

## Lichens and Fungi. Part 16.<sup>1</sup> The Crystal and Molecular Structures of Stictane-3 $\beta$ ,22 $\alpha$ -diol and 22 $\alpha$ -Hydroxy-3,4-secostictan-3-oic Acid

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The crystal and molecular structures of the title compounds have been determined from X-ray diffractometer data by direct methods. Crystals of stictane-3 $\beta$ ,22 $\alpha$ -diol (1) are monoclinic, space group *C*2 with  $a = 24.14(1)$ ,  $b = 7.606(3)$ ,  $c = 15.900(7)$  Å,  $\beta = 117.3(1)^\circ$ , and  $Z = 4$ . The structure was refined by full-matrix least-squares to  $R$  0.057 for 1 973 observed reflections. The structure confirmed the boat conformation proposed for the B ring of the triterpane. Crystals of 22 $\alpha$ -hydroxy-3,4-secostictan-3-oic acid (3b) are monoclinic, space group *P*2<sub>1</sub>, with  $a = 8.938(2)$ ,  $b = 27.789(7)$ ,  $c = 6.687(2)$  Å,  $\beta = 111.36(2)^\circ$ , and  $Z = 2$ . The structure was refined by full-matrix least-squares to  $R$  0.087 for 887 observed reflections. The B ring is shown to have a slightly flattened chair conformation and to possess one equatorial and three axial substituent groups.

THE chair, boat, chair, chair, chair conformational sequence illustrated in structure (1) was proposed<sup>2</sup> by us for stictane, the parent of the ten new triterpanes isolated from the extractives of three New Zealand *Pseudocyphellaria* lichen species. Subsequently, we demonstrated<sup>3</sup> the identity of stictane-3 $\beta$ ,22 $\alpha$ -diol (1) with retigeradiol for which structure (2) (taraxerane-3 $\beta$ ,19 $\beta$ -diol) had been advanced.<sup>4</sup> The physical and spectroscopic properties of the triterpane hydrocarbon, stictane, derived from the title diol (1) differed<sup>5</sup> from those of taraxerane.

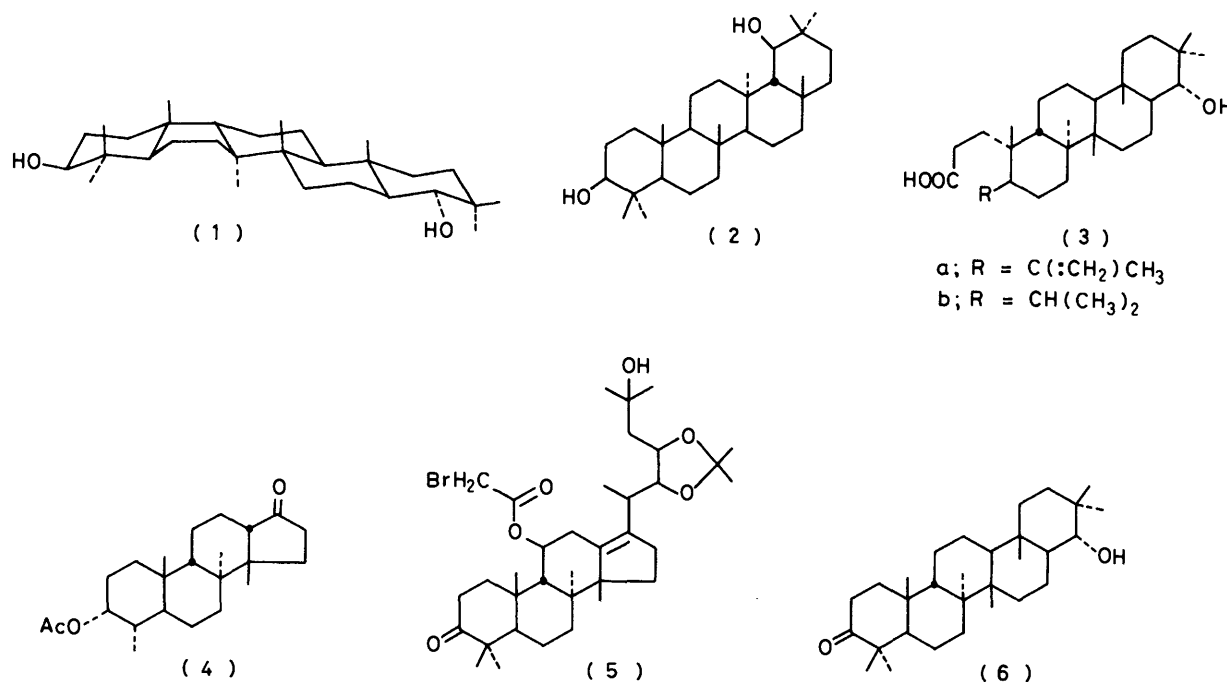
More recently we proposed<sup>6</sup> structure (3a) for one of three new triterpenoids isolated from *Pseudocyphellaria degelii*. These new triterpenoids were considered to be the tetracyclic analogues of the parent group of pentacyclic stictane triterpanes. Since the structures of neither of the new groups of triterpenoids have been

rigorously established (the published structures being deduced principally from analyses of spectral data<sup>2,7,8</sup>) X-ray crystallographic determinations of stictane-3 $\beta$ ,22 $\alpha$ -diol (1) and a derivative of compound (3a), the saturated tetracyclic triterpane acid (3b), were undertaken.

