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Studies on the reactions of N-bromosuccinimide in dimethyl sulfoxide: Part IV—Action on lupenyl acetate

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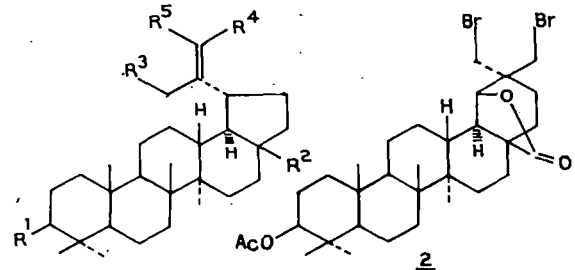
Action of N-bromosuccinimide on lupenyl acetate (**1**) in dimethyl sulfoxide has been studied. The compounds so formed have been identified as 30-bromolupenyl acetate (**1a**), 29-(*E*-*Z*)-bromolupenyl acetates (**1c** and **1d**), and 29,30-dibromo-18-iso-oleanan-19α-hydroxy 3β-yl acetate (**3a**). Further treatment of **1a** and mixture of **1c** and **1d** with NBS in DMSO containing water afforded 30-oxo-lupeol (**1k**) and 20-(*E*-*Z*)-bromo-lupeol (**1l** and **1m**) respectively; compound **1a** on alumina column afforded 30-hydroxylupenyl acetate (**1h**) and 30-hydroxylupeol (**1i**).

The action of N-bromosuccinimide (NBS) in CCl_4 on lupenyl acetate has been studied by Ramachandra Rao *et al.*[1] who have reported the isolation of 30-bromolupenyl acetate (**1a**) as the reaction product. The action of NBS in dimethyl sulfoxide (DMSO) on methyl acetylbetulenate (**1b**) has been reported from our laboratory[2], and the isolation of rearranged dibromolactone (**2**) prompted us to explore the applicability of the reaction on lupenyl acetate (**1**). Lupenyl acetate in chloroform when treated with NBS in DMSO furnished the compounds A, B and C (see Experimental). The compounds A and B on oxidation with NBS in DMSO in the presence of water yielded compounds F and G. The hydrolysis of A on alumina column furnishing compounds H and I has also been studied. Determination of structures of all the compounds (A-I) was fully corroborated by chemical and spectral studies. From IR and PMR spectral data (see Experimental) the compound A was characterised as 30-bromolup-20(29)-en-3β-yl-acetate (**1a**)[1].

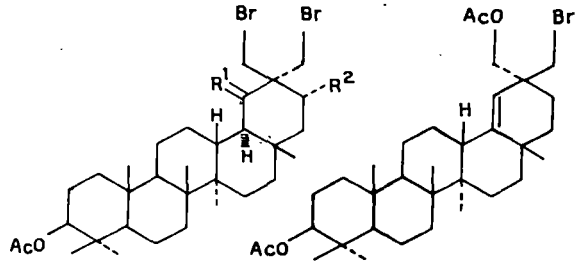
Compound B in its PMR spectrum showed two pairs of singlets at δ 1.71 and 1.72 and 5.72 and 5.90 which integrated for three protons and one proton respectively and were attributed to the presence of E and Z isomers arising out of the C-20(29) olefinic group with bromine atom with it. Thus the product 29-bromolupenylacetate[3] is a mixture of 29-*E*-bromo (**1c**) and 29-*Z*-bromo (**1d**) lup-20(29)-en-3β-yl-acetate.

