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STRUCTURE OF TERMINIC ACID, A DIHYDROXYTRITERPENE CARBOXYLIC ACID FROM *TERMINALIA ARJUNA**

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Key Word Index—*Terminalia arjuna*; Combretaceae; terminic acid; dihydroxytriterpene carboxylic acid; 3β,13β-dihydroxylup-20(29)-en-28-oic acid.

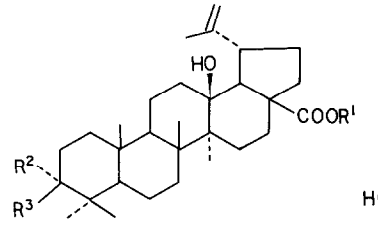
Abstract—The structure of terminic acid, a new dihydroxytriterpene carboxylic acid isolated from the roots of *Terminalia arjuna*, has been established as 3β,13β-dihydroxylup-20(29)-en-28-oic acid by a study of its chemical reactions and spectroscopic data. Terminic acid and its derivatives were found to undergo skeletal rearrangement under protonic conditions to yield oleanene lactone.

INTRODUCTION

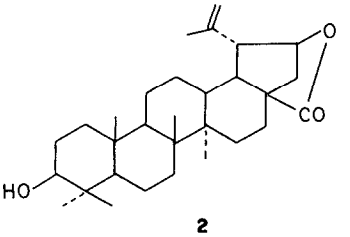
The isolation of a new dihydroxytriterpene carboxylic acid (0.0003%), terminic acid, along with several triterpenoid glycosides was reported earlier by us from the *n*-hexane extract of root bark of *Terminalia arjuna* [1, 2]. The same acid has now been obtained in a slightly better yield (0.005%) from the *n*-hexane extract of its heartwood along with sitosterol. The structure of terminic acid has been established as 3β,13β-dihydroxylup-20(29)-en-28-oic acid by using chemical and spectroscopic data.

RESULTS AND DISCUSSION

Terminic acid (**1**), mp 292–294°, $[\alpha]_D$ +5.88° gave a positive Liebermann–Burchard test for triterpenes and a pale yellow colour with tetranitromethane for a double bond. It analysed for $C_{30}H_{48}O_4$ and showed the presence of hydroxyl (*br* 3480 cm^{-1}) and carboxyl groups



1 $R^1 = R^2 = H, R^3 = OH$
1a $R^1 = R^2 = H, R^3 = OAc$
1b $R^2 = R^3 = O, R^1 = H$
1c $R^1 = Me, R^2 = H, R^3 = OH$
1d $R^1 = Me, R^2 = H, R^3 = OAc$



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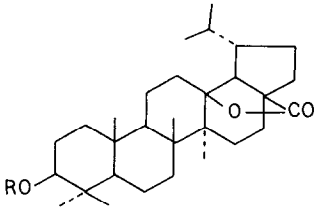

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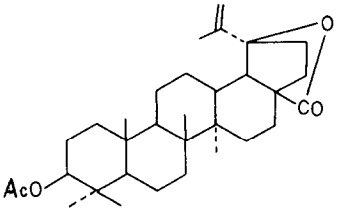
3a R = Ac



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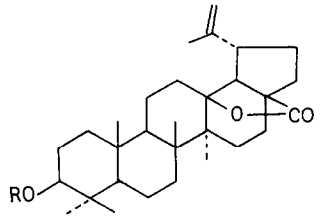


5 R = H
5a R = Ac

*Part 3 in the series "Chemical Examination of the Roots of *Terminalia arjuna*". For Part 2 see ref. [2].

(1680 cm^{-1}) and a vinylidene double bond (1660 and 880 cm^{-1}) in its IR spectrum. No UV absroption characteristic of the α- and β-amyrin series [3] was noticed. The appearance of the characteristic absorptions of a methylene group in its IR spectrum suggested that it might belong to the lupene, hopene or taraxastene series.

