# Application of Tris(dipivaloylmethanato)europium(III) to the Assignments of the Methyl Resonances of Triterpenes related to Serratenediol [C(14a)-Homo-27-norgammacer-14-ene-3β,21α-diol]

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The n.m.r. spectra of triterpenes related to serratenediol was examined by use of the shift reagent $Eu(DPM)_3$. The upfield and downfield shifts of methyl resonances were observed for the same molecule and this is an example of the importance of the angle dependence term in the McConell and Robertson equation. The relative strength of association at the competing sites in a polyacetoxytriterpene was different, and the association coefficient at each co-ordinating site was taken as a measure of the relative strength of association. Assignment of the methyl resonances of serratenediol diacetate [C(14a)-homo-27-norgammacer-14-ene-3β,21α-diyl diacetate] and serratriol triacetate [C(14a)-homo-27-norgammacer-14-ene-3β,21α,24-triyl triacetate] has been achieved.

EVER since the effectiveness of the dipyridine adduct of the rare earth complex, $Eu(DPM)_3$, as a shift reagent was shown by Hinckley,[1] there have been reported a number of investigations of the applications for this reagent.[2] We examined simplifications of the spectra of triterpenes related to serratenediol,[3] possessing more than one co-ordinating function, using $Eu(DPM)_3$ as a shift reagent. In addition, the effectiveness of the shift reagent in aiding the assignments of methyl signals in the spectra of the triterpenes was investigated.

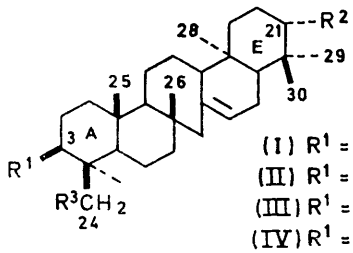
The n.m.r. spectra of serraten-3β-ol acetate (I) at various ratios of shift reagent to substrate are shown in Figure 1. Upon addition of the shift reagent, the

[1] C. C. Hinkley, *J. Amer. Chem. Soc.*, 1969, **91**, 5160.

[2] K. J. Liska, A. F. Fentiman, and R. L. Foltz, *Tetrahedron Letters*, 1970, 4657; O. Achmatowicz, A. Ejchart, J. Jurczak, L. Kozerski, and J. St. Pyrek, *Chem. Comm.*, 1971, 98; F. I. Carroll and J. T. Blackwell, *Tetrahedron Letters*, 1970, 4173; T. H. Siddall, tert., *Chem. Comm.*, 1971, 452; P. H. Mazzocchi, H. J. Tamburin, and G. R. Miller, *Tetrahedron Letters*, 1971, 1819.

[3] Y. Inubushi, T. Sano, and Y. Tsuda, *Tetrahedron Letters*, 1964, 1303; Y. Tsuda, T. Sano, K. Kawaguchi, and Y. Inubushi, *ibid.*, p. 1279; Y. Inubushi, Y. Tsuda, T. Sano, T. Konita, S. Suzuki, H. Ageta, and Y. Otake, *Chem. and Pharm. Bull. (Japan)*, 1967, **15**, 1153.

spectrum was simplified without serious broadening effects. Increasing the amount of $Eu(DPM)_3$ resolved




(I) $R^1$ = OAc $R^2$ = H $R^3$ = H
(II) $R^1$ = H $R^2$ = OAc $R^3$ = H
(III) $R^1$ = OAc $R^2$ = OAc $R^3$ = H
(IV) $R^1$ = OAc $R^2$ = OAc $R^3$ = OAc
(V) $R^1$ = OAc $R^2$ = H $R^3$ = OAc

the spectrum such that, at a molar ratio 1 : 2 of shift reagent to substrate, all seven methyl signals could be 23-$H_3$(*eq*) and that of 2*eq*-H is larger than that of 2*ax*-H. Furthermore, the europium atom in the complex will be *ca.* 2—3 Å from the two oxygen atoms of the acetoxy-group.[4,5] From these facts, the europium atom was estimated to be located at the place shown in Figure 2.