Similarly 29-*E* and *Z*-bromomethylacetyl betule-



2

1, R^1 = OAc, R^2 = CH_3, R^3 = R^4 = R^5 = H
1a, R^1 = OAc, R^2 = CH_3, R^3 = Br, R^4 = R^5 = H
1b, R^1 = OAc, R^2 = COOMe, R^3 = R^4 = R^5 = H
1c, R^1 = OAc, R^2 = CH_3, R^3 = R^5 = H, R^4 = Br
1d, R^1 = OAc, R^2 = CH_3, R^3 = R^4 = H, R^5 = Br
1e, R^1 = OAc, R^2 = COOMe, R^3 = R^5 = H, R^4 = Br
1f, R^1 = OAc, R^2 = COOMe, R^3 = R^4 = H, R^5 = Br
1g, R^1 = R^3 = OAc, R^2 = CH_3, R^4 = Br, R^5 = H
1h, R^1 = OAc, R^2 = CH_3, R^3 = OH, R^4 = R^5 = H
1i, R^1 = R^3 = OH, R^2 = CH_3, R^4 = R^5 = H
1j, R^1 = R^3 = OAc, R^2 = CH_3, R^4 = R^5 = H
1k, R^1 = OH, R^2 = CH_3, R^3 = O, R^4 = R^5 = H
1l, R^1 = OH, R^2 = CH_3, R_3 = R^4 = H, R^5 = Br
1m, R^1 = OH, R^2 = CH_3, R_3 = R^5 = H, R^4 = Br
1n, R^1 = OAc, R^2 = CH_3, R^3 = O, R^4 = R^5 = H



4

3, R^1 = H_2, R^2 = OH
3a, R^1 = =O, R^2 = H
3b, R^1 = O, R^2 = H
3c, R^1 = H, OH, R^2 = H

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nates [**1e** and **1f**] crystallised from $CHCl_3$-MeOH analysed for $C_{33}H_{51}O_4Br$, m.p. 228-30°; IR 1735, 1725, 1240, 900 cm^{-1}; PMR: δ 0.78-1.0 (15H, 5t-CH_3), 1.71 and 1.78 (*s*, 3H, C=C-CH_3), 2.05 (*s*, 3H, O-COCH_3), 3.65 and 3.70 (*s*, 3H, -COOCH_3), 4.45 (*m*, 1H, *H*-C-3-O-CO-), 5.76 and 5.97 (*s*, 1H, C=C(Br)H) were isolated (not reported earlier[2]) as the products of the reaction of NBS/DMSO with **1b**.

The most polar product C was purified by crystallisations from $CHCl_3$-MeOH. Its PMR spectrum showed the presence of six tertiary methyls (δ 0.84,0.85, 0.87, 0.89, 0.95 and 1.06) and acetoxy group (δ 2.04) and exhibited two *AB* quartets centered at δ 3.64 (J = 16 Hz) and 3.02 (J = 10 Hz) due to four protons of the two $-CH_2Br$ groups, a one proton doublet of a doublet centered at δ 4.05 (J = 6 and 12 Hz) suggested the presence of a CH bearing a hydroxyl group as evident from the IR band (3330 cm^{-1}). The high J value indicated the hydroxyl to be axially oriented. Such a situation is satisfied if a lupane skeleton rearranges to oleanane skeleton with the hydroxyl group being situated at C-21 for which the structure **3** could be proposed. ^{13}C NMR data could also be accounted for the structure **3**.

Though structure **3** was initially suggested, one of the alternative structures **3a** and **3c** was also highly desired on mechanistic ground. In order to decide amongst the three structures possible **3**, **3a** and **3c**, the following experiments were performed.

Compound C was oxidised with CrO_3-Py in usual manner giving the product D which crystallised from $CHCl_3$-MeOH and analysed for $C_{32}H_{50}O_3Br_2$ m.p. 248-49°. Its IR spectrum showed the absence of hydroxyl band but gave a new band at 1705 beside the acetoxy carbonyl absorption at 1725 and 1245 cm^{-1}. The mass spectrum of D gave peaks at *m/z* 584, 582, 580 in the ratio 1:2:1 indicating the presence of two bromine atoms in the molecule. The peaks could arise by the loss of acetic acid molecule (60 mass units) from the molecular ions which did not appear in the spectrum. The PMR spectrum of D furnished a convincing proof for the structure **3b**. It showed peaks at δ 0.62, 0.75, 0.78, 0.88, 0.94 for the six tertiary methyls, a singlet at 1.94 for the methyl protons of acetoxy group, a one proton doublet at 2.45 with the coupling constant of 12.5 Hz showing that this proton coupled with a single proton which must be *trans* di-axial further indicating that the newly formed carbonyl group has only one neighbouring proton. This suggested the carbonyl group to be at C-19 that has an α-proton as C-18 α-H couples with C-13 β-H. Thus, structure **3a** was assigned for C. The structure of D as **3b** suggested the compound C to be 29,30-di-bromo-19-hydroxyl-18-iso-oleanan-3β-yl-acetate.