Terminic acid gave a monoacetate (**1a**), $C_{32}H_{50}O_5$, mp 262–264°, $[\alpha]_D$ +20° whose IR spectrum (3480 cm^{-1}) indicated the presence of another hydroxyl which was either a hindered secondary or a tertiary group. It resisted further acetylation with acetic anhydride even in the presence of perchloric acid and it gave only a monoketo derivative (**1b**), $C_{30}H_{46}O_4$, mp 255–258°, $[\alpha]_D$ +28.4°, with Sarett's reagent, which also showed a hydroxyl peak absorption at 3500 cm^{-1} in its IR spectrum supporting the presence of a tertiary hydroxyl. The ketone gave a positive Zimmerman test revealing the possible presence of a 3-keto group.

Terminic acid gave a monomethyl ester (**1c**), $C_{31}H_{50}O_4$, mp 254–256°, $[\alpha]_D$ +10° whose IR spectrum showed two clear, sharp hydroxyl peaks at 3540 and 3420 cm^{-1}. The methyl ester gave an ester acetate (**1d**), $C_{33}H_{52}O_5$, mp 196–198°, $[\alpha]_D$ +15°, which exhibited the resistant hydroxyl peak at 3500 cm^{-1} in its IR spectrum.

The ^1H NMR spectra of terminic acid and its derivatives (Table 1) were very characteristic of the lup-20(29)-en system. All of them showed the methylene protons as doublets around δ 4.6 and methyl on a double bond around 1.6–1.7. The acetate and the methyl ester acetate showed only one α-H to an acetoxyl group. The coupling constants of H-3 (J = 8 and 2 Hz) in terminic acid acetate indicated it to be a 3α-axial H and that the hydroxyl was a 3β-equatorial group.

From the above observations terminic acid was indicated to be a dihydroxy-lup-20(29)-en-28-oic acid. Its physical constants were quite different from those of alphitolic acid [4–6], the only dihydroxy acid reported so far in this series. However, it is pertinent here to refer to three related lactones reported in the literature [7–14] which may be considered as derived from the respective hypothetical dihydroxy acids. Of these, thurberogenin (**2**) is the 28–21-lactone isolated from *Lamaireocerous thurberi* [7–9]; **3** is a 20(29)-dihydro-28–13-lactone from *Dellinia indica* [14] and the third one (**4**) [10–13], obtained by synthesis through mercuric acetate oxidation of 3-acetylbetulinic acid.

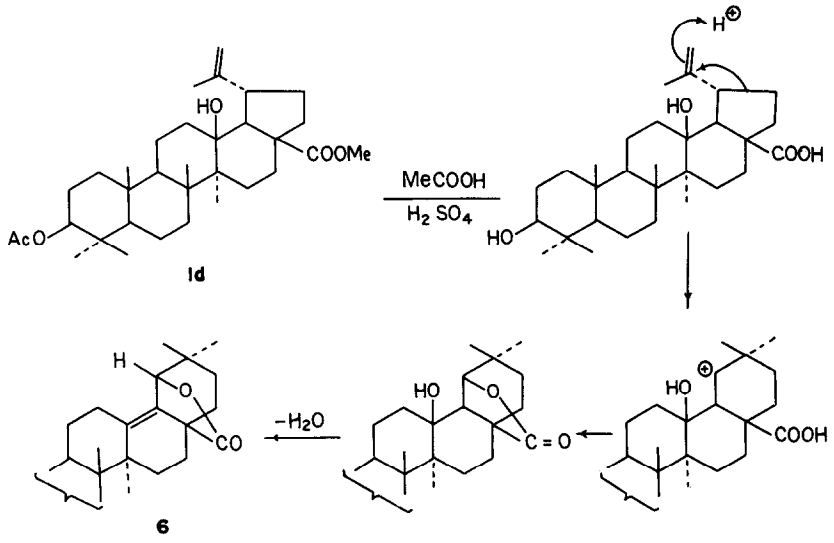
With the ubiquitous 3β-hydroxyl [15, 16], the tertiary hydroxyl in terminic acid may be present at C-5, C-9, C-13, C-18 or C-19. The mass spectral fragmentation (Scheme 1) of the methyl ester acetate of terminic acid (**1c**), as well as that of 3-ketoterminic acid (**1b**), resembled that of compounds with the lupane skeleton [17]. The ions at m/z 262, 249, 189 from **1c** and 218 and 205 from **1b**, comprising rings A/B, suggested that the tertiary hydroxyl was in rings D/E, which was supported by the appearance of ions at m/z 278 and 249 from **1c** and m/z 235 from **1b**.

