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# The Structure of the Methylene Dibromide Adduct of Sporidesmin at —150°C

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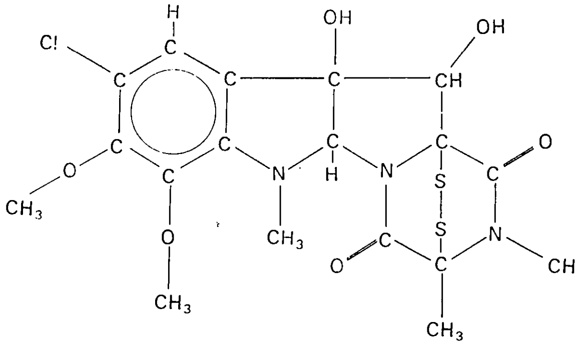
The structure of sporidesmin, the causative agent of facial eczema in sheep, isolated by Synge & White from cultures of the fungus *Pithomyces chartarum* (previously *Sporidesmium bakerii* Syd.) has been determined from its $CH_2Br_2$ adduct.

The compound crystallizes in the orthorhombic space group $P2_12_12_1$ with cell dimensions $a = 9{\cdot}681$, $b = 10{\cdot}629$, $c = 23{\cdot}358$ Å at − 150 °C. Data were collected for 0–7 layers about *a* and the 0-layer about *b*. The positions of the Br atoms (occupied only 0·65) and also the S atoms were determined from normal and generalized Patterson projections and Harker sections. Two three-dimensional electron-density distributions with two-dimensional $\varrho_0$ and $\Delta\varrho$ distributions led to the structure (I), corresponding to the formula $C_{18}H_{20}O_6N_3S_2Cl \, . \, 0{\cdot}65 \; CH_2Br_2$.



(I)

The structure was refined by several cycles of full-matrix least-squares calculations, the final *R* being 0·144.

## Introduction

The serious disease in sheep, known as 'facial eczema', which causes extensive liver damage and ultimate death is widely spread in New Zealand and outbreaks have occurred also in Australia (Janes, 1959). Extensive research (Thornton & Percival, 1958, 1959) has established the disease as due to the ingestion of spores of the fungus *Pithomyces chartarum* (previously known as *Sporidesmium bakeri* Syd.), found frequently on pasture grass in the tropics and subtropics (Ellis, 1960), but detected also in Britain in one case (Lacey & Gregory, (1962).

Synge & White (1959) were able to isolate from cultures of this fungus the main metabolic toxic agent which they named sporidesmin and which could be obtained in crystalline form as a $CCl_4$ adduct, the chemical analysis of which indicated the composition $C_{19}H_{21}O_6N_3S_2Cl \, . \, CCl_4$. Preliminary cell parameter measurements, carried out by Mrs M. M. Harding, University of Oxford, gave for this substance $a=9{\cdot}65$, $b=10{\cdot}57$, $c=24{\cdot}9$ Å, space group $P2_12_12_1$ with $Z=4$ and the measured density, 1·607 g.cm$^{-3}$, corresponded to a molecular weight of the asymmetric unit of approximately 615 (compared with the formula weight of 641).

In view of the importance of establishing the structure of the toxic agent, the small amounts of the material available at that time and the difficulties in solving the problem by chemical methods, we undertook the derivation of the structure by X-ray diffraction methods on the suggestion of Dr Synge and with the concurrence of the New Zealand Department of Agriculture and the research team at Ruakura Animal Research Station in New Zealand who were engaged in the investigation of the structure and chemistry of the substance.

The first attempt, using crystals of the $CCl_4$ adduct provided by Dr White of Ruakura Research Station, proved unsuccessful owing to the difficulty of extracting from the Patterson distribution the positions of 7 medium-weight atoms (2S+5Cl). In 1961, Dr White succeeded in preparing a new derivative, a $CH_2Br_2$ adduct, and with crystals of this compound the analysis was carried through, establishing the complete stereochemical configuration of the novel skeletal structure.

A short note on the essential features of the structure has been published (Fridrichsons & Mathieson, 1962*a*) and the main results of the analysis were reported at the Rome Congress of the International Union of Crystallography in 1963 (Fridrichsons & Mathieson, 1963).

## Experimental

The crystals of the $CH_2Br_2$ adduct are lath-shaped and belong to the orthorhombic system. The cell dimensions, determined against Si as standard (Fridrichsons, 1959) are $a=9{\cdot}681$, $b=10{\cdot}629$, $c=23{\cdot}358$ Å at −150 °C, the corresponding values at room temperature being $a=9{\cdot}64$, $b=10{\cdot}58$, $c=23{\cdot}88$ Å. The crystals deteriorate markedly in air and for extended use had to be sealed in capillary tubes. Density determinations by flotation in magnesium bromide and potassium iodide solutions gave a value of 1·65, indicating four molecules in the unit cell, the space group established from extinctions being $P2_12_12_1$.

Intensity data were collected at −150 °C from equi-inclination Weissenberg photographs with the use of Cu $K\alpha$ radiation (for experimental details see Fridrichsons & Mathieson, 1962*b*) and a multiple-film technique with visual intensity estimation against a set of timed exposures of a single reflexion. Eight layers on the *a* axis ($h=0$–7) with the zero-layer of the *b* axis for cross-correlation were recorded. A total of 1925 reflexions were measured, representing about 80% of the total possible in the recorded layers.

Calculations of $\sin^2\theta$ values, intensity correction factors (no absorption corrections applied), the $h0l$ and $0kl$ structure factors, Patterson and Harker distributions and electron-density projections were computed on the University of Sydney computer SILLIAC (Freeman, 1957, 1958). The three-dimensional structure-factor calculations and the three-dimensional Fourier syntheses were computed on the University of New South Wales computer UTECOM (Rollett, 1960) and the three-dimensional least-squares calculations on an IBM 7090 computer (Busing & Levy, 1959). Scattering factors used were those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for C, N and O, of Thomas & Umeda (1959) for Cl and Br and of Dawson (1960) for S.

