observation, the structure of the trisubstituted olefin (**4**), formed by the forced Wolff-Kishner reduction of methyl 2α,3β,23-triacetoxy-19-oxoolean-12-en-28-oate (**2**)[4,10] and by successive methylation and acetylation, was suggested to be methyl 2α,3β,23-triacetoxy-13α*H*-olean-18-en-28-oate. The spectral data are compatible with the proposed structure (**4**). The mass spectrum of **4** showed peaks characteristic for Δ^{18}-oleanene derivatives[8] at *m/e* 249, 248, and 189. In the PMR spectrum, a sharp singlet due to an olefinic proton at C-19 appeared at δ 5.30. This δ-value was identical with that for $C_{(19)}$–H of methyl 2α,3β-diacetoxyolean-18-en-28-oate (**7**) with a 13α*H*-configuration, while differed from those for $C_{(19)}$–H of the 13β*H*-18-ene (**10**; δ 5.10) and of methyl *O*-acetylmorolate (**14**; δ 5.07)[11] with a 13β*H*-configuration.

Triterpenes with an olean-18-ene framework hitherto reported, germanicol (**24**),[12] miliacin (**25**),[13] morolic acid (**26**),[9,14] germanidiol (**27**; =2β-hydroxygermanicol),[15] and epigermanidiol (**28**; =2α-hydroxygermanicol)[16], are all in $C_{(13)}$–β*H* configuration, and neither isolation nor preparation of olean-18-ene derivative with a 13α*H*-configuration has yet been described. Methyl 2α,3β,23-triacetoxy-13α*H*-olean-18-en-28-oate (**4**) and methyl 2α,3β-diacetoxy-13α*H*-olean-18-en-28-oate (**7**) are the first examples of 13α*H*-olean-18-ene derivatives.

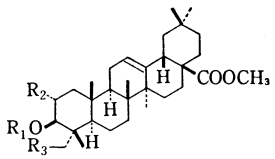
The structure of the α,β-unsaturated ketone (**8**), obtained by the forced Wolff-Kishner reduction of **5**, was inferred to be **8** from the IR (1730 and 1680 cm^{-1}), UV λ_{max} 253 nm (log ε 3.81), PMR (absence of olefinic proton), and mass spectral data *m/e* 584.3682 (M^+; *m/e* 584.3709 calcd for $C_{35}H_{52}O_7$) and *m/e* 188.



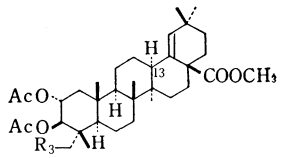
	R_1	R_2	R_3	R_4
1	H	OH	OH	COOH
6	H	OH	H	COOH
13	Ac	OAc	H	$COOCH_3$
15	Ac	H	H	$COOCH_3$



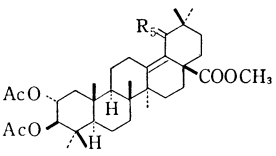
	R_3
2	OAc
5	H



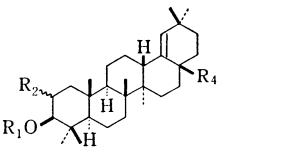
	R_1	R_2	R_3
3	Ac	OAc	OAc
9	Ac	OAc	H
29	H	OH	OH



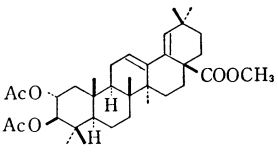
	R_3
4	OAc
7	H



	R_5
8	O
23	H_2



	R_1	R_2	R_4
10	Ac	α-OAc	$COOCH_3$
14	Ac	H	$COOCH_3$
24	H	H	CH_3
25	CH_3	H	CH_3
26	H	H	COOH
27	H	β-OH	$COOCH_3$
28	H	α-OH	$COOCH_3$



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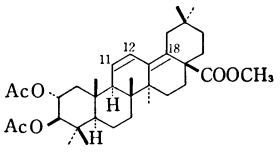