When 3-acetylterminic acid (**1c**) was treated with $POCl_3$–pyridine, a γ-lactone (1785 cm^{-1}) (**5a**), $C_{32}H_{48}O_4$, mp 296–298°, $[\alpha]_D$ +16°, was obtained. Its ^1H NMR spectrum (4.6 and 4.7, 2H, *br s*, methylene group; 1.66, 3H, *s*, vinylic methyl) showed that the five-membered ring E is intact. The formation of a γ-lactone rules out position C-18 for the tertiary hydroxyl leaving the choice between C-13 or C-19, suggesting at the same time that the tertiary hydroxyl is β-oriented and *cis* to the 28-β-carboxyl. The mass spectrum of 3β-acetylterminic acid lactone, (M^+ at m/z 496) gave the crucial fragments m/z 262, 249, 189, 218 and 217 in support of its structure. The lactone (**5a**) on careful hydrolysis with 3% methanolic potassium hydroxide gave the corresponding 3β-hydroxy lactone (**5**), $C_{30}H_{46}O_3$, mp 305–306°, $[\alpha]_D$ +26°.

If the tertiary hydroxyl in terminic acid were at C-19 the lactone (**5a**) would have been identical with the synthetic lactone (**4**) for which varied physical constants are reported in the literature. The two lactones showed a marked difference in their physical characteristics, particularly in their optical rotations (Table 2). The difference was more conspicuous in their ^1H NMR spectra. While the chemical

Table 1. ^1H NMR spectra of terminic acid and its derivatives

Terminic acid (**1**)	Methylterminate (**1c**)	Acetylterminic acid (**1a**)	Terminic acid ester acetate (**1d**)	3-Ketoterminic acid (**1b**)	Assignment
0.64 *s* 0.75 *s* 0.86 *s* 1.22 *s* } 15H	0.75 *s* 0.82 *s* 0.96 *s* 1.26 *s* } 15H	0.85 *s* 0.95 *s* 1.25 *s* } 15H	0.76 *s* 0.78 *s* 0.81 *s* 0.88 *s* 0.89 *s* } 15H	0.80 *s* 0.98 *s* 1.04 *s* 1.22 *s* } 15H	5 × Me
1.62	1.60	1.70	1.64	1.66	$-C(=CH_2)-Me$
—	—	2.05	1.92	—	OAc-3β
—	—	—	—	2.32 *br m*	H-2α, H-2β
2.96 *br m*	3.20 *br m*	3.05 *br m*	2.85 *br m*	3.00 *br m*	H-18α, OH-13β
—	3.66	—	3.6	—	COOMe-28
4.22 *br m*	4.10 *m*	4.44 *dd* *J* = 8, 2 *Hz*	4.36 *m*	—	H-3α
4.52 *br s* 4.64 *br s*	4.58 *br s* 4.72 *br s*	4.71 *br s* 4.82 *br s*	4.51 *br s* 4.66 *br s*	4.58 *br s* 4.70 *br s*	$-C(=CH_2)-Me$



Scheme 1.

Table 2. Physical and spectral characteristics of lup-28,19- and 28,13-lactones

	3β-Acetyl-lup-20(29)-en-28,19β-lactone (4)	3β-Acetylterminic acid lactone (5a)	Assignment
mp	315–317°; 300°; 350°	296–298°	—
$[\alpha]_D$	+60°; +58°; +55°	+16°	—
^{1}H NMR	0.85–0.95, 15H, all *s*	0.82–0.95 15H, all *s*	5 × ter. Me
	1.79 3H, *s*	1.66 3H, *s*	–C(=CH$_2$)–Me
	2.04 3H, *s*	2.00 3H, *s*	OCO Me-3β
	4.48 *m*	4.40 *d*, *J* = 8 Hz	H-3α
	4.95, 5.33 } 2H, *m*	4.60, 4.70 } 2H, two *br s*	–C(=CH$_2$)–Me