In the acetate (I), the three methyl signals suffering the most significant shifts to lower field are assigned to 24*ax*-, 23*eq*-, and 25-positions, respectively, by consideration of the distance of each methyl group from the co-ordinating metal ion. The signal showing the fourth large induced change is assignable to 26-Me because the shift parameter of this group is greater than that of the olefinic proton which is farther from the metal ion than 26-$H_3$. The remaining three methyl signals showed upfield shifts suggesting the importance of the

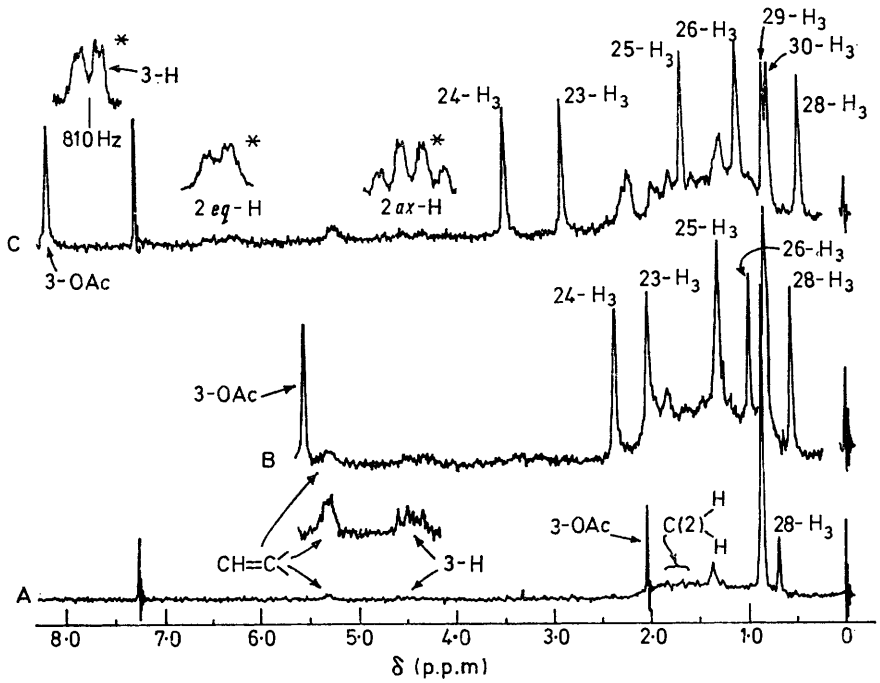



FIGURE 1 60 MHz N.m.r. spectra of serraten-3β-ol acetate (I) (10 mg) in $CDCl_3$ (0·4 ml) containing various amounts of $Eu(DPM)_3$; A, without $Eu(DPM)_3$; B, with 0·011M-$Eu(DPM)_3$; and C, with 0·018M-$Eu(DPM)_3$. The signals marked with * are the accumulated signals

recognised separately instead of only two distinct peaks in the absence of the shift reagent. The chemical shifts of signals due to methyl groups, an acetoxy-methyl group, an olefinic proton and a methine proton geminal to an acetoxy-group varied linearly with the molar ratio of shift reagent to substrate and the induced chemical shift ($\delta_E$) was given by the equation $\delta_E = \delta + S[Eu(DPM)_3/\text{substrate}]$,[4] where $\delta$ is the chemical shift in the uncomplexed substrate and $S$ is the europium shift parameter, the slope of the line.

As shown in Figure 1, the induced chemical shifts of 2*ax*-H and 2*eq*-H are larger than those of 24-$H_3$(*ax*) and angle dependence term of the McConnell and Robertson equation.[6] Supposing that the axis of the magnetic dipole in the $Eu(DPM)_3$–acetoxy association is in the direction from the midway position between the two

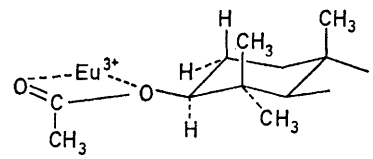



FIGURE 2

oxygen atoms of an acetoxy-group toward the europium atom, the europium atom is situated in such a position

[4] A. F. Cockerill and D. M. Rackham, *Tetrahedron Letters*, 1970, 5149; 5153.