## Structure analysis

The analytical composition of the crystal sample received from Dr White was given as $C_{18}H_{20\text{-}22}O_6N_3S_2Cl\,.\,CH_2Br_2$, and to determine the positions of the Br and possibly also the S and Cl atoms, sharpened $P(u, w)$ and $P(v, w)$ projections, generalized Patterson distributions $P_1(v, w)$ to $P_7(v, w)$ and Harker sections $H(\frac{1}{2}, v, w)$ and $H(0, v, w)$ were computed. The internal and space-group symmetry relationships between the Br–Br vectors, to be expected for two Br atoms linked through the methylene group in $CH_2Br_2$, did not eventuate in an obvious manner in the vector distribution maps and doubts therefore arose about the presence of $CH_2Br_2$ in the crystals used which could have been lost since the chemical analysis. To test this, a mass spectrum of the compound (using a few crystals of the batch and heating to release the solvent) was taken and this definitely indicated the presence of $CH_2Br_2$. To explain the absence of dominant obvious Br–Br vectors, the possibility remained that the $CH_2Br_2$ was present in a ratio of less than 1:1. This conclusion was substantiated by the measured value of the density, which for the cell dimensions determined for the crystals of the sample would require a molecular weight of 605 (instead of 650 calculated from the analytical composition) corresponding to an average content of 0·75 $CH_2Br_2$ per molecule of sporidesmin.

A similar loss of solvent molecules appears to occur in the $CCl_4$ adduct, as can be inferred from the difference in the molecular weights cited in the *Introduction*, and this would provide additional reason for the failure to initiate the analysis of that compound.

In this more complex situation, with the effective $Z$ for Br (∼26) not greatly above those of S and Cl, the internal Br–Br vector in $CH_2Br_2$ was sought and located from its known length (*ca.* 3·2 Å) in the near-origin regions of the vector distributions and correlation with possible vectors in general positions attempted, the correct choice being ambiguous because of the incidental near-coincidence of the $z$ parameters of the two Br atoms. With the alternative choices of $z_1$ and $z_2$ for Br(1) and Br(2), $\varrho_0$ and $\Delta\varrho$ distributions for the *a*- and *b*-axis projections were calculated, first to select the correct choice and also to assist, if possible, in the ex-