shifts of the methylene protons as well as the methyl on the double bond in 3-acetylterminic acid lactone (**5a**) were almost the same as in other terminic acid derivatives, these appeared deshielded in 3β-acetylbetulinic acid lactone (**4**). This deshielding effect noticed in the latter lactone might be reasonably attributed to the presence of the 28,19-lactone. A similar effect was also noticed in dihydroceanothenic acid ester lactone [13]. These considerations strongly favour location of the tertiary hydroxyl in terminic acid at C-13, in which case the dihydro derivative of terminic acid lactone (**5a**) should be identical with the 3β-acetate (**3a**) of the natural lactone (**3**). Their identity was in fact proved by hydrogenating **5a** over Pd–C when it gave a product identical in its physical characteristics with those of **3a**. However, direct comparison could not be made as an authentic specimen was not available.

Terminic acid (**1**) has, therefore, been identified as 3β,13β-dihydroxylup-20(29)-en-28-oic acid. Its ^{13}C NMR spectrum compared well with that of methlybetulinate [18] (Table 3) lending further support to its proposed structure.

The easy lactonizable 13β-hydroxyl and 28-carboxyl groups, added to the acid sensitive 20(29)-double bond, led to some interesting rearrangements in terminic acid. In an attempt to obtain the 13-anhydro derivative, the methyl ester acetate of terminic acid was chosen instead of the free acid, but when treated with $POCl_3$–pyridine it underwent no reaction. However, when treated with acetic acid–sulphuric acid it gave an entirely rearranged product whose IR spectrum indicated it to be a hydroxy lactone (3460 and 1786 cm^{-1}). The acetate and the ester groups as well as the vinylidene group were absent. Its ^{1}H NMR spectrum showed no methyl group on a double bond, no olefinic protons and no acetate or ester methyls. Instead, its methyl region integrated for seven tertiary methyls remniscent of the oleanane skeleton. In addition, a one proton multiplet appeared at δ 3.69 due to the 3α-hydrogen and a broad singlet was seen at 3.83 accounting for the hydrogen α to the lactonic oxygen.

On the basis of the above evidence the rearranged product can be assigned the structure, 3β-hydroxy-olean-13(18)-en-19,28-lactone (**6**) which may have been formed

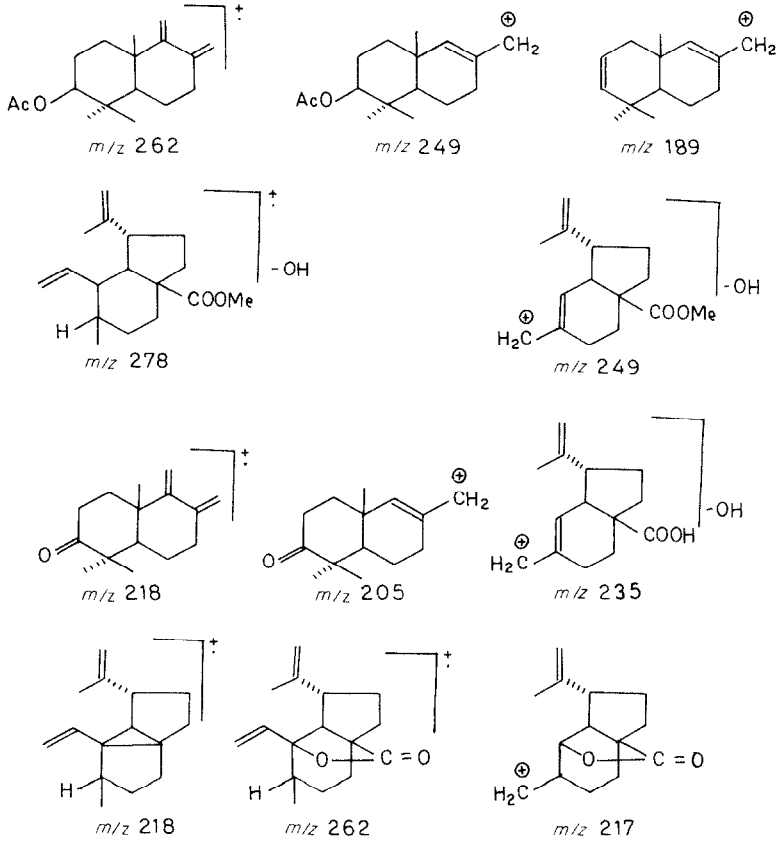
Table 3. ^{13}C NMR spectral data of terminic acid and methylbetulinate*