The compound C on acetylation furnished compound E which analysed for $C_{34}H_{53}O_4Br$, m.p. 180-81°. Its mass spectrum showed its molecular ion-peaks at *m/z* 606 $[M_1]^+$ and 604 $[M_2]^+$. Its PMR spectrum showed the existence of six tertiary methyls in the region δ 0.70-0.95 two acetoxy methyls at 1.94 and 2.02 a proton at C-3 geminal to acetoxyl group at its usual position of 4.45, a two proton *AB* quartet at 4.65 (J = 14.5 Hz) assignable to the methylene protons geminal to acetoxyl group which must have replaced one of the bromine atoms, and a one proton downfield singlet at 6.1 assignable to an isolated olefinic proton.

The isolated olefinic proton (6.1) could be attributed to the C-19 proton of the derivative **4** which could arise by dehydration of hydroxyl group if it is α-oriented as observed in the case of 19α-hydroxyl-18-iso-oleanan derivative[4]. Thus structure **3c** could be assigned to compound C. However, structure **3c** was rejected on the basis of the fact that E showed the absence of second pair of methylene protons carrying the bromine atom though it still contained a bromine atom. The downfield appearance of this olefinic proton at 6.1 as a singlet suggested it to be attached to the carbon containing the bromine. Thus, the presence of the grouping C=C(H)Br group was envisaged. This is possible only if compound C rearranges under the reaction condition (Py-Ac_2O) from 18-iso-oleanane to lupane skeleton giving rise E. This transformation further suggested that the hydroxyl group at C-19 is *cis* to the 18α-proton. Such a rearrangement is well documented in literature[4], where the 19α-hydroxy-18α-*H*-oleanan-3β-ol on acetylation furnishes lupenyl acetate. Since identical group and stereochemical factors are involved in the present case (C) the stereochemistry of the isopropenyl group in E is also established to be alpha oriented. Thus, E was identified as 29-bromo-3,30-diacetoxy lup-20(29)-ene (**1g**). Further, since a single sharp singlet for the olefinic proton appears in E, only one isomer (**1g**) appears to be formed due to electronic repulsion of the bromine and acetoxy carbonyl groupings. The above observations led to conclude the structure of C as 29,30-dibromo-oleanan-18α*H*-19α-ol-3β-yl acetate (**3a**). The structure **3a** was further confirmed by comparison

of its ^{13}C NMR spectral data with those of compounds **1** and **2** [Table 1].

Compound **1a** was allowed to be adsorbed over alumina column for 3 days. Elution of the column with pet. ether-benzene (3:2) afforded a compound that crystallised from $CHCl_3$ – MeOH and analysed for $C_{32}H_{52}O_3$ (M^+ 484), m.p. 348-59°, $[\alpha]_D \pm 0°$; IR spectra showed the presence of a hydroxyl (3500), an acetoxyl (1715, 1240) and an olefinic methylene (3040, 1640, 890) groupings, PMR spectra showed the presence of six tertiary methyls in the region δ 0.78-1.03 as six singlets, one acetoxy methyl as a singlet at 2.04, a doublet (J = 8 Hz) of two protons that appeared at 4.025 have been assigned to the methylene carbon (C-30) bearing a hydroxyl group; the methine proton geminal to the C-3 acetoxyl group appeared at the usual position at 4.48; the C-29 methylene protons appeared as multiplet at 4.90. Thus on the basis of spectral data this compound was assigned the structure as 30-hydroxy-lupenyl acetate (**1h**).

Table 1—Carbon-13 NMR spectral data (δ, ppm) of **1** (lupenyl acetate)[8], **2** and **3a**