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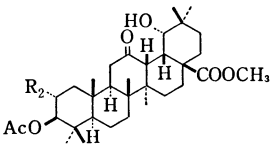
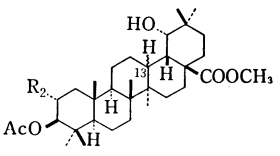
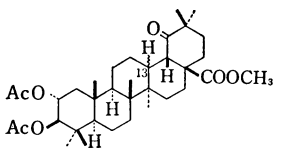


	R_2
16	H
18	OAc



	R_2	13H
17	H	β
19	OAc	β
20	OAc	α



21	13β-H
22	13α-H

Although the formation mechanism of 13α*H*-olean-18-ene derivatives from 19-oxoolean-12-enes is not clearly elucidated, a mechanism *via* 19-oxoolean-13(18)-ene seems to be likely. It has been reported that olean-12-en-19-one derivatives undergo isomerization in the presence of alkali to give the corresponding olean-13(18)-en-19-one derivatives.[6,10,17] And α,β-unsaturated carbonyl compounds, on Wolff-Kishner reduction, often afford abnormal deoxygenated products in which a migration of the double bond has occurred, together with the normal products.[18] Under the forced Wolff-Kishner reduction conditions, a 19-oxoolean-12-ene derivative (**5**) must have isomerized into the corresponding α,β-unsaturated ketone (**8**). This compound (**8**) was subjected to the forced Wolff-Kishner reduction to give 13α*H*-olean-18-ene (**7**) in 19 % yield, after acetylation and methylation of the product, while the corresponding normal deoxygenated product, olean-13(18)-ene derivative (**23**) was not obtained.

The formation reaction of 13α*H*-olean-18-ene derivatives (**4** and **7**) was stereospecific and no 13β*H*-diastereomer was detected. The stereospecificity may be due to a structure feature around the C/D/E rings of olean-13(18)-en-19-one derivatives and/or of their nitrogen-containing intermediates.

Experimental

General indications in Experimental were the same as described in a previous paper.[4] Anhydrous hydrazine was prepared by Kusama's procedure.[19] Diethylene glycol was distilled and dried over Molecular Sieves. The forced Wolff-Kishner reduction was carried out in an argon atmosphere.

Forced Wolff-Kishner Reduction of Methyl 2α,3β,23-Triacetoxy-19-oxoolean-12-en-28-oate (2) Followed by Methylation and Acetylation. Methyl 2α,3β,23-triacetoxy-19-oxoolean-12-en-28-oate (**2**; 66 mg)[4] was treated with diethylene glycol (3 ml), sodium (68 mg), and anhydrous hydrazine (1 ml) according to the Barton procedure.[2] The reaction product, without purification, was subjected to methylation with diazomethane in ether and then to acetylation with acetic anhydride in pyridine to give a crude product (*ca.* 47 mg). The product in benzene was passed through a column of silica gel (10 g) and the following solvents were used as eluent (each 40 ml): fr. 1, benzene; fr. 2, benzene-acetone (200:3); frs. 3—8, benzene-acetone (100:3). Fractions 5 and 6 were combined (*ca.* 17 mg) and purified by preparative TLC, developed with benzene-acetone (16:1) to give methyl 2α,3β,23-triacetoxy-13α*H*-olean-18-en-28-oate (**4**; 13 mg), as amorphous solid, $[\alpha]_D$ +70° (*c* 0.16, EtOH), IR (Nujol) 1740 (br), 1730, 1715 (sh), 1240, 1225, 1045, and 1030 cm^{-1}; PMR* ($CDCl_3$) δ 0.83, 0.90, 1.12 (each 3H, s; *t*-Me), 0.98 (9H, s; 3×*t*-Me), 1.99, 2.01, 2.08 (each 3H, s; -OAc), 3.65 (3H, s; $-CO_2Me$), 3.58, 3.82 (2H, ABq, *J*=12 Hz; $C_{(23)}H_2$-OAc), 5.10 (2H, m; $C_{(2\beta)}$-H and $C_{(3\alpha)}$-H), 5.30 (1H, s; $C_{(19)}$-H); MS *m/e* 628 (M^+), 626, 569, 568, 466, 449, 448, 435, 433, 392, 262, 249, 248, 245, 203, 189 (base peak), 185, and 175.