Carbon No.	Methylbetulinate	Terminic acid	Carbon No.	Methylbetulinate	Terminic acid
C-1	38.7	38.968	C-17	56.4	55.708
C-2	27.3	28.117	C-18	49.3	49.102
C-3	78.6	78.525	C-19	46.8	46.749
C-4	38.7	38.658	C-20	150.1	150.355
C-5	55.2	55.243	C-21	30.5	30.443
C-6	18.2	18.135	C-22	36.8	36.984
C-7	34.2	34.225	C-23	15.3	15.624
C-8	40.5	40.518	C-24	27.0	27.311
C-9	50.4	50.345	C-25	16.0†	15.996†
C-10	37.0	37.914	C-26	15.9†	15.903†
C-11	20.8	20.706	C-27	14.6	14.508
C-12	25.4	25.356	C-28	176.2	177.573
C-13	38.1	79.021	C-29	109.3	109.34
C-14	42.2	42.223	C-30	19.3	19.158
C-15	29.6	29.450	COOMe	50.1	—

*The ^{13}C NMR spectrum was recorded in the FT mode on a Brucker WH 270 spectrometer operating at 67.89 MHz and controlled by a NICOLET BNC-12 (20 bits word, 16 000 memory computer). The spectrum was measured in $CDCl_3$ + DMSO-d_6 solution with TMS as the internal standard, at room temperature with a pulse width of 15 sec and a repetition time of 3 sec, 8000 data points and using quadrate detection. 3 W power was used for the broad-band off-resonance proton decoupled spectrum.

†Interchangeable.

as shown in Scheme 2. In the ^1H NMR spectrum of this lactone the α-hydrogen over the lactone appeared shielded at δ 3.83 compared to the signal for the corresponding proton in other lactones, for example H-21 (δ 4.6) in thurberogenin (**2**)[7–9] and H-21 in acacic acid lactone and sapogenin-B (*ca* δ 4.2) [19]. The shielding influence



Scheme 2.

in compound **6** might be attributed to the presence of the 13,18-double bond. It is not difficult to understand the multiple steps involved in this rearrangement, such as hydrolysis of the 3-acetate and the 28-methyl ester and even the isomerization of the 20(29)-double bond, which is known to be very labile under protonic conditions, leading to a host of rearranged products [20]. The same double bond was, however, found to be intact during $POCl_3$ treatment. This contrasting behaviour of the lup-20(29)-double bond is in accord with similar observations made in our laboratories during Wagner–Meerwein rearrangements of lupane derivatives [21]. 3β-Acetylterminic acid, as well as terminic acid, when heated with acetic acid–sulphuric acid gave the same lactone (**6**).

The present isolation of terminic acid from the roots of *T. arjuna* is very significant since it is the first lup-20(29)-en derivative to be isolated from nature with a hydroxyl free at the rare C-13 position and also it is the first report of the occurrence of a lupane derivative in any *Terminalia* species.

EXPERIMENTAL

Mps were uncorr. ^1H NMR spectra were taken in $CDCl_3$ soln with TMS as internal standard.

The pale reddish heartwood of the roots of *Terminalia arjuna* was dried and powdered. The powder (5 kg) was successively extracted with *n*-hexane and rectified spirit. The yellow *n*-hexane extract (5 l). was concd and chromatographed on a Si gel 100–200 mesh column to yield fractions 1–10, hexane, 0.2 g, an oil; fractions 11–15, hexane–C_6H_6 (4:1), 0.1 g, a mixture; fractions 16–20, hexane–C_6H_6 (1:1), 0.1 g, sitosterol; fractions 21–40, C_6H_6, 0.5 g, terminic acid.