Table 1. *Comparison of $F_o$ and $F_c$ values*

| | $F_o$ | $\lvert F_c \rvert$ |
|---|---|---|
| **00ℓ** | | |
| 2 | 45 | 92 |
| 4 | 181 | 147 |
| 6 | 286 | 220 |
| 8 | 54 | 26 |
| 10 | 100 | 112 |
| 12 | 116 | 103 |
| 14 | 19 | 17 |
| 16 | 19 | 19 |
| 18 | 34 | 30 |
| 20 | 91 | 80 |
| 22 | 14 | 19 |
| 24 | 50 | 51 |
| 26 | 34 | 35 |
| 28 | 16 | 16 |
| **01ℓ** | | |
| 1 | 44 | 48 |
| 2 | 45 | 98 |
| 3 | 8 | 14 |
| 4 | 81 | 59 |
| 5 | 84 | 79 |
| 6 | 69 | 65 |
| 7 | 39 | 33 |
| 8 | 108 | 96 |
| 9 | 36 | 41 |
| 10 | 66 | 42 |
| 11 | 78 | 70 |
| 12 | 124 | 103 |
| 13 | 37 | 36 |
| 14 | 10 | 10 |
| 15 | 24 | 30 |
| 16 | 13 | 19 |
| 17 | - | 1 |
| 18 | 19 | 22 |
| 19 | 28 | 28 |
| 20 | 20 | 17 |
| 21 | 13 | 11 |
| 22 | 26 | 23 |
| 23 | 11 | 8 |
| 24 | 8 | 6 |
| 25 | 17 | 14 |
| 26 | 10 | 8 |
| 27 | 25 | 28 |
| **02ℓ** | | |
| 0 | 15 | 24 |
| 1 | 86 | 96 |
| 2 | 9 | 4 |
| 3 | 55 | 57 |
| 4 | 35 | 24 |
| 5 | 56 | 48 |
| 6 | 8 | 17 |
| 7 | 84 | 72 |
| 8 | 34 | 23 |
| 9 | 91 | 84 |
| 10 | 24 | 31 |
| 11 | 36 | 29 |
| 12 | - | 5 |
| 13 | 16 | 20 |
| 14 | - | 3 |
| 15 | 10 | 13 |
| 16 | 11 | 5 |
| 17 | 20 | 19 |
| 18 | 24 | 23 |
| 19 | 10 | 7 |
| 20 | 23 | 18 |
| 21 | 21 | 20 |
| 22 | - | 4 |
| 23 | 30 | 28 |
| 24 | - | 7 |
| 25 | 24 | 20 |
| 26 | 8 | 7 |
| 27 | - | 3 |
| 28 | - | 2 |
| 29 | 15 | 14 |
| **03ℓ** | | |
| 1 | 37 | 39 |
| 2 | 23 | 24 |
| 3 | 28 | 13 |
| 4 | 103 | 104 |
| 5 | 82 | 51 |
| 6 | 14 | 18 |
| 7 | - | 3 |
| 8 | 49 | 44 |
| 9 | 106 | 87 |
| 10 | 9 | 7 |
| 11 | 61 | 54 |
| 12 | 8 | 3 |
| 13 | 41 | 38 |
| 14 | 11 | 14 |
| 15 | 51 | 47 |
| 16 | 27 | 27 |
| 17 | - | 2 |
| 18 | 11 | 9 |
| 19 | - | 1 |
| 20 | 12 | 14 |
| 21 | - | 0 |
| 22 | 14 | 13 |
| 23 | 31 | 33 |
| 24 | 22 | 23 |
| 25 | 9 | 7 |
| 26 | 10 | 9 |
| 27 | 8 | 4 |
| 28 | 25 | 23 |
| **04ℓ** | | |
| 0 | 183 | 193 |
| 1 | 171 | 142 |
| 2 | 31 | 40 |
| 3 | 183 | 169 |
| 4 | 44 | 33 |
| 5 | 66 | 68 |
| 6 | 27 | 23 |
| 7 | 121 | 102 |
| 8 | 13 | 6 |
| 9 | 66 | 54 |
| 10 | 82 | 69 |
| 11 | - | 4 |
| 12 | - | 2 |
| 13 | 36 | 43 |
| 14 | 25 | 26 |
| 15 | 40 | 34 |
| 16 | 27 | 30 |
| 17 | - | 4 |
| 18 | - | 6 |
| 19 | 45 | 44 |
| **04ℓ** | | |
| 20 | 31 | 31 |
| 21 | 59 | 50 |
| 22 | 11 | 8 |
| 23 | 39 | 40 |
| 24 | 14 | 12 |
| 25 | - | 1 |
| 26 | 16 | 15 |
| 27 | 17 | 16 |
| **05ℓ** | | |
| 1 | 73 | 57 |
| 2 | 68 | 78 |
| 3 | 72 | 47 |
| 4 | 80 | 79 |
| 5 | 88 | 55 |
| 6 | 8 | 6 |
| 7 | 22 | 14 |
| 8 | 17 | 14 |
| 9 | 48 | 43 |
| 10 | 15 | 10 |
| 11 | 21 | 30 |
| 12 | 76 | 73 |
| 13 | 9 | 5 |
| 14 | 19 | 14 |
| 15 | 27 | 22 |
| 16 | - | 2 |
| 17 | 26 | 29 |
| 18 | 13 | 12 |
| 19 | 20 | 15 |
| 20 | 16 | 15 |
| 21 | - | 7 |
| 22 | 48 | 45 |
| 23 | - | 7 |
| 24 | - | 8 |
| 25 | - | 1 |
| 26 | - | 1 |
| 27 | 15 | 13 |
| **06ℓ** | | |
| 0 | 88 | 70 |
| 1 | 56 | 51 |
| 2 | 6 | 1 |
| 3 | 92 | 65 |
| 4 | 53 | 41 |
| 5 | 13 | 15 |
| 6 | 9 | 17 |
| 7 | 22 | 28 |
| 8 | 12 | 7 |
| 9 | 37 | 31 |
| 10 | 40 | 46 |
| 11 | 15 | 16 |
| 12 | - | 10 |
| 13 | 57 | 52 |