Carbon	**1**[8]	**2**	**3a**
1	38.3	38.6	38.3
2	23.6	23.7	23.6
3	80.7	80.9	80.9
4	37.7	37.7	37.7
5	55.3	55.6	55.2
6	18.2	18.1	18.2
7	34.1	33.7	34.1
8	40.7	41.3	41.2
9	50.2	46.7	49.4
10	37.0	36.4	36.33
11	20.9	21.3	21.2
12	25.0	26.9	25.0
13	37.9	37.8	37.8
14	42.7	40.6	42.8
15	27.4	28.3	28.3
16	35.5	36.6	36.5
17	42.9	51.1	44.4
18	48.2	45.7	45.6
19	47.9	80.8	73.9
20	150.5	35.3	36.9
21	29.8	29.7	26.4
22	39.9	31.1	37.6
23	27.9	27.9	27.9
24	16.5	16.6	16.5
25	16.1	16.5	16.1
26	15.9	15.5	16.0
27	14.4	13.6	14.4
28	18.0	178.0	18.3
29	109.2	39.7	38.6
30	19.2	40.0	43.0

Note: ^{13}C NMR data of **2** not reported in earlier paper[2]

The most polar fraction eluted by benzene-ethyl-acetate (9:1) and crystallised from $CHCl_3$ – MeOH was analysed for $C_{30}H_{50}O_2$, m.p. 235-36°C MS: 442 $[M]^+$; its IR spectrum showed the presence of two hydroxyl groups (3330, 3500) and the olefinic methylene double bond (3040, 1640, 890). The PMR spectrum exhibited signals at (δ): 0.77-1.07 (6*s*, 18H, 6x-t-CH_3), 4.15 (*d*, 2H, $-CH_2OH$, J = 6 Hz), 3.18 (*m*, 1H, HO – C_3H), 4.9 (*m*, 2H, C = CH_2). From these spectral data the compound was identified as lup-20(29)-ene-3β,30-diol[7] (**1i**). Acetylation of **1h** and **1i** with Ac_2O – Py separately furnished the same compound $C_{34}H_{54}O_4$, m.p. 164-65°, M^+ 526; IR 1745, 1730, 1245, 1240 cm^{-1}, identical with 3β,30-diacetoxylup-20(29)-ene (**1g**). Similar adsorption of compound B gave back the starting material (B).

A mixture of A and B was further treated with NBS in DMSO containing 5% water and kept in dark for 25 days. The mixture after usual work-up and chromatography over silica gel furnished two compounds (F and G). Compound F was analysed for $C_{30}H_{49}OBr$ (M^+ 514) m.p. 174-75°, gave positive test for halogen (Beilstein test) and unsaturation (TNM); its IR spectrum showed the presence of hydroxyl group (3400 cm^{-1}) and tri-substituted double bond (910 cm^{-1}). It was identified as 29-bromo-lupeol (**1l** and **1m**) by acetylation to B. Acetylation of F with Py – Ac_2O afforded an acetate $C_{32}H_{51}O_2Br$, m.p. 185-6°, identical with B. The second compound (G) was crystallised from $CHCl_3$ – MeOH. It analysed for $C_{30}H_{50}O_2$ m.p. 234-35°C, MS: 440 $[M]^+$; UV 228 nm and IR 1690, 1630 (α,β-unsaturated carbonyl group), the peak at 3320 cm^{-1} (OH); did not respond to Beilstein test for halogen but gave yellow colouration with TNM. It was identified as 30-oxolupeol (**1k**). Its acetate was identical with 30-oxo-lupenyl acetate[7] (**1n**).

The formation of **1a** and a mixture of **1c** and **1d** indicated that with NBS in polar solvent both allylic bromination by free radical mechanism and bromonium ion attack takes place with equal ease at the isopropyl group of lupane skeleton. In case of methyl acetyl betulenate (**1b**) the bromonium ion attack gives rise to the lactone **2** when the lactonic oxygen is β-oriented at C-19 whereas the lupenyl acetate (**1**) the ring expansion is accompanied by hydroxylation at C-19 but its orientation is alpha. It is to be noted that the stereochemistry of C-18 proton remains intact as alpha showing that no olefinic double bond is formed to give the germanicene type skeleton (**4**) before lactonisation in the case of **1b**[2] or hydroxyla-

tion in the case of **1**. Further, since only the dibromo compounds give rise to the oleanane derivatives, it may be suggested that a small amount of bromonium ion may attack the olefinic bond in two different ways; in isopropyl derivative the three membered ring bromonium ion can open up with the loss of a proton from the C-29 give **1c** + **1d**/**1e** + **1f** from **1**/**1b** whereas the isopropyl group with allylic bromine at C-30 opens up in a different manner giving rise to a cation at C-20 or may undergo simultaneous ring expansion and addition to furnish **3a**/**2**.

