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# The Crystal and Molecular Structure of Bacogenin-A$_1$ Dibromoacetate

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The crystal structure of bacogenin-A$_1$ dibromoacetate, $C_{34}H_{50}O_6Br_2$, has been determined in order to elucidate the molecular structure and absolute configuration of bacogenin-A$_1$, $C_{30}H_{48}O_4$, a triterpenoid sapogenin isolated from *Bacopa monniera*. The crystals are orthorhombic with space group $P2_12_12_1$ and the unit-cell dimensions are $a=13{\cdot}36$, $b=36{\cdot}24$, $c=7{\cdot}15$ Å, $Z=4$. The crystal structure was solved by the heavy-atom method and refined by the block-matrix least-squares method including anisotropic thermal parameters. The final $R$ value for 1288 observed structure factors was 0·084. The absolute configuration was determined by the use of the anomalous dispersion of bromine atoms for Mo $K\alpha$ radiation. The molecular structure of bacogenin-A$_1$ was determined to be a partially modified dammarane-type triterpene.

## Introduction

Bacogenin-A$_1$, $C_{30}H_{48}O_4$, is one of the sapogenins obtained on acid hydrolysis of bacoside A which was isolated from an Indian plant, *Bacopa monniera* (Kulshreshtha & Rastogi, 1973). On the basis of the chemical and spectroscopic data, bacogenin-A$_1$ was shown to be a tetracyclic triterpene having a chemical structure formulated as (I) (Fig. 1). However, an alternative formula having a methyl at C(24) could not be ruled out.

Therefore, an X-ray structure analysis of bacogenin-A$_1$ dibromoacetate (II) (Fig. 1), has been undertaken in order to establish the chemical structure of bacogenin-A$_1$ including its absolute configuration.

## Experimental

Bacogenin-A$_1$ was treated with bromoacetyl bromide in chloroform containing a few drops of pyridine to give bacogenin-A$_1$ dibromoacetate. The product was recrystallized from MeOH to obtain colourless prisms

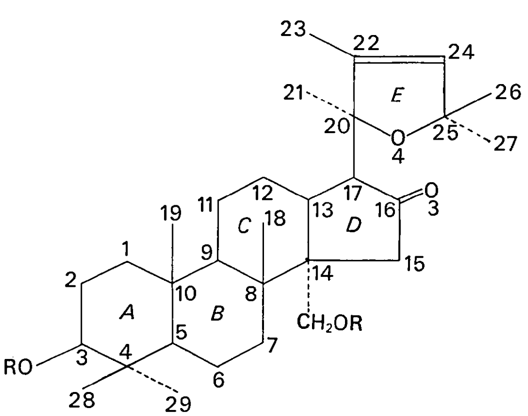

Fig. 1. Chemical formulae: (I) bacogenin-A$_1$; (II) bacogenin-A$_1$ dibromoacetate. (I) R=H; (II) R=$COCH_2Br$.

elongated along the *c* axis. The density was measured by flotation using an aqueous solution of potassium iodide.

*Crystal data*

Bacogenin-A$_1$ dibromoacetate, $C_{34}H_{50}O_6Br_2$: M.W. 714·57, m.p. 183·5–185°.
Orthorhombic
$a = 13{\cdot}36 \pm 0{\cdot}01$, $b = 36{\cdot}24 \pm 0{\cdot}04$, $c = 7{\cdot}151 \pm 0{\cdot}007$ Å
$U = 3463$ Å$^3$
$D_m = 1{\cdot}36_6$ g cm$^{-3}$, $D_x = 1{\cdot}370$ g cm$^{-3}$, $Z = 4$
$\mu$ for Mo $K\alpha = 19{\cdot}0$ cm$^{-1}$
$F(000) = 1482$.
Absent spectra: $h00$ when $h$ is odd, $0k0$ when $k$ is odd, and $00l$ when $l$ is odd. Space group: $P2_12_12_1$.

The lattice constants and the three-dimensional intensity data were derived from the measurements made on a four-circle diffractometer using Zr-filtered Mo $K\alpha$ radiation. All the intensity data were then corrected for Lorentz and polarization factors to obtain

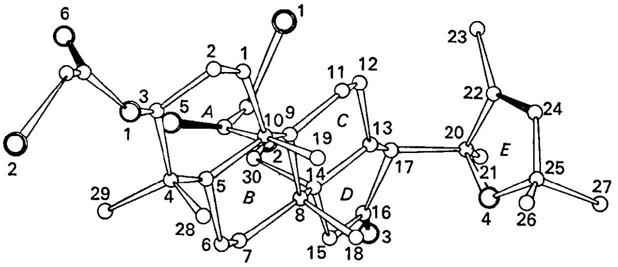

Fig. 2. The molecular structure in the correct absolute configuration. Carbon atoms are shown by a single circle, oxygen by a double circle and bromine by a triple circle. The double bond is shown by a black rod.

Table 1. *Final atomic parameters*

Temperature factors are expressed as $T = \exp\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\}$.

The thermal parameters are multiplied by $10^4$. The e.s.d.'s are given in the parentheses denoting least significant digits. To represent the correct absolute configuration the coordinates should be referred to the right-handed coordinate system.

| | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Br(1) | 0·6807 (2) | 0·3727 (1) | −0·1993 (6) | 104 (2) | 20 (0) | 605 (12) | −6 (1) | −75 (5) | −27 (2) |
| Br(2) | 1·6365 (3) | 0·5357 (1) | 0·1399 (7) | 116 (3) | 18 (0) | 717 (15) | −8 (1) | −123 (6) | −7 (2) |
| C(1) | 1·2833 (15) | 0·3990 (5) | −0·0734 (26) | 77 (15) | 9 (2) | 81 (47) | −10 (5) | 11 (25) | 13 (8) |
| C(2) | 1·3903 (14) | 0·4167 (5) | −0·0840 (30) | 51 (14) | 9 (2) | 222 (60) | −13 (4) | −9 (26) | −8 (9) |
| C(3) | 1·3860 (13) | 0·4514 (5) | 0·0444 (30) | 30 (12) | 12 (2) | 202 (56) | −15 (4) | 33 (24) | −4 (10) |
| C(4) | 1·3613 (15) | 0·4432 (5) | 0·2528 (29) | 64 (14) | 7 (2) | 214 (54) | −3 (4) | 64 (28) | −5 (9) |
| C(5) | 1·2596 (13) | 0·4223 (4) | 0·2501 (28) | 46 (12) | 5 (1) | 204 (53) | −1 (4) | −27 (25) | −6 (9) |
| C(6) | 1·2208 (14) | 0·4139 (5) | 0·4531 (27) | 58 (14) | 8 (2) | 126 (48) | −9 (4) | −39 (25) | −10 (9) |
| C(7) | 1·1108 (14) | 0·4026 (5) | 0·4382 (27) | 65 (14) | 9 (2) | 153 (51) | −19 (4) | 63 (26) | −24 (9) |
| C(8) | 1·0973 (12) | 0·3664 (5) | 0·3135 (25) | 44 (12) | 11 (2) | 67 (41) | 1 (4) | 67 (22) | −5 (8) |
| C(9) | 1·1464 (14) | 0·3723 (5) | 0·1196 (25) | 52 (12) | 10 (2) | 110 (44) | −4 (4) | 45 (23) | 2 (9) |
| C(10) | 1·2571 (13) | 0·3861 (4) | 0·1288 (24) | 57 (12) | 6 (1) | 62 (40) | 4 (4) | −29 (22) | −6 (7) |
| C(11) | 1·1298 (15) | 0·3398 (5) | −0·0104 (28) | 71 (15) | 8 (2) | 153 (51) | −4 (4) | 58 (27) | −22 (8) |
| C(12) | 1·0201 (14) | 0·3297 (5) | −0·0367 (27) | 53 (13) | 8 (2) | 116 (47) | −5 (4) | 18 (24) | 0 (8) |
| C(13) | 0·9733 (12) | 0·3238 (4) | 0·1550 (26) | 44 (12) | 7 (2) | 90 (43) | −5 (4) | 5 (22) | −9 (8) |
| C(14) | 0·9820 (12) | 0·3581 (5) | 0·2812 (32) | 39 (11) | 7 (2) | 273 (61) | −2 (4) | 19 (26) | 5 (9) |
| C(15) | 0·9151 (13) | 0·3493 (5) | 0·4403 (32) | 31 (11) | 11 (2) | 245 (59) | −13 (4) | −19 (26) | −6 (10) |
| C(16) | 0·8340 (15) | 0·3280 (5) | 0·3623 (32) | 72 (15) | 7 (2) | 297 (64) | 10 (4) | 95 (30) | 15 (10) |
| C(17) | 0·8648 (13) | 0·3117 (4) | 0·1742 (30) | 51 (12) | 5 (1) | 244 (55) | −6 (4) | 71 (28) | −7 (8) |
| C(18) | 1·1402 (15) | 0·3338 (5) | 0·4344 (25) | 69 (14) | 9 (2) | 87 (45) | −6 (5) | −67 (27) | 11 (8) |
| C(19) | 1·3320 (13) | 0·3552 (5) | 0·1930 (34) | 48 (12) | 8 (2) | 326 (66) | 1 (4) | −13 (29) | −3 (10) |
| C(20) | 0·8515 (14) | 0·2675 (4) | 0·1731 (27) | 70 (13) | 3 (1) | 177 (47) | 1 (3) | 10 (29) | −9 (8) |
| C(21) | 0·7419 (14) | 0·2573 (6) | 0·1954 (34) | 45 (13) | 12 (2) | 281 (66) | −12 (4) | 51 (28) | −11 (11) |
| C(22) | 0·8973 (14) | 0·2495 (5) | 0·0045 (36) | 47 (13) | 5 (1) | 265 (51) | −3 (4) | 35 (24) | −8 (8) |
| C(23) | 0·8540 (18) | 0·2588 (6) | −0·1953 (27) | 112 (18) | 11 (2) | 90 (49) | −4 (5) | −33 (32) | −11 (9) |
| C(24) | 0·9613 (14) | 0·2248 (5) | 0·0586 (35) | 42 (12) | 10 (2) | 334 (71) | −6 (4) | 12 (30) | −15 (11) |
| C(25) | 0·9723 (14) | 0·2244 (4) | 0·2679 (30) | 73 (14) | 5 (1) | 236 (59) | −1 (4) | −6 (29) | −13 (9) |
| C(26) | 1·0790 (17) | 0·2309 (5) | 0·3366 (41) | 91 (17) | 8 (2) | 425 (82) | −0 (5) | −35 (38) | 24 (12) |
| C(27) | 0·9271 (20) | 0·1868 (5) | 0·3430 (39) | 149 (23) | 6 (2) | 324 (73) | 3 (5) | 68 (42) | −6 (11) |
| C(28) | 1·4496 (14) | 0·4247 (5) | 0·3602 (33) | 57 (14) | 9 (2) | 252 (61) | −6 (4) | −57 (28) | 25 (10) |
| C(29) | 1·3438 (15) | 0·4830 (6) | 0·3482 (34) | 55 (14) | 12 (2) | 293 (65) | −7 (4) | 46 (31) | −19 (11) |
| C(30) | 0·9357 (11) | 0·3940 (5) | 0·1908 (32) | 18 (10) | 11 (2) | 269 (62) | −5 (4) | −21 (25) | 9 (11) |
| C(31) | 0·7651 (16) | 0·4105 (5) | 0·0955 (34) | 90 (17) | 4 (1) | 355 (77) | −5 (4) | −39 (34) | −2 (10) |
| C(32) | 0·6716 (13) | 0·3976 (4) | 0·0387 (42) | 36 (12) | 4 (1) | 704 (105) | −2 (4) | 70 (34) | −26 (12) |
| C(33) | 1·5100 (16) | 0·4939 (5) | −0·0769 (34) | 72 (16) | 9 (2) | 274 (66) | 9 (5) | −58 (30) | 1 (10) |
| C(34) | 1·6178 (16) | 0·5045 (5) | −0·0753 (31) | 67 (15) | 11 (2) | 192 (54) | −7 (5) | −19 (28) | 4 (10) |
| O(1) | 1·4869 (9) | 0·4669 (3) | 0·0466 (21) | 48 (8) | 10 (1) | 256 (39) | −0 (3) | 5 (17) | 9 (6) |
| O(2) | 0·8344 (9) | 0·3849 (3) | 0·1402 (28) | 54 (8) | 5 (1) | 665 (66) | 3 (2) | −29 (24) | 3 (8) |
| O(3) | 0·7467 (11) | 0·3257 (4) | 0·4216 (23) | 87 (11) | 11 (1) | 318 (48) | −5 (3) | 71 (22) | −13 (7) |
| O(4) | 0·9068 (9) | 0·2537 (3) | 0·3225 (19) | 72 (9) | 7 (1) | 151 (31) | 4 (3) | −9 (17) | −1 (6) |
| O(5) | 0·7955 (12) | 0·4411 (4) | 0·0814 (34) | 76 (11) | 10 (1) | 801 (85) | −3 (3) | −39 (29) | −0 (10) |
| O(6) | 1·4502 (11) | 0·5049 (4) | −0·1902 (26) | 88 (11) | 13 (1) | 375 (51) | −1 (4) | −19 (24) | 36 (8) |