Characterization of terminic acid (**1**). Terminic acid crystallized from $CHCl_3$–MeOH as colourless plates, mp 290–292°, $[\alpha]_D$ + 5.88° (MeOH; *c* 0.51). (Found: C, 76.18; H, 10.20. $C_{30}H_{48}O_4$ requires: C, 76.23; H, 10.24%.) IR ν_{max}^{nujol} cm^{-1}: 3480, 1680, 1660, 1460, 1380, 1140, 880.

3β-Acetylterminic acid (**1a**). A mixture of **1** (100 mg) in dry pyridine (10 ml) and Ac_2O (5 ml) was heated on a steam-bath for 2 hr. The acetate (**1a**) crystallized from $CHCl_3$–MeOH as colourless needles, mp 262–264°, $[\alpha]_D$ + 20° ($CHCl_3$; *c* 0.25). (Found: C, 74.62, H, 9.76. $C_{32}H_{50}O_5$ requires: C, 74.67; H, 9.79%.) IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3480, 1725, 1690, 1440, 1360, 1250, 1100, 1000, 975, 885.

Methylterminate (**1c**). Compound **1** (50 mg) was taken in dry Et_2O and treated with excess ethereal CH_2N_2 and kept overnight at 0°. The ester (**1c**), (52 mg) crystallized from $CHCl_3$–MeOH as colourless plates, mp 254–256°, $[\alpha]_D$ + 10° ($CHCl_3$; *c* 0.6). (Found: C, 76.40; H, 10.30. $C_{31}H_{50}O_4$ requires C, 76.50; H, 10.35%.) IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3540, 3420, 1740, 1580, 1380, 1080, 1070, 950, 880.

Methyl-3β-acetylterminate (**1d**). The acetate (**1a**) (25 mg) in dry Et_2O was esterified with dry ethereal CH_2N_2 and the ester acetate (**1d**) (25 mg) crystallized from $CHCl_3$–MeOH as colourless needles, mp 196–198°, $[\alpha]_D$ + 15° ($CHCl_3$; *c* 0.5). (Found: C, 74.86; H, 9.80; $C_{33}H_{52}O_5$ requires: C, 74.96; H, 9.91%.) IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500, 1740, 1640, 1460, 1250, 980, 885. MS *m/z* (rel. int.): 528 $[M]^+$ (0), 510 (12.8), 450 (59.8), 435 (30.7), 393 (25.6), 322 (8.5), 278 (40.2), 269 (10.4), 262 (51.3), 249 (34.2), 231 (9.6), 219 (18.4), 190 (73.2), 189 (100), 172 (10.4), 121 (63.3).

Attempted forced acetylation of 3β-acetylterminic acid. The monoacetate (**1a**) (20 mg) was taken-up in dry Ac_2O (6 ml) and two drops of $HClO_4$ added and the mixture was kept for 1 hr at room temp. The starting compound was recovered unchanged.

Sarett's oxidation of terminic acid to yield 3-ketoterminic acid (**1b**). Terminic acid (**1**) (100 mg) in dry pyridine (8 ml) was treated with Sarett's reagent (1 ml) and kept at room temp. for 24 hr. After usual work-up the keto product (50 mg) crystallized from $CHCl_3$–MeOH as colourless needles, mp 255–258°, $[\alpha]_D$ + 28.4° ($CHCl_3$; *c* 0.4). (Found: C, 76.45; H, 9.80. $C_{30}H_{46}O_4$ requires: C, 76.55; H, 9.85%.) IR ν_{max}^{nujol} cm^{-1}: 3500, 1700, 1600, 1640, 1460, 1380, 1100, 885. MS *m/z* (rel. int.): 470 $[M]^+$ (1.1), 452 (61.6), 427 (8.4), 408 (39.0), 393 (12.8), 384 (12.4), 370 (4.7), 365 (9.2), 246 (92.5), 235 (57.3), 219 (61.1), 218 (38.9), 217 (18.4), 205 (100), 201 (40.1), 192 (10.4), 190 (36.4), 161 (39.0), 118 (68.0).

