

Studies on the reaction of N-bromosuccinimide in dimethyl sulphoxide: Part IX—Action on moretenyl acetate

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Received 19 April 1994; revised and accepted 25 January 1995

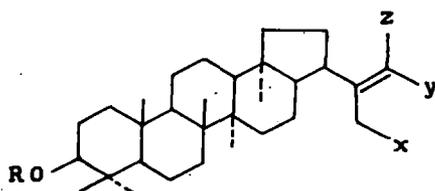
The action of N-bromosuccinimide on moretenyl acetate (**1**) in dimethyl sulphoxide affords 30-bromomoretenyl acetate (**1a**), 22,29,30-tribromomoretenyl acetate (**2a**) and 29,30-dibromo-22-hydroxymoreten-3 β -yl acetate (**2b**). **2a** on adsorption over basic alumina for 7 days furnishes **1a**, **2b**, 30-bromomoretenol (**1b**), and *E/Z*-29-bromomoretenols (**1c** + **1d**).

In continuation of our studies^{1,2} on the action of N-bromosuccinimide (NBS) in dimethyl sulphoxide (DMSO) on isopropenyl group of lupane skeleton, we report herein the isolation and characterization of the products **A**, **B** and **C** obtained by the reaction of NBS in DMSO on moretenyl acetate (3 β -acetyl-21 α H-hop-22(29)-ene) (**1**)^{3,4}, a compound of isohopane skeleton having an isopropenyl group attached to a cyclopentane ring. Also the action of basic alumina on the tribromo product **B** is reported in this paper.

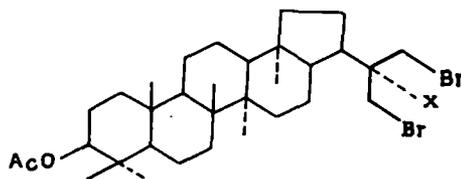
Compound **A**—Eluted by petrol was analysed for C₃₂H₅₁O₂Br, m.p. 222-24°. IR spectrum showed the presence of a vinyl group (3040, 840 cm⁻¹) and acetate group (1720, 1245 cm⁻¹). The presence of double bond was confirmed by the TNM test for unsaturation. It gave green coloured flame in Beilstein's test showing the presence of bromine in the molecule and in the mass spectrum the presence of two peaks of the same height at *m/z* 548 and 546 indicated that there is a bromine atom in **A**. ¹H NMR

spectrum of **A** showed the presence of six *tert*-methyls in the region δ 0.69 to 1.23. The *AB* quartet centered at 4.1 ppm (*J* = 10 Hz) integrating for two protons indicated that the carbon atom bearing these two protons is attached to a sufficiently electronegative element or group to cause the downfield shift of the protons. Thus the bromine atom must be attached to a primary carbon showing the presence of -CH₂Br group. The vinyl protons that appeared at δ 4.9 and 5.9 integrated for one proton each were attributed to =CH₂ group. Thus **A** has been assigned the structure 30-bromomoretenyl acetate (30-bromo-3 β -acetoxy-21 α H-hop-22(29)-ene) (**1a**).

Compound **B**—It analysed for C₃₂H₅₁O₂Br₃, m.p. 241-42°, [α]_D + 23. Its IR spectrum showed the presence of acetate group (1725, 1245 cm⁻¹). Its mass spectrum showed the molecular ion peaks at *m/z* 710, 708, 706, 704 in the ratio 1:3:3:1 indicating the presence of three bromine atoms in the molecule of compound **B**. Further, the existence of molecular ion



- 1**, R = Ac, x = y = z = H
1a, R = Ac, x = Br, y = z = H
1b, R = H, x = Br, y = z = H
1c, R = H, x = y = H, z = Br
1d, R = H, x = z = H, y = Br



- 2a**, x = Br
2b, x = OH

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peak at m/z 427 indicated loss of all the three bromine atoms along with the isopropyl group showing that all the three bromine atoms belong to the isopropyl group⁴.

The structure of **B** was further confirmed from the ¹H NMR spectrum. It exhibited six singlets in the region δ 0.75 to 1.27 each integrating for three protons accounting for six tertiary methyls; a multiplet in the region δ 3.8 to 4.2 integrating for four protons was due to two *AB* quartets, superimposed on each other by plotting a COSY spectrum, that were assignable to the isolated two $-\text{CH}_2\text{Br}$ groups (the protons of each pair resonated at δ 3.81 and 3.97 and 3.94 and 4.15 ppm with the same coupling value of 11 Hz). This was further supported by addition of C_6D_6 to the solution that clearly separated the two *AB* quartets.

¹³C NMR spectrum of compound **B** showed the presence of 32 carbons in the region 171 to 15 ppm and the DEPT experiments showed the presence of seven quartets one of which was due to acetoxy methyl (21,0) (thus two less than in the starting compound **1**), twelve triplets for twelve CH_2 carbons (two more than those in **1**), two of which were due to $-\text{CH}_2\text{Br}$ carbons (38.86 and 40.2), six doublets for six $-\text{CH}$ carbons (one less than that in **1**) and seven singlets for tertiary carbons (one more than that in **1**). The one peak at 76.06 ppm was definitely due to a tertiary carbon bearing an electronegative halogen atom showing that C-22 carries a bromine atom. Thus **B** has been assigned structure 22,29,30-tribromo-moretenyl acetate (22,29,30-tribromo-3 β -acetoxy-21 α H-hopane) (**2a**).