| 14 | 19 | 27 |
| 15 | - | 7 |
| 16 | 17 | 14 |
| 17 | 30 | 25 |
| 18 | 21 | 23 |
| 19 | 30 | 29 |
| 20 | - | 4 |
| 21 | - | 1 |
| 22 | 24 | 25 |
| 23 | - | 2 |
| 24 | 15 | 16 |
| 25 | - | 4 |
| 26 | 9 | 8 |
| **07ℓ** | | |
| 1 | 34 | 34 |
| 2 | 24 | 13 |
| 3 | 67 | 51 |
| 4 | 21 | 14 |
| 5 | 62 | 62 |
| 6 | 113 | 92 |
| 7 | 11 | 19 |
| 8 | 72 | 54 |
| 9 | - | 0 |
| 10 | 36 | 39 |
| 11 | 18 | 12 |
| 12 | 90 | 74 |
| 13 | 24 | 23 |
| 14 | 30 | 27 |
| 15 | 27 | 23 |
| 16 | - | 6 |
| 17 | - | 1 |
| 18 | 35 | 27 |
| 19 | 11 | 12 |
| 20 | 21 | 18 |
| 21 | - | 1 |
| 22 | 18 | 17 |
| 23 | 24 | 21 |
| 24 | 9 | 6 |
| 25 | 12 | 10 |
| **08ℓ** | | |
| 0 | 120 | 91 |
| 1 | 30 | 27 |
| 2 | 11 | 10 |
| 3 | 14 | 11 |
| [illegible] | 73 | 57 |
| 5 | 17 | 17 |
| 6 | 75 | 60 |
| 7 | 12 | 5 |
| 8 | 10 | 7 |
| 9 | 22 | 19 |
| 10 | 73 | 63 |
| 11 | 27 | 31 |
| 12 | - | 9 |
| 13 | 20 | 20 |
| 14 | 63 | 51 |
| 15 | - | 2 |
| 16 | - | 3 |
| 17 | - | 6 |
| 18 | 9 | 8 |
| 19 | - | 2 |
| 20 | - | 5 |
| 21 | 27 | 24 |
| 22 | 7 | 12 |
| 23 | 15 | 11 |
| 24 | 4 | 7 |
| **09ℓ** | | |
| 1 | 12 | 21 |
| 2 | 73 | 56 |
| 3 | - | 7 |
| 4 | 27 | 25 |
| **09ℓ** | | |
| 5 | 12 | 7 |
| 6 | 20 | 15 |
| 7 | 17 | 14 |
| 8 | - | 6 |
| 9 | - | 1 |
| 10 | - | 4 |
| 11 | 14 | 11 |
| 12 | 30 | 29 |
| 13 | 45 | 43 |
| 14 | - | 2 |
| 15 | 17 | 14 |
| 16 | - | 6 |
| 17 | 11 | 10 |
| 18 | 15 | 14 |
| 19 | 19 | 15 |
| 20 | - | 3 |
| 21 | 9 | 13 |
| 22 | 19 | 19 |
| **0,10,ℓ** | | |
| 0 | 39 | 30 |
| 1 | 14 | 12 |
| 2 | 27 | 26 |
| 3 | 50 | 45 |
| 4 | - | 2 |
| 5 | 13 | 9 |
| 6 | - | 1 |
| 7 | 11 | 9 |
| 8 | 15 | 7 |
| 9 | 12 | 9 |
| 10 | 11 | 9 |
| 11 | - | 8 |
| 12 | 18 | 13 |
| 13 | 27 | 24 |
| 14 | - | 2 |
| 15 | - | 7 |
| 16 | 13 | 12 |
| 17 | - | 3 |
| 18 | 20 | 17 |
| 19 | 13 | 13 |
| 20 | 16 | 14 |
| **0,11,ℓ** | | |
| 1 | 19 | 13 |
| 2 | - | 3 |
| 3 | 42 | 40 |
| 4 | - | 1 |
| 5 | 24 | 26 |
| 6 | 15 | 11 |
| 7 | 24 | 19 |
| 8 | 21 | 21 |
| 9 | 56 | 44 |
| 10 | 15 | 12 |
| 11 | 38 | 25 |
| 12 | 11 | 9 |
| 13 | - | 2 |
| 14 | 21 | 20 |
| 15 | 47 | 37 |
| 16 | 14 | 11 |
| 17 | 25 | 23 |
| **0,12,ℓ** | | |
| 0 | 28 | 26 |
| 1 | 22 | 21 |
| 2 | 21 | 15 |
| 3 | 45 | 40 |
| 4 | 28 | 24 |
| 5 | 12 | 10 |
| 6 | - | 0 |
| 7 | 35 | 34 |
| 8 | 18 | 14 |
| 9 | 39 | 30 |
| 10 | 20 | 16 |
| 11 | 35 | 30 |
| 12 | 7 | 8 |
| 13 | 18 | 19 |
| 14 | 9 | 8 |
| **0,13,ℓ** | | |
| 1 | 23 | 19 |
| 2 | - | 1 |
| 3 | 17 | 15 |
| 4 | - | 7 |
| 5 | - | 7 |
| 6 | - | 1 |
| 7 | 16 | 12 |
| **10ℓ** | | |
| 1 | 90 | 87 |
| 2 | 73 | 25 |
| 3 | 167 | 127 |
| 4 | 50 | 29 |
| 5 | 14 | 1 |
| 6 | 108 | 65 |
| 7 | 45 | 25 |
| 8 | 154 | 119 |
| 9 | 16 | 21 |
| 10 | 38 | 34 |
| 11 | 31 | 43 |
| 12 | 132 | 94 |
| 13 | 31 | 12 |
| 14 | 46 | 49 |
| 15 | 12 | 12 |
| 16 | 29 | 30 |
| 17 | 15 | 18 |
| 18 | 13 | 12 |
| 19 | 12 | 13 |
| 20 | 45 | 45 |
| 21 | 24 | 20 |
| 22 | - | 8 |
| 23 | 21 | 21 |
| 24 | - | 2 |
| 25 | 17 | 21 |
| 26 | 13 | 12 |
| **11ℓ** | | |
| 0 | 15 | 16 |
| 1 | 64 | 110 |