The formation of **1h** during column chromatography showed that the bromine on sp^3 carbon undergoes facile hydrolysis than the 3-acetate, whereas the aqueous NBS causes allylic bromination, hydrolysis and oxidation to yield the allylic aldehyde **1k**.

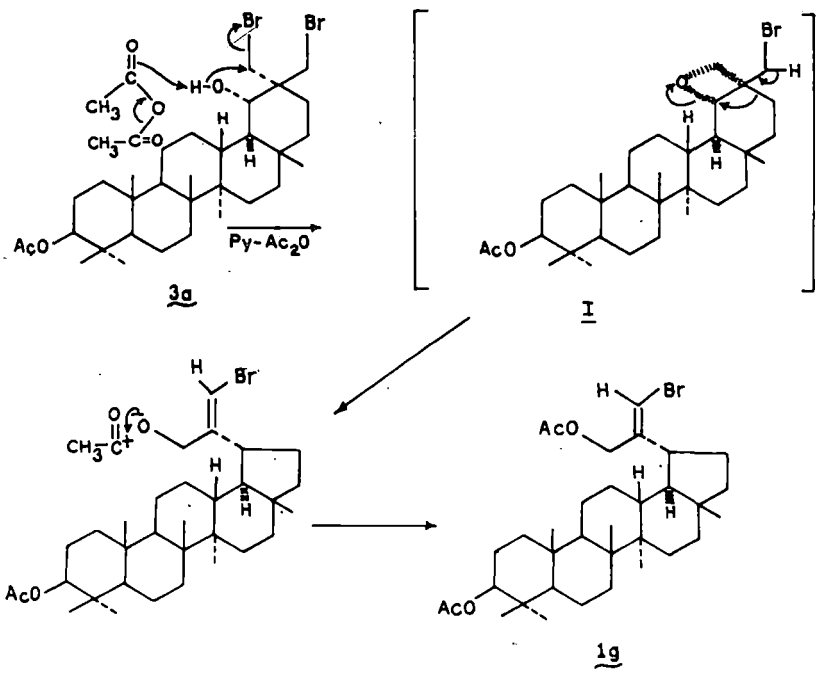
The rearrangement of **3a** to **1g** during acetylation is almost similar to the previous observation[4] (where acetylation of 3β,19α-dihydroxy-18α-H-oleanane-yielded lupenyl acetate). It has been observed that 30-bromolupenyl acetate (**1a**) when treated with Ac_2O – Py under usual acetylation conditions no 30-acetoxylupenyl acetate (**1j**) was formed showing that the bromine at C-30 in **1a** is unreactive with Ac_2O – Py. Under acetylation conditions the hydroxyl oxygen being at a closer proximity to the C-30 bromine and bromine being a better leaving group a nucleophillic attack takes place with the liberation of bromide ion to give an unstable four membered ring **I**. This immediately undergoes E-ring contraction with opening of the oxo-ring giving rise to **1g**.

Experimental Procedure

Melting points are uncorrected. The pet. ether used had b.p. 60-80°. Alumina (S. Merck) deactivated with 5% or 10% AcOH was used for column chromatography. TLC plates were coated with silica gel G and the spots located by exposing to iodine vapours. All optical rotations were determined in chloroform. IR spectra were recorded as nujol mulls on a Beckmann IR-20 spectrophotometer, UV spectra in MeOH on a Beckmann DU-2 spectrophotometer, PMR spectra in $CDCl_3$ on Varian A-60 or T-60 or EM-360 spectrometer. ^{13}C NMR spectra in $CDCl_3$ on an FT-80A instrument using TMS as internal standard. Mass spectra were recorded by solid probe C1/CH4 method.

Treatment of Lupenyl acetate with NBS in Dimethyl Sulfoxide: Formation of 30-bromo-lup-20(29)-en-3β-yl acetate (**1a**), *29(E-Z)-bromo-lup-20(29)-en-3β-yl-acetate* (**1c** *and* **1d**) *and 29,30-di-bromo oleanan-18α-H-19α-ol-3β-yl acetate* (**3a**)

To a solution of lupenyl acetate (1 g) in $CHCl_3$ (10 ml) and DMSO (25 ml), crystals of NBS (1 g) were added in lots of 100 mg each with constant shaking and the solution was kept in dark for 24 hr. The mixture was diluted with water, the $CHCl_3$ layer washed, dried and concentrated to give a residue (900 mg) which was chromatographed over alumina column. Elution with solvents of increasing polarity furnished compounds A (500 mg, pet. ether benzene) 4:1), B (200 mg, pet. ether benzene 3:2) and C (160 mg, benzene-chloroform 9:1).