¹³C NMR spectra of compound **B** are given in Table I.

Compound **C**—It was analysed for $\text{C}_{32}\text{H}_{52}\text{O}_3\text{Br}_2$, m.p. 258–59°, $[\alpha]_D + 25$. Its IR spectrum showed the presence of a hydroxyl group (3360 cm^{-1}) and acetoxy group (1730, 1250 cm^{-1}). Its mass spectrum showed molecular ion peaks at m/z 645, 643, 641 in the ratio (1:2:1) typical for the compound with two bromine atoms^{1,2}, that the two bromine atoms and the hydroxyl groups are present on the isopropyl group was indicated by the molecular ion peak at m/z 427 which is caused by the homolytic cleavage of C-21 side chain [$\text{M}^+ - 217$].

¹H NMR spectrum of **C** showed the presence of six *tert*-methyls in the region δ 0.72–0.98 ppm, the acetoxy methyl at δ 2.06 and the C-3 methine proton at δ 4.45. It showed a pair of *AB* quartets centered at δ 3.57 and 3.72 ($J = 10$ Hz), two singlets at δ 3.48 and 3.66 ppm typical of a pair of $-\text{CH}_2\text{Br}$ without restricted rotation and another set of non-resolvable peaks in the region δ 3.42 to 3.56 ppm. The total

Table I—¹³C NMR signals (δ , ppm) of compounds **2a** and **2b**

Carbon No.	2a	2b
1	38.4	38.4
2	23.6	23.6
3	80.9	80.9
4	37.8	37.9
5	55.2	55.2
6	18.2	18.2
7	33.2	33.2
8	41.5	41.6
9	50.2	50.2
10	37.0	36.9
11	20.9	20.9
12	23.7	24.0
13	48.4	48.4
14	41.9	41.6
15	32.8	32.6
16	26.6	24.0,24.4
17	54.2	52.0
18	45.4	45.1
19	40.8	40.4
20	23.6	23.6
21	45.9	47.6
22	76.1	75.2,73.8,74.6
23	28.0	28.0
24	16.0	16.0
25	15.9	15.2
26	16.5	16.4
27	18.8	16.8
28	16.1	16.4
29	38.9	39.2,39.4,39.6
30	40.3	39.6,39.8,40.0
$-\text{OCOCH}_3$	170.0	171.0
$-\text{OCOCH}_3$	21.3	21.2

number of protons integrated were four, an indication that the pairs of $-\text{CH}_2\text{Br}$ are in three different geometries where one pair had restricted rotation and the other two pairs had free rotation. This interpretation was confirmed by its ¹³C NMR spectrum that showed three singlets around 74.00 ppm integrating for one carbon pointing to the fact that this carbon had three different stereoisomers carrying either a hydroxyl or bromine atom and it must be the C-22 carbon. Such an observation was also reported by Wenkert *et al.*⁵ in the case of C-22 hydroxyl hopane. Thus, compound **C** has been assigned the structure 29,30-dibromo-22-hydroxy-21 α H-hopane-3 β -yl acetate (**2b**).

The ¹³C NMR spectra of compound **C** are given in Table I.

Effect of basic alumina on compound 2a

2a was subjected to basic alumina hydrolysis by keeping it adsorbed for seven days. On the 8th day it was eluted first with petrol to yield a solid compound, m.p. 222-23°C. It was found to be identical to 1a.

The next compound, m.p. 258-59° that followed was eluted by petrol-benzene (4:1). It was found to be identical to 2b.

The third compound, m.p. 238-39°C, eluted by petrol-benzene (3:2) showed in its IR spectrum the presence of hydroxyl group (3280-3320 cm^{-1}) and methylenic double bond (3040, 1620 and 890 cm^{-1}) but did not show any absorption for the carbonyl group indicating that the 3-acetoxy group is hydrolysed. Its mass spectrum showed molecular ion peaks of equal intensity at m/z 506 and 504, showing the presence of one bromine atom. The compound on acetylation (Py - Ac_2O) furnished an acetate, m.p. 222-24°C, identical to 1a. Thus, the compound is 30-bromomoretanol (1b).

The last fraction eluted by petrol-benzene (2:3) had m.p. 206-8°C. Its mass spectrum showed molecular ion peaks of equal intensity at m/z 506, 504 indicating the presence of a bromine atom and its IR spectrum showed the presence of hydroxyl group (3340 cm^{-1}) and olefinic double bond (820 cm^{-1}). Its ^1H NMR spectrum showed the presence of six *tert*-methyls as singlets in the region of δ 0.64 to 0.95 ppm, a methyl at δ 1.67 and 1.69 that appeared in the ratio 1:2, indicated that there is a methyl situated on a double bonded carbon which was confirmed by appearance of an olefinic proton at δ 5.8 and 5.76 once again in 1:2 ratio which was probably due to the existence of *cis-trans* isomers of vinyl bromo derivatives 1c and 1d as observed in the previous cases². Thus, this compound was a mixture of *E/Z*-bromomoretanols (1c and 1d).