finally 1288 independent structure factors having net intensities above $3\sigma$ level. A Wilson plot gave an approximate overall temperature factor of 6·6 Å$^2$.

### Determination of the structure

The positions of the two bromine atoms were determined from a three-dimensional sharpened Patterson function and the Harker sections. Subsequent Fourier and difference Fourier synthesis revealed all the 42 atoms. The oxygen atoms were identified on the difference Fourier map with the help of chemical and structural considerations.

Refinement of the structural parameters was carried out by the block-matrix least-squares calculation using the program *HBLS* (Okaya & Ashida, 1967). Twelve cycles of calculation with anisotropic temperature factors for all atoms gave the *R* value of 0·084 for 1288

Table 2. *Observed and calculated structure factors*

| H | FO | FC |
|---|---|---|
| K,L= 0 0 | | |
| 2 | 77 | 82 |
| 4 | 173 | 149 |
| 6 | 85 | 84 |
| 8 | 55 | 51 |
| 10 | 30 | 29 |
| 12 | 14 | 13 |
| K,L= 1 0 | | |
| 2 | 120 | 112 |
| 3 | 25 | 28 |
| 4 | 100 | 94 |
| 5 | 128 | 116 |
| 7 | 53 | 51 |
| 8 | 17 | 14 |
| 10 | 22 | 24 |
| 11 | 16 | 12 |
| K,L= 2 0 | | |
| 0 | 61 | 74 |
| 1 | 65 | 80 |
| 2 | 43 | 36 |
| 3 | 28 | 25 |
| 4 | 45 | 47 |
| 5 | 84 | 94 |
| 6 | 49 | 51 |
| 7 | 41 | 46 |
| 8 | 34 | 33 |
| 9 | 31 | 31 |
| 11 | 28 | 30 |
| 12 | 14 | 15 |
| K,L= 3 0 | | |
| 1 | 30 | 41 |
| 2* | 3 | 2 |
| 3 | 63 | 63 |
| 4 | 22 | 22 |
| 5 | 53 | 53 |
| 6 | 14 | 11 |
| 7 | 71 | 76 |
| 8 | 14 | 12 |
| 9 | 31 | 37 |
| 10 | 33 | 34 |
| 11 | 12 | 14 |
| 12 | 28 | 28 |
| K,L= 4 0 | | |
| 0 | 96 | 88 |
| 1 | 70 | 67 |
| 2 | 181 | 191 |
| 3 | 41 | 45 |
| 4 | 36 | 43 |
| 5 | 9 | 4 |
| 6 | 46 | 42 |
| 7 | 58 | 41 |
| 8 | 71 | 73 |
| 10 | 12 | 13 |
| 12 | 20 | 25 |
| K,L= 5 0 | | |
| 1 | 66 | 54 |
| 2 | 296 | 310 |
| 3 | 9 | 1 |
| 4 | 78 | 82 |
| 6 | 99 | 73 |
| 7 | 126 | 125 |
| 8 | 31 | 27 |
| 9 | 35 | 40 |
| 10 | 33 | 34 |
| K,L= 6 0 | | |
| 0 | 28 | 22 |
| 1 | 43 | 29 |
| 2 | 101 | 101 |
| 3 | 238 | 229 |
| 4 | 15 | 10 |
| 5 | 67 | 65 |
| 6 | 110 | 94 |
| 7 | 23 | 20 |
| 8 | 14 | 12 |
| 9 | 27 | 26 |
| 10 | 10 | 8 |
| K,L= 7 0 | | |
| 1 | 44 | 52 |
| 2 | 169 | 150 |
| 3 | 7 | 2 |
| 4 | 95 | 96 |
| 5 | 27 | 23 |
| 6 | 55 | 45 |
| 7 | 29 | 32 |
| 8 | 46 | 42 |
| 11 | 17 | 19 |
| K,L= 8 0 | | |
| 0 | 176 | 179 |
| 1 | 137 | 133 |
| 2 | 28 | 22 |
| 3 | 21 | 27 |
| 4 | 63 | 47 |
| 5 | 37 | 39 |
| 6 | 48 | 52 |
| 7 | 25 | 30 |
| 8 | 52 | 55 |
| 11 | 24 | 22 |
| 12 | 28 | 33 |
| K,L= 9 0 | | |
| 1 | 47 | 38 |
| 2 | 63 | 57 |
| 3 | 52 | 40 |
| 4 | 16 | 23 |
| 5 | 101 | 83 |
| 6 | 89 | 84 |
| 7 | 35 | 31 |
| 8 | 23 | 25 |
| 9 | 18 | 22 |
| 10 | 24 | 24 |
| 11 | 11 | 14 |
| K,L= 10 0 | | |
| 0 | 94 | 98 |
| 1 | 44 | 35 |
| 2 | 7 | 4 |
| 3 | 20 | 17 |
| 4 | 91 | 95 |
| 5 | 153 | 141 |
| 6 | 16 | 17 |
| 7 | 28 | 24 |
| 8 | 33 | 33 |
| 9 | 11 | 9 |
| 10 | 17 | 16 |
| 11 | 30 | 27 |
| K,L= 11 0 | | |
| 1 | 128 | 119 |
| 2 | 30 | 33 |
| 3 | 29 | 20 |
| 4 | 18 | 4 |
| 5 | 35 | 39 |
| 6 | 22 | 26 |
| 7 | 8 | 11 |
| 8 | 24 | 24 |
| 9 | 21 | 24 |
| 10 | 35 | 31 |
| 12 | 29 | 24 |
| K,L= 12 0 | | |
| 0 | 31 | 11 |
| 1 | 62 | 51 |
| 2 | 41 | 47 |
| 3 | 23 | 23 |
| 4 | 77 | 75 |
| 5 | 27 | 29 |
| 6 | 118 | 109 |
| 7 | 17 | 13 |
| 8 | 23 | 25 |
| 9 | 21 | 20 |
| 11 | 23 | 24 |
| K,L= 13 0 | | |
| 1 | 104 | 108 |
| 2 | 88 | 84 |
| 3 | 29 | 34 |
| 4 | 37 | 37 |
| 5 | 74 | 79 |
| 6 | 9 | 6 |
| 7 | 50 | 59 |
| 9 | 20 | 21 |
| 10 | 26 | 28 |
| 11 | 10 | 9 |
| K,L= 14 0 | | |
| 0 | 135 | 133 |
| 1 | 29 | 30 |
| 2 | 42 | 43 |
| 3 | 71 | 75 |
| 4 | 63 | 70 |
| 6 | 14 | 11 |
| 8 | 45 | 47 |
| 10 | 25 | 23 |
| K,L= 15 0 | | |
| 1 | 45 | 44 |
| 2 | 47 | 46 |
| 3 | 55 | 56 |
| 4 | 22 | 22 |
| 6 | 31 | 34 |
| 7 | 36 | 35 |
| 8 | 29 | 27 |
| 9 | 23 | 22 |
| 10 | 16 | 14 |
| 11 | 44 | 46 |
| K,L= 16 0 | | |
| 0 | 44 | 42 |
| 1 | 53 | 50 |
| 2 | 42 | 38 |
| 3 | 72 | 65 |
| 4 | 6 | 2 |
| 7 | 38 | 42 |
| 8 | 42 | 40 |
| 9 | 21 | 25 |
| 10 | 19 | 12 |
| K,L= 17 0 | | |
| 1 | 58 | 66 |
| 2 | 26 | 23 |
| 3 | 36 | 35 |
| 4 | 39 | 41 |
| 6 | 38 | 33 |
| 7 | 25 | 24 |
| 8 | 14 | 13 |
| 9 | 21 | 20 |
| K,L= 18 0 | | |
| 0 | 13 | 10 |
| 1 | 32 | 36 |
| 2 | 12 | 14 |
| 3 | 34 | 33 |
| 4 | 37 | 28 |
| 5 | 10 | 11 |
| 7 | 11 | 13 |
| 8 | 18 | 18 |
| 10 | 13 | 18 |
| K,L= 19 0 | | |
| 1 | 59 | 61 |
| 2 | 73 | 72 |
| 3 | 12 | 8 |
| 4 | 9 | 6 |
| 5 | 49 | 47 |
| 6 | 36 | 39 |
| 9 | 15 | 16 |
| K,L= 20 0 | | |
| 0 | 44 | 47 |
| 1 | 6 | 7 |
| 2 | 26 | 23 |
| 3 | 19 | 20 |
| 4 | 28 | 30 |
| 5 | 23 | 22 |
| 6 | 57 | 53 |
| 7 | 35 | 33 |
| 8 | 19 | 14 |
| 9 | 17 | 16 |
| 10 | 29 | 27 |
| K,L= 21 0 | | |
| 1 | 8 | 6 |
| 2 | 15 | 13 |
| 3 | 9 | 12 |
| 4 | 28 | 29 |
| 5 | 20 | 17 |
| 6 | 22 | 23 |
| 7 | 22 | 21 |
| 8 | 45 | 44 |
| 9 | 21 | 28 |
| 10 | 36 | 35 |
| K,L= 22 0 | | |
| 0 | 55 | 53 |
| 1 | 7 | 5 |
| 2 | 20 | 20 |
| 3 | 25 | 26 |
| 4 | 10 | 13 |
| 5 | 14 | 10 |
| 7 | 32 | 28 |
| 10 | 13 | 10 |
| K,L= 23 0 | | |
| 1 | 20 | 15 |
| 2 | 8 | 7 |
| 3 | 33 | 36 |
| 4 | 16 | 21 |
| 5 | 16 | 14 |
| 6 | 19 | 19 |
| 7 | 9 | 7 |
| 8 | 12 | 10 |
| K,L= 24 0 | | |
| 0 | 45 | 46 |
| 1 | 23 | 17 |
| 2 | 18 | 19 |
| 3 | 49 | 52 |
| 4 | 14 | 14 |
| 7 | 28 | 26 |
| 8 | 20 | 23 |
| 9 | 15 | 16 |
| K,L= 25 0 | | |
| 1 | 18 | 21 |
| 2 | 46 | 50 |
| 3 | 24 | 28 |
| 4 | 21 | 21 |