Forced Wolff-Kishner Reduction of Methyl 2α,3β-Diacetoxy-18-oxoolean-12-en-28-oate (5) Followed by Acetylation and Methylation. Methyl 2α,3β-diacetoxy-19-oxoolean-12-en-28-oate (**5**; 120 mg) was subjected to the forced Wolff-Kishner reduction by the same procedure [diethylene glycol (*ca.* 6 ml), sodium (136 mg), and anhydrous hydrazine (1.5 ml)] as above, and the reaction product (*ca.* 84 mg) was acetylated with acetic anhydride in pyridine to give an acetylated product. This was purified by column chromatography on silica gel (15 g) eluting with the following solvents; fr. 1, benzene-acetone (100:1, 30 ml); fr. 2, benzene-acetone (50:1, 30 ml); frs. 3 and 4, benzene-acetone (100:3, each 30 ml); frs. 5—10, benzene-acetone (25:1, each 15 ml), and frs. 11—21, benzene-acetone (20:1, each 30 ml). From the fractions 6—8, a diacetate (*ca.* 52 mg) was obtained as amorphous solid, IR (KBr) 1738, 1700, 1630, 1250, 1230, 1045, and 1035 cm^{-1}; PMR ($CDCl_3$) δ 0.92, 0.98 (each 9H, s; 3×*t*-Me), 1.09 (3H, s; *t*-Me), 1.98, 2.05 (each 3H, s; -OAc), 4.75 (1H, d, *J*=11 Hz; $C_{(2\alpha)}$-H), 5.15 (1H, ddd, *J*=11, *J*=11, and *J*=4 Hz; $C_{(2\beta)}$-H), and 5.34 (1H, s; $C_{(19)}$-H); MS *m/e* 512 (M^+-CO_2), 510, 497, 452, 437, 409, 392, 349, 334, 247, 233, 215, 203, and 190 (base peak). Fractions 14—19 gave an α,β-unsaturated keto acid (23 mg).

The diacetate, above obtained, was treated with diazomethane in ether to give methyl 2α,3β-diacetoxy-13α*H*-olean-18-en-23-oate (**7**), which was crystallized from ethanol to afford white needles (38 mg), mp 224—225 °C, $[\alpha]_D$ +71° (*c* 1.38, EtOH); IR (KBr) 1740, 1725 (sh), 1630, 1250, and 1230 cm^{-1}; PMR ($CDCl_3$) δ 0.83, 1.10 (each 3H, s; *t*-Me), 0.91 (9H, s; 3×*t*-Me), 0.98 (6H, s; 2×*t*-Me), 1.98, 2.05 (each 3H, s; -OAc), 3.64 (3H, s; $-CO_2Me$), 4.75 (1H, d, *J*=11 Hz; $C_{(2\alpha)}$-H), 5.15 (1H, ddd, *J*=11, *J*=11, and *J*=4 Hz; $C_{(2\beta)}$-H), and 5.30 (1H, s; $C_{(19)}$-H); mol wt *m/e* 570.3830. Calcd for $C_{35}H_{54}O_6$: *m/e* 570.3917. MS *m/e* 570 (M^+), 568, 511, 510, 495, 450, 435, 409, 407, 334, 259, 249, 248, 247, 235, 234, 233, 215, 203, 189 (base peak), 187, and 175.

The α,β-unsaturated keto acid, on treatment with diazomethane, was converted into methyl 2α,3β-diacetoxy-19-oxoolean-13(18)-en-28-oate (**8**), mp 223—224°C (crystallized from ether); $[\alpha]_D$ −154° (*c* 0.94, $CHCl_3$); IR (KBr) 1730, 1660, 1240, 1230, and 1040 cm^{-1}; UV (EtOH) λ_{max} 253 nm (log ε 3.81); PMR ($CDCl_3$) δ 0.85, 1.12, 1.23 (each 3H, s; *t*-Me), 0.90, 1.06 (each 6H, s; 2×*t*-Me), 1.99, 2.06 (each 3H, s; -OAc), 3.64 (3H, s; $-CO_2Me$), 4.76 (1H, d, *J*=11 Hz; $C_{(3\alpha)}$-H), 5.18 (1H, ddd, *J*=11, *J*=11 and *J*=4 Hz; $C_{(2\beta)}$-H), and the absence of olefinic proton; mol wt *m/e* 584.3682. Calcd for $C_{35}H_{52}O_7$: *m/e* 584.3709. MS *m/e* 584 (M^+), 524, 482, 464, 405, and 188 (base peak).