### EXPERIMENTAL

Suitable needle-shaped crystals of the title diol (1) were obtained from acetone solution.

*Crystal Data.*— $C_{30}H_{52}O_2$ ,  $M = 444.8$ . Monoclinic,  $a = 24.14(1)$ ,  $b = 7.606(3)$ ,  $c = 15.900(7)$  Å,  $\beta = 117.3(1)^\circ$ ,  $U = 2594$  Å<sup>3</sup>,  $D_m = 1.13$ ,  $D_c = 1.14$  g cm<sup>-3</sup>,  $Z = 4$ . Space group was uniquely determined as *C*2 for the enantiomeric molecule from systematic absences ( $h0l$  if  $h = 2n$  and  $hk0$  if  $h + k = 2n$ ). Space group and unit cell information were obtained from precession photography (Cu- $K\alpha$ ,  $\lambda = 1.5418$  Å). Three-dimensional intensity data were collected using the  $\theta$ - $2\theta$  scanning mode with nickel-filtered



Cu- $K_{\alpha}$  radiation on a Hilger and Watts four-circle, computer-controlled diffractometer. The intensities were corrected for Lorentz and polarisation effects but no absorption corrections were applied. Of the 1893 reflections collected, 1793 had values of  $F_o^2$  that were greater than three times their estimated standard deviations and these were used in the final refinement of structural parameters.

Hydrogenation of 22 $\alpha$ -hydroxy-3,4-secostict-4(23)-en-3-oic acid (3a) over Adam's catalyst afforded the title hydroxy-acid (3b). Suitable rectangular prisms were obtained from acetone solution.

**Crystal Data.**— $C_{30}H_{52}O_3(CH_3)_2CO$ ,  $M = 518.8$ . Monoclinic,  $a = 8.938(2)$ ,  $b = 27.789(7)$ ,  $c = 6.687(2)$  Å,  $\beta = 111.36(2)^\circ$ ,  $U = 1546.7$  Å<sup>3</sup>,  $D_m = 1.12$ ,  $D_o = 1.11$  g cm<sup>-3</sup>,  $Z = 2$ . The space group was uniquely determined as  $P2_1$  from systematic absences ( $0k0$  if  $k = 2n + 1$ ). Space group and unit cell information were obtained from precession photography (Cu- $K_{\alpha}$ ,  $\lambda = 1.5418$  Å). Three-dimensional intensity data were collected using the  $\theta$ - $2\theta$  scanning mode with zirconium-filtered Mo- $K_{\alpha}$  radiation on a Hilger and Watts four-circle, computer-controlled diffractometer. The intensities were corrected for Lorentz and polarisation effects, but not for absorption which was very small. Of the 1863 reflections collected, 887 had values of  $F_o^2$  that were equal or greater than twice their estimated standard deviations and these were used in the final refinement of structural parameters.

**Structure Solution of Stictane-3 $\beta$ ,22 $\alpha$ -diol (1) and Refinement.**—The structure of the diol (1) was solved by direct methods using the program MULTAN.<sup>9</sup> Inputting stereochemical information on the ring C-D-E fragment, as determined for (3b) (see below), into the structure factor normalisation procedure yielded an  $E$  map in which 18 carbon atoms appeared to be located in reasonable positions and the remaining heavy atoms were found in subsequent difference-Fourier, least-squares refinement cycles using the program system SHELX.<sup>10</sup> Two cycles of full-matrix least-squares refinement with isotropic thermal parameters for the ring carbon atoms and anisotropic refinement of the methyl carbon and hydroxy carbon atoms resulted in  $R$  0.118. A difference Fourier synthesis revealed electron density maxima in reasonable locations for the hydrogen atoms and these were input with idealised positions and C-H = 1.00 Å. An overall isotropic thermal parameter was assigned to each type of hydrogen atom and a weighting scheme based on counting statistics was introduced. Examination of observed and calculated structure factors revealed evidence for secondary extinction. Two cycles of refinement, in which the calculated structure factor was empirically modified using an isotropic extinction parameter,<sup>11</sup> reduced the discrepancies between observed and calculated structure factors to acceptable values. The final conventional  $R$  factor was 0.057 and  $R'$  ( $=\sum w^{\frac{1}{2}}\Delta/\sum w^{\frac{1}{2}}F_o$ ) 0.073. A final difference Fourier synthesis revealed no peaks higher than those earlier assigned to hydrogen atoms and the weighting scheme appeared reasonable. Figure 1 is a perspective view of the molecule looking towards the  $\alpha$ -face.