[5] J. K. M. Sanders and D. H. Williams, *J. Amer. Chem. Soc.*, 1971, **93**, 641; G. M. Whitesides and D. W. Lewis, *ibid.*, 1970, **92**, 6979.

[6] H. McConnell and R. E. Robertson, *J. Chem. Phys.*, 1958, **29**, 1361.

that the value of the $(3\cos^2\theta - 1)$ term of the McConnell and Robertson equation for the olefinic proton is positive and those for the methyl groups on ring E are negative. In the molecular model, these three methyl groups are approximately in a straight line, when seen from the europium atom position. The shift parameter of each methyl group, therefore, only depends on the distance from the metal ion. Accordingly, methyl resonances showing upfield shifts are assigned to 29-, 30-, and 28-$H_3$, respectively, in order of their appearance from low to high field. In order to confirm the dependence on the angle term, the spectra of serraten-3β-ol (I; $R^1 = OH$) obtained by co-ordination of the shift reagent were examined and in this case, all methyl groups experienced downfield shifts. Consequently, it is clear that the direction of the axis of the magnetic dipole for $Eu(DPM)_3$–acetoxy association varies remarkably compared with that for $Eu(DPM)_3$–hydroxy association. The observed $S_{n=1}$ values of signals where $n$ is a molar ratio of shift reagent to substrate were obtained by good linear extrapolations and are shown in the Table.

Some chemical shifts (in Hz downfield from tetramethylsilane) of compounds (I)—(V)

| | Serraten-3β-ol acetate (I) | | Serraten-21α-ol acetate (II) | | Serratenediol diacetate (III) | | | Serratriol triacetate (IV) | | | 21-Deoxyserratriol diacetate (V) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | δ | $S_{obs}$ | δ | $S_{obs}$ | δ | $S_{obs}$ | $S_{calc}$ | δ | $S_{obs}$ | $S_{calc}$ | δ | $S_{obs}$ | $S$[C(24)–OAc–Eu] |
| 23-$H_3$ | 51 | 139 | 51 | −7 | 51 | 92 | 95 | 60 | 154 | 154 | 60 | 220 | 105 |
| 24-$H_3$ | 51 | 180 | 49 | −14 | 51 | 130 | 119 | | | | | | |
| 25-$H_3$ | 51 | 54 | 49 | −32 | 51 | 18 | 14 | 51 | 43 | 43 | 51 | 89 | 45 |
| 26-$H_3$ | 51 | 11 | 51 | −26 | 51 | −6 | −14 | 51 | −1 | −2 | 51 | 21 | 12 |
| 28-$H_3$ | 40 | −14 | 42 | 47 | 42 | 30 | 27 | 42 | 29 | 26 | 40 | −8 | 4 |
| 29-$H_3$ | 51 | −2 | 54 | 145 | 55 | 110 | 113 | 55 | 86 | 96 | 51 | −3 | −1 |
| 30-$H_3$ | 51 | −4 | 51 | 185 | 51 | 148 | 143 | 51 | 126 | 119 | 53 | −9 | −6 |
| CH=C | 319 | 0 | 319 | 17 | 321 | 13 | 13 | 321 | 13 | 12 | 318 | 5 | 5 |
| 3-OAc | 122 | 416 | | | 122 | 294 | | 123 | 241 | | 123 | 339 | |
| 21-OAc | | | 123 | 436 | 122 | 350 | | 122 | 295 | | | | |
| 24-OAc | | | | | | | | 123 | 161 | | 122 | 232 | |
| 3-H | 269 | 610 | | | 270 | 454 | | 270 | 401 | | 272 | 508 | |
| 21-H | | | 271 | 630 | 270 | 490 | | 270 | 428 | | | | |
| 24-$H_2$ | | | | | | | | 255 | 251 | | 254 | 358 | |

Measurements were made on the spectra of serraten-21α-ol acetate (II) at various ratios of shift reagent to substrate and the assignments of signals were performed in analogy with the 3β-acetate (I). The observed $S_{n=1}$ values were obtained by linear extrapolations and are shown in the Table.