Oxidation of Methyl 2α,3β-Diacetoxy-13αH-olean-18-en-28-oate (7) with Selenium Dioxide. A mixture of **7** (32.5 mg) and selenium dioxide (15.2 mg) in acetic acid (3 ml) was heated under reflux for 6 h. Usual work-up gave a residue (33 mg), which was subjected to purification by preparative TLC, developed with benzene-acetone (50:3), to give methyl 2α,3β-diacetoxyoleana-12,18-dien-28-oate (**11**; 21 mg), mp 245—247 °C (crystallized from ethanol); $[\alpha]_D$ +64° (*c* 1.0, EtOH); IR (KBr) 1733, 1720 (sh), 1630, 1250, 1225, and 1040 cm^{-1}; UV (EtOH) λ_{max} 235 nm (log ε 3.9); PMR ($CDCl_3$) δ 0.90, 1.11 (each 3H, s; *t*-Me), 0.91 (6H, s; 2×*t*-Me), 1.00 (9H, s; 3×*t*-Me), 1.99, 2.05 (each 3H, s; -OAc), 3.61 (3H, s; $-CO_2Me$), 4.76 (1H, d, *J*=11 Hz; $C_{(2\alpha)}$-H), 5.16 (1H, ddd, *J*=11, *J*=11, and *J*=4 Hz; $C_{(2\beta)}$-H), 5.47 (1H, s; $C_{(19)}$-H), and 5.57 (1H, t-like; $C_{(12)}$-H); mol wt *m/e* 568.3708. Calcd for $C_{35}H_{52}O_6$: *m/e* 568.3760; MS *m/e* 568 (M^+), 509, 448, 433, 389, 367, 260, 247, and 201 (base peak).

Isomerization of Methyl 2α,3β-Diacetoxyoleana-12,18-dien-28-oate (11) into Methyl 2α,3β-Diacetoxyoleana-11,13-dien-28-oate (12). The diene (**11**; 21 mg) was dissolved in chloroform (3 ml) and dry hydrogen chloride was passed through the solution for 1.5 h. Usual treatment gave a residue (16 mg), which

* PMR spectra were measured using a Hitachi R-20 (60 MHz) spectrometer unless otherwise stated.

was shown to be completely isomerized into methyl 2α,3β-diacetoxyoleana-11,13-dien-28-oate (**12**) by PMR examination. The diene (**12**): mp 186.5—188.5 °C (crystallized from ethanol); $[\alpha]_D$ −128° (*c* 0.125, EtOH); IR (KBr) 1730, 1725 (sh), 1700 (sh), 1630, 1245, 1230 (sh), 1042, and 1030 cm^{-1}; UV (EtOH) λ_{max} 243.5 (log ε 4.31), 251.5 (4.36), and 260.5 nm (4.16); PMR ($CDCl_3$) δ 0.80 (6H, s; 2×*t*-Me), 0.91 (12H, s; 4×*t*-Me), 1.08 (3H, s; *t*-Me), 2.00, 2.06 (each 3H, s; -OAc), 3.66 (3H, s; $-CO_2Me$), 4.76 (1H, d, *J*=11 Hz; $C_{(3\alpha)}$-H), 5.15 (1H, ddd, *J*=11, *J*=11, and *J*=4 Hz; $C_{(2\beta)}$-H), 5.58 (1H, d, *J*=11 Hz; $C_{(12)}$-H), and 6.48 (1H, dd, *J*=11 and *J*=2 Hz; $C_{(11)}$-H); mol wt *m/e* 568.3698. Calcd for $C_{35}H_{52}O_6$: *m/e* 568.3760; MS *m/e* 568 (M^+), 509, 448, 433, 389, 367, and 187 (base peak). This diene was found to be identical with the diene (**12**)[6] prepared from methyl 2,3-di-*O*-acetylarjunate (**13**)[4,6] according to the known procedures.[6]