**Structure Solution of 22 $\alpha$ -Hydroxy-3,4-secostictan-3-oic Acid (3b) and Refinement.**—The structure was solved by direct methods using the program MULTAN. A plausible 26 atom fragment was recognized in the seventh ranked figure of merit solution offered by the program. Inputting these atoms with isotropic temperature factors into the refinement program SHELX gave, after one cycle of full-matrix least-squares refinement, an  $R$  value of 0.32, and also revealed the

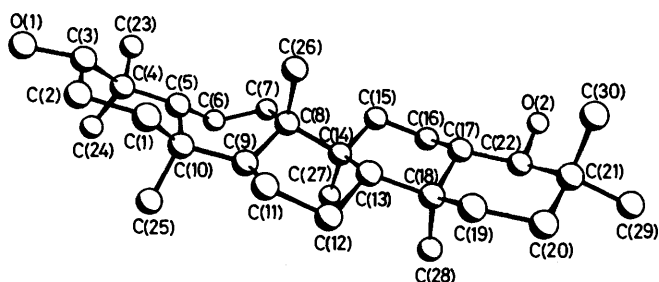


FIGURE 1 General view of the molecule of stictane-3 $\beta$ ,22 $\alpha$ -diol, looking towards the  $\alpha$ -face, showing the atom numbering scheme

presence of an acetone solvate molecule hydrogen bonded to the C(22) hydroxy-group. Isotropic least-squares refinement of this resulted in  $R$  0.13. A difference Fourier synthesis revealed electron density maxima in reasonable locations for the hydrogen atoms and these were input with idealised positions and C-H 1.08 Å. An overall isotropic thermal parameter was assigned to each type of hydrogen atom, and a weighting scheme based on counting statistics was introduced. Four further cycles of full-matrix calculations converged with  $R$  0.087 and  $R'$  ( $=\sum w^{\frac{1}{2}}\Delta/\sum w^{\frac{1}{2}}F_o$ )

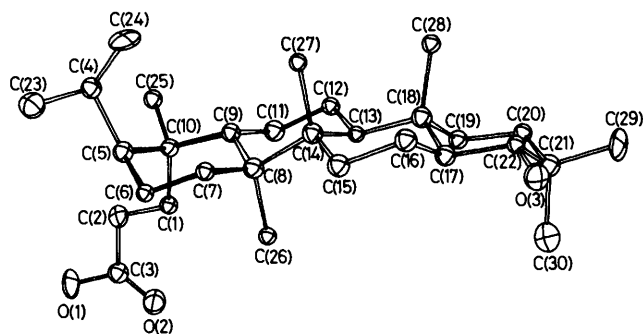


FIGURE 2 A perspective view of 22 $\alpha$ -hydroxy-3,4-secostictan-3-oic acid showing the atom numbering scheme

0.078. No abnormal discrepancies were found between observed and calculated structure factors for the reflections not used in the refinement. Figure 2 is a perspective view of the molecule showing the atomic numbering scheme.

## RESULTS AND DISCUSSION

The final bond lengths and angles of the title compounds appear in Table 1. Final atom co-ordinates appear in Tables 2 and 3. Tables of the thermal parameters, torsion angle and mean plane data, calculated and observed structure factors, and views of the respective unit cells have been deposited in Supplementary Publication No. SUP 233841 (31 pp.).\* The torsion angle and mean plane data show that in the diol (1) ring B adopts a twisted boat conformation essentially identical to that determined<sup>12</sup> for the structurally analogous fusidic acid-derived steroid 4 $\alpha$ ,8 $\alpha$ ,14 $\beta$ -trimethyl-18-nor-5 $\alpha$ ,9 $\beta$ ,13 $\beta$ -androstan-17-one (4). In accord with expectations<sup>12-14</sup> steric crowding around the C(8), C(9), and

\* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc., Perkin Trans. 2*, 1981, Index Issue.

TABLE 1

Interatomic distances (Å) and angles (°) for stictane-3 $\beta$ ,22 $\alpha$ -diol (1a) and 22 $\alpha$ -hydroxy-3,4-secostictan-3-oic acid (3b) with standard deviations in parentheses

## (a) Bonds

|             | (1a)     | (3b)      |             | (1a)     | (3b)      |
|-------------|----------|-----------|-------------|----------|-----------|
| C(1)-C(2)   | 1.524(6) | 1.542(26) | C(13)-C(14) | 1.564(6) | 1.552(25) |
| C(1)-C(10)  | 1.537(6) | 1.579(24) | C(13)-C(18) | 1.563(6) | 1.538(25) |
| C(2)-C(3)   | 1.514(8) | 1.514(27) | C(14)-C(15) | 1.557(7) | 1.550(26) |
| C(3)-C(4)   | 1.559(8) |           | C(14)-C(27) | 1.546(7) | 1.574(23) |
| C(4)-C(5)   | 1.555(6) | 1.580(24) | C(15)-C(16) | 1.522(6) | 1.557(25) |
| C(4)-C(23)  | 1.536(9) | 1.484(28) | C(16)-C(17) | 1.532(7) | 1.474(25) |
| C(4)-C(24)  | 1.546(6) | 1.532(29) | C(17)-C(18) | 1.559(7) | 1.576(26) |
| C(5)-C(6)   | 1.509(8) | 1.543(26) | C(17)-C(22) | 1.532(6) | 1.551(26) |
| C(5)-C(10)  | 1.547(7) | 1.578(26) | C(18)-C(19) | 1.539(7) | 1.547(24) |
| C(6)-C(7)   | 1.532(5) | 1.508(24) | C(18)-C(28) | 1.540(8) | 1.539(25) |
| C(7)-C(8)   | 1.561(7) | 1.547(26) | C(19)-C(20) | 1.519(6) | 1.551(26) |
| C(8)-C(9)   | 1.552(6) | 1.563(25) | C(20)-C(21) | 1.535(7) | 1.562(26) |
| C(8)-C(14)  | 1.614(6) | 1.583(27) | C(21)-C(22) | 1.543(7) | 1.488(27) |
| C(8)-C(26)  | 1.546(7) | 1.596(24) | C(21)-C(29) | 1.536(6) | 1.578(28) |
| C(9)-C(10)  | 1.588(6) | 1.576(24) | C(21)-C(30) | 1.522(8) | 1.560(28) |
| C(9)-C(11)  | 1.530(7) | 1.533(25) | C(3)-O(1)   | 1.419(6) | 1.308(24) |
| C(10)-C(25) | 1.556(7) | 1.555(23) | C(3)-O(2)   |          | 1.150(23) |
| C(11)-C(12) | 1.536(6) | 1.523(25) | C(22)-O(2)  | 1.425(7) |           |
| C(12)-C(13) | 1.532(7) | 1.536(23) | C(22)-O(3)  |          | 1.405(21) |