| 2 | 112 | 120 |
| 3 | 51 | 42 |
| 4 | 119 | 110 |
| 5 | 87 | 72 |
| 6 | 50 | 26 |
| 7 | 88 | 79 |
| 8 | 55 | 42 |
| **11ℓ** | | |
| 9 | 174 | 139 |
| 10 | 95 | 78 |
| 11 | 95 | 82 |
| 12 | 9 | 9 |
| 13 | 136 | 108 |
| 14 | 22 | 16 |
| 15 | 36 | 46 |
| 16 | 33 | 35 |
| 17 | 21 | 24 |
| 18 | - | 7 |
| 19 | 34 | 29 |
| 20 | 14 | 19 |
| 21 | 24 | 20 |
| 22 | 17 | 17 |
| 23 | 26 | 20 |
| 24 | 20 | 20 |
| 25 | 21 | 16 |
| 26 | 10 | 8 |
| **12ℓ** | | |
| 0 | 40 | 36 |
| 1 | 108 | 116 |
| 2 | 54 | 69 |
| 3 | 103 | 78 |
| 4 | 94 | 69 |
| 5 | 46 | 46 |
| 6 | 30 | 36 |
| 7 | 19 | 23 |
| 8 | 66 | 69 |
| 9 | 26 | 19 |
| 10 | 23 | 32 |
| 11 | 39 | 39 |
| 12 | 66 | 56 |
| 13 | 26 | 34 |
| 14 | 30 | 28 |
| 15 | - | 5 |
| 16 | 17 | 14 |
| 17 | 44 | 39 |
| 18 | 48 | 45 |
| 19 | 21 | 15 |
| 20 | 22 | 19 |
| 21 | 27 | 27 |
| 22 | 23 | 21 |
| 23 | - | 8 |
| 24 | 31 | 33 |
| **13ℓ** | | |
| 0 | 10 | 10 |
| 1 | 129 | 121 |
| 2 | 75 | 58 |
| 3 | 158 | 139 |
| 4 | 79 | 66 |
| 5 | 42 | 52 |
| 6 | 71 | 41 |
| 7 | 28 | 13 |
| 8 | 85 | 59 |
| 9 | 37 | 47 |
| 10 | 105 | 82 |
| 11 | 34 | 32 |
| 12 | 69 | 66 |
| 13 | - | 4 |
| 14 | 21 | 24 |
| 15 | 26 | 22 |
| 16 | 71 | 63 |
| 17 | 30 | 30 |
| 18 | 22 | 18 |
| 19 | 38 | 32 |
| 20 | 24 | 22 |
| 21 | 12 | 13 |
| 22 | 25 | 18 |
| 23 | 21 | 23 |
| 24 | - | 4 |
| 25 | 15 | 17 |
| 26 | 15 | 12 |
| **14ℓ** | | |
| 0 | 86 | 67 |
| 1 | 82 | 64 |
| 2 | 23 | 30 |
| 3 | 53 | 48 |
| 4 | 92 | 60 |
| 5 | 94 | 66 |
| 6 | 39 | 27 |
| 7 | 14 | 17 |
| 8 | 33 | 28 |
| 9 | 122 | 94 |
| 10 | 22 | 16 |
| 11 | 75 | 64 |
| 12 | 19 | 17 |
| 13 | 21 | 16 |
| 14 | - | 8 |
| 15 | 82 | 68 |
| 16 | - | 6 |
| 17 | 39 | 34 |
| 18 | 18 | 13 |
| 19 | 30 | 25 |
| 20 | 20 | 13 |
| 21 | 12 | 14 |
| 22 | 23 | 21 |
| 23 | - | 10 |
| 24 | - | 9 |
| 25 | 23 | 21 |
| **15ℓ** | | |
| 0 | 74 | 72 |
| 1 | 100 | 79 |
| 2 | 19 | 3 |
| 3 | 23 | 25 |
| 4 | 31 | 31 |
| 5 | 59 | 51 |
| 6 | 65 | 50 |
| 7 | 53 | 46 |
| 8 | 53 | 43 |
| 9 | 62 | 62 |
| 10 | 38 | 38 |
| 11 | 40 | 45 |
| 12 | 59 | 59 |
| 13 | 78 | 71 |
| 14 | 49 | 51 |
| 15 | 32 | 34 |
| 16 | 35 | 37 |
| 17 | 14 | 16 |
| 18 | 12 | 14 |
| 19 | 24 | 21 |
| 20 | 12 | 9 |
| 21 | 14 | 10 |
| 22 | 25 | 22 |
| **15ℓ** | | |
| 23 | 19 | 17 |
| 24 | 10 | 8 |
| **16ℓ** | | |
| 0 | 24 | 20 |
| 1 | 79 | 61 |
| 2 | 40 | 42 |
| 3 | 119 | 96 |
| 4 | 34 | 20 |
| 5 | 11 | 10 |
| 6 | 36 | 20 |
| 7 | 27 | 25 |
| 8 | 15 | 18 |
| 9 | 21 | 27 |
| 10 | 27 | 27 |
| 11 | 21 | 22 |
| 12 | 13 | 9 |
| 13 | 47 | 48 |
| 14 | 36 | 32 |
| 15 | 37 | 31 |
| 16 | 19 | 24 |
| 17 | - | 3 |
| 18 | 17 | 16 |
| 19 | 15 | 18 |
| 20 | - | 9 |
| 21 | 22 | 23 |
| 22 | - | 0 |
| 23 | 19 | 21 |
| 24 | 12 | 11 |
| **17ℓ** | | |
| 0 | 54 | 51 |
| 1 | 38 | 35 |
| 2 | 80 | 72 |
| 3 | 51 | 52 |
| 4 | 40 | 37 |
| 5 | 52 | 41 |
| 6 | 63 | 60 |
| 7 | 10 | 4 |
| 8 | 15 | 17 |
| 9 | 49 | 51 |
| 10 | 19 | 15 |
| 11 | 27 | 31 |
| 12 | 18 | 18 |
| 13 | 22 | 20 |
| 14 | - | 4 |
| 15 | 39 | 37 |
| 16 | - | 7 |
| 17 | 29 | 26 |