*Oxidation of Methyl 2,3-Di-O-acetylarjunate (**13**) with Hydrogen Peroxide.* A solution of methyl 2,3-di-*O*-acetylarjunate (**13**; 102 mg)[4,6] in acetic acid (8 ml) was treated dropwise at 70—75 °C with a mixture of acetic acid (1 ml) and hydrogen peroxide (35 %, 1 ml) according to the Barton procedure.[9] Usual treatment gave a residue (*ca.* 100 mg), which was purified by column chromatography on silica gel (15 g). Elution was carried out with the following solvents: fr. 1, benzene–acetone (50:1, 30 ml); fr. 2, benzene–acetone (100:3, 30 ml); frs. 3 and 4, benzene–acetone (25:1, each 15 ml), frs. 5—10 (each 10 ml), frs. 11 and 12 (each 15 ml). Fractions 6—8, on evaporation of the solvents, gave a residue (*ca.* 70 mg), which was crystallized from ether to give methyl 2α,3β-diacetoxy-19α-hydroxy-12-oxooleanan-28-oate (**18**; 32 mg) as white needles, mp 272—273 °C; $[\alpha]_D$ −25° (*c* 1.11, $CHCl_3$); IR (Nujol) 3500, 1750, 1730, 1720, 1690, 1260, 1230, and 1045 cm^{-1}; PMR ($CDCl_3$) δ 0.91, 0.98, 1.01 (each 6H, s; 2×*t*-Me), 1.15 (3H, s; *t*-Me), 1.99, 2.05 (each 3H, s; -OAc), 2.90 (1H, dd, *J*=7 and *J*=3.5 Hz; $C_{(18)}$-H), 3.10 (1H, d, *J*=7 Hz; $C_{(13)}$-H), 3.70 (3H, s; $-CO_2Me$), 4.55 [1H, t-like; $C_{(19\beta)}$-H; on addition of D_2O, this signal changes into a doublet (*J*=3.5 Hz)], 4.75 (1H, d, *J*=11 Hz; $C_{(3\alpha)}$-H), and 5.10 (1H, ddd, *J*=11, *J*=11, and *J*=4 Hz; $C_{(2)}$-H); MS *m/e* 602 (M^+), 584, 569, 543, 525, 524, 482, 465, 464, and 276 (base peak); Found: C, 68.59; H, 9.09%. Calcd for $C_{35}H_{54}O_8 \cdot 1/2\ H_2O$: C, 68.71; H, 9.06%.

*Treatment of Methyl 2α,3β-Diacetoxy-19α-hydroxy-12-oxooleanan-28-oate (**18**) with Alkali.* A mixture of **18** (28 mg) in methanol (5 ml) containing potassium hydroxide (400 mg) was heated under reflux for 2 h. After usual work-up, a residue was acetylated with acetic anhydride in pyridine and crystallized from ether to afford white needles, which were chromatographed on silica gel (5 g), eluting with the following solvents: fr. 1, benzene–acetone (50:1, 10 ml); fr. 2, benzene–acetone (100:3, 10 ml); and frs. 3—11, benzene–acetone (25:1, each 5 ml). Fractions 6—8, on evaporation of the solvents, afforded crystals, which were identical with the starting material in respect to IR, PMR, and TLC.