It is worth noting that the majority of the products B and C are possibly formed first by allylic bromination to give 30-bromo derivative A which undergoes attack by bromonium ion to form the dibromo carbonium ion, followed by nucleophilic attack by either a bromide ion (Br^-) or hydroxyl ion (OH^-) to furnish B and C respectively. The 29-bromo derivatives (1c/1d) are probably formed by shift of hydrogen from $-\text{CH}_2\text{Br}$ (2a) that is more acidic in basic Al_2O_3 to form the less acidic isomer.

Experimental Section

Melting points are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded in Varian XL-300, 400 spectrometers operating at 75 MHz in the FT model using CDCl_3 as solvent and TMS as internal standard (chemical shifts in δ , ppm downfield from

TMS). Mass spectra were recorded in JMS-D400 at 70 eV; IR spectra in Beckmann-20 spectrophotometer and optical rotations in Jasco-180 using CHCl_3 as solvent. The chromatography columns were prepared from alumina of mesh-60-120 neutralized by 4 ml of 10% AcOH per 100g of alumina and TLC on chromatoplates of silica gel G [E-Merk] using petrolbenzene (1:9) as eluent and the spots were developed in iodine chamber.

In the mass spectra of 1a, 2a and 2b: M_1^+ stands for molecular ion when all the bromine isotopes are 81; M_2^+ when all the bromine isotopes are 79; M_3^+ when one of the bromine isotopes is 79; and M_4^+ when one of the bromine isotopes is 81.

Oxidation of moretenyl acetate 1 with NBS in DMSO

To a solution of 1 (0.5g) in CHCl_3 (2 ml), NBS (0.5g) was added in portions followed by addition of DMSO (20 ml) and the reaction mixture kept in the dark. After 48 hr the mixture was poured in ice cold water when a white solid separated out that was extracted with CHCl_3 . The CHCl_3 layer was thoroughly washed with water and dried (Na_2SO_4). The solvent was removed by distillation and the residue (0.5g) dissolved in benzene was poured in a column of alumina (20g). The column was eluted with solvents of increasing polarity. Petrol eluted solid A, m.p. 215-18°; petrol-benzene (9:1) eluted solid B, m.p. 233-37° and petrol-benzene (3:2) eluted solid C, m.p. 245-50°.

30-Bromomoretanyl acetate (1a)—Compound A (0.1g) was crystallised from CHCl_3 - MeOH, m.p. 222-24°; (Found: C, 70.12; H, 9.30. $\text{C}_{32}\text{H}_{51}\text{O}_2\text{Br}$ requires C, 70.75; H, 9.36%); IR: 3040, 1640, 840 ($=\text{CH}_2$), 1720, 1245 cm^{-1} ($-\text{OCOCH}_3$); MS: m/z (Rel. int.), 548 (M_1 , 6.5)⁺, 546 (M_2 , 6.6)⁺, 533 ($M_1 - \text{CH}_3$, 1.7)⁺, 531 ($M_2 - \text{CH}_3$)⁺, 488 ($M_1 - \text{CH}_3\text{COOH}$, 4.0)⁺, 486 ($M_2 - \text{CH}_3\text{COOH}$, 3.0)⁺, 467(4.5), 269(2), 267(20), 249(17), 203(25), 189(100); ^1H NMR: δ 0.69, 0.76, 0.84, 0.94, 0.97, 1.05, (6s, 6 \times *t*- CH_3), 2.03 (s, 3H, $-\text{OCOCH}_3$), 4.1 (AB_{q} , $J = 10$ Hz, 2H, $-\text{CH}_2\text{Br}$), 4.45 (m, 1H, $H - C - 3 - O$), 4.9 and 5.9 (2s, 2H, $C = H_2$).

22,29,30-Tribromomoretanyl acetate (2a)—Fraction B (0.2g) was crystallised from CHCl_3 - MeOH, m.p. 241-42°; $[\alpha]_{\text{D}} + 23.14$ (Found: C, 54.37; H, 7.3. $\text{C}_{32}\text{H}_{51}\text{O}_2\text{Br}_3$ requires C, 54.32; H, 7.26%); IR: 1725, 1245 cm^{-1} ($-\text{OCOCH}_3$), MS: m/z 710 (M_1 , 2.5)⁺, 708 (M_3 , 7.5)⁺, 706 (M_4 , 7.3)⁺, 704 (M_2 , 2.2)⁺, 649 ($M_1 - \text{AcOH}$, 2.4)⁺, 648 ($M_3 - \text{AcOH}$, 6.0)⁺, 646 ($M_4 - \text{AcOH}$, 5.9)⁺, 644 ($M_2 - \text{AcOH}$, 2.0)⁺, 635(2), 633(6), 631(6.1), 629(2.3), 548(3.9), 547(8), 546(3), 545(7), 429(7.3), 428(14), 426(15), 348, 346, 268,

266(15), 249(20), 205(14), 204(15), 203(16), 189(79 base); $^1\text{H NMR}$: δ 0.75, 0.84, 0.85, 0.95, 1.00, 1.27 (6s, 18H, $6 \times t\text{-CH}_3$), 2.05 (s, 3H, $-\text{OCOCH}_3$), 3.8-4.2 (2 AB_q , 4H, $2 \times \text{CH}_2\text{Br}$).