## (b) Angles

|                  | (1a)     | (3b)       |                   | (1a)     | (3b)       |
|------------------|----------|------------|-------------------|----------|------------|
| C(2)-C(1)-C(10)  | 112.2(3) | 114.7(1.5) | C(11)-C(12)-C(13) | 112.0(4) | 114.1(1.6) |
| C(1)-C(2)-C(3)   | 113.6(4) | 111.5(1.6) | C(12)-C(13)-C(14) | 110.9(3) | 110.0(1.4) |
| C(2)-C(3)-C(4)   | 115.5(5) |            | C(12)-C(13)-C(18) | 114.1(4) | 116.6(1.6) |
| C(2)-C(3)-O(1)   | 109.6(4) | 109.8(2.0) | C(14)-C(13)-C(18) | 116.3(4) | 117.1(1.6) |
| C(2)-C(3)-O(2)   |          | 126.1(2.3) | C(8)-C(14)-C(13)  | 108.8(4) | 110.1(1.6) |
| O(1)-C(3)-O(2)   |          | 124.1(2.4) | C(8)-C(14)-C(15)  | 108.5(3) | 110.8(1.5) |
| C(4)-C(3)-O(1)   | 111.1(4) |            | C(8)-C(14)-C(27)  | 109.8(3) | 110.0(1.5) |
| C(3)-C(4)-C(23)  | 107.2(5) |            | C(13)-C(14)-C(15) | 108.6(3) | 110.9(1.5) |
| C(3)-C(4)-C(24)  | 111.9(4) |            | C(13)-C(14)-C(27) | 112.2(4) | 111.1(1.6) |
| C(5)-C(4)-C(23)  | 108.9(4) | 119.8(1.8) | C(15)-C(14)-C(27) | 108.0(4) | 103.8(1.6) |
| C(5)-C(4)-C(24)  | 115.4(4) | 107.1(1.8) | C(14)-C(15)-C(16) | 113.6(4) | 110.8(1.7) |
| C(23)-C(4)-C(24) | 107.1(4) | 109.2(1.9) | C(15)-C(16)-C(17) | 110.1(4) | 112.0(1.7) |
| C(4)-C(5)-C(6)   | 117.6(4) | 116.1(1.6) | C(16)-C(17)-C(18) | 111.3(3) | 106.8(1.7) |
| C(4)-C(5)-C(10)  | 117.2(4) | 117.0(1.6) | C(16)-C(17)-C(22) | 113.2(4) | 114.8(1.7) |
| C(6)-C(5)-C(10)  | 109.7(4) | 109.7(1.6) | C(13)-C(18)-C(17) | 107.9(4) | 109.4(1.6) |
| C(5)-C(6)-C(7)   | 108.6(4) | 115.8(1.7) | C(13)-C(18)-C(19) | 109.4(4) | 107.3(1.7) |
| C(6)-C(7)-C(8)   | 114.5(4) | 112.0(1.6) | C(13)-C(18)-C(28) | 112.3(3) | 111.5(1.7) |
| C(7)-C(8)-C(9)   | 109.8(3) | 110.4(1.7) | C(17)-C(18)-C(19) | 106.3(3) | 104.6(1.6) |
| C(7)-C(8)-C(14)  | 109.7(4) | 112.1(1.6) | C(17)-C(18)-C(28) | 112.8(4) | 114.3(1.7) |
| C(7)-C(8)-C(26)  | 108.3(4) | 106.6(1.7) | C(19)-C(18)-C(28) | 107.9(4) | 109.2(1.7) |
| C(9)-C(8)-C(14)  | 107.4(4) | 107.8(1.5) | C(18)-C(19)-C(20) | 113.2(4) | 114.2(1.7) |
| C(9)-C(8)-C(26)  | 110.2(4) | 110.2(1.4) | C(19)-C(20)-C(21) | 115.2(5) | 110.3(1.9) |
| C(14)-C(8)-C(26) | 113.3(3) | 109.7(1.5) | C(20)-C(21)-C(22) | 109.9(3) | 111.4(1.9) |
| C(8)-C(9)-C(10)  | 117.9(4) | 118.5(1.6) | C(20)-C(21)-C(29) | 108.0(5) | 107.5(1.9) |
| C(8)-C(9)-C(11)  | 111.6(3) | 110.8(1.6) | C(20)-C(21)-C(30) | 109.6(5) | 111.4(1.8) |
| C(10)-C(9)-C(11) | 112.2(4) | 113.2(1.5) | C(22)-C(21)-C(29) | 109.9(4) | 108.2(1.9) |
| C(1)-C(10)-C(5)  | 107.1(4) | 108.0(1.5) | C(22)-C(21)-C(30) | 110.8(5) | 112.3(1.9) |
| C(1)-C(10)-C(9)  | 115.5(3) | 111.4(1.4) | C(29)-C(21)-C(30) | 110.6(4) | 105.8(1.9) |
| C(1)-C(10)-C(25) | 107.8(4) | 106.4(1.5) | C(17)-C(22)-C(21) | 113.7(4) | 111.3(1.8) |
| C(5)-C(10)-C(9)  | 108.8(4) | 110.8(1.6) | C(17)-C(22)-O(2)  | 109.2(4) |            |
| C(5)-C(10)-C(25) | 114.0(3) | 110.4(1.6) | C(21)-C(22)-O(2)  | 111.4(3) |            |
| C(9)-C(10)-C(25) | 103.9(4) | 109.7(1.6) | C(17)-C(22)-O(3)  |          | 108.7(1.7) |
| C(9)-C(11)-C(12) | 112.3(4) | 112.2(1.7) | C(21)-C(22)-O(3)  |          | 112.4(1.7) |