Next, the effect of $Eu(DPM)_3$ on the chemical shift behaviour of signals in serratenediol diacetate (III), in which two acetoxy-functions are present, were examined. The assignment of the signals of the acetoxy-groups was performed as follows. First, the spectrum of [21-$^2$H]-serratenediol diacetate derived from serratenediol 3-acetate [7] was taken in order to establish the assignment of the methine proton at C(3). From this result, the signal due to the methine proton at C(21) was in turn readily assignable. Since the conformations of rings A and E are identical, the shift parameters of the 3- and 21-acetoxy-methyl groups will be parallel to those of 3-H and 21-H, respectively. Accordingly, the resonances of the two acetoxy-methyl groups were also assigned. The nature of the shift reagent interaction was normal and the observed $S_{n=1}$ values of these protons together with those of other methyl groups are shown in the Table.

In the diacetate (III), the spatial environment of each acetoxy-group at C(3) and C(21) is identical. In fact, the carbonyl i.r. absorption bands overlap one another and in the n.m.r. spectrum, the proton signals of the two acetoxy-groups lie over each other. Further, the acetoxy-methyl group and the methine proton of ring A in the acetate (I) had approximately the same $S_{n=1}$ values as those of the corresponding protons of ring E in the diacetate (II). From these observations, it was anticipated that $Eu(DPM)_3$ would associate similarly with 3- and 21-OAc. Contrary to our expectations, the observed $S_{n=1}$ values of these protons on rings A and E significantly differ from one another.

At this point, the following assumptions were made. First, the concomitant association of the shift reagent to two acetoxy-functions is improbable under the experimental conditions. Secondly, the association effect due to 3-OAc for protons on ring E and that due to 21-OAc for protons on ring A would be negligible in the diacetate (III). In fact, the $S_{n=1}$ values for 29- and 30-$H_3$ in the acetate (I) are −2 and −4 Hz, respectively, whereas those for these groups in the diacetate (II) are +145 and +185 Hz, respectively.

The ratios of the $S_{n=1}$ values for two acetoxymethyl groups and two methine protons at C(3) and C(21) in diacetate (III) to those for the corresponding protons in monoacetate (I) and (II) were then calculated as 3-OAc (III) : 3-OAc (I) 0·707, 21-OAc (III) : 21-OAc (II) 0·803, 3-H( III) : 3-H (I) 0·744, and 21-H (III) : 21-H (II) 0·778.

These ratios suggest that the relative strength of association at the competing sites is different and this difference may arise from unanalysed factors such as the conformation of the molecule as a whole, *etc.* The association coefficient at each site was taken as a measure of the relative strength of association and evaluated by equation (1), where $S^{(III)}$ calc. is the

$$S^{(III)}\text{ calc.} = a \,.\, S^{(I)}[\text{C(3)–OAc–Eu}] + b \,.\, S^{(II)}[\text{C(21)–OAc–Eu}] \quad (1)$$

[7] Y. Inubushi, Y. Tsuda, H. Ishii, T. Sano, M. Hosokawa, and T. Harayama, *J. Pharm. Soc. Japan*, 1964, **84**, 1108.

calculated value of $S_{n=1}$ for each methyl signal in compound (III), $S^{(I)}$[C(3)–OAc–Eu] is the $S_{n=1}$ value of each methyl signal in the (I)–Eu(DPM)$_3$ complex, $S^{(II)}$[(C(21)–OAc–Eu] is the $S_{n=1}$ value of each methyl signal in the (II)–Eu(DPM)$_3$ complex, $a$ is the association coefficient for the C(3)–OAc function in compound (III) [equation (2)], and $b$ is the association coefficient for the

$$a = 1/2 \left\{ \frac{S^{(III)}_{n=1}[C(3)\cdot O\cdot CO\cdot CH_3]}{S^{(I)}_{n=1}[C(3)\cdot O\cdot CO\cdot CH_3]} + \frac{S^{(III)}_{n=1}[C(3)-H]}{S^{(I)}_{n=1}[C(3)-H]} \right\} = 0{\cdot}725 \quad (2)$$

C(21)–OAc function in compound (III) [equation (3)].

$$b = 1/2 \left\{ \frac{S^{(III)}_{n=1}[C(21)\cdot O\cdot CO\cdot CH_3]}{S^{(II)}_{n=1}[C(21)\cdot O\cdot CO\cdot CH_3]} + \frac{S^{(III)}_{n=1}[C(21)-H]}{S^{(II)}_{n=1}[C(21)-H]} \right\} = 0{\cdot}790 \quad (3)$$

Application of the relationship given by the equation (1) to all seven methyl groups in the diacetate (III) readily leads to the assignments indicated in the Table.