| 5 | 34 | 35 |
| 6 | 16 | 17 |
| 8 | 33 | 31 |
| K,L= 26 0 | | |
| 1 | 11 | 8 |
| 2 | 19 | 19 |
| 3 | 12 | 12 |
| 4 | 13 | 14 |
| K,L= 27 0 | | |
| 1 | 10 | 7 |
| 2 | 9 | 11 |
| 3 | 38 | 39 |
| 5 | 44 | 43 |
| 6 | 14 | 16 |
| 7 | 20 | 20 |
| 8 | 11 | 2 |
| K,L= 28 0 | | |
| 0 | 18 | 18 |
| 1 | 21 | 24 |
| 2 | 27 | 26 |
| 3 | 19 | 16 |
| 5 | 11 | 5 |
| K,L= 29 0 | | |
| 1 | 28 | 26 |
| 2 | 48 | 51 |
| 3 | 14 | 17 |
| K,L= 30 0 | | |
| 0 | 18 | 15 |
| 1 | 27 | 27 |
| 3 | 10 | 10 |
| 6 | 25 | 24 |
| K,L= 31 0 | | |
| 1 | 14 | 14 |
| 2 | 10 | 11 |
| 3 | 15 | 14 |
| 4 | 6 | 9 |
| 5 | 21 | 18 |
| K,L= 32 0 | | |
| 0 | 10 | 12 |
| 3 | 7 | 12 |
| 4 | 13 | 16 |
| 5 | 33 | 33 |
| K,L= 33 0 | | |
| 1 | 18 | 23 |
| 2 | 14 | 14 |
| 4 | 22 | 23 |
| K,L= 34 0 | | |
| 1 | 8 | 8 |
| 3 | 12 | 9 |
| 4 | 14 | 15 |
| K,L= 36 0 | | |
| 0 | 17 | 16 |
| K,L= 0 1 | | |
| 2 | 31 | 30 |
| 3 | 4 | 10 |
| 4 | 32 | 30 |
| 5 | 51 | 60 |
| 6 | 61 | 51 |
| 7 | 56 | 62 |
| 8 | 59 | 32 |
| 9 | 34 | 30 |
| 10 | 28 | 28 |
| 11 | 42 | 42 |
| K,L= 1 1 | | |
| 0 | 99 | 94 |
| 1 | 138 | 141 |
| 2 | 37 | 35 |
| 3 | 78 | 77 |
| 4 | 78 | 78 |
| 5 | 89 | 82 |
| 6 | 100 | 95 |
| 7 | 48 | 49 |
| 8 | 19 | 19 |
| 9 | 32 | 34 |
| 10 | 31 | 30 |
| 12 | 14 | 11 |
| K,L= 2 1 | | |
| 0 | 113 | 91 |
| 1 | 138 | 138 |
| 2 | 73 | 72 |
| 3 | 60 | 69 |
| 4 | 38 | 38 |
| 5 | 51 | 48 |
| 6 | 74 | 72 |
| 7 | 68 | 67 |
| 8 | 58 | 55 |
| 9 | 23 | 26 |
| 10 | 29 | 28 |
| 11* | 0 | 12 |
| 12 | 17 | 17 |
| K,L= 3 1 | | |
| 0 | 46 | 47 |
| 1 | 197 | 201 |
| 2 | 119 | 139 |
| 3 | 53 | 50 |
| 4 | 67 | 72 |
| 5 | 36 | 37 |
| 6 | 20 | 20 |
| 7 | 64 | 58 |
| 8 | 48 | 45 |
| 9 | 34 | 35 |
| 10 | 22 | 18 |
| 11 | 18 | 19 |
| 12 | 18 | 17 |
| K,L= 4 1 | | |
| 0 | 7 | 8 |
| 1 | 80 | 81 |
| 2 | 23 | 24 |
| 3 | 183 | 188 |
| 4 | 80 | 78 |
| 5 | 92 | 85 |
| 6 | 40 | 44 |
| 7 | 36 | 37 |
| 8 | 44 | 39 |
| 9 | 25 | 27 |
| 10 | 18 | 20 |
| 11 | 16 | 16 |
| 12* | 0 | 15 |
| K,L= 5 1 | | |
| 0 | 22 | 15 |
| 1 | 11 | 23 |
| 2 | 64 | 70 |
| 3 | 100 | 90 |
| 4 | 60 | 62 |
| 5 | 9 | 9 |
| 6 | 82 | 73 |
| 7 | 33 | 37 |
| 8 | 30 | 25 |
| 9 | 52 | 54 |
| 10 | 30 | 32 |
| K,L= 6 1 | | |
| 0 | 45 | 36 |
| 1 | 70 | 70 |
| 2 | 159 | 155 |
| 3 | 72 | 66 |
| 4 | 51 | 46 |
| 5 | 59 | 58 |
| 6 | 45 | 41 |
| 7 | 16 | 18 |
| 8 | 52 | 52 |
| 9 | 18 | 20 |
| 10 | 26 | 24 |
| K,L= 7 1 | | |
| 0 | 151 | 146 |
| 1 | 56 | 44 |
| 2 | 135 | 129 |
| 3 | 58 | 66 |
| 4 | 101 | 99 |
| 5 | 33 | 34 |
| 6 | 30 | 32 |
| 7 | 33 | 35 |
| 8 | 19 | 23 |
| 9 | 27 | 31 |
| 10 | 52 | 46 |
| 12 | 37 | 30 |
| K,L= 8 1 | | |
| 0 | 20 | 27 |
| 1 | 156 | 168 |
| 2 | 62 | 67 |
| 3 | 54 | 65 |
| 4 | 62 | 63 |
| 5 | 46 | 45 |
| 6 | 19 | 17 |
| 7 | 13 | 11 |
| 8 | 21 | 20 |
| 9 | 33 | 34 |
| 10 | 14 | 14 |
| 11 | 23 | 18 |
| K,L= 9 1 | | |
| 0 | 12 | 5 |
| 1 | 149 | 146 |
| 2 | 50 | 46 |
| 3 | 72 | 57 |
| 4 | 64 | 71 |
| 5 | 108 | 111 |
| 6 | 28 | 29 |
| 7 | 41 | 43 |
| 9 | 14 | 13 |
| 10 | 24 | 26 |
| K,L= 10 1 | | |
| 0 | 137 | 153 |
| 1 | 87 | 79 |
| 2 | 71 | 68 |
| 3 | 61 | 49 |
| 5 | 33 | 28 |
| 6 | 43 | 43 |
| 7 | 33 | 31 |
| 8 | 10 | 13 |
| 9 | 18 | 18 |
| 11 | 26 | 26 |
| 12 | 19 | 18 |
| K,L= 11 1 | | |
| 0 | 22 | 14 |
| 1 | 93 | 89 |
| 2 | 11 | 15 |
| 3 | 11 | 14 |
| 4 | 65 | 60 |
| 5 | 23 | 24 |
| 6 | 45 | 47 |
| 7 | 18 | 24 |
| 8 | 23 | 22 |
| 10 | 36 | 33 |
| 12 | 23 | 22 |
| K,L= 12 1 | | |
| 0 | 5 | 4 |
| 1 | 40 | 36 |
| 2 | 56 | 49 |
| 3 | 81 | 72 |
| 4 | 53 | 47 |
| 5 | 85 | 80 |
| 6 | 26 | 25 |
| 7 | 27 | 24 |
| 8 | 22 | 17 |
| 9 | 31 | 30 |
| 11 | 23 | 20 |
| K,L= 13 1 | | |
| 0 | 44 | 38 |
| 1 | 91 | 96 |
| 2 | 64 | 63 |
| 3 | 35 | 33 |
| 4 | 46 | 43 |
| 5 | 11 | 11 |
| 6 | 44 | 47 |
| 7 | 34 | 33 |
| 8 | 12 | 16 |
| 9 | 30 | 24 |
| 10 | 17 | 19 |
| K,L= 14 1 | | |
| 0 | 45 | 51 |
| 1 | 36 | 39 |
| 2 | 51 | 53 |
| 3 | 23 | 20 |
| 4 | 22 | 24 |
| 6 | 14 | 19 |
| 7 | 30 | 34 |
| 8 | 38 | 32 |
| 9 | 29 | 29 |
| K,L= 15 1 | | |
| 0 | 52 | 51 |
| 1 | 28 | 27 |
| 2 | 63 | 68 |
| 3 | 38 | 41 |
| 4 | 77 | 77 |
| 5 | 28 | 29 |
| 6* | 0 | 10 |
| 7 | 9 | 13 |
| 8 | 18 | 17 |
| 10 | 14 | 16 |
| 11 | 20 | 20 |
| K,L= 16 1 | | |
| 0 | 8 | 9 |
| 1 | 87 | 85 |
| 2 | 44 | 39 |
| 3 | 89 | 85 |
| 4 | 14 | 16 |
| 5 | 35 | 34 |
| 6 | 35 | 29 |
| 7 | 22 | 21 |
| 9 | 18 | 15 |
| K,L= 17 1 | | |
| 0 | 3 | 0 |
| 1 | 64 | 63 |
| 2 | 76 | 81 |
| 3 | 40 | 41 |
| 4 | 55 | 55 |
| 5 | 14 | 14 |
| 6 | 32 | 30 |
| 7 | 64 | 58 |
| 8 | 19 | 18 |
| 9 | 20 | 16 |
| K,L= 18 1 | | |
| 0 | 29 | 21 |
| 1 | 45 | 46 |
| 2 | 29 | 23 |
| 3 | 32 | 29 |
| 4 | 26 | 23 |
| 5 | 37 | 34 |
| 6 | 20 | 21 |
| 7 | 26 | 25 |
| 8 | 40 | 40 |
| 9 | 26 | 27 |
| 10 | 23 | 22 |
| K,L= 19 1 | | |
| 0 | 24 | 25 |
| 2 | 10 | 13 |
| 3 | 16 | 14 |
| 4 | 24 | 22 |
| 5 | 29 | 31 |
| 6 | 46 | 38 |
| 9 | 15 | 14 |
| K,L= 20 1 | | |
| 0 | 45 | 46 |
| 1 | 20 | 14 |
| 2 | 28 | 23 |
| 3 | 49 | 56 |
| 4 | 45 | 45 |
| 5 | 39 | 39 |
| 7 | 22 | 21 |
| 8 | 12 | 11 |
| 9 | 19 | 20 |
| K,L= 21 1 | | |
| 0 | 23 | 26 |
| 1 | 57 | 61 |
| 2 | 34 | 39 |
| 4 | 12 | 12 |
| 5 | 24 | 20 |
| 6 | 19 | 19 |
| 9 | 22 | 24 |
| K,L= 22 1 | | |
| 0 | 74 | 69 |
| 1 | 45 | 46 |
| 2 | 14 | 12 |
| 3* | 0 | 12 |
| 4 | 43 | 47 |
| 5 | 30 | 25 |
| 6 | 26 | 27 |
| 9 | 22 | 26 |
| K,L= 23 1 | | |
| 0 | 9 | 9 |
| 1 | 40 | 42 |
| 2 | 28 | 30 |
| 3 | 30 | 31 |
| 4 | 35 | 32 |
| 5 | 28 | 26 |