C(14) atoms results in the lengthening of the C(8)-C(14) [1.614(6)] and C(9)-C(10) [1.588(6)] bonds whilst the C(5)-C(6) [1.509(8) Å] bond appears to have been shortened to a greater extent in 4 $\alpha$ ,8 $\alpha$ ,14 $\beta$ -trimethyl-18-nor-5 $\alpha$ ,9 $\beta$ ,13 $\beta$ -androstane-17-one (4). The presence in the hydroxy-acid (3b) of a chair ring B system is consistent with the view that the parent naturally occurring triterpene acid (3a) is derived from a parent pentacyclic triterpenoid [most probably the ketol (6)], by rupture of the C(3)-C(4) bond and with reversion of the boat ring B system to a chair conformation.

Since the interconversion of stictane-3 $\beta$ ,22 $\alpha$ -diol (1)

and 22 $\alpha$ -hydroxystictan-3-one (6) has been achieved<sup>2</sup> the absolute configuration of the diol can be assigned from a comparison of the o.r.d. curves of the ketol (6) and alisol-A (23,24)-acetone 11-monobromoacetate (5).<sup>15,16</sup> Because of the close correspondence in the signs and magnitudes of their respective o.r.d. curves it follows that the ring A-B portions of these substances have identical absolute configurations. Although caution must be exercised in the correlation of solid and solution state conformations, it is now apparent that in fusidic acid type boat ring B steroids and triterpenoids, the presence in ring A at C(3), but not at C(2),<sup>2</sup> of a keto functionality

TABLE 2

Atom positional parameters for stictane-3 $\beta$ ,22 $\alpha$ -diol (1)

(a) Non-hydrogen atoms

| Atom  | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> |
|-------|------------|------------|------------|
| C(1)  | 0.890 2(2) | 1.228 7(0) | 1.125 6(3) |
| C(2)  | 0.923 5(2) | 1.257 2(8) | 1.232 4(3) |
| C(3)  | 0.926 1(2) | 1.094 1(7) | 1.288 7(3) |
| C(4)  | 0.951 2(2) | 0.925 1(7) | 1.262 2(3) |
| C(5)  | 0.915 7(2) | 0.911 1(6) | 1.152 5(3) |
| C(6)  | 0.924 5(2) | 0.745 7(7) | 1.107 6(3) |
| C(7)  | 0.864 2(2) | 0.708 4(7) | 1.017 2(3) |
| C(8)  | 0.834 5(2) | 0.873 1(6) | 0.953 9(3) |
| C(9)  | 0.882 3(2) | 1.026 2(6) | 0.985 5(3) |
| C(10) | 0.917 4(2) | 1.073 2(6) | 1.095 0(3) |
| C(11) | 0.855 7(2) | 1.189 2(7) | 0.923 6(3) |
| C(12) | 0.833 4(2) | 1.150 2(7) | 0.818 2(3) |
| C(13) | 0.787 6(2) | 0.995 7(6) | 0.783 5(3) |
| C(14) | 0.816 7(2) | 0.828 2(7) | 0.845 2(3) |
| C(15) | 0.767 2(2) | 0.678 3(7) | 0.809 1(3) |
| C(16) | 0.738 9(2) | 0.647 5(7) | 0.702 9(3) |
| C(17) | 0.707 6(2) | 0.816 0(7) | 0.649 4(3) |
| C(18) | 0.755 6(2) | 0.968 6(7) | 0.673 8(3) |
| C(19) | 0.717 8(2) | 1.133 8(7) | 0.624 7(3) |
| C(20) | 0.678 5(2) | 1.111 2(7) | 0.518 7(3) |
| C(21) | 0.633 6(2) | 0.954 1(7) | 0.488 7(3) |
| C(22) | 0.668 4(2) | 0.787 7(7) | 0.542 7(3) |
| C(23) | 0.933 1(3) | 0.768 2(8) | 1.305 2(4) |
| C(24) | 1.023 1(2) | 0.925 8(8) | 1.305 6(3) |
| C(25) | 0.984 2(2) | 1.125 6(7) | 1.112 3(3) |
| C(26) | 0.776 2(2) | 0.926 8(7) | 0.964 4(3) |
| C(27) | 0.875 2(2) | 0.763 0(7) | 0.838 5(3) |
| C(28) | 0.803 2(2) | 0.936 3(8) | 0.636 2(3) |
| C(29) | 0.609 0(3) | 0.926 6(9) | 0.381 8(3) |
| C(30) | 0.578 8(2) | 0.994 7(8) | 0.508 1(4) |
| O(1)  | 0.960 1(2) | 1.131 0(6) | 1.386 9(2) |
| O(2)  | 0.626 3(2) | 0.645 5(5) | 0.527 1(2) |