Next, the spectra of serratriol triacetate (IV) were studied. First, the spectra of 21-deoxyserratriol diacetate (V) were taken at various ratios of reagent to substrate and the feature of the shift reagent interactions was normal and the observed $S_{n=1}$ values are shown in the Table. In the diacetate (V), the induced changes of methyl signals affected by the C(3)–OAc–Eu(DPM)$_3$ association can be estimated from the $S_{n=1}$ values for C(3)·O·CO·C$H_3$ and C(3)–$H$. These signals, however, are also affected by the C(24)–OAc–Eu(DPM)$_3$ association. Because the latter effect could not be estimated independently, the observed $S_{n=1}$ values were regarded as those affected by C(3)–OAc–Eu(DPM)$_3$ association. In other words, the effect of the C(3)–OAc–Eu(DPM)$_3$ association in the diacetate (V) is identical with that in the monoacetate (I) but the association coefficient related to this acetoxy-group is different for compounds (I) and (V). The $S_{n=1}$ values of methyl signals affected by the C(24)–OAc–Eu(DPM)$_3$ association in the diacetate (V) were calculated by the relationship (4), where

$$S^{(V)}[C(24)\text{–OAc–Eu}] = S^{(V)} - a'' \cdot S^{(I)}[C(3)\text{–OAc–Eu}] \quad (4)$$

$S^{(V)}$[C(24)–OAc–Eu) is the calculated $S_{n=1}$ value of each methyl signal for C(24)–OAc–Eu(DPM)$_3$ association in compound (V), $a''$ is the association coefficient for the C(3)–OAc function in compound (V) [equation (5)], and

$$a'' = 1/2 \left\{ \frac{S^{(V)}_{n=1}[C(3)\cdot O\cdot CO\cdot CH_3]}{S^{(I)}_{n=1}[C(3)\cdot O\cdot CO\cdot CH_3]} + \frac{S^{(V)}_{n=1}[C(3)-H]}{S^{(I)}_{n=1}[C(3)-H]} \right\} = 0{\cdot}824 \quad (5)$$

$S^{(V)}$ is the observed $S_{n=1}$ value of each methyl signal in compound (V). The values are given in the Table.

Measurements were then made on the spectra of the triacetate (IV) at various ratios of shift reagent to substrate and the observed $S_{n=1}$ values of signals were obtained by good linear extrapolations and are shown in the Table. For the triacetate (IV), one of three acetoxy-methyl signals, which showed the least induced change, is assignable to 24-OAc judging from the $S_{n=1}$ value. For the diacetate (V), the $S_{n=1}$ value of 3-OAc is *ca.* 1·4 times that of 24-OAc. From this relationship, the acetyoxy-methyl signal, the $S_{n=1}$ value of which is 1·5 that of 24-OAc, is assigned to 3-OAc. The remaining acetoxy-methyl signal which undergoes the greatest shift, is therefore, assigned to 21-OAc. By analogy with the compound (III), the association coefficient related to each acetoxy-function in the triacetate (IV) was evaluated as follows, and application of the relationship (6),

$$S^{(IV)}\text{ calc.} = a' \cdot S^{(I)}[C(3)\text{–OAc–Eu}] + b' \cdot S^{(II)}[C(21)\text{–OAc–Eu}] + c \cdot S^{(V)}[C(24)\text{–OAc–Eu}] \quad (6)$$

where $S^{(IV)}$ calc. is the calculated $S_{n=1}$ value of each methyl signal in compound (IV), $a'$ is the association coefficient for the C(3)–OAc function in compound (IV) [equation (7)], $b'$ is the association coefficient for the

$$a' = 1/2 \left\{ \frac{S^{(IV)}_{n=1}[C(3)\cdot O\cdot CO\cdot CH_3]}{S^{(I)}_{n=1}[C(3)\cdot O\cdot CO\cdot CH_3]} + \frac{S^{(IV)}_{n=1}[C(3)-H]}{S^{(I)}_{n=1}[C(3)-H]} \right\} = 0{\cdot}618 \quad (7)$$