Action of $POCl_3$ on 3β-acetylterminic acid to yield 3β-acetylterminic acid lactone (**5a**). Compound **1a** (50 mg) was dissolved in dry pyridine (5 ml) and freshly distilled $POCl_3$ (0.5 ml) was added. The mixture was heated on a steam-bath for 4 hr. The product (25 mg) was crystallized from $CHCl_3$–MeOH as colourless prisms, mp 296–298°, $[\alpha]_D$ + 16° ($CHCl_3$; *c* 0.4). (Found: C, 77.30; H, 9.70. $C_{32}H_{48}O_4$ requires: C, 77.38; H, 9.74%.) IR ν_{max}^{nujol} cm^{-1}: 1785, 1725, 1640, 1460, 1360, 1250, 980, 920. MS *m/z* (rel. int.): 496 $[M]^+$ (1), 453 (2.4), 452 (3.0), 438 (4.7), 353 (9.5), 262 (9.5), 249 (8.4), 218 (28.5), 217 (12.4), 204 (10), 189 (12.4), 173 (10.0), 141 (83.3), 71 (32.6).

Hydrolysis of **5a** *to give 3β-hydroxyterminic acid lactone* (**5**). Compound **5a** (25 mg) was hydrolysed with 3% methanolic KOH (5 ml) to give the hydroxy lactone (**5**) (15 mg) which crystallized from $CHCl_3$–MeOH as colourless plates, mp 305–306°, $[\alpha]_D$ + 26° ($CHCl_3$; *c* 0.3). (Found: C, 79.24; H, 9.96. $C_{30}H_{46}O_3$ requires: C, 79.30; H, 10.13%.) IR ν_{max}^{nujol} cm^{-1}: 3480, 1780, 1665, 1450, 1340, 1080, 885.

Attempted dehydration of methyl-3β-acetylterminate. To methyl-3β-acetylterminate (10 mg) in dry pyridine (4 ml) freshly distilled $POCl_3$ (0.5 ml) was added and the mixture heated on a steam-bath for 4 hr. The starting material was recovered unchanged.

Action of H_2SO_4–HOAc on methyl-3β-acetylterminate to produce 3β-hydroxyolean-13(18)-en-19,28-lactone (**6**) Methyl-3β-acetylterminate (20 mg) was taken-up in glacial HOAc (5 ml), conc. H_2SO_4 (five drops) was added and the mixture was heated on a steam-bath for 4 hr. The product (12 mg) was crystallized from $CHCl_3$–MeOH as colourless needles, mp 150–152°. UV λ_{max}^{EtOH} nm: 215. IR ν_{max}^{nujol} cm^{-1}: 3460, 1786, 1600, 1465, 1380, 1160, 1025, 984. ^1H NMR (CCl_4): δ 0.74, 0.80, 0.86, 0.94, 1.04 (21H, all *s*, 7 × tert. –Me), 3.69 (1H, *m*, H-3α), 3.83 (1H, *br s*, H-19α).

Action of H_2SO_4–HOAc on terminic acid (**1**) *to form a lactone* (**6**). Terminic acid (**1**) (20 mg) in glacial HOAc (5 ml) with conc. H_2SO_4 (five drops) was heated for 4 hr on a steam-bath to give the above lactone (**6**) (10 mg).

Action of H_2SO_4–HOAc on 3β-acetylterminic acid. Compound **1a** (10 mg) in glacial HOAc (2 ml) with conc. H_2SO_4 (3 drops) was heated as above to give the lactone (**6**) (5 mg).

Hydrogenation of 3β-acetylterminic acid lactone to yield 3β-acetyllupane-13,18-lactone (**3a**). Compound **5a** (50 mg) in dry EtOAc (10 ml) was hydrogenated in the presence of Pd–C (10%, 100 mg) catalyst for 4 hr at room temp. The hydrogenated product (15 mg) crystallized from $CHCl_3$–MeOH, mp 317–319°, $[\alpha]_D$ + 82° (lit. [14] mp 319–320°, $[\alpha]_D$ + 82.1°).

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