| 18 | 34 | 31 |
| 19 | 18 | 20 |
| 20 | 14 | 13 |
| 21 | - | 8 |
| 22 | 10 | 13 |
| 23 | 13 | 12 |
| 24 | 14 | 14 |
| **18ℓ** | | |
| 0 | 41 | 40 |
| 1 | 62 | 57 |
| 2 | 45 | 44 |
| 3 | 24 | 21 |
| 4 | 23 | 24 |
| 5 | 28 | 26 |
| 6 | 40 | 36 |
| 7 | 29 | 27 |
| 8 | 46 | 45 |
| 9 | 26 | 27 |
| 10 | 11 | 12 |
| 11 | - | 7 |
| 12 | 37 | 33 |
| 13 | 16 | 15 |
| 14 | 21 | 22 |
| 15 | 27 | 25 |
| 16 | - | 4 |
| 17 | - | 6 |
| 18 | 22 | 18 |
| 19 | 22 | 20 |
| 20 | 10 | 9 |
| 21 | 17 | 19 |
| **19ℓ** | | |
| 0 | 34 | 26 |
| 1 | 19 | 19 |
| 2 | - | 4 |
| 3 | 21 | 18 |
| 4 | 11 | 12 |
| 5 | 41 | 37 |
| 6 | 33 | 30 |
| 7 | 30 | 29 |
| 8 | 24 | 21 |
| 9 | 27 | 28 |
| 10 | 37 | 29 |
| 11 | 10 | 9 |
| 12 | 39 | 34 |
| 13 | 18 | 19 |
| 14 | 22 | 20 |
| 15 | - | 1 |
| 16 | 10 | 8 |
| 17 | 24 | 20 |
| 18 | - | 8 |
| 19 | - | 8 |
| 20 | - | 5 |
| 21 | - | 7 |
| 22 | 13 | 14 |
| **1,10,ℓ** | | |
| 0 | 57 | 48 |
| 1 | 10 | 12 |
| 2 | 31 | 29 |
| 3 | 28 | 27 |
| 4 | 30 | 30 |
| 5 | 10 | 11 |
| 6 | 30 | 25 |
| 7 | 18 | 18 |
| 8 | 15 | 16 |
| 9 | 21 | 17 |
| 10 | 12 | 14 |
| 11 | 23 | 22 |
| 12 | 11 | 11 |
| 13 | 30 | 27 |
| 14 | - | 3 |
| 15 | - | 9 |
| 16 | 15 | 12 |
| 17 | - | 6 |
| 18 | 17 | 18 |
| **1,11,ℓ** | | |
| 0 | - | 8 |
| 1 | 22 | 23 |
| 2 | 42 | 42 |
| 3 | 40 | 39 |
| 4 | 11 | 10 |
| 5 | 16 | 14 |
| 6 | 31 | 33 |
| 7 | 13 | 15 |
| 8 | - | 10 |
| 9 | 20 | 18 |
| 10 | 13 | 14 |
| 11 | 15 | 14 |
| 12 | 15 | 14 |
| 13 | 12 | 10 |
| 14 | 15 | 11 |
| 15 | 18 | 14 |
| 16 | - | 8 |
| 17 | 13 | 14 |
| **1,12,ℓ** | | |
| 0 | 14 | 14 |
| 1 | 33 | 34 |
| 2 | 27 | 21 |
| 3 | 13 | 11 |
| 4 | 13 | 11 |
| 5 | 36 | 34 |
| 6 | 40 | 36 |
| 7 | - | 8 |
| 8 | - | 6 |
| 9 | - | 7 |
| 10 | 17 | 14 |
| 11 | 11 | 11 |
| 12 | - | 6 |
| 13 | - | 2 |
| 14 | 8 | 12 |
| **1,13,ℓ** | | |
| 0 | - | 3 |
| 1 | - | 3 |
| 2 | 20 | 20 |
| 3 | 17 | 18 |
| 4 | 13 | 10 |
| 5 | 11 | 12 |
| 6 | 9 | 11 |
| 7 | 19 | 21 |
| **20ℓ** | | |
| 0 | 36 | 32 |
| 1 | 45 | 75 |
| 2 | 20 | 8 |
| 3 | 9 | 5 |
| 4 | 26 | 3 |
| 5 | 105 | 84 |
| 6 | 32 | 21 |
| 7 | 56 | 54 |
| 8 | 88 | 88 |
| 9 | 71 | 69 |
| 10 | 76 | 80 |
| 11 | 21 | 16 |
| 12 | 10 | 2 |
| 13 | 24 | 24 |
| 14 | 64 | 52 |
| 15 | 21 | 23 |
| 16 | 23 | 17 |
| 17 | 31 | 28 |
| 18 | - | 5 |
| 19 | - | 4 |
| 20 | 8 | 8 |
| 21 | 9 | 8 |
| 22 | 30 | 26 |
| 23 | 19 | 19 |
| 24 | - | 1 |
| 25 | - | 1 |
| 26 | 12 | 7 |
| 27 | 24 | 20 |
| **21ℓ** | | |
| 0 | 79 | 111 |
| 1 | 51 | 43 |
| 2 | 72 | 92 |
| 3 | 177 | 161 |
| 4 | 41 | 36 |
| 5 | 83 | 82 |
| 6 | 22 | 20 |
| 7 | 7 | 25 |
| 8 | 30 | 31 |
| 9 | 73 | 73 |
| 10 | 22 | 16 |
| 11 | 52 | 52 |
| 12 | 61 | 52 |
| 13 | 27 | 32 |
| 14 | - | 11 |
| 15 | 60 | 52 |
| 16 | 16 | 14 |
| 17 | 34 | 34 |
| 18 | 22 | 19 |
| 19 | 31 | 29 |
| 20 | 22 | 21 |
| 21 | 41 | 40 |
| 22 | - | 8 |
| 23 | 23 | 22 |
| 24 | - | 7 |
| 25 | - | 7 |
| 26 | 13 | 12 |
| 27 | 13 | 13 |
| 28 | 12 | 11 |
| 29 | 6 | 4 |
| **22ℓ** | | |
| 0 | 130 | 112 |
| 1 | 135 | 149 |
| 2 | 86 | 76 |
| 3 | 125 | 131 |