*Wolff-Kishner Reduction of Methyl 2α,3β-Diacetoxy-19α-hydroxy-12-oxooleanan-28-oate (**18**) Followed by Methylation and Acetylation. i) By the Barton Procedure.* To a boiling mixture of sodium (106 mg) in diethylene glycol (5 ml) and anhydrous hydrazine (1 ml), methyl 2α,3β-diacetoxy-19α-hydroxy-12-oxo-oleanan-28-oate (**18**; 100 mg) was added. The reaction mixture was treated according to the Barton procedure[2] to afford a residue, which was methylated with diazomethane and then acetylated with acetic anhydride in pyridine. The product, dissolved in benzene, was passed through a column of silica gel (15 g) and eluted with the following solvents: fr. 1, benzene–acetone (100:1, 30 ml); frs. 2 and 3, benzene–acetone (50:1, each 15 ml); frs. 4—15, benzene–acetone (100:3, each 10 ml). A 13β*H*-alcohol (**19**; 33 mg) was obtained from fractions 7 and 8, as amorphous solid, IR (Nujol) 3500, 1740, 1240, and 1230 cm^{-1}; PMR ($CDCl_3$) δ 0.88 (12H, s; 4×*t*-Me), 0.96 (6H, s; 2×*t*-Me), 1.17 (3H, s; *t*-Me), 1.97, 2.03 (each 3H, s; -OAc), 3.37 (1H, d, *J*=2 Hz; $C_{(19)}$-H), 3.70 (3H, s; $-CO_2Me$), 4.75 (1H, d, *J*=11 Hz; $C_{(3\alpha)}$-H), and 5.13 (1H, ddd, *J*=11, *J*=11, *J*=4 Hz; $C_{(2)}$-H); MS *m/e* 570 (M^+-H_2O), 528, 510, 495, 486, 468, 450, 435, and 189 (base peak). Fractions 9—12 gave a 13α*H*-alcohol (**20**; 26 mg) as amorphous solid, IR (Nujol) 3500, 1740, 1725 (sh), 1245, and 1225 cm^{-1}; PMR ($CDCl_3$) δ 0.90 (9H, s; 3×*t*-Me), 0.97, 1.03, 1.09, 1.25 (each 3H, s; *t*-Me), 1.98, 2.04 (each 3H, s; -OAc), 3.40 (1H, d, *J*=5 Hz; $C_{(19)}$-H), 3.69 (3H, s; $-CO_2Me$), 4.75 (1H, d, *J*=11 Hz; $C_{(3\alpha)}$-H), and 5.15 (1H, ddd, *J*=11, *J*=11, and *J*=4 Hz; $C_{(2)}$-H); MS *m/e* 570 (M^+-H_2O), 528, 510, 495, 486, 468, 450, 435, and 189 (base peak). *ii) By the Huang-Minlon Procedure.* A mixture of **18** (47 mg), potassium hydroxide (500 mg), anhydrous hydrazine (0.6 ml), and diethylene glycol (4.7 ml) was heated under reflux for 1.5 h and excess hydrazine and water were distilled off. Then reflux was continued at 220 °C for 7 h. After usual work-up, acetylation and methylation were followed. The reaction mixture was subjected to column chromatographic separation on silica gel (5 g), eluting with benzene–acetone (100:1, 10 ml; fr. 1); benzene–acetone (50:1, 10 ml; fr. 2), and then benzene–acetone (100:3, each 5 ml; frs. 3—12). Fractions 5 and 6 gave the 13β*H*-alcohol (**19**; 21.4 mg) and fractions 7—9 the 13α*H*-alcohol (**20**; 14.5 mg).

*Oxidation of Methyl 2α,3β-Diacetoxy-19α-hydroxyoleanan-28-oate (**19**) with Jones Reagent.* A solution of **19** (19 mg) in acetone (1.5 ml) was cooled at 0 °C and Jones reagent (0.2 ml) was added with stirring. After usual work-up, the reaction product was dissolved in benzene and passed through a column of silica gel (5 g) and eluted with the following solvents: fr. 1, benzene–acetone (200 : 1, 20 ml); frs. 2—17, benzene–acetone (50 : 1, each 2.5 ml). Fractions 10 and 11, on evaporation of the solvents, gave methyl 2α,3β-diacetoxy-19-oxooleanan-28-oate (**21**; 9.6 mg) as amorphous solid, IR (KBr) 1730, 1720 (sh), 1695 (sh), 1245, and 1230 cm^{-1}; CD (*c* 0.0024, EtOH) $\Delta\varepsilon_{302}$ +1.60; PMR (100 MHz**, $CDCl_3$) δ 0.84, 0.94, 0.98, 1.01, 1.12 (each 3H, s; *t*-Me), 0.86 (6H, s; 2×*t*-Me), 1.94, 2.01 (each 3H, s; -OAc), 3.15 (1H, d, $J_{13\beta,18\beta}$=4 Hz; $C_{(18\beta)}$-H), 3.70 (3H, s; $-CO_2Me$), 4.70 (1H, d, *J*=11 Hz; $C_{(3\alpha)}$-H), and 5.06 (1H, ddd, *J*=11, *J*=11, and *J*=4 Hz; $C_{(2)}$-H); mol wt *m/e* 586.3899. Calcd for $C_{35}H_{54}O_7$: *m/e* 586.3867; MS *m/e* 586 (M^+), 527, 526, 484, 467, 466, 451, 425, 407, and 205 (base peak).