29,30-Dibromo-22-hydroxymoretanyl acetate (2b)—Fraction C (0.2g) was crystallised from $\text{CHCl}_3\text{-MeOH}$, m.p. 258-59°, $[\alpha]_D + 25$; showed positive Beilstein test for halogen but no colouration with TNM (Found: C, 59.40; H, 8.03. $\text{C}_{32}\text{H}_{52}\text{O}_3\text{Br}_2$ requires C, 59.63; H, 8.13%); IR: 3360 (OH), 1730, 1250 cm^{-1} ($-\text{OCOCH}_3$); MS: m/z 645 ($M_1\text{-H}$, 0.1) $^+$, 643 ($M_3\text{-H}$, 0.2) $^+$, 641 ($M_2\text{-H}$, 0.1) $^+$, 585 (645-AcOH, 0.1), 583 (643-AcOH, 0.2), 581 (641-AcOH), 570 (585- CH_3 , 0.5), 567 (583- CH_3 , 0.4), 565 (645-Br, 0.4), 563 (543-Br, 0.4), 547 (565- H_2O , 3), 545 (563- H_2O , 2), 532, 530, 466, 465, 425, 407, 410, 367, 269, 267, 249, 205, 203, 189 (base); $^1\text{H NMR}$: δ 0.72, 0.84, 0.85, 0.86, 0.94, 0.98 (6s, 18H, $6 \times t\text{-CH}_3$), 2.06 (s, 3H, $-\text{COCH}_3$), 3.57-3.72 (2 AB_q + 2s + m, 4H, $2 \times \text{CH}_2\text{Br}$), 4.45 (m, 1H, H-C-3-OAc).

Effect of basic alumina on 2a—The mother liquor obtained after crystallisation of B was dried and the residue (0.1g) dissolved in benzene was adsorbed over basic alumina (10g). It was kept for 7 days while the surface was kept submerged in petrol. On the 8th day it was eluted with solvents of increasing polarity. The following fractions were collected. Fraction D (0.02g) [Petrol], Fraction E (0.025g) [petrol:benzene (4:1)], Fraction F (0.015g) [petrol:benzene; 3:2], Fraction G (0.02g) [petrol:benzene; 2:3].

Fraction D; crystallised from $\text{CHCl}_3\text{-MeOH}$, m.p. 222-24° was identical [m.m.p., co-TLC and co-IR] with 30-bromomoretanyl acetate (1a).

Fraction E; crystallised from $\text{CHCl}_3\text{-MeOH}$ m.p. 258-59° was identical (m.m.p., co-IR and co-TLC) with 29,30-dibromo-22-hydroxymoretanyl acetate (2b).

Fraction F; crystallised from $\text{CHCl}_3\text{-MeOH}$ m.p. 238-39°; Acetate (Py-Ac₂O), m.p. 222-23°. It was identical with (m.m.p., co-TLC and co-IR) 1a. Thus, the compound obtained from fraction F was identical to 1b.

Fraction G, crystallised from $\text{CHCl}_3\text{-MeOH}$ m.p. 206-8°C. Compound obtained from the fraction G was found to be a mixture of *E/Z*-29-bromomoretanols (1c + 1d).

Acknowledgement

The authors thank Dr J N Shoolery, Variar Associate, Palo Alto, USA, for the $^1\text{H NMR}$, $^{13}\text{C NMR}$ and 2D NMR spectra; to Prof K K Balasubramanium, IIT, Madras, for some of the $^1\text{H NMR}$ spectra and to the Director, CDRI Lucknow for the mass spectra and the optical rotations. One of them (SC) is grateful to CSIR for the award of a Research Associateship.

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Studies on the reaction of N-bromosuccinimide in dimethyl sulphoxide.
Part IX—Action on moretenyl acetate

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Received 19 April 1994, revised and accepted 25 January 1995

The action of N-bromosuccinimide on moretenyl acetate (1) in dimethyl sulphoxide affords 30-bromo-moretenyl acetate (1a), 22,29,30-tribromomoretanyl acetate (2a) and 29,30-dibromo-22-hydroxy-moreten-3 β -yl acetate (2b). 2a on adsorption over basic alumina for 7 days furnishes 1a, 2b, 30-bromo-moretenol (1b), and *E/Z*-29-bromomoretanols (1c + 1d).

OC-6348A, d/15, PD

In continuation of our studies^{1,2} on the action of N-bromosuccinimide (NBS) in dimethyl sulphoxide (DMSO) on isopropenyl group of lupane skeleton, we report herein the isolation and characterization of the products A, B and C obtained by the reaction of NBS in DMSO on moretenyl acetate (3 β -acetyl-21 α H-hop-22(29)-ene) (1)^{3,4}, a compound of isohopane skeleton having an isopropenyl group attached to a cyclopentane ring. Also the action of basic alumina on the tribromo product B is reported in this paper.