| 4 | 72 | 83 |
| 5 | 58 | 42 |
| 6 | 92 | 83 |
| 7 | 7 | 10 |
| 8 | 80 | 87 |
| 9 | 68 | 59 |
| 10 | 63 | 56 |
| 11 | 42 | 51 |
| 12 | 107 | 102 |
| 13 | 24 | 18 |
| 14 | 38 | 41 |
| 15 | 28 | 28 |
| 16 | 20 | 19 |
| **22ℓ** | | |
| 17 | 21 | 21 |
| 18 | - | 8 |
| 19 | 21 | 17 |
| 20 | 27 | 27 |
| 21 | 21 | 19 |
| 22 | 30 | 24 |
| 23 | 32 | 30 |
| 24 | 26 | 22 |
| 25 | 12 | 9 |
| 26 | 14 | 16 |
| 27 | 7 | 8 |
| 28 | 8 | 6 |
| **23ℓ** | | |
| 0 | 163 | 163 |
| 1 | 79 | 79 |
| 2 | 70 | 68 |
| 3 | 22 | 27 |
| 4 | 102 | 105 |
| 5 | 44 | 60 |
| 6 | 75 | 73 |
| 7 | 24 | 19 |
| 8 | 44 | 43 |
| 9 | 30 | 29 |
| 10 | 29 | 35 |
| 11 | 29 | 32 |
| 12 | 18 | 10 |
| 13 | 18 | 17 |
| 14 | 36 | 34 |
| 15 | 20 | 18 |
| 16 | 9 | 6 |
| 17 | 17 | 19 |
| 18 | 33 | 34 |
| 19 | 18 | 16 |
| 20 | 19 | 17 |
| 21 | 28 | 23 |
| 22 | 7 | 8 |
| 23 | 28 | 25 |
| 24 | 23 | 22 |
| 25 | 18 | 18 |
| 26 | - | 5 |
| 27 | - | 3 |
| 28 | 5 | 7 |
| **24ℓ** | | |
| 0 | 25 | 37 |
| 1 | 32 | 29 |
| 2 | 23 | 24 |
| 3 | 36 | 33 |
| 4 | 80 | 66 |
| 5 | 17 | 22 |
| 6 | 59 | 47 |
| 7 | 36 | 41 |
| 8 | 41 | 46 |
| 9 | 36 | 39 |
| 10 | 30 | 22 |
| 11 | 39 | 38 |
| 12 | 44 | 46 |
| 13 | 34 | 32 |
| 14 | 26 | 27 |
| 15 | 11 | 7 |
| 16 | 30 | 30 |
| 17 | 27 | 26 |
| 18 | 16 | 13 |
| 19 | 17 | 18 |
| 20 | 17 | 17 |
| 21 | 16 | 15 |
| 22 | 14 | 12 |
| 23 | 12 | 9 |
| 24 | 13 | 10 |
| 25 | 10 | 10 |
| 26 | 12 | 10 |
| 27 | 13 | 13 |
| 28 | 7 | 10 |
| **25ℓ** | | |
| 0 | 118 | 101 |
| 1 | 23 | 13 |
| 2 | 62 | 51 |
| 3 | 59 | 40 |
| 4 | 77 | 66 |
| 5 | 17 | 17 |
| 6 | 76 | 69 |
| 7 | 20 | 24 |
| 8 | 66 | 55 |
| 9 | 13 | 16 |
| 10 | 8 | 7 |
| 11 | 12 | 12 |
| 12 | 77 | 67 |
| 13 | 20 | 19 |
| 14 | 19 | 21 |
| 15 | 25 | 24 |
| 16 | 32 | 29 |
| 17 | 30 | 29 |
| 18 | 41 | 38 |
| 19 | 22 | 20 |
| 20 | 19 | 15 |
| 21 | 21 | 18 |
| 22 | 10 | 9 |
| 23 | - | 4 |
| 24 | 25 | 25 |
| 25 | 20 | 19 |
| 26 | 15 | 17 |
| **26ℓ** | | |
| 0 | 77 | 71 |
| 1 | 30 | 18 |
| 2 | 83 | 74 |
| 3 | 73 | 63 |
| 4 | 69 | 54 |
| 5 | 30 | 26 |
| 6 | 34 | 30 |
| 7 | 40 | 35 |
| 8 | 33 | 29 |
| 9 | 108 | 96 |
| 10 | 14 | 18 |
| 11 | 72 | 54 |
| 12 | 18 | 16 |
| 13 | 33 | 37 |
| 14 | - | 1 |
| 15 | 40 | 45 |
| 16 | 22 | 19 |
| 17 | 25 | 20 |
| 18 | 22 | 21 |
| 19 | 27 | 23 |
| 20 | 29 | 31 |
| 21 | - | 5 |
| **26ℓ** | | |
| 22 | - | 8 |
| 23 | 20 | 16 |
| 24 | 26 | 22 |
| 25 | 17 | 14 |
| 26 | 9 | 11 |
| **27ℓ** | | |
| 0 | 35 | 44 |
| 1 | 43 | 46 |
| 2 | 18 | 23 |
| 3 | 33 | 24 |
| 4 | 31 | 31 |
| 5 | 60 | 55 |
| 6 | 22 | 17 |
| 7 | 35 | 28 |
| 8 | 18 | 18 |
| 9 | 13 | 10 |
| 10 | 24 | 23 |
| 11 | 25 | 18 |
| 12 | 26 | 21 |
| 13 | 22 | 17 |
| 14 | 27 | 27 |
| 15 | 25 | 21 |
| 16 | 11 | 9 |
| 17 | 26 | 22 |
| 18 | 16 | 17 |
| 19 | 20 | 20 |
| 20 | 22 | 18 |
| 21 | 16 | 14 |
| 22 | 21 | 16 |
| 23 | - | 4 |
| 24 | 10 | 11 |
| 25 | 10 | 13 |
| **28ℓ** | | |
| 0 | 18 | 15 |
| 1 | 34 | 32 |
| 2 | 15 | 15 |
| 3 | 27 | 28 |
| 4 | 20 | 24 |
| 5 | 34 | 34 |
| 6 | 32 | 29 |
| 7 | 22 | 20 |
| 8 | 34 | 28 |