Compound A: 30-*Bromo lupenyl acetate* (**1a**)

It was crystallised from $CHCl_3$–MeOH, m.p. 236-37° [Lit[1] m.p. 235-36°] $[\alpha]_D$ +12°, gave Beilstein test positive, IR 1725, 1255 ($OCOCH_3$) 3015, 1640 and 880 cm^{-1} (C=CH_2); PMR: δ0.79, 0.83, 0.84, 0.85, 0.95,1.02 (6*s*, 6×t-CH_3), 2.04 (*s*, 3H, $OCOCH_3$), 3.99 (*s*, 2H, CH_2Br), 4.48 (*m*, 1H, AcO–C_3–*H*), 5.04, 5.12 (2*s*, 2H, C=CH_2) (Found: C, 70.12; H, 9.3. Calc. for $C_{32}H_{51}O_2Br$: C, 70.2; H, 9.3%).

Compound B: 29(*E-Z*)-*Bromolupenyl acetate* (**1c** *and* **1d**)

It was crystallised four times from $CHCl_3$–MeOH m.p. 186-88°, $[\alpha]_D$ +32°; IR: 1735, 1240 ($OCOCH_3$) and 1265 cm^{-1} (=CHBr); MS: m/z 548, 546 (M^+), 467, 407, 203, 189, 109 (base); PMR: δ 0.79, 0.84, 0.85, 0.86, 0.92, 1.02 (6*s*, 18H, 6×t–Me), 1.71 and 1.73 (*s*, 3H, =C–CH_3), 2.05 (*s*, $OCOCH_3$), 4.48 (*m*, 1H, AcO–C_3–αH), 5.72, 5.91 (2*s*, 1H, C_{29}–H), identical (m.m.p., co-TLC) with an authentic sample of 29-bromolupenyl acetate (**1c**) and (**1d**).

Compound C: 29,30-*Dibromo*-19α-*hydroxy*-18α*H*,3β-*yl acetate* (**3a**)

It was crystallised from $CHCl_3$–MeOH, m.p. 258-60°; TNM test: negative; Beilstein test tor halogen: positive; IR: 3330 (–OH) 1732 and 1250 ($OCOCH_3$) cm^{-1}; MS[+]: ** 646 [M_1, 1%]**, 644 [M_3, 2%]+, 642 [M_2, 1%]+, 626 [M_1–HBr, 2%]+, 624 [M_3–HBr]+, 622 [M_2–HBr, 2%]+, 586, 584, 582 [M–HOAc, 1:2:1, 5%], 565, 564, 563, 562 [M–HBr, 5%], 547 (4%), 531 (2%), 505, 504, 503, 501 (5%), 483 (20%), 466 (7%), 452 (3%), 423 (10%), 313 (4%), 297 (5%), 283 (5%), 269 (4%), 249 (6%), 204 (15%), 189 (100%); PMR: δ 0.84, 0.85, 0.87, 0.89, 0.95, 1.06 (6*s*, 6×t-CH_3), 2.04 (*s*, 3H, $OCOCH_3$), 3.64 (*ABq*, 2H, CH_2–Br, J=16 Hz), 3.02 (*ABq*, 2H, –CH_2Br, J=10 Hz), 4.05 (*dd*, 1H, HO–$C_{19}\beta$–H, J=6 and 12 Hz), 4.45 (*m*, 1H, AcO–$C_3\alpha$–H) (Found: C, 59.6; H, 8.05. $C_{32}H_{52}O_3Br_2$ requires C,59.6; H, 8.1%).