| 7 | 17 | 15 |
| 9 | 23 | 22 |
| K,L= 24 1 | | |
| 0 | 9 | 10 |
| 1 | 21 | 19 |
| 2 | 23 | 20 |
| 3 | 29 | 32 |
| 4 | 31 | 32 |
| 5 | 21 | 16 |
| 8 | 24 | 20 |
| K,L= 25 1 | | |
| 1 | 22 | 17 |
| 2 | 19 | 15 |
| 3 | 12 | 11 |
| 5 | 16 | 19 |
| 6 | 11 | 13 |
| 7 | 23 | 23 |
| K,L= 26 1 | | |
| 1 | 14 | 11 |
| 2 | 13 | 9 |
| 3 | 22 | 24 |
| 4 | 8 | 12 |
| 5 | 13 | 11 |
| 6 | 20 | 23 |
| 7* | 0 | 15 |
| 8 | 18 | 23 |
| K,L= 27 1 | | |
| 1 | 12 | 15 |
| 2 | 21 | 20 |
| 4 | 20 | 17 |
| 5 | 29 | 26 |
| 7 | 13 | 14 |
| K,L= 28 1 | | |
| 1 | 13 | 11 |
| 2 | 31 | 26 |
| 3 | 38 | 34 |
| K,L= 29 1 | | |
| 0 | 9 | 10 |
| 1 | 22 | 18 |
| 2 | 19 | 21 |
| 3 | 29 | 32 |
| 4 | 23 | 25 |
| 5 | 17 | 14 |
| 6 | 23 | 20 |
| K,L= 30 1 | | |
| 0 | 32 | 33 |
| 1 | 16 | 18 |
| 2 | 16 | 16 |
| 3 | 13 | 10 |
| 4 | 25 | 25 |
| K,L= 31 1 | | |
| 0 | 10 | 12 |
| 2 | 16 | 16 |
| 4 | 16 | 17 |
| 5 | 14 | 14 |
| K,L= 32 1 | | |
| 0 | 29 | 28 |
| 2 | 14 | 13 |
| 3 | 13 | 10 |
| K,L= 33 1 | | |
| 1 | 10 | 10 |
| 3* | 0 | 12 |
| K,L= 34 1 | | |
| 0 | 23 | 21 |
| K,L= 35 1 | | |
| 0 | 11 | 7 |
| K,L= 0 2 | | |
| 1 | 72 | 76 |
| 2 | 32 | 29 |
| 3 | 68 | 66 |
| 4 | 21 | 20 |
| 5 | 14 | 14 |
| 6 | 23 | 22 |
| 8 | 41 | 43 |
| 9 | 38 | 36 |
| 10 | 18 | 15 |
| K,L= 1 2 | | |
| 0 | 10 | 15 |
| 1 | 36 | 38 |
| 2 | 53 | 45 |
| 3 | 43 | 50 |
| 4 | 40 | 40 |
| 5 | 55 | 52 |
| 6 | 35 | 35 |
| 7 | 26 | 26 |
| 8 | 43 | 45 |
| 9 | 25 | 23 |
| 10 | 29 | 31 |
| 11 | 33 | 34 |
| 12* | 0 | 12 |
| K,L= 2 2 | | |
| 0 | 55 | 53 |
| 1 | 105 | 105 |
| 2 | 105 | 110 |
| 3 | 93 | 94 |
| 4 | 56 | 58 |
| 5 | 59 | 61 |
| 6 | 23 | 22 |
| 7* | 0 | 10 |
| 8 | 19 | 20 |
| 9 | 12 | 11 |
| 10 | 18 | 15 |
| K,L= 3 2 | | |
| 0 | 54 | 67 |
| 1 | 118 | 113 |
| 2 | 67 | 60 |
| 3 | 98 | 96 |
| 4 | 49 | 53 |
| 5 | 27 | 24 |
| 6 | 30 | 27 |
| 7 | 48 | 53 |
| 8 | 17 | 16 |
| 9 | 21 | 20 |
| 10 | 21 | 16 |
| 12* | 0 | 15 |
| K,L= 4 2 | | |
| 0 | 9 | 13 |
| 1 | 93 | 89 |
| 2 | 34 | 39 |
| 3 | 26 | 27 |
| 4 | 44 | 39 |
| 5 | 51 | 54 |
| 6 | 59 | 54 |
| 7 | 28 | 34 |
| 8 | 41 | 39 |
| 9 | 25 | 23 |
| 10 | 23 | 22 |
| 11 | 34 | 31 |
| K,L= 5 2 | | |
| 0 | 18 | 17 |
| 1 | 61 | 55 |
| 2 | 32 | 33 |
| 3 | 37 | 36 |
| 4 | 48 | 59 |
| 5 | 32 | 32 |
| 6 | 9 | 8 |
| 7 | 40 | 39 |
| 8 | 21 | 20 |
| 9 | 30 | 28 |
| 10* | 0 | 25 |
| 11 | 19 | 19 |
| K,L= 6 2 | | |
| 0 | 35 | 29 |
| 1 | 94 | 88 |
| 2 | 34 | 31 |
| 3 | 61 | 66 |
| 4 | 15 | 15 |
| 5 | 43 | 42 |
| 6 | 49 | 45 |
| 8 | 31 | 29 |
| 9 | 17 | 16 |
| 10 | 41 | 43 |
| 12* | 0 | 16 |
| K,L= 7 2 | | |
| 0 | 98 | 96 |
| 1 | 17 | 27 |
| 2 | 43 | 41 |
| 3 | 68 | 61 |
| 4 | 32 | 29 |
| 5 | 46 | 44 |
| 6* | 0 | 16 |
| 7 | 43 | 41 |
| 9 | 31 | 30 |
| 11* | 0 | 20 |
| K,L= 8 2 | | |
| 0 | 115 | 117 |
| 1 | 61 | 60 |
| 2 | 100 | 91 |
| 3 | 53 | 56 |
| 4 | 19 | 15 |
| 5 | 38 | 39 |
| 6 | 32 | 31 |
| 7 | 14 | 11 |
| 8 | 42 | 40 |
| 9 | 33 | 36 |
| 10* | 0 | 21 |
| K,L= 9 2 | | |
| 0 | 36 | 33 |
| 1 | 60 | 56 |
| 2 | 45 | 50 |
| 3 | 105 | 103 |
| 4 | 37 | 31 |
| 5 | 29 | 23 |
| 6 | 41 | 41 |
| 7 | 47 | 44 |
| 8 | 12 | 12 |
| 9 | 39 | 38 |
| 10 | 27 | 21 |
| 11 | 23 | 22 |
| K,L= 10 2 | | |
| 0 | 25 | 27 |
| 1 | 56 | 45 |
| 2 | 65 | 76 |
| 3 | 34 | 41 |
| 4 | 41 | 42 |
| 5 | 29 | 31 |
| 6 | 27 | 26 |
| 7 | 28 | 25 |
| 8 | 31 | 33 |
| 9 | 35 | 35 |
| 10 | 23 | 17 |
| 11 | 24 | 21 |
| K,L= 11 2 | | |
| 0 | 63 | 91 |
| 1 | 71 | 75 |
| 2 | 35 | 34 |
| 3 | 100 | 92 |
| 4 | 54 | 51 |
| 5 | 16 | 11 |
| 6 | 20 | 19 |
| 7 | 41 | 41 |
| 8 | 43 | 47 |
| 9 | 23 | 20 |
| K,L= 12 2 | | |
| 0 | 84 | 87 |
| 1 | 27 | 29 |
| 2 | 49 | 49 |
| 3 | 39 | 36 |
| 4 | 67 | 68 |
| 5 | 46 | 44 |
| 6 | 14 | 17 |
| 7 | 28 | 26 |
| 8 | 17 | 14 |
| 10* | 0 | 25 |
| K,L= 13 2 | | |
| 0 | 161 | 147 |
| 1 | 40 | 42 |
| 2 | 66 | 73 |
| 3 | 42 | 37 |
| 4 | 53 | 52 |
| 5 | 16 | 13 |
| 7* | 0 | 14 |
| 8 | 31 | 30 |
| 9* | 0 | 12 |
| 10 | 17 | 18 |
| K,L= 14 2 | | |
| 0 | 49 | 39 |
| 1 | 42 | 43 |
| 2 | 59 | 58 |
| 3 | 44 | 41 |
| 4 | 41 | 40 |
| 5 | 77 | 74 |
| 6 | 20 | 21 |
| 7 | 22 | 19 |
| 9 | 32 | 31 |
| 10 | 20 | 17 |
| K,L= 15 2 | | |
| 0 | 90 | 84 |
| 1 | 44 | 36 |
| 2 | 22 | 21 |
| 3 | 67 | 62 |
| 4 | 51 | 49 |
| 5 | 16 | 14 |
| 6 | 31 | 31 |
| 7 | 32 | 33 |
| 9 | 27 | 24 |
| K,L= 16 2 | | |
| 0 | 102 | 95 |
| 1 | 83 | 80 |
| 2 | 41 | 40 |
| 3 | 37 | 40 |
| 4* | 0 | 14 |
| 5 | 44 | 39 |
| 6 | 32 | 33 |
| 7 | 27 | 23 |
| 8 | 23 | 21 |
| 9* | 0 | 15 |
| 10* | 0 | 20 |
| K,L= 17 2 | | |
| 0 | 10 | 12 |
| 1 | 17 | 17 |
| 2 | 35 | 35 |
| 3 | 19 | 16 |
| 4 | 21 | 21 |
| 5 | 32 | 32 |
| 6 | 28 | 29 |
| 7 | 20 | 26 |
| 8* | 0 | 11 |
| 9 | 20 | 21 |
| K,L= 18 2 | | |
| 0 | 38 | 35 |
| 1 | 13 | 14 |
| 2 | 30 | 28 |
| 3 | 18 | 22 |
| 5 | 34 | 30 |
| 6 | 38 | 35 |
| 7 | 42 | 41 |
| 9 | 23 | 22 |
| 10 | 16 | 14 |
| K,L= 19 2 | | |
| 1 | 35 | 35 |
| 2 | 30 | 28 |
| 3 | 12 | 13 |
| 4* | 0 | 14 |
| 5 | 22 | 24 |
| 7 | 33 | 27 |
| 8 | 24 | 25 |
| 10* | 0 | 15 |
| K,L= 20 2 | | |
| 0 | 40 | 42 |
| 1 | 40 | 37 |
| 2 | 49 | 45 |
| 3 | 42 | 43 |
| 4 | 23 | 28 |
| 5 | 23 | 21 |
| 6 | 24 | 24 |
| 7 | 38 | 33 |
| 9 | 13 | 12 |
| K,L= 21 2 | | |
| 0 | 12 | 9 |
| 1 | 38 | 37 |
| 2 | 26 | 21 |
| 3 | 44 | 43 |
| 4 | 26 | 22 |
| 5 | 26 | 25 |
| 7 | 36 | 36 |
| K,L= 22 2 | | |
| 0 | 15 | 13 |
| 2 | 33 | 33 |
| 3 | 15 | 16 |
| 4 | 21 | 20 |
| 5 | 37 | 35 |
| 7 | 25 | 29 |
| K,L= 23 2 | | |
| 0 | 32 | 36 |