C(21)–OAc function in compound (IV) [equation (8)], and

$$b' = 1/2 \left\{ \frac{S^{(IV)}_{n=1}[C(21)\cdot O\cdot CO\cdot CH_3]}{S^{(II)}_{n=1}[C(21)\cdot O\cdot CO\cdot CH_3]} + \frac{S^{(IV)}_{n=1}[C(21)-H]}{S^{(II)}_{n=1}[C(21)-H]} \right\} = 0{\cdot}678 \quad (8)$$

$c'$ is the association coefficient for the C(24)–OAc function in compound (IV) [equation (9)], to all six methyl

$$c' = 1/2 \left\{ \frac{S^{(IV)}_{n=1}[C(24)\cdot O\cdot CO\cdot CH_3]}{S^{(V)}_{n=1}[C(24)\cdot O\cdot CO\cdot CH_3]} + \frac{S^{(IV)}_{n=1}[C(24)-H]}{S^{(V)}_{n=1}[C(24)-H]} \right\} = 0{\cdot}698 \quad (9)$$

groups of compound (IV) readily leads to the assignments in the Table.

## EXPERIMENTAL

M.p.s were determined with a microscopic hot-stage and are uncorrected. Unless otherwise stated, the i.r. spectra were measured for solutions in chloroform with a Hitachi KPI spectrometer and measurements of n.m.r. were made for deuteriochloroform solutions ranging in concentration from 0·1 to 0·3M with increasing amounts of Eu(DPM)$_3$ with a Varian A-60 instrument. The line positions of signals are given on the $\delta$ scale with reference to tetramethylsilane as the internal standard. The molar ratio of Eu(DPM)$_3$ to the substrate was estimated by integrating the area of tertiary methyl group or acetoxymethyl group

and the area of the pivaloyl methyl groups of $Eu(DPM)_3$. Mass spectral determinations were performed with a Hitachi RMU-6C mass spectrometer with a direct heated inlet system. Column chromatography was performed on alumina (Brockmann alumina, Activity II—III).

*Serraten-3β-ol Acetate* (I).—A mixture of sodium (290 mg) and hydrazine (0·6 ml) was added to diethylene glycol (5 ml) and heated at 180° for 1 h. After cooling, 21-oxoserraten-3β-ol acetate (244 mg) was added and heated at 180° for 2 h. After removal of the excess of hydrazine, the mixture was refluxed at 235° for 3 h, poured into ice–water and extracted with ether. The extract was washed with water and dried ($MgSO_4$). The solvent was evaporated off to leave the crude serraten-3β-ol which was acetylated with acetic anhydride–pyridine. The acetate was recrystallised from chloroform–methanol to give *serraten-3β-ol acetate* (I) as needles (62 mg), m.p. 308—310°, $\nu_{max.}$ 1720 and 1255 $cm^{-1}$ (Found: C, 82·0; H, 11·2. $C_{32}H_{52}O_2$ requires C, 81·95; H, 10·9%).

*Serraten-21α-ol Acetate* (II).—To a solution of serratenediol 3-acetate [7] (100 mg) in pyridine (10 ml) was added benzoyl chloride (2 ml), and the mixture was stood at room temperature overnight, concentrated *in vacuo*, poured into ice–water, and extracted with chloroform. The chloroform extract was washed with the saturated aqueous hydrogen carbonate solution, dried ($MgSO_4$), and evaporated. The residue in benzene was chromatographed with benzene on alumina and the eluate was recrystallised from chloroform–methanol to afford serratenediol 3-acetate 21-benzoate as needles, m.p. 324—326°, $\nu_{max.}$ 1710 and 1265 $cm^{-1}$, n.m.r. 0·75 (3H, s), 0·87 (12H, s), 0·93 (3H, s), 1·07 (3H, s), 2·05 (3H, s), 4·62 (2H, m), 5·37 (1H, m), 7·50 (3H, m), and 8·05 (2H, m), *m/e* 588 ($M^+$, 43%), 573 ($M^+ - CH_3$, 6), 528 ($M^+ - C_2H_4O_2$, 50), 466 ($M^+ - C_7H_6O_2$, 68), 391 (100), 344 (6), 338 (19), 300 (3), and 249 (58).