(b) Calculated positions for hydrogen atoms

| Atom   | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> |
|--------|------------|------------|------------|
| H(11)  | 0.845 1(2) | 1.205 8(0) | 1.105 5(3) |
| H(12)  | 0.894 5(2) | 1.337 5(0) | 1.093 9(3) |
| H(21)  | 0.901 1(2) | 1.351 8(8) | 1.248 3(3) |
| H(22)  | 0.967 2(2) | 1.295 7(8) | 1.251 0(3) |
| H(31)  | 0.881 6(2) | 1.066 5(7) | 1.271 3(3) |
| H(5)   | 0.872 9(2) | 0.905 3(6) | 1.147 5(3) |
| H(61)  | 0.959 7(2) | 0.762 2(7) | 1.091 6(3) |
| H(62)  | 0.934 1(2) | 0.644 8(7) | 1.152 5(3) |
| H(71)  | 0.873 7(2) | 0.620 5(7) | 0.978 8(3) |
| H(72)  | 0.833 2(2) | 0.657 5(7) | 1.035 7(3) |
| H(9)   | 0.916 7(2) | 0.976 1(6) | 0.974 5(3) |
| H(111) | 0.889 1(2) | 1.280 8(7) | 0.943 9(3) |
| H(112) | 0.819 8(2) | 1.234 8(7) | 0.932 4(3) |
| H(121) | 0.870 3(2) | 1.120 7(7) | 0.808 2(3) |
| H(122) | 0.812 3(2) | 1.257 1(7) | 0.780 4(3) |
| H(13)  | 0.751 1(2) | 1.027 9(6) | 0.793 9(3) |
| H(151) | 0.733 0(2) | 0.709 5(7) | 0.825 2(3) |
| H(152) | 0.787 7(2) | 0.567 0(7) | 0.842 3(3) |
| H(161) | 0.772 4(2) | 0.612 1(7) | 0.685 8(3) |
| H(162) | 0.707 0(2) | 0.551 8(7) | 0.684 5(3) |
| H(17)  | 0.677 4(2) | 0.852 5(7) | 0.673 1(3) |
| H(191) | 0.747 3(2) | 1.234 0(7) | 0.636 3(3) |
| H(192) | 0.689 4(2) | 1.161 6(7) | 0.653 1(3) |
| H(201) | 0.653 2(2) | 1.220 3(7) | 0.493 2(3) |
| H(202) | 0.707 5(2) | 1.096 6(7) | 0.490 1(3) |
| H(22)  | 0.697 9(2) | 0.757 8(7) | 0.516 8(3) |
| H(231) | 0.886 5(3) | 0.766 1(8) | 1.274 5(4) |
| H(232) | 0.949 7(3) | 0.789 5(8) | 1.374 7(4) |
| H(233) | 0.948 9(3) | 0.652 7(8) | 1.294 9(4) |
| H(241) | 1.038 6(2) | 1.032 7(8) | 1.286 4(3) |
| H(242) | 1.033 5(2) | 0.818 7(8) | 1.279 2(3) |
| H(243) | 1.043 5(2) | 0.917 7(8) | 1.376 3(3) |
| H(251) | 1.009 1(2) | 1.175 1(7) | 1.177 3(3) |
| H(252) | 0.981 2(2) | 1.214 7(7) | 1.064 2(3) |
| H(253) | 1.005 0(2) | 1.017 2(7) | 1.105 0(3) |
| H(261) | 0.756 8(2) | 1.030 5(7) | 0.922 5(3) |
| H(262) | 0.786 8(2) | 0.958 2(7) | 1.031 2(3) |
| H(263) | 0.746 1(2) | 0.826 3(7) | 0.943 2(3) |
| H(271) | 0.904 2(2) | 0.863 2(7) | 0.847 2(3) |
| H(272) | 0.865 3(2) | 0.701 3(7) | 0.777 7(3) |