| 1 | 19 | 20 |
| 2 | 24 | 22 |
| 3 | 21 | 18 |
| 4 | 17 | 15 |
| 5 | 23 | 24 |
| 7* | 0 | 15 |
| 8 | 21 | 25 |
| K,L= 24 2 | | |
| 1 | 19 | 21 |
| 2 | 23 | 24 |
| 3 | 13 | 10 |
| 4 | 21 | 22 |
| 5 | 18 | 17 |
| 6 | 23 | 21 |
| 8 | 27 | 28 |
| K,L= 25 2 | | |
| 0 | 12 | 9 |
| 1 | 24 | 28 |
| 2 | 28 | 28 |
| 3 | 11 | 15 |
| 4* | 0 | 12 |
| 5 | 35 | 35 |
| 7 | 13 | 14 |
| 8* | 0 | 15 |
| K,L= 26 2 | | |
| 1 | 28 | 27 |
| 3 | 21 | 21 |
| 5 | 39 | 37 |
| 6 | 20 | 16 |
| 7* | 0 | 9 |
| K,L= 27 2 | | |
| 0 | 45 | 45 |
| 1 | 24 | 22 |
| 2 | 18 | 15 |
| 3 | 12 | 11 |
| 4 | 27 | 27 |
| 6 | 17 | 16 |
| 7 | 20 | 20 |
| K,L= 28 2 | | |
| 2 | 12 | 10 |
| 3* | 0 | 8 |
| 5 | 13 | 14 |
| 6 | 13 | 17 |
| K,L= 29 2 | | |
| 0 | 10 | 11 |
| 3 | 18 | 18 |
| 6 | 25 | 25 |
| K,L= 30 2 | | |
| 1 | 19 | 24 |
| 3 | 18 | 15 |
| 4* | 0 | 12 |
| K,L= 31 2 | | |
| 1 | 16 | 11 |
| K,L= 32 2 | | |
| 2 | 10 | 10 |
| K,L= 33 2 | | |
| 0 | 14 | 13 |
| K,L= 0 3 | | |
| 2 | 55 | 66 |
| 3 | 35 | 32 |
| 4 | 36 | 37 |
| 5 | 33 | 35 |
| 6 | 17 | 18 |
| 9 | 23 | 20 |
| 11 | 18 | 17 |
| K,L= 1 3 | | |
| 0 | 18 | 16 |
| 1 | 43 | 47 |
| 2 | 93 | 90 |
| 3 | 48 | 52 |
| 4 | 62 | 61 |
| 5 | 10 | 10 |
| 6 | 40 | 43 |
| 7 | 18 | 20 |
| 8* | 0 | 13 |
| 9 | 22 | 19 |
| 10 | 21 | 25 |
| K,L= 2 3 | | |
| 0 | 66 | 68 |
| 1 | 33 | 40 |
| 2 | 79 | 78 |
| 3 | 37 | 36 |
| 4 | 36 | 31 |
| 5 | 7 | 8 |
| 6 | 38 | 40 |
| 7 | 37 | 38 |
| 8 | 34 | 32 |
| 9 | 30 | 33 |
| 10 | 23 | 25 |
| K,L= 3 3 | | |
| 0 | 20 | 19 |
| 1 | 47 | 44 |
| 2 | 31 | 31 |
| 3 | 45 | 44 |
| 4 | 17 | 14 |
| 5 | 47 | 46 |
| 6 | 24 | 24 |
| 8 | 41 | 40 |
| 9 | 22 | 21 |
| 11 | 32 | 30 |
| K,L= 4 3 | | |
| 0 | 19 | 18 |
| 1 | 47 | 43 |
| 2 | 49 | 41 |
| 3 | 27 | 28 |
| 4 | 54 | 53 |
| 5 | 31 | 32 |
| 6 | 30 | 31 |
| 7 | 26 | 23 |
| 8 | 26 | 23 |
| 9 | 23 | 20 |
| 10 | 31 | 31 |
| 11 | 22 | 19 |
| K,L= 5 3 | | |
| 0 | 127 | 120 |
| 1 | 37 | 39 |
| 2 | 56 | 51 |
| 4 | 52 | 55 |
| 5 | 12 | 13 |
| 6 | 22 | 20 |
| 7 | 19 | 18 |
| 9 | 12 | 11 |
| K,L= 6 3 | | |
| 0 | 45 | 44 |
| 1 | 41 | 39 |
| 2 | 60 | 52 |
| 3 | 19 | 19 |
| 4 | 65 | 59 |
| 5 | 44 | 48 |
| 6 | 28 | 30 |
| 7* | 0 | 13 |
| 8 | 20 | 22 |
| 9 | 35 | 33 |
| 10 | 21 | 27 |
| K,L= 7 3 | | |
| 0 | 112 | 114 |
| 1 | 76 | 76 |
| 2 | 49 | 46 |
| 3 | 27 | 30 |
| 4 | 45 | 48 |
| 5 | 51 | 52 |
| 6 | 58 | 50 |
| 7 | 33 | 30 |
| 8 | 17 | 20 |
| 10 | 25 | 27 |
| K,L= 8 3 | | |
| 0 | 4 | 3 |
| 1 | 18 | 16 |
| 2 | 9 | 10 |
| 3 | 28 | 26 |
| 4 | 34 | 35 |
| 5 | 49 | 44 |
| 6 | 33 | 32 |
| 7 | 29 | 25 |
| 9 | 19 | 19 |
| 10* | 0 | 7 |
| K,L= 9 3 | | |
| 0 | 35 | 34 |
| 1 | 30 | 31 |
| 2 | 54 | 51 |
| 3 | 30 | 32 |
| 4 | 31 | 31 |
| 6 | 39 | 41 |
| 7 | 24 | 23 |
| 8 | 51 | 50 |
| 9 | 41 | 43 |
| 10* | 0 | 20 |
| K,L= 10 3 | | |
| 0 | 5 | 14 |
| 1 | 34 | 32 |
| 2 | 43 | 41 |
| 3 | 30 | 30 |
| 5 | 25 | 24 |
| 7 | 38 | 37 |
| 9 | 40 | 39 |
| 10 | 20 | 20 |
| K,L= 11 3 | | |
| 0 | 25 | 23 |
| 1 | 37 | 39 |
| 2 | 13 | 12 |
| 3 | 49 | 54 |
| 4 | 27 | 22 |
| 6 | 13 | 11 |
| 7 | 19 | 17 |
| 8 | 36 | 40 |
| 9 | 23 | 24 |
| K,L= 12 3 | | |
| 0 | 23 | 21 |
| 1 | 49 | 53 |
| 2 | 45 | 47 |
| 3 | 48 | 49 |
| 4 | 20 | 24 |
| 5 | 28 | 26 |
| 6* | 0 | 9 |
| 7 | 16 | 16 |
| 8 | 38 | 42 |
| 9* | 0 | 14 |
| 10 | 19 | 16 |
| K,L= 13 3 | | |
| 0 | 52 | 51 |
| 1 | 13 | 14 |
| 2 | 44 | 42 |
| 3 | 37 | 32 |
| 4 | 29 | 33 |
| 5 | 18 | 20 |
| 6 | 34 | 35 |
| 8 | 28 | 26 |
| 9 | 18 | 14 |
| K,L= 14 3 | | |
| 0 | 11 | 11 |
| 1 | 31 | 29 |
| 2 | 47 | 42 |
| 3 | 23 | 21 |
| 4 | 24 | 21 |
| 5 | 23 | 24 |
| 6 | 47 | 47 |
| 7 | 20 | 18 |
| 8 | 24 | 27 |
| 9 | 28 | 24 |
| K,L= 15 3 | | |
| 0 | 27 | 27 |
| 1 | 21 | 23 |
| 2 | 22 | 22 |
| 3 | 14 | 14 |
| 4 | 16 | 20 |
| 5 | 33 | 29 |
| 6 | 35 | 32 |
| 7 | 41 | 41 |
| 9 | 17 | 17 |
| 10 | 29 | 31 |
| K,L= 16 3 | | |
| 0 | 27 | 27 |
| 1 | 14 | 14 |
| 2 | 11 | 13 |
| 3 | 7 | 11 |
| 4 | 13 | 10 |
| 6* | 0 | 12 |
| 7 | 43 | 43 |
| 8 | 22 | 18 |
| 9 | 18 | 15 |
| K,L= 17 3 | | |
| 0 | 26 | 25 |
| 1 | 25 | 26 |
| 2 | 34 | 34 |
| 3 | 18 | 22 |
| 5 | 21 | 21 |
| 6 | 37 | 41 |
| 7 | 16 | 23 |
| K,L= 18 3 | | |
| 0 | 27 | 28 |
| 1 | 52 | 50 |
| 2 | 50 | 51 |
| 3 | 19 | 17 |
| 5 | 23 | 26 |
| 6 | 29 | 27 |
| 7 | 25 | 29 |
| 8 | 16 | 13 |
| K,L= 19 3 | | |
| 0 | 32 | 30 |
| 1 | 28 | 27 |
| 2 | 14 | 15 |
| 3 | 27 | 26 |
| 4 | 23 | 24 |
| 5 | 18 | 12 |
| 6* | 0 | 7 |
| 8* | 0 | 18 |
| K,L= 20 3 | | |
| 0 | 23 | 24 |
| 1 | 14 | 14 |
| 2 | 18 | 19 |
| 3 | 30 | 24 |
| 4 | 35 | 34 |
| 5 | 23 | 19 |
| 8* | 0 | 26 |
| K,L= 21 3 | | |
| 2 | 19 | 17 |
| 3 | 25 | 24 |
| 4* | 0 | 11 |
| 5 | 25 | 27 |
| 6* | 0 | 14 |
| 7* | 0 | 18 |
| 8 | 15 | 12 |
| K,L= 22 3 | | |
| 0 | 23 | 26 |
| 1 | 15 | 13 |
| 4 | 22 | 23 |
| 5 | 13 | 13 |
| 6 | 19 | 17 |
| 7 | 23 | 22 |
| K,L= 23 3 | | |
| 0 | 17 | 16 |
| 1 | 25 | 22 |
| 2 | 11 | 11 |
| 3 | 25 | 26 |
| 4 | 21 | 22 |
| K,L= 24 3 | | |
| 1 | 10 | 10 |
| 2 | 42 | 43 |
| 3 | 14 | 11 |
| 6* | 0 | 19 |
| K,L= 25 3 | | |
| 1 | 16 | 15 |
| 3 | 10 | 9 |
| 4 | 19 | 18 |
| 5 | 16 | 16 |
| 6* | 0 | 9 |
| K,L= 26 3 | | |
| 0 | 12 | 13 |
| 1 | 15 | 20 |
| 2 | 26 | 27 |
| 3 | 15 | 13 |
| 4* | 0 | 16 |
| 5* | 0 | 18 |
| K,L= 27 3 | | |
| 4 | 11 | 13 |
| K,L= 28 3 | | |
| 1 | 10 | 11 |
| 3 | 15 | 17 |
| K,L= 29 3 | | |
| 1* | 0 | 15 |
| 3* | 0 | 14 |
| K,L= 30 3 | | |
| 0 | 20 | 18 |
| K,L= 0 4 | | |
| 1 | 37 | 35 |