A solution of the diester (60 mg) in 3% ethanolic hydrochloric acid (120 ml) was heated under reflux on a water-bath for 4 h. After cooling, the mixture was evaporated to dryness *in vacuo* and the residue in benzene was chromatographed on alumina with benzene. The eluate, without further purification, was dissolved in pyridine (6 ml) and to this solution was added $CrO_3$–pyridine complex [from $CrO_3$ (250 mg) and pyridine (10 ml)]. The mixture was stirred at room temperature overnight, poured into ice–water and extracted with chloroform. The chloroform extract was washed with water and dried ($MgSO_4$). The solvent was evaporated off to leave the crude keto-benzoate, which in benzene was chromatographed on alumina with benzene. The eluate was recrystallised from chloroform–methanol to afford 3-oxoserraten-21α-ol benzoate as crystals (69 mg), m.p. 220—223°, $\nu_{max.}$ 1703 and 1265 $cm^{-1}$, *m/e* 544 ($M^+$, 20%), 529 ($M^+ - CH_3$, 6), 422 ($M^+ - C_7H_6O_2$, 60), 338 (4), 300 (12), 295 (2), 220 (10), 204 (100), and 205 (16). A mixture of sodium (0·5 g) and hydrazine (0·7 ml) was added to diethylene glycol (7 ml) and heated at 160° for 1 h. After cooling the keto-benzoate (60 mg) was added to the mixture and refluxed at 180° for 2 h. After removal of the excess of hydrazine, the mixture was refluxed at 235° for 3 h, poured into ice–water, and extracted with chloroform. The chloroform extract was washed with water and dried ($MgSO_4$). The solvent was evaporated off and the residue was acetylated with acetic anhydride–pyridine. The acetate was recrystallised from chloroform–methanol to give serraten-21α-ol acetate (II) as needles (30 mg), m.p. 252—256°, $\nu_{max.}$ 1720 and 1255 $cm^{-1}$, *m/e* 468 ($M^+$, 28%), 453 ($M^+ - CH_3$, 8), 408 ($M^+ - C_2H_4O_2$, 8), 344 (1), 277 (6), 262 (36), 206 (60), and 186 (100).

21-*Deoxyserratriol Diacetate* (V).—A mixture of sodium (0·5 g) and hydrazine (0·7 ml) was added to diethylene glycol (7 ml) and heated at 180° for 1 h. After cooling, the serratriol keto-acetonide [8] (55 mg) was added to the mixture and refluxed at 180° for 2 h. After removal of the excess of hydrazine, the mixture was refluxed at 240° for 4 h, poured into ice–water, and extracted with chloroform. The chloroform extract was washed with water and dried ($MgSO_4$). The residue (39 mg) was added to 3% ethanolic hydrochloric acid (10 ml) and the mixture was heated on a water bath for 30 min and evaporated to dryness *in vacuo*. The residue was acetylated with acetic anhydride–pyridine and the crude diacetate was recrystallised from chloroform–methanol to give 21-deoxyserratriol diacetate (V) as needles (28 mg), m.p. 219—221°, $\nu_{max.}$ 1720 and 1255 $cm^{-1}$, *m/e* 526 ($M^+$, 90%), 511 ($M^+ - CH_3$, 84), 466 ($M^+ - C_2H_4O_2$, 7), 295 (10), 230 (6), 216 (7), and 205 (100).

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[8] Y. Tsuda, T. Sano, and Y. Inubushi, *Tetrahedron Letters*, 1966, 5933.