*Oxidation of Methyl 2α,3β-Diacetoxy-19α-hydroxy-13α*H*-oleanan-28-oate (**20**) with Jones Reagent.* A solution of **20** (14 mg) in acetone (1.5 ml) was oxidized with Jones reagent (0.2 ml) as the same as above. Usual treatment and purification gave methyl 2α,3β-diacetoxy-19-oxo-13α*H*-oleanan-28-oate (**22**), mp 204—209 °C; IR (KBr) 1730, 1710 (sh), 1690, 1240, and 1225 cm^{-1}; CD (*c* 0.0025, EtOH) $\Delta\varepsilon_{302}$ −0.11; PMR (100 MHz, $CDCl_3$) δ 0.86, 0.88, 1.08, 1.14 (each 3H, s; *t*-Me), 1.02 (9H, s; 3×*t*-Me), 1.95, 2.00 (each 3H, s; -OAc), 3.28 (1H, d, $J_{13\alpha,18\beta}$=12 Hz, $C_{(18\beta)}$-H), 3.64 (3H, s; $-CO_2Me$), 4.69 (1H, d, *J*=11 Hz; $C_{(3\alpha)}$-H), and 5.10 (1H, ddd, *J*=11, *J*=11, and *J*=4 Hz; $C_{(2)}$-H); MW *m/e* 586.3879. Calcd for $C_{35}H_{54}O_7$: *m/e* 586.3867; MS *m/e* 586 (M^+), 527, 526, 484, 467, 466, 451, 425, 407, and 205 (base peak).

** PMR (100 MHz) spectra were measured with a JEOL 4H-100 spectrometer.

*Dehydration of Methyl 2α,3β-Diacetoxy-19α-hydroxyoleanan-28-oate (**19**).* A solution of **19** (21 mg) in pyridine (0.7 ml) and phosphoryl chloride (0.1 ml) was heated under reflux for 4 h and then treated as usual to afford a residue (19 mg). The residue was dissolved in benzene and passed through a column of silica gel (3 g) and eluted with benzene (6 ml; fr. 1), benzene–acetone (100 : 1, 6 ml; fr. 2), and with benzene–acetone (50 : 1, each 6 ml; frs. 3—9) successively. The fractions 5 and 6 were combined and further subjected to purification by preparative TLC on Kieselgel PF_{254} developed with benzene–acetone (20 : 1) to give methyl 2α,3β-diacetoxy-olean-18-en-28-oate (**10**; 6 mg), mp 232—233 °C (crystallized from ethanol), $[\alpha]_{450}$ −38° (*c* 0.13, EtOH); IR (KBr) 1740 (br), 1630, 1245, and 1230 cm^{-1}; PMR ($CDCl_3$) δ 0.78, 1.02 (each 3H, s; *t*-Me), 0.90 (6H, s; 2×*t*-Me), 0.98 (9H, s; 3×*t*-Me), 1.98, 2.04 (each 3H, s; -OAc), 3.66 (3H, s; $-CO_2Me$), 4.75 (1H, d, J=11 Hz; $C_{(3\alpha)}$–H), 5.10 (1H, s; $C_{(19)}$–H), and 5.15 (1H, ddd, J=11, J=11, and J=4 Hz; $C_{(2\beta)}$–H); mol wt *m/e* 570.3912. Calcd for $C_{35}H_{54}O_6$: *m/e* 570.3917; MS *m/e* 570 (M^+), 555, 538, 511, 510, 495, 468, 451, 450, 436, 435, 409, 407, 391, 249, 203, and 189 (base peak). This ester (**10**) gave the same R_f value on TLC as that of **7**, but the IR and PMR spectra were distinctly different to each other.