Oxidation of **3c**: 29,30-*Dibromo-oleanan*-18α*H*-19-*one* (**3b**)

Compound C (0.1 g) dissolved in pyridine (1 ml) was mixed with CrO_3 (0.1 g) in pyridine (1 ml) in cold. After usual work-up and purification of the product by chromatography and crystallisations furnished crystals of **3b**, m.p. 248-49°, IR: 1725, 1245 ($OCOCH_3$) and 1705 cm^{-1} (CO); MS (*m/z*): 584 [M_1–AcOH]+, 582 [M_3–AcOH]+, 580 [M_2–AcOH]+, 569, 567, 565, 503, 502, 501, 475, 474, 473, 393, 391, 191, 189, PMR: δ 0.6, 0.75, 0.78, 0.88, 0.94 (6*s*, 6×t-CH_3), 1.94 (*s*, $OCOCH_3$), 2.45 (*d*, 1H, 18αH, J=12.5 Hz), 3.46 and 3.82 (dd, 2H, –CH_2Br, J=465; 12, 2 Hz) 3.67 and 3.81 (dd, 2H, CH_2Br, J=195, 12 Hz), 4.39 (*m*, H, C_3–αH), (Found: C, 59.6; H, 7.8; $C_{32}H_{50}O_3Br_2$, requires C, 59.63; H, 7.8%).

Acetylation of compound C

Compound C (0.1 g) dissolved in Py (1 ml) was mixed with Ac_2O (1 ml) and the mixture kept on a water bath overnight. Usual work-up and chromatography followed by crystallisation furnished the acetate E (0.1 g), m.p. 180-81°, IR: 1730, 1725, 1250, 1245 (2×$OCOCH_3$), 3015, 1640 and 840 cm^{-1} (>C=C<H); MS [*m/z*] 606, 604 [M^+], 546, 544, 466, 465, 406, 405, 189; PMR: δ 0.70, 0.76, 0.78, 0.79, 0.81, 0.96 (6*s*, 6×t-CH_3), 1.94, 2.02 (2*s*, 2×–$OCOCH_3$), 4.45 (*m*, 1H, C_3–αH), 4.65 (*ABq*, 2H, CH_2OAc), 6.10 (*s*, 1H, =C*H*Br), identified as 29-bromo-3β,30-diacetoxy-lup-20(29)-ene (**1g**).

Treatment of compound A and B with NBS in DMSO containing water. Isolation of compounds **1l**, **1m** *and* **1k**

To a mixture of compounds A and B (500 mg) in $CHCl_3$ (12 ml), DMSO (12.5 ml), crystals of NBS (500 mg) were added with constant shaking followed by water (2 ml). The mixture was kept in dark for 25 days and diluted with water, extracted with $CHCl_3$ and washed with water, dried and concentrated to give yellow residue (425 mg) which was chromatographed over silica gel. Elution with solvents of increasing polarity gave compounds **1l** and **1m** (200 mg). These were crystallised from $CHCl_3$–MeOH, m.p. 174-75°, TNM test: positive and Beilstein test: positive. IR 3400 (–OH) and 910 cm^{-1} (>C=C<H), MS: (*m/z*) 506 [M_1]+, 504 [M_2]+, 425, 408, 407, 207, 203; PMR: δ 0.75, 0.81, 0.82, 0.91, 0.95, 1.01 (6*s*, 6×t-CH_3), 1.71 (*s*, 3H, C=C–CH_3), 3.2 (*m*, H, C_3–αH), 5.89 (C=C*H*Br) (Found: C, 71.2; H, 9.8. Requires C, 71.3; H, 9.8%). The identity of these compounds was further confirmed by preparing its acetate, which was identical with compound B. m.p. and m.m.p. 185-86°C.

*M_1^+ represents molecular mass due to bromine 81, M_2^+ due to bromine 79 and M_3^+ due to bromine of isotropic masses 79 and 81 when two bromine atoms are present.

Compound **1k** was crystallised from $CHCl_3-MeOH$ to give crystals m.p. 235-6°, UV 228; IR 3320 ($-OH$), 1690 and 1630 cm^{-1} ($C=C-C=O$), Beilstein test for halogen: negative; TNM test: positive; MS: (*m/z*) 440 $[M]^+$, 422 $[M-H_2O]^+$, 407 $[422-CH_3]^+$, 207, 203, 190, 189; PMR: δ 0.75, 0.81, 0.82, 0.92,0.96, 1.01 (6*s*, 6 × t-CH_3), 3.18 (*m*, 1H, $C_3\alpha H$),5.91 and 6.28 (2*s*, 2H, $-C=CH_2$), 9.51 (*s*, H, $-CHO$). This compound (**1k**) which was identified as 30-oxo lupeol by preparation of its acetate which was identical with 30-oxo-lupenyl acetate (**1n**).