Compound A—Eluted by petrol was analysed for C₃₂H₅₁O₂Br, m.p. 222–24°. IR spectrum showed the presence of a vinyl group (3040, 840 cm⁻¹) and acetate group (1720, 1245 cm⁻¹). The presence of double bond was confirmed by the 1NM test for unsaturation. It gave green coloured flame in Beilstein's test showing the presence of bromine in the molecule and in the mass spectrum the presence of two peaks of the same height at m/z 548 and 546 indicated that there is a bromine atom in A. ¹H NMR spectrum of A showed the presence of six tertiary methyls in the region δ 0.69 to 1.23. The AB quartet centered at 4.1 ppm (*J* = 10 Hz) integrating for two protons indicated that the carbon atom bearing these two protons is attached to a sufficiently electronegative element or group to cause the downfield shift of the protons. Thus the bromine atom must be attached to a primary carbon showing the presence of -CH₂Br group. The vinyl protons that appeared at δ 4.9 and 5.9 integrated for one proton each were attributed to =CH₂ group. Thus A has been assigned the structure 30-bromomoretanyl acetate (30-bromo-3 β -acetoxy-21 α H-hop-22(29)-ene) (1a).

Compound B—It analysed for C₃₂H₅₁O₂Br₃, m.p. 241–42°, [α]_D + 23.14. Its IR spectrum showed the presence of acetate group (1725, 1245 cm⁻¹). Its mass spectrum showed the molecular ion peaks m/z 710, 708, 706, 704 in the ratio 1:3:3:1 indicating the presence of three bromine atoms in the molecule of compound B. Further, the existence of molecular ion peak at m/z 427 indicated loss of all the three bromine atoms along with the isopropyl group showing that all the three bromine atoms belong to the isopropyl group⁴.

The structure of B was further confirmed from the ¹H NMR spectrum. It exhibited six singlets in the region δ 0.75 to 1.27 each integrating for three protons accounting for six tertiary methyls; a multiplet in the region δ 3.8 to 4.2 integrating for four protons was due to two AB quartets, superimposed on each other by plotting a Copsy spectrum, that were assignable to the isolated two -CH₂Br groups (the protons of each pair resonated at δ 3.81 and 3.97 and 3.94 and 4.15 ppm with the same coupling value of 11 Hz). This was further supported by addition of C₆D₆ to the solution that clearly separated the two AB quartets.

¹³C NMR spectrum of compound B showed the presence of 32 carbons in the region 171 to 15 ppm and the DEPT experiments showed the presence of seven quartets one of which was due to acetoxy methyl (21.0) (thus two less than in the starting compound 1), twelve triplets for twelve CH₂ carbons (two more than those in 1), two of which were due to -CH₂Br carbons (38.86 and 40.2), six doublets for six -CH carbons (one less than that in 1) and seven singlets for tertiary carbons (one more than that in 1). The one peak at 76.06 ppm was definitely due to a tertiary carbon bearing an electronegative halogen atom showing that C-22 carries a bromide atom. Thus B has been assigned structure 22,29,30-tribromomoretanyl acetate (22,29,30-tribromo-3 β -acetoxy-21 α H-hopane) (2a).

¹³C NMR spectra of compound B are given in Table 1.

Compound C—It was analysed for C₃₂H₅₁O₃Br₂, m.p. 258–59°, [α]_D + 25. Its IR spectrum showed the presence of a hydroxyl group (3360 cm⁻¹) and acetoxy group (1730, 1250 cm⁻¹). Its mass spectrum showed molecular ion peaks at m/z 645, 643, 641 in the ratio (1:2:1) typical for the compound with two bromine atoms^{1,2}, that the two bromine atoms and the hydroxyl groups are present on the isopropyl group was indicated by the molecular ion peak at m/z 427 which is caused by the homolytic cleavage of C-21 side chain [M⁺ - 217].

¹H NMR spectrum of C showed the presence of six *tert*-methyls in the region δ 0.72-0.93 ppm, the acetoxy methyl at δ 2.06 and the C-3 methine proton at δ 4.45. It showed a pair of AB quartets centered at δ 3.57 and 3.72 ($J = 10$ Hz), two singlets at δ 3.48 and 3.66 ppm typical of a pair of $-\text{CH}_2\text{Br}$ without restricted rotation and another set of non-resolvable peaks in the region δ 3.42 to 3.56 ppm. The total number of protons integrated were four, an indication that the pairs of $-\text{CH}_2\text{Br}$ are in three different geometries where one pair had restricted rotation and the other two pairs had free rotation. This interpretation was confirmed by its ¹³C NMR spectrum that showed three singlets around 74.00 ppm integrating for one carbon pointing to the fact that this carbon had three different stereoisomers carrying either a hydroxyl or bromine atom and it must be the C-22 carbon. Such an observation was also reported by Wenkert *et al.*¹ in the case of C-22 hydroxyl hopane. Thus, compound C has been assigned the structure 29,30-dibromo-22-hydroxy-21 α H-hopane-3 β -yl acetate (2b).