TABLE 2 (continued)

| Atom   | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> |
|--------|------------|------------|------------|
| H(273) | 0.895 5(2) | 0.678 7(7) | 0.892 4(3) |
| H(281) | 0.827 7(2) | 0.824 5(8) | 0.656 7(3) |
| H(282) | 0.823 0(2) | 1.038 8(8) | 0.662 8(3) |
| H(283) | 0.782 0(3) | 0.943 2(8) | 0.565 5(3) |
| H(291) | 0.580 1(3) | 0.823 3(9) | 0.360 0(3) |
| H(292) | 0.645 0(3) | 0.905 3(9) | 0.368 3(3) |
| H(293) | 0.586 1(3) | 1.034 6(9) | 0.347 6(3) |
| H(301) | 0.595 2(2) | 1.011 1(8) | 0.577 8(4) |
| H(302) | 0.544 5(2) | 1.905 5(8) | 0.484 9(4) |
| H(303) | 0.562 3(2) | 1.109 1(8) | 0.475 1(4) |
| H(01)  | 0.960 2(2) | 1.017 9(6) | 1.419 0(2) |
| H(02)  | 0.606 0(2) | 0.611 4(5) | 0.458 8(2) |

TABLE 3

Atom positional parameters for 22 $\alpha$ -hydroxy-3,4-secostictan-3-oic acid (3b)

(a) Non-hydrogen atoms

| Atom  | <i>x/a</i>   | <i>y/b</i>  | <i>z/c</i>   |
|-------|--------------|-------------|--------------|
| C(1)  | 0.179 1(24)  | 0.833 0(11) | 0.265 3(32)  |
| C(2)  | 0.224 8(22)  | 0.886 8(10) | 0.286 6(34)  |
| C(3)  | 0.150 3(28)  | 0.913 2(11) | 0.425 1(37)  |
| C(4)  | 0.578 9(24)  | 0.791 3(11) | 0.191 0(38)  |
| C(5)  | 0.450 5(23)  | 0.797 0(10) | 0.301 0(32)  |
| C(6)  | 0.465 0(22)  | 0.761 3(11) | 0.484 1(29)  |
| C(7)  | 0.400 7(21)  | 0.711 4(10) | 0.415 2(32)  |
| C(8)  | 0.220 8(24)  | 0.712 0(10) | 0.269 3(34)  |
| C(9)  | 0.189 5(21)  | 0.750 2(10) | 0.086 9(32)  |
| C(10) | 0.268 9(22)  | 0.801 5(10) | 0.147 4(30)  |
| C(11) | 0.010 5(23)  | 0.752 4(10) | -0.053 4(33) |
| C(12) | -0.056 1(22) | 0.703 4(9)  | -0.144 6(29) |
| C(13) | -0.020 8(21) | 0.663 3(10) | 0.024 5(30)  |
| C(14) | 0.161 9(24)  | 0.661 5(0)  | 0.159 7(33)  |
| C(15) | 0.200 5(25)  | 0.621 0(10) | 0.330 6(32)  |
| C(16) | 0.112 3(24)  | 0.573 6(10) | 0.230 3(34)  |
| C(17) | -0.063 7(25) | 0.579 4(10) | 0.145 5(35)  |
| C(18) | -0.106 4(24) | 0.614 9(11) | -0.051 2(34) |
| C(19) | -0.288 9(23) | 0.624 0(10) | -0.118 2(34) |
| C(20) | -0.393 0(26) | 0.577 8(10) | -0.178 7(34) |
| C(21) | -0.336 0(27) | 0.540 8(11) | 0.009 9(37)  |
| C(22) | -0.160 1(23) | 0.531 9(11) | 0.081 2(34)  |
| C(23) | 0.596 2(30)  | 0.744 6(12) | 0.094 3(42)  |
| C(24) | 0.741 8(27)  | 0.806 1(14) | 0.357 5(41)  |
| C(25) | 0.255 2(26)  | 0.829 2(10) | -0.060 5(31) |
| C(26) | 0.123 5(21)  | 0.725 8(10) | 0.419 5(32)  |
| C(27) | 0.261 1(21)  | 0.647 1(11) | 0.016 9(28)  |
| C(28) | -0.072 0(24) | 0.594 8(10) | -0.244 5(31) |
| C(29) | -0.426 0(27) | 0.491 8(10) | -0.076 0(44) |
| C(30) | -0.388 2(26) | 0.556 4(11) | 0.198 9(35)  |
| O(1)  | 0.218 7(21)  | 0.955 3(10) | 0.479 3(36)  |
| O(2)  | 0.043 9(22)  | 0.900 1(9)  | 0.468 5(30)  |
| O(3)  | -0.105 1(17) | 0.499 7(9)  | 0.255 1(24)  |