The acetate **1k** (50 mg) was obtained by its treatment with pyridine (2.5 ml) and Ac_2O (2 ml) on a water-bath for 4 hr followed by usual work-up, m.p. 224-26° ($CHCl_3-MeOH$), identical with an authentic sample of 30-oxo-lupenyl acetate (**1n**).

Adsorption of compound A on alumina: Isolation of 30-hydroxy lupenyl acetate (**1h**) *and 30-hydroxy-lupeol* (**1i**)

Compound **1a** (250 mg) in benzene (1 ml) was adsorbed over active alumina column (30 gm) developed with petroleum ether and allowed to stand for 24 hr. Elution with solvents of increasing polarity afforded compounds **1h** (benzene) and **1i** [benzene-$CHCl_3$ (4:1)].

Compound **1h** was crystallised from $CHCl_3-MeOH$ as needle shaped crystals, m.p. 248-49° $[\alpha]_D \pm 0°$; TNM test positive; Beilstein test negative; IR: 3500 ($-OH$), 1715, 1240 ($-O-CO-CH_3$),3040, 1640, 890 cm^{-1} ($>C=CH_2$), MS (*m/z*): 483 $[M-1]^+$, 465, 425, 424 $[M-AcOH]^+$ 408, 380, 356, 248, 233, 203, 189 (base); PMR: δ 0.78, 0.83, 0.84, 0.85, 0.94, 1.03 (6*s*, 18H, 6 × t-CH_3), 2.04 (*s*, 3H, $-OCO-CH_3$), 4.15 (q, $J_{AB}=6$ Hz, 2H, $-CH_2OH$), 4.48 (*m*, 1H, $H-C-O-C-CH_3$), 4.94 (*m*, 2H, $>C=CH_2$) (Found: C, 79.3; H, 10.8. $C_{32}H_{52}O_3$ requires C, 79.3; H, 10.81); Acetylation of **1h** with Ac_2O-Py gave the diacetate **1j**, m.p. 166-67°, $[\alpha]_D + 8°$, IR: 1750, 1730, 1250, 1265, (2 × $OCOCH_3$), 3080, 1640 and 840 cm^{-1} ($=CH_2$).

Compound **1i**: *30-hydroxy lupeol*

It was crystallised from $CHCl_3-MeOH$, m.p. 226-28°, $[\alpha]_D + 4°$; responded to TNM test but did not respond to Beilstein test. IR: 3300-3400 ($-OH$), 3100, 1640 and 880 cm^{-1} ($>C=CH_2$). (Found: C, 81.2; H, 11.4; $C_{30}H_{50}O_2$ requires C, 81.4; H, 11.4). It was identified by preparation of its diacetate **1j** ($Py-Ac_2O$), m.p. 163-64°, $[\alpha]_D + 8°$ [Lit[7] m.p. 163-64°, $[\alpha]_D + 9.7°$] which was identical with **1j** prepared from **1h**.

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References

1 Ramachandra Rao L, Sankara Rao C & Sundara Ramaian T, *Indian J Chem*, (1968) 16.

2 Pradhan B P, Mukherjee M M & Chakraborty D K, *Indian J Chem*, 22B (1983) 12.

3 Gupta S R, Halsall T G & Jones E R H, *J chem Soc*, (1961) 5353.

4 Simonsen J & Ross W C J, *The Terpenes*, Vol. 5 (The Cambridge University Press, London), 1957, Jones E R H & Meakins R J, *J chem Soc*, (1941) 757.

5 Ruzicka L & Rosenkrauz G, *Helv chim Acta*, 22 (1939) 778.

6 Simonsen J & Ross W C J, *The Terpenes*, Vol. 4 (The Cambridge University Press, London), 1957.

7 Wenkart E, Baddeley G V, Burfitt I R & Moreno L N, *Organic magnetic Reson*, (1978) 337.