| 2 | 20 | 18 |
| 3 | 34 | 37 |
| 4 | 22 | 30 |
| 5 | 25 | 28 |
| 7 | 42 | 40 |
| 9 | 22 | 21 |
| 10 | 32 | 31 |
| K,L= 1 4 | | |
| 1 | 25 | 28 |
| 2 | 17 | 18 |
| 3 | 21 | 24 |
| 5 | 28 | 27 |
| 6 | 30 | 32 |
| 7 | 18 | 20 |
| 8 | 29 | 28 |
| 9 | 26 | 27 |
| K,L= 2 4 | | |
| 0 | 27 | 27 |
| 1 | 19 | 13 |
| 2 | 48 | 46 |
| 3 | 67 | 70 |
| 4 | 18 | 23 |
| 5 | 19 | 14 |
| 6* | 0 | 7 |
| 10 | 26 | 25 |
| K,L= 3 4 | | |
| 0 | 39 | 38 |
| 1 | 58 | 54 |
| 2 | 34 | 35 |
| 3 | 14 | 14 |
| 5 | 16 | 13 |
| 10 | 19 | 18 |
| K,L= 4 4 | | |
| 0 | 10 | 5 |
| 1 | 66 | 63 |
| 2 | 13 | 10 |
| 3 | 33 | 29 |
| 5 | 25 | 28 |
| 6 | 21 | 19 |
| 7 | 20 | 22 |
| 8 | 9 | 9 |
| K,L= 5 4 | | |
| 0 | 37 | 37 |
| 1 | 37 | 36 |
| 3 | 25 | 25 |
| 5 | 18 | 16 |
| 6 | 28 | 24 |
| 7* | 0 | 17 |
| K,L= 6 4 | | |
| 0 | 20 | 22 |
| 1 | 48 | 45 |
| 2 | 41 | 36 |
| 3 | 15 | 18 |
| 4 | 29 | 35 |
| 5* | 0 | 16 |
| 6 | 26 | 25 |
| 7 | 32 | 32 |
| 10 | 30 | 29 |
| K,L= 7 4 | | |
| 0 | 41 | 37 |
| 1 | 49 | 46 |
| 2 | 30 | 30 |
| 3 | 28 | 29 |
| 5 | 31 | 28 |
| 6 | 28 | 26 |
| 8 | 24 | 27 |
| 9 | 37 | 37 |
| K,L= 8 4 | | |
| 0 | 6 | 6 |
| 1 | 23 | 22 |
| 3 | 20 | 19 |
| 5 | 20 | 20 |
| 8 | 31 | 29 |
| K,L= 9 4 | | |
| 0 | 16 | 12 |
| 1 | 48 | 45 |
| 3 | 25 | 23 |
| 4 | 18 | 25 |
| 5 | 22 | 22 |
| K,L= 10 4 | | |
| 0 | 16 | 18 |
| 1 | 32 | 30 |
| 2 | 42 | 41 |
| 3 | 20 | 21 |
| 4 | 23 | 24 |
| 6 | 17 | 10 |
| 7 | 31 | 31 |
| K,L= 11 4 | | |
| 0 | 61 | 64 |
| 1 | 22 | 19 |
| 2 | 25 | 22 |
| 3 | 41 | 42 |
| 4* | 0 | 27 |
| 5 | 20 | 17 |
| K,L= 12 4 | | |
| 0 | 11 | 11 |
| 1* | 0 | 8 |
| 2 | 16 | 16 |
| 3 | 36 | 31 |
| 4 | 17 | 23 |
| 7 | 40 | 42 |
| 8 | 20 | 22 |
| K,L= 13 4 | | |
| 0 | 30 | 28 |
| 1 | 19 | 21 |
| 2 | 22 | 28 |
| 3 | 34 | 32 |
| 5 | 28 | 26 |
| 6 | 25 | 21 |
| 7 | 22 | 19 |
| 8 | 28 | 27 |
| K,L= 14 4 | | |
| 0 | 30 | 29 |
| 1* | 0 | 15 |
| 2 | 32 | 32 |
| 3 | 34 | 34 |
| 4* | 0 | 20 |
| K,L= 15 4 | | |
| 0 | 59 | 62 |
| 1 | 34 | 27 |
| 3 | 20 | 18 |
| 6 | 24 | 23 |
| 7 | 19 | 19 |
| K,L= 16 4 | | |
| 1 | 20 | 24 |
| 2 | 27 | 26 |
| 3 | 14 | 12 |
| 4* | 0 | 0 |
| 5 | 15 | 14 |
| 7 | 25 | 25 |
| K,L= 17 4 | | |
| 1 | 28 | 28 |
| 2 | 26 | 22 |
| 3 | 22 | 26 |
| 4 | 29 | 35 |
| 5 | 44 | 36 |
| 6 | 17 | 19 |
| K,L= 18 4 | | |
| 1* | 0 | 14 |
| 2 | 20 | 21 |
| 4 | 21 | 27 |
| K,L= 19 4 | | |
| 0 | 22 | 20 |
| 3 | 24 | 25 |
| 5 | 10 | 12 |
| 6 | 17 | 14 |
| K,L= 20 4 | | |
| 0 | 19 | 21 |
| 1 | 10 | 6 |
| 2* | 0 | 15 |
| 4 | 21 | 24 |
| K,L= 21 4 | | |
| 1* | 0 | 13 |
| 2* | 0 | 13 |
| 5 | 25 | 24 |
| K,L= 22 4 | | |
| 1* | 0 | 11 |
| 3 | 24 | 23 |
| 4 | 14 | 18 |
| 5* | 0 | 14 |
| K,L= 23 4 | | |
| 0 | 8 | 9 |
| 1 | 19 | 17 |
| 2 | 21 | 21 |
| 3* | 0 | 12 |
| 5 | 25 | 23 |
| K,L= 24 4 | | |
| 1 | 16 | 13 |
| 5* | 0 | 13 |
| K,L= 25 4 | | |
| 1* | 0 | 8 |
| 2* | 0 | 14 |
| 5* | 0 | 13 |
| K,L= 26 4 | | |
| 1* | 0 | 17 |
| K,L= 27 4 | | |
| 0 | 23 | 22 |
| 3 | 21 | 18 |
| K,L= 0 5 | | |
| 7 | 11 | 15 |
| K,L= 1 5 | | |
| 0 | 28 | 26 |
| 2 | 22 | 22 |
| 4 | 14 | 16 |
| 5 | 18 | 17 |
| 6 | 24 | 25 |
| K,L= 2 5 | | |
| 1 | 39 | 38 |
| 3 | 19 | 20 |
| 4 | 13 | 18 |
| 5* | 0 | 10 |
| 6 | 12 | 17 |
| 8 | 16 | 14 |
| K,L= 3 5 | | |
| 2 | 25 | 30 |
| 3 | 18 | 18 |
| 5 | 23 | 19 |
| 8 | 29 | 30 |
| K,L= 4 5 | | |
| 0 | 35 | 35 |
| 2 | 28 | 24 |
| 4 | 24 | 26 |
| 5* | 0 | 11 |
| 7 | 21 | 23 |
| 8* | 0 | 24 |
| K,L= 5 5 | | |
| 0 | 8 | 9 |
| 1 | 21 | 19 |
| 3 | 25 | 23 |
| 7 | 23 | 27 |
| K,L= 6 5 | | |
| 0 | 29 | 24 |
| 1 | 22 | 21 |
| 2 | 17 | 16 |
| 3 | 14 | 15 |
| K,L= 7 5 | | |
| 1 | 22 | 21 |
| 2 | 16 | 14 |
| 3* | 0 | 12 |
| 4 | 16 | 17 |
| 7* | 0 | 12 |
| K,L= 8 5 | | |
| 0 | 28 | 29 |
| 4 | 21 | 21 |
| 5 | 17 | 14 |
| 6 | 15 | 15 |
| K,L= 9 5 | | |
| 0 | 19 | 17 |
| 1 | 21 | 26 |
| 2 | 41 | 36 |
| 3 | 22 | 17 |
| K,L= 10 5 | | |
| 0 | 15 | 12 |
| 1 | 34 | 33 |
| 2 | 33 | 30 |
| 4* | 0 | 15 |
| 5 | 11 | 11 |
| 6* | 0 | 18 |
| K,L= 11 5 | | |
| 1 | 28 | 30 |
| 2 | 32 | 25 |
| 3 | 9 | 13 |
| K,L= 12 5 | | |
| 2 | 14 | 10 |
| K,L= 13 5 | | |
| 2 | 26 | 22 |
| 3 | 21 | 18 |
| K,L= 14 5 | | |
| 1 | 35 | 27 |
| 2 | 22 | 20 |
| 3 | 27 | 30 |
| 5* | 0 | 14 |
| K,L= 15 5 | | |
| 0 | 23 | 19 |
| 1 | 29 | 27 |
| 2 | 15 | 18 |
| 3 | 35 | 39 |
| K,L= 16 5 | | |
| 1 | 24 | 23 |
| 3 | 21 | 23 |
| 4 | 36 | 31 |
| 5* | 0 | 15 |
| K,L= 17 5 | | |
| 2 | 18 | 17 |
| 5* | 0 | 19 |
| K,L= 18 5 | | |
| 0 | 39 | 34 |
| 1* | 0 | 21 |
| 2* | 0 | 13 |
| 4* | 0 | 14 |
| K,L= 19 5 | | |
| 5 | 19 | 20 |
| K,L= 20 5 | | |
| 0 | 10 | 18 |
| K,L= 21 5 | | |
| 3* | 0 | 17 |
| K,L= 0 6 | | |
| 4 | 23 | 24 |
| K,L= 1 6 | | |
| 0 | 28 | 29 |
| 1 | 18 | 24 |
| 2 | 17 | 16 |
| K,L= 2 6 | | |
| 0 | 31 | 30 |
| 2 | 23 | 24 |
| 4 | 13 | 12 |
| K,L= 3 6 | | |
| 0 | 30 | 31 |
| 2 | 17 | 21 |
| K,L= 4 6 | | |
| 0 | 18 | 14 |
| K,L= 5 6 | | |
| 0 | 11 | 15 |
| 2 | 25 | 24 |
| 6 | 16 | 12 |
| K,L= 6 6 | | |
| 0 | 6 | 7 |
| 2 | 22 | 17 |
| K,L= 7 6 | | |
| 0 | 23 | 23 |
| 1 | 25 | 24 |
| K,L= 8 6 | | |
| 0 | 9 | 17 |
| 2 | 18 | 13 |
| 4 | 15 | 14 |
| K,L= 9 6 | | |
| 0 | 20 | 16 |
| 1 | 15 | 16 |
| K,L= 10 6 | | |
| 0 | 19 | 21 |
| 1 | 16 | 15 |
| K,L= 11 6 | | |
| 4* | 0 | 17 |
| K,L= 12 6 | | |
| 1 | 18 | 10 |
| 2* | 0 | 12 |
| K,L= 13 6 | | |
| 2 | 30 | 28 |
| K,L= 14 6 | | |
| 0 | 20 | 19 |
| 2* | 0 | 15 |
| K,L= 16 6 | | |
| 0 | 17 | 19 |
| K,L= 17 6 | | |
| 0 | 5 | 11 |