The ¹³C NMR spectra of compound C are given in Table I.

Effect of basic alumina on compound 2a ^B

2a was subjected to basic alumina hydrolysis by keeping it adsorbed for seven days. On the 8th day it was eluted first with petrol to yield a solid compound, m.p. 222-23°C. It was found to be identical to 1a.

The next compound, m.p. 258-59° that followed was eluted by petrol-benzene (4:1). It was found to be identical to 2b. ^C

The third compound, m.p. 238-39°C, eluted by petrol-benzene (3:2) showed in its IR spectrum the presence of hydroxyl group (3280-3320 cm^{-1}) and methylenic double bond (3040, 1620 and 890 cm^{-1}) but did not show any absorption for the carbonyl group indicating that the 3-acetoxy group is hydrolysed. Its mass spectrum showed molecular ion peaks of equal intensity at m/z 506 and 504, showing the presence of one bromine atom. The compound on acetylation (Py-Ac₂O) furnished an acetate, m.p. 222-24°C, identical to 1a. Thus, the compound is 30-bromomoretenol (1b). ^D

The last fraction eluted by petrol-benzene (2:3) had m.p. 206-8°C. Its mass spectrum showed molecular ion peaks of equal intensity at m/z 506, 504 indicating the presence of a bromine atom and its IR spectrum showed the presence of hydroxyl group (3340 cm^{-1}) and olefinic double bond (820 cm^{-1}). Its ¹H NMR spectrum showed the presence of six *tert*-methyls as singlets in the region of δ 0.64 to 0.95 ppm, a methyl at δ 1.67 and 1.69 that appeared in the ratio 1:2, indicated that there is a methyl situated on a double bonded carbon which was confirmed by appearance of an olefinic proton at δ 5.8 and 5.76 once again in 1:2 ratio which was probably due to the existence of *cis-trans* isomers of vinyl bromo derivatives 1c and 1d, as observed in the previous cases². Thus, this compound was a mixture of *E/Z*-bromomoretenols (1c and 1d).

It is worth noting that the majority of the products B and C are possibly formed first by allylic bromination to give 30-bromo derivative A which undergoes attack by bromonium ion to form the dibromo carbonium ion, followed by nucleophilic attack by either a bromide ion (Br^-) or hydroxyl ion (OH^-) to furnish B and C respectively. The 29-bromo derivatives (1c/1d) are probably formed by shift of hydrogen from $-\text{CH}_2\text{Br}$ (2a) that is more acidic in basic Al_2O_3 to form the less acidic isomer. ^E

Experimental Section

Melting points are uncorrected. ¹H NMR and ¹³C NMR spectra were recorded in Varian XL-300, 400 spectrometers operating at 75 MHz in the FT model using CDCl_3 as solvent and TMS as internal standard (chemical shifts in δ , ppm downfield from TMS). Mass spectra were recorded in JMS-D400 at 70 eV; IR spectra in Beckmann-20 spectrophotometer and optical rotations in Jasco-180 using CHCl_3 as solvent. The chromatography columns were prepared from alumina of mesh-60-120 neutralized by 4 ml of 10% AcOH per 100g of alumina and TLC on chromatoplates of silica gel G [E-Merk] using petrolbenzene (1:9) as eluent and the spots were developed in iodine chamber.

In the mass spectra of 1a, 2a and 2b: M_1^+ stands for molecular ion when all the bromine isotopes are 81; M_2^+ when all the bromine isotopes are 79; M_3^+ when one of the bromine isotopes is 79; and M_4^+ when one of the bromine isotopes is 81. ^F

Oxidation of moretenyl acetate 1 with NBS in DMSO

To a solution of 1 (0.5g) in CHCl_3 (2 ml), NBS (0.5g) was added in portions followed by addition of DMSO (20 ml) and the reaction mixture kept in the dark. After 48 hr the mixture was poured in ice cold water when a white solid separated out that was extracted with CHCl_3 . The CHCl_3 layer was thoroughly washed with water and dried (Na_2SO_4). The solvent was removed by distillation and the residue (0.5g) dissolved in benzene was poured in a column of alumina (20g). The column was eluted with solvents of increasing polarity. Petrol eluted solid A, m.p. 215-18°; petrol-benzene (9:1) eluted solid B, m.p. 233-37° and petrol-benzene (3:2) eluted solid C, m.p. 245-50°. ^G