(b) Calculated positions for hydrogen atoms

| Atom   | <i>x/a</i>   | <i>y/b</i>  | <i>z/c</i>   |
|--------|--------------|-------------|--------------|
| H(11)  | 0.051 3(24)  | 0.829 4(11) | 0.179 4(32)  |
| H(12)  | 0.210 3(24)  | 0.818 6(11) | 0.425 4(32)  |
| H(21)  | 0.181 1(22)  | 0.902 5(10) | 0.128 0(34)  |
| H(22)  | 0.353 7(22)  | 0.890 8(10) | 0.357 0(34)  |
| H(4)   | 0.529 5(24)  | 0.814 2(11) | 0.051 7(38)  |
| H(5)   | 0.484 4(23)  | 0.831 7(10) | 0.376 3(32)  |
| H(61)  | 0.400 7(22)  | 0.776 2(11) | 0.578 6(29)  |
| H(62)  | 0.590 9(22)  | 0.758 2(11) | 0.582 4(29)  |
| H(71)  | 0.469 4(21)  | 0.695 5(10) | 0.328 8(32)  |
| H(72)  | 0.414 1(21)  | 0.690 0(10) | 0.555 4(32)  |
| H(9)   | 0.255 5(21)  | 0.736 4(10) | -0.007 5(32) |
| H(111) | -0.005 4(23) | 0.776 5(10) | -0.186 3(33) |
| H(112) | -0.056 2(23) | 0.765 7(10) | 0.041 1(33)  |
| H(121) | -0.185 0(22) | 0.705 9(9)  | -0.221 9(29) |
| H(122) | -0.004 4(22) | 0.693 3(9)  | -0.261 5(29) |
| H(13)  | -0.070 8(21) | 0.671 2(10) | 0.145 5(30)  |
| H(151) | 0.158 5(25)  | 0.632 7(10) | 0.455 0(32)  |
| H(152) | 0.328 4(25)  | 0.614 8(10) | 0.399 1(32)  |
| H(161) | 0.143 9(24)  | 0.546 6(10) | 0.355 1(34)  |
| H(162) | 0.153 1(24)  | 0.562 2(10) | 0.104 2(34)  |
| H(17)  | -0.101 3(25) | 0.593 5(10) | 0.270 5(35)  |

TABLE 3 (continued)

| Atom   | x/a          | y/b         | z/c          |
|--------|--------------|-------------|--------------|
| H(191) | -0.308 4(23) | 0.640 7(10) | 0.016 1(34)  |
| H(192) | -0.327 6(23) | 0.648 2(10) | -0.254 0(34) |
| H(201) | -0.517 1(26) | 0.587 4(10) | -0.214 0(34) |
| H(202) | -0.380 7(26) | 0.561 8(10) | -0.319 1(34) |
| H(22)  | -0.138 5(23) | 0.516 4(11) | -0.054 0(34) |
| H(231) | 0.468 6(30)  | 0.738 5(12) | 0.016 9(42)  |
| H(232) | 0.646 1(30)  | 0.718 6(12) | 0.221 4(42)  |
| H(233) | 0.653 4(30)  | 0.740 8(12) | -0.022 0(42) |
| H(241) | 0.752 6(27)  | 0.837 7(14) | 0.456 0(41)  |
| H(242) | 0.830 1(27)  | 0.807 7(14) | 0.282 3(41)  |
| H(243) | 0.761 7(27)  | 0.774 3(14) | 0.456 5(41)  |
| H(251) | 0.302 9(26)  | 0.804 2(10) | -0.145 7(31) |
| H(252) | 0.339 0(26)  | 0.858 5(10) | 0.001 1(31)  |
| H(253) | 0.142 0(26)  | 0.843 3(10) | -0.168 6(31) |
| H(261) | 0.018 8(21)  | 0.741 3(10) | 0.298 1(32)  |
| H(262) | 0.183 4(21)  | 0.752 9(10) | 0.537 1(32)  |
| H(263) | 0.087 1(21)  | 0.696 4(10) | 0.497 3(32)  |
| H(271) | 0.208 4(21)  | 0.664 4(11) | -0.137 6(28) |
| H(272) | 0.267 4(21)  | 0.608 7(11) | -0.005 7(28) |
| H(273) | 0.380 6(21)  | 0.661 0(11) | 0.099 3(28)  |
| H(281) | 0.035 2(24)  | 0.575 3(10) | -0.233 7(31) |
| H(282) | -0.084 5(24) | 0.626 1(10) | -0.344 9(31) |
| H(283) | -0.175 5(24) | 0.571 8(10) | -0.313 3(31) |
| H(291) | -0.548 9(27) | 0.504 3(10) | -0.140 1(44) |
| H(292) | -0.417 1(27) | 0.461 2(10) | 0.027 3(44)  |
| H(293) | -0.388 8(27) | 0.481 4(10) | -0.206 5(44) |
| H(301) | -0.360 3(26) | 0.594 1(11) | 0.195 0(35)  |
| H(302) | -0.318 8(26) | 0.541 7(11) | 0.354 8(35)  |
| H(303) | -0.514 7(26) | 0.552 3(11) | 0.168 8(35)  |

will generally result in ring A also adopting a twisted boat conformation. In accord with these observations the o.r.d. curves of the ketol (6) and of alisol-A (23,24)-acetone 11-monobromoacetate differ significantly from those of other 3-oxo-4 $\alpha$ ,4 $\beta$ -dimethyl steroids and triterpenoids in which ring A adopts the more normal flattened

chair conformation. On the other hand ring A retains a chair conformation if C(3) is equatorially or axially<sup>13</sup> substituted. <sup>1</sup>H N.m.r. data support these observations.

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