Table 3. *Comparison of the calculated and observed intensity ratios used for the establishment of the absolute configuration*

| $h\ k\ l$ | $\lvert F_c\rvert^2(hkl)/\lvert F_c\rvert^2(\bar{h}\bar{k}\bar{l})$ | $I_o^2(hkl)/I_o^2(\bar{h}\bar{k}\bar{l})$ |
|---|---|---|
| 7 1 1 | 1·1646 | > 1 |
| 6 2 1 | 1·1515 | > 1 |
| 7 3 1 | 1·1897 | > 1 |
| 8 4 1 | 1·2053 | > 1 |
| 4 5 1 | 0·8277 | < 1 |
| 8 6 1 | 1·3251 | > 1 |
| 4 8 1 | 0·8404 | < 1 |
| 5 8 1 | 1·2999 | > 1 |
| 2,12,1 | 1·1515 | > 1 |
| 2,14,1 | 0·8001 | < 1 |

Table 4. *Least-squares planes through various groups of atoms and deviations of atoms from the planes*

Equations of the planes are of the form $AX+BY+CZ=D$, where $X$, $Y$, $Z$ and $D$ are in Å units relative to the orthogonal axes $X\|\mathbf{a}$, $Y\|\mathbf{b}$ and $Z\|\mathbf{c}$.

*A* ring $0·6960X-0·6301Y+0·3443Z=2·9302$

| | | | |
|---|---|---|---|
| C(1) | −0·2867 | C(19) | 1·8212* |
| C(2) | 0·2781 | C(28) | 1·7408* |
| C(3) | −0·2399 | C(29) | −0·6061* |
| C(4) | 0·2308 | O(1) | 0·3513* |
| C(5) | −0·2444 | | |
| C(10) | 0·2621 | | |

*B* ring $0·5333X-0·7169Y+0·4492Z=-0·9003$

| | | | |
|---|---|---|---|
| C(5) | −0·2931 | C(18) | 1·7830* |
| C(6) | 0·3026 | C(19) | 1·7484* |
| C(7) | −0·2370 | | |
| C(8) | 0·2060 | | |
| C(9) | −0·2203 | | |
| C(10) | 0·2418 | | |

*C* ring $0·4335X-0·7884Y+0·4366Z=-3·3966$

| | | | |
|---|---|---|---|
| C(8) | 0·2610 | C(18) | 1·8199* |
| C(9) | −0·2287 | C(30) | −1·8446* |
| C(11) | 0·2005 | | |
| C(12) | −0·2311 | | |
| C(13) | 0·2676 | | |
| C(14) | −0·2690 | | |

*D* ring $0·3417X-0·8171Y+0·4643Z=-4·7035$

| | | | |
|---|---|---|---|
| C(15) | −0·0000 | C(13) | 0·0735* |
| C(16) | 0·0000 | C(14) | −0·4845* |
| C(17) | −0·0000 | | |

*E* ring $0·7108X+0·7021Y-0·0437Z=14·8510$

| | | | |
|---|---|---|---|
| C(20) | −0·0104 | C(23) | −0·0934* |
| C(22) | 0·0188 | O(4) | 0·1159* |
| C(24) | −0·0190 | | |
| C(25) | 0·0105 | | |

Ester $-0·2333X+0·7194Y+0·6542Z=7·7684$

| | |
|---|---|
| O(1) | −0·0128 |
| O(33) | 0·0405 |
| O(34) | −0·0118 |
| O(6) | −0·0159 |

Ester $-0·2908X+0·1194Y+0·9493Z=-0·6080$

| | |
|---|---|
| O(2) | −0·0175 |
| C(31) | 0·0589 |
| C(32) | −0·0191 |
| O(5) | −0·0223 |

* These atoms are not included in the least-squares calculation. Interplanar angles: *A*/*B* 168°, *B*/*C* 173°, *C*/*D* 175°.

observed reflexions. The weighting factors used were,

$$\sqrt{w}=35/F_o,\ \text{when } F_o>35,$$
$$\sqrt{w}=1,\ \text{when } 5<F_o\le 35,$$
$$\sqrt{w}=0,\ \text{when } F_o\le 5.$$

The atomic scattering factors used were those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for oxygen and carbon and those of Thomas & Umeda (1957) for bromine. The final atomic parameters are presented in Table 1 along with their standard deviations. The observed and calculated structure factors are given in Table 2.

The absolute configuration of the structure was determined by the anomalous-dispersion method. The dispersion terms of the bromine scattering factor for Mo $K\alpha$ radiation were assumed to be $\Delta f'=-0·3$ and $\Delta f''=2·6$, according to Dauben & Templeton (1955). A comparison between observed and calculated intensities indicated the absolute configuration as shown in Fig. 2. In Table 3 are listed the calculated and observed

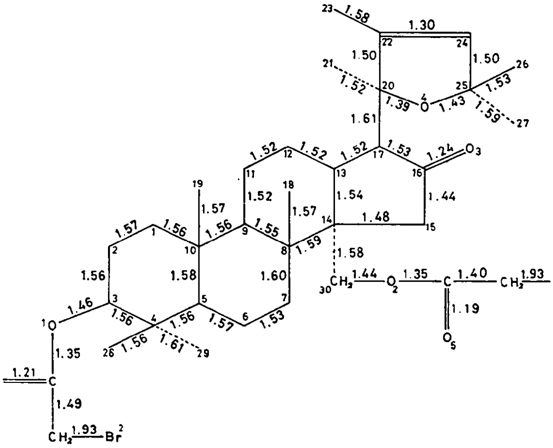

Fig. 3. Bond lengths (Å).

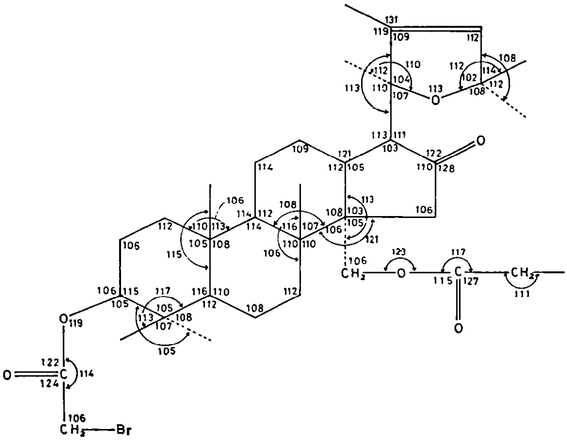

Fig. 4. Bond angles (°).