30-Bromomoretenyl acetate (1a) -- Compound A (0.1g) was crystallised from CHCl_3 -MeOH, m.p. 222-24°; (Found: C, 70.12; H, 9.30. $\text{C}_{32}\text{H}_{51}\text{O}_2\text{Br}$ requires C, 70.75; H, 9.36%); IR: 3040, 1640, 840 ($=\text{CH}_2$)/1720, 1245 cm^{-1} ($-\text{OCOCH}_3$); MS: m/z (Rel. int.), 548 (M_1 , 6.5)⁺, 546 (M_2 , 6.6)⁺, 533 ($M_1-\text{CH}_3$, 1.7)⁺, 531 ($M_2-\text{CH}_3$)⁺, 488 ($M_1-\text{CH}_2\text{COOH}$, 4.0)⁺, 486 ($M_2-\text{CH}_2\text{COOH}$, 3.0)⁺, 467(4.5), 269(2), 267(20), 249(17), 203(25), 189(100); ¹H NMR: δ 0.69, 0.76, 0.84, 0.94, 0.97, 1.05, (6s, 6 \times $-\text{CH}_3$), 2.03 (s, 3H, $-\text{OCOCCH}_3$), 4.1 (ABq, $J = 10$ Hz, 2H, $-\text{CH}_2\text{Br}$), 4.45 (m, 1H, H C-3-O), 4.9 and 5.9 (2s, 2H, C-11₂). ^H

22,29,30-Tribromomoretanyl acetate (2a)—Fraction B (0.2g) was crystallised from CHCl_3 - MeOH, m.p. 241-42°; $[\alpha]_D^{25} + 23.14$ (Found: C, 54.37; H, 7.3. $\text{C}_{22}\text{H}_{21}\text{O}_3\text{Br}_3$ requires C, 54.32; H, 7.26%); IR: 1725 (1245 cm^{-1} (-COCH₃)), MS: m/z 710 (M_1 , 2.5)⁺, 708 (M_3 , 7.5)⁺, 706 (M_4 , 7.3)⁺, 704 (M_3 , 2.2)⁺, 649 (M_1 -AcOH, 2.4)⁺, 648 (M_3 -AcOH, 6.0)⁺, 646 (M_4 -AcOH, 5.9)⁺, 644 (M_2 -AcOH, 2.0)⁺, 635(2), 633(6), 631(6.1), 629(2.3), 548(3.9), 547(8), 546(3), 545(7), 429(7.3), 428(14), 426(15), 348, 346, 268, 266(15), 249(20), 205(14), 204(15), 203(16), 189(79 base); ¹H NMR: δ 0.75, 0.84, 0.85, 0.95, 1.00, 1.27 (6s, 18H, 6 × $1-\text{CH}_3$), 2.05 (s, 3H, -COCH₃), 3.8-4.2 (2 AB₂, 4H, 2 × CH₂Br).

29,30-Dibromo-22-hydroxymoretanyl acetate (2b)—Fraction C (0.2g) was crystallised from CHCl_3 - MeOH, m.p. 258-59°, $[\alpha]_D^{25} + 25$; showed positive Beilstein test for halogen but no colouration with TNM (Found: C, 59.40; H, 8.03. $\text{C}_{22}\text{H}_{21}\text{O}_3\text{Br}_2$ requires C, 59.63; H, 8.13%); IR: 3360 (OH), 1730, 1250 cm^{-1} (-COCH₃); MS: m/z 645 (M_1 -H, 0.1)⁺, (M_3 -H, 0.2)⁺, 641 (M_2 -H, 0.1)⁺, 585 (645-AcOH, 0.1), 583 (643-AcOH, 0.2), 581 (641-AcOH), 570 (585-CH₃, 0.5), 567 (583-CH₃, 0.4), 565 (645-Br, 0.4), 563 (543-Br, 0.4), 547 (565-H₂O, 3), 545 (563-H₂O, 2), 532, 530, 466, 465, 425, 407, 410, 367, 269, 267/249, 205, 203, 189 (base); ¹H NMR: δ 0.72, 0.84, 0.85, 0.86, 0.94, 0.98 (6s, 18H, 6 × $1-\text{CH}_3$), 2.06 (s, 3H, -COCH₃), 3.57/3.72 (2AB₂ + 2s + m, 4H, 2 × CH₂Br), 4.45 (m, 1H, H-C-3-OAc).

Effect of basic alumina on 2a—The mother liquor obtained after crystallisation of B was dried and the residue (0.1g) dissolved in benzene was adsorbed over basic alumina (10g). It was kept for 7 days while the surface was kept submerged in petrol. On the 8th day it was eluted with solvents of increasing polarity. The following fractions were collected. Fraction D (0.02g) [Petrol], Fraction E (0.025g) [petrol:benzene (4:1)], Fraction F (0.015g) [petrol:benzene: 3:2], Fraction G (0.02g) [petrol:benzene: 2:3].

Fraction D; crystallised from CHCl_3 - MeOH, m.p. 222-24° was identical [m.m.p., co-TLC and co-IR] with 30-bromomoretanyl acetate (1a).

Fraction E; crystallised from CHCl_3 - MeOH, m.p. 258-59° was identical (m.m.p., co-IR and co-TLC) with 29,30-dibromo-22-hydroxymoretanyl acetate (2b).

Fraction F; crystallised from CHCl_3 - MeOH, m.p. 238-39°; Acetate (Py-Ac₂O), m.p. 222-23°. It was identical with (m.m.p., co-TLC and co-IR) 1a. Thus, the compound obtained from fraction F was identical to 1b.

Fraction G; crystallised from CHCl_3 - MeOH, m.p. 206-8°C. Compound obtained from the fraction G was found to be a mixture of *E/Z*-29-bromomoretanols (1c + 1d).