*Dehydration of Methyl 2α,3β-Diacetoxy-19α-hydroxy-13αH-oleanan-28-oate (**20**).* A solution of **20** (12 mg) in pyridine (0.7 ml) and phosphoryl chloride (0.1 ml) was refluxed for 1 h. After usual treatment, purification by preparative TLC was carried out as before. Methyl 2α,3β-diacetoxyolean-13(18)-en-28-oate (**23**) was obtained, mp 202—203 °C (crystallized from ether); IR (KBr) 1720, 1700 (sh), 1620, 1240, 1230, and 1030 cm^{-1}; PMR ($CDCl_3$) δ 0.74, 1.02, 1.15 (each 3H, s; *t*-Me), 0.90 (12H, s; 4×*t*-Me), 1.98, 2.04 (each 3H, s; -OAc), 3.65 (3H, s; $-CO_2Me$), 4.75 (1H, d, J=11 Hz; $C_{(3\alpha)}$–H), 5.15 (1H, ddd, J=11, J=11, and J=4 Hz; $C_{(2\beta)}$–H), and the absence of olefinic proton; mol wt *m/e* 570.3916. Calcd for $C_{35}H_{54}O_6$: *m/e* 570.3917; MS *m/e* 570 (M^+), 555, 538, 511, 510, 495, 468, 451, 450, 436, 435, 407, 391, 249, 203, and 189 (base peak).

*Catalytic Hydrogenation of Methyl 2α,3β-Diacetoxyoleana-11,13-dien-28-oate (**12**).* The 11,13-diene (**12**; 23 mg) in acetic acid was hydrogenated under an atmospheric pressure in the presence of platinum oxide (5 mg) for 20 h and worked up as usual to give a residue. The residue was subjected to preparative TLC on Kieselgel PF_{254} developed with benzene–acetone (50 : 3). The crude product (11 mg) was crystallized from ether to afford methyl 2α,3β-diacetoxyolean-13(18)-en-28-oate (**23**), mp 205.5—206.5 °C; $[\alpha]_{450}$ −66° (*c* 0.076, EtOH); mol wt *m/e* 570.3827. Calcd for $C_{35}H_{54}O_6$: *m/e* 570.3917. The IR, PMR, and MS spectra and TLC were completely identical with those of the specimen obtained by the dehydration of **20**.

*Forced Wolff-Kishner Reduction of Methyl 2α,3β-Diacetoxy-19-oxoolean-13(18)-en-28-oate (**8**) Followed by Acetylation and Methylation.* The α,β-unsaturated keto ester (**8**; 38 mg) was subjected to the forced Wolff-Kishner reduction (sodium 38 mg, diethylene glycol 1.5 ml, and anhydrous hydrazine 0.4 ml) under the same conditions as before. After usual work-up, a residue was acetylated with acetic anhydride in pyridine. The crude acetate was purified by column chromatography on silica gel (5 g), using the following solvents as eluent (each 10 ml): fr. 1, benzene–acetone (100 : 1); fr. 2, benzene–acetone (50 : 1); frs. 3 and 4, benzene–acetone (100 : 3); frs. 5—8, benzene-acetone (25 : 1); fr. 9, benzene–acetone (20 : 1). Fractions 5 and 6 were combined and methylated with diazomethane in ether. The reaction product was purified by preparative TLC on Kieselgel PF_{254} developed with benzene–acetone (20 : 1) to afford methyl 2α,3β-diacetoxy-13α*H*-olean-18-en-28-oate (**7**), which was shown to be identical (IR, PMR, MS, and TLC) with a specimen obtained by the forced Wolff-Kishner reduction of **5**.

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