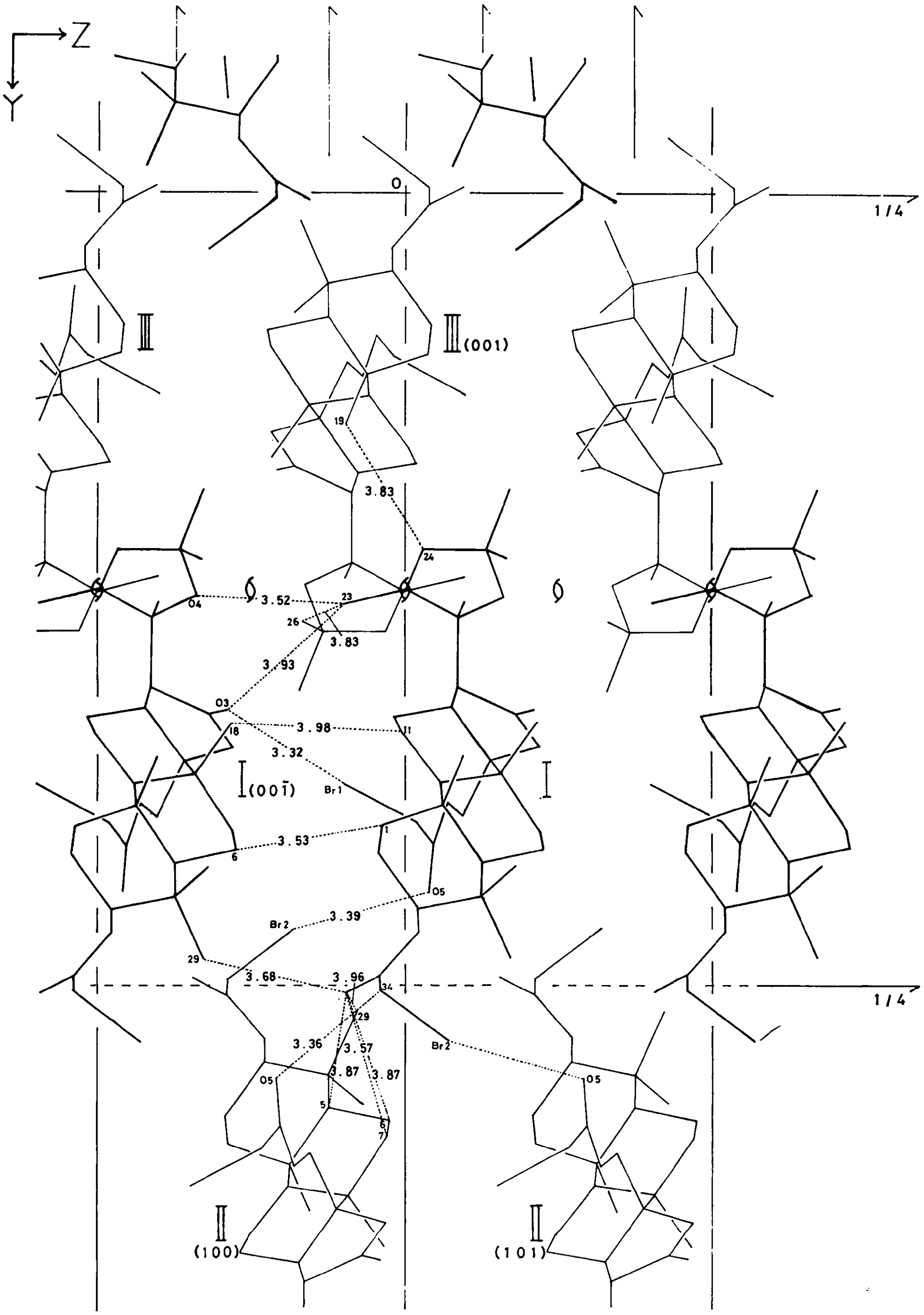

Fig. 5. Projection of the crystal structure along the $a$ axis. The positions of the molecules are: I at $x,y,z$; II at $1\frac{1}{2}-x,1-y,-\frac{1}{2}+z$; III at $-\frac{1}{2}+x,\frac{1}{2}-y,-1-z$; IV at $-x,\frac{1}{2}+x,\frac{1}{2}-z$; where $x,y$, and $z$ are the coordinates given in Table 1. Intermolecular short distances less than 4 Å are shown by dotted lines.

intensity ratios of the Friedel pairs of reflexions used for the establishment of the absolute configuration.

## Discussion of the structure

### *The molecular structure*

The present X-ray analysis of bacogenin $A_1$ dibromoacetate established the structure of bacogenin $A_1$ as (I) in accordance with the result of chemical and spectroscopic investigations. The structure is a partially modified dammarane-type triterpene having all-*trans* fusions of *A*/*B*, *B*/*C* and *C*/*D* rings. The stereochemistry at C(20) was *S* and the methyl group in the dihydrofurane ring was established at C(22).

The bond lengths and angles are shown in Figs. 3 and 4 respectively. These values are not significantly different from the expected ones. The mean estimated standard deviations in interatomic distances are 0·025 Å for C–Br, 0·027 Å for C–C and 0·023 Å for C–O, and those in bond angles are 1·5° for tetrahedral C–C–C bonds. The mean value of the C–C single-bond lengths for the various types of bonds is calculated to be 1·54 Å.

The deviations of atoms from the best planes through the various atoms and the torsion angles within each ring are shown in Tables 4 and 5. Each of the *A*, *B* and *C* rings takes a chair and the five-membered ring *D* a slightly deformed half-chair conformation, while the dihydrofuran ring *E* shows an envelope form. The distortions of the *B* ring seem to be caused by the interactions between the bulky axial groups which push each other in order to relieve the mutual repulsive

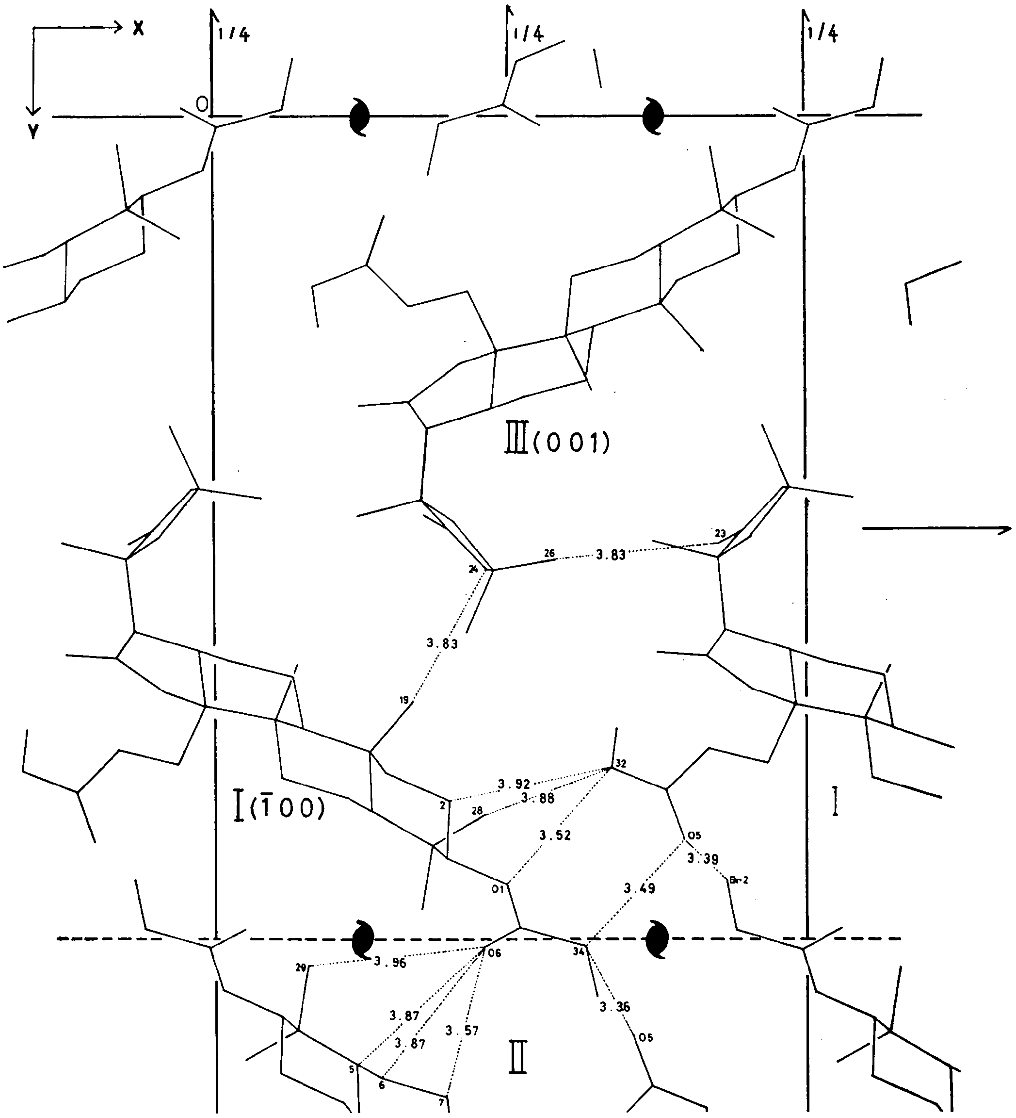

Fig. 6. Projection of the crystal structure along the *c* axis. Intermolecular short distances less than 4 Å are shown by dotted lines.

forces. In a six-membered ring, the non-bonded distances between 1·3 diaxial methyl groups would have been 2·52 Å, if the ring took a regular chair form. This distance is here increased to 3·19 Å between C(18) and C(19) and 3·20 Å between C(19) and C(28). As is usually seen in related triterpenes the skeleton of the molecule is slightly bent in a direction opposite to the axial methyl groups at the ring juncture. This may be clear by seeing that the dihedral angle between the least-squares planes formed by the *A* and *B* rings is 168° and that between *B* and *C* is 173°.

Table 5. *Torsion angles within the ring*

| *A* ring | $\varphi(A–B)$ | *B* ring | $\varphi(A–B)$ |
|---|---|---|---|
| C(1)—C(2) | −62·6° | C(5)—C(6) | −64·6° |
| C(2)—C(3) | 60·6 | C(6)—C(7) | 61·0 |
| C(3)—C(4) | −56·8 | C(7)—C(8) | −54·7 |
| C(4)—C(5) | 56·6 | C(8)—C(9) | 51·9 |
| C(5)—C(10) | −59·6 | C(9)—C(10) | −55·3 |
| C(10)-C(1) | 61·4 | C(10)-C(5) | 60·5 |
| *C* ring | | *D* ring | |
| C(8)—C(9) | −55·8 | C(13)-C(14) | 35·8 |
| C(9)—C(11) | 55·3 | C(14)-C(15) | −34·0 |
| C(11)-C(12) | −54·1 | C(15)-C(16) | 19·9 |
| C(12)-C(13) | 58·4 | C(16)-C(17) | 2·8 |
| C(13)-C(14) | −61·9 | C(17)-C(13) | −23·4 |
| C(14)-C(8) | 58·2 | | |
| *E* ring | | | |
| C(20)-C(22) | 7·8 | | |
| C(22)-C(24) | −3·6 | | |
| C(24)-C(25) | −1·8 | | |
| C(25)-O(4) | 7·2 | | |
| O(4)—C(20) | −9·2 | | |

$\varphi(A–B)$, a simplified notation of $\varphi(C–A–B–D)$, is the torsional angle about the *A–B* bond, in which *A*, *B*, *C* and *D* are all involved in the ring in question. $\varphi(C–A–B–D)$ is defined as the angle between the projections of *C–A* and *B–D* bonds, when the projection is taken along the *A–B* bond. The positive angle is taken in the same sense as that of the turning direction of a right-handed screw advancing along the *A–B* bond.

The orientation of the *E* ring with respect to the *D* ring is such that the conformation about the C(17)–C(20) bond adopts a staggered form, the internal rotation angle C(13)–C(17)–C(20)–O(4) being 59°. The overall conformation of the present compound resembles closely that of a dammarane-type triterpene reported by Tanaka, Tanaka, Ohsawa, Iitaka & Shibata (1968).

### *The crystal structure*

The projections of the crystal structure viewed along the *a* and *c* axes are shown in Figs. 5 and 6 respectively. The short intermolecular distances less than 4 Å are also shown in these Figures.

The molecules are packed together mainly by van der Waals forces and there are no hydrogen bonds. The molecules are more closely packed in the **c** direction through van der Waals interactions between bromine and oxygen atoms.

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