Acknowledgement

The authors thank Dr J N Shoolery, Varian Associate, Palo Alto, USA, for the ¹H NMR, ¹³C NMR and 2D NMR spectra; to Prof K K Balasubramaniam, IIT, Madras, for some of the ¹H NMR spectra and to the Director, CDRI, Lucknow for the mass spectra and the optical rotations. One of them (SC) is grateful to CSIR for the award of a Research Associateship.

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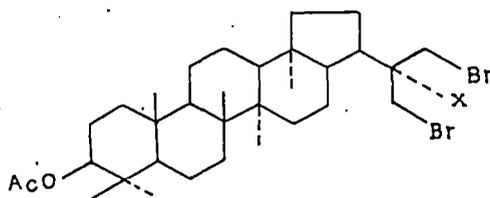
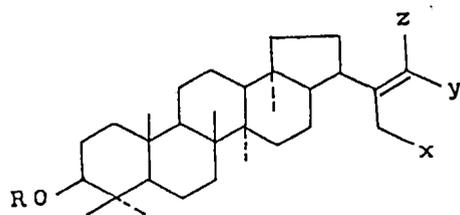
¹Present address: Chemistry Dept., Dinhatia College, Cough Behar.

Table I—¹³C NMR signals (δ , ppm) of compounds 2a and 2b

Carbon No.	2a	2b
1	38.4	38.4
2	23.6	23.6
3	80.9	80.9
4	37.8	37.9
5	55.2	55.2
6	18.2	18.2
7	33.2	33.2
8	41.5	41.6
9	50.2	50.2
10	37.0	36.9
11	20.9	20.9
12	23.7	24.0
13	48.4	48.4
14	41.9	41.6
15	32.8	32.6
16	26.6	24.0, 24.4
17	54.2	52.0
18	45.4	45.1
19	40.8	40.4
20	23.6	23.6
21	45.9	47.6
22	76.1	75.2, 73.8, 74.6
23	28.0	28.0
24	16.0	16.0
25	15.9	15.2
26	16.5	16.4
27	18.8	16.8
28	16.1	16.4
29	38.9	39.2, 39.4, 39.6
30	40.3	39.6, 39.8, 40.0
COCH ₃	170.0	171.0
COCH ₂ Br	21.3	21.2

Carbon No. 2a 2b

Carbon No. 2a 2b



- 1 , R = Ac , x = y = z = H
1a , R = Ac , x = Br , y = z = H
1b , R = H , x = Br , y = z = H
1c , R = H , x = y = H , z = Br
1d , R = H , x = z = H , y = Br

- 2a , x = Br
2b , x = OH

all the three bromine atoms (as well as the hydroxyl group).

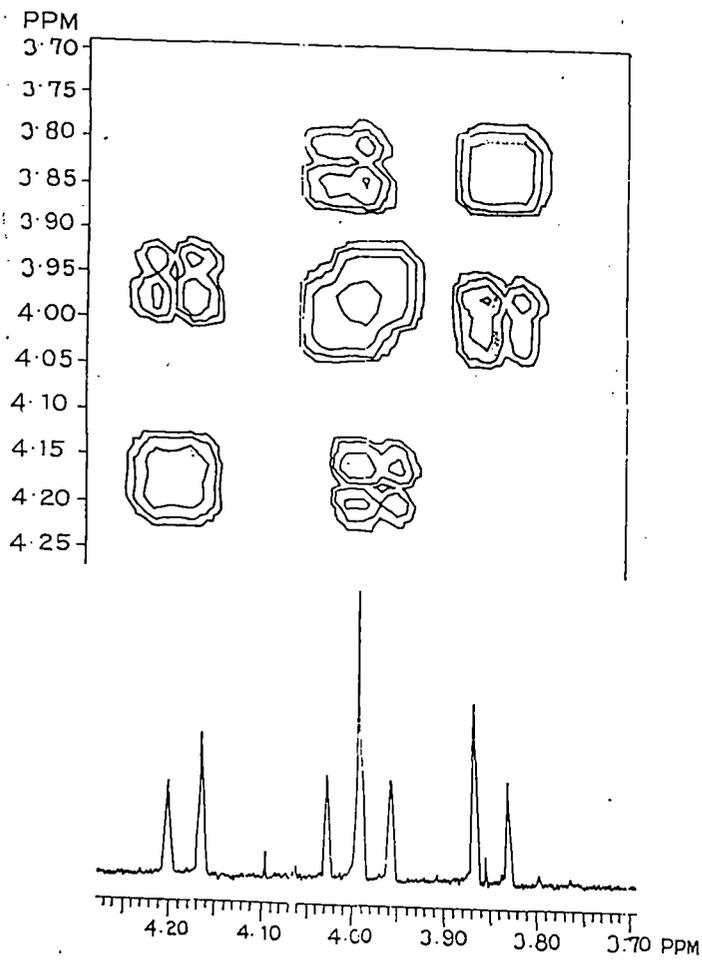


Fig. 1.

g with the isopropyl group containing two
 bromine atoms belong to the isopropyl