| 9 | 37 | 35 |
| 10 | 35 | 33 |
| 11 | 9 | 16 |
| 12 | 19 | 17 |
| 13 | - | 3 |
| 14 | 24 | 18 |
| 15 | 18 | 17 |
| 16 | 28 | 29 |
| 17 | 16 | 15 |
| 18 | 29 | 27 |
| 19 | 6 | 6 |
| 20 | 16 | 15 |
| 21 | 11 | 13 |
| 22 | 9 | 11 |
| **29ℓ** | | |
| 0 | 46 | 50 |
| 1 | 36 | 30 |
| 2 | 25 | 23 |
| 3 | 41 | 38 |
| 4 | 47 | 43 |
| 5 | 52 | 51 |
| 6 | 11 | 12 |
| 7 | 20 | 19 |
| 8 | - | 5 |
| 9 | 43 | 36 |
| 10 | 23 | 20 |
| 11 | 18 | 16 |
| 12 | - | 2 |
| 13 | - | 6 |
| 14 | 22 | 21 |
| 15 | 36 | 34 |
| 16 | 7 | 5 |
| 17 | 8 | 12 |
| 18 | 19 | 16 |
| 19 | 12 | 11 |
| 20 | 14 | 12 |
| **2,10,ℓ** | | |
| 0 | 30 | 33 |
| 1 | 24 | 24 |
| 2 | 14 | 14 |
| 3 | 45 | 41 |
| 4 | 10 | 14 |
| 5 | 13 | 14 |
| 6 | 29 | 28 |
| 7 | - | 4 |
| 8 | 35 | 33 |
| 9 | 33 | 30 |
| 10 | 34 | 33 |
| 11 | 13 | 11 |
| 12 | 34 | 36 |
| 13 | 7 | 8 |
| 14 | 30 | 27 |
| 15 | 6 | 2 |
| 16 | 13 | 12 |
| 17 | 10 | 11 |
| 18 | 4 | 4 |
| 19 | 11 | 10 |
| 20 | 9 | 11 |
| **2,11,ℓ** | | |
| 0 | 15 | 18 |
| 1 | 11 | 12 |
| 2 | 21 | 21 |
| 3 | 7 | 9 |
| 4 | 29 | 27 |
| 5 | 6 | 7 |
| 6 | 27 | 23 |
| 7 | 12 | 10 |
| 8 | 12 | 15 |
| 9 | - | 4 |
| 10 | 22 | 22 |
| 11 | - | 6 |
| 12 | 11 | 9 |
| 13 | 8 | 5 |
| 14 | 21 | 19 |
| 15 | - | 4 |
| 16 | 11 | 11 |
| 17 | 4 | 6 |
| **2,12,ℓ** | | |
| 0 | 11 | 12 |
| 1 | 13 | 12 |
| 2 | 36 | 36 |
| 3 | 8 | 7 |
| 4 | 10 | 10 |
| 5 | 14 | 13 |
| 6 | 35 | 35 |
| 7 | 12 | 13 |
| 8 | 5 | 4 |
| 9 | - | 3 |
| 10 | 7 | 12 |
| 11 | - | 3 |
| 12 | 7 | 7 |
| 13 | 11 | 13 |
| 14 | 9 | 18 |
| **2,13,ℓ** | | |
| 0 | - | 5 |
| 1 | 10 | 13 |
| 2 | 8 | 10 |
| 3 | 24 | 25 |
| 4 | - | 5 |
| 5 | 16 | 16 |
| 6 | 21 | 22 |
| 7 | 10 | 11 |
| 8 | 9 | 16 |
| **30ℓ** | | |
| 1 | - | 5 |
| 2 | 75 | 90 |
| 3 | - | 6 |
| 4 | 70 | 71 |
| 5 | 90 | 62 |
| 6 | 75 | 38 |
| 7 | 78 | 66 |
| 8 | 34 | 15 |
| 9 | 16 | 17 |
| 10 | 61 | 46 |
| 11 | 53 | 42 |
| 12 | 61 | 49 |
| 13 | 33 | 32 |
| 14 | - | 1 |
| 15 | 21 | 23 |
| 16 | - | 1 |
| 17 | - | 9 |
| 18 | 33 | 35 |
| 19 | 15 | 15 |
| 20 | - | 8 |
| 21 | 25 | 21 |
| 22 | 50 | 46 |
| 23 | 10 | 13 |
| 24 | 20 | 21 |
| 25 | - | 3 |
| 26 | - | 5 |
| 27 | - | 7 |
| 28 | 12 | 17 |
| **31ℓ** | | |
| 0 | 209 | 186 |
| 1 | 146 | 141 |
| 2 | 80 | 60 |
| 3 | 127 | 105 |
| 4 | 73 | 56 |
| 5 | 5 | 23 |
| 6 | 44 | 34 |
| 7 | 73 | 62 |
| 8 | 23 | 19 |
| 9 | 25 | 21 |
| 10 | 41 | 36 |
| 11 | 33 | 41 |
| 12 | 37 | 36 |
| 13 | 31 | 24 |
| 14 | - | 7 |
| 15 | 20 | 23 |
| 16 | - | 4 |
| 17 | - | 12 |
| 18 | 33 | 30 |
| 19 | 22 | 25 |
| 20 | 17 | 25 |
| 21 | 36 | 33 |
| 22 | 18 | 19 |
| 23 | 18 | 20 |
| 24 | 20 | 24 |
| 25 | - | 8 |
| 26 | - | 3 |
| 27 | 11 | 16 |
| **32ℓ** | | |
| 0 | 125 | 106 |
| 1 | 70 | 43 |
| 2 | 50 | 55 |
| 3 | 91 | 76 |
| 4 | 81 | 66 |
| 5 | 107 | 88 |
| 6 | 87 | 63 |
| 7 | 65 | 42 |
| 8 | 139 | 101 |
| 9 | 69 | 57 |
| 10 | 51 | 49 |
| 11 | 68 | 63 |
| 12 | 46 | 46 |
| 13 | 66 | 60 |
| 14 | 48 | 51 |
| 15 | 37 | 31 |
| 16 | 67 | 56 |
| 17 | 11 | 19 |
| 18 | 32 | 31 |
| 19 | 19 | 16 |
| 20 | 10 | 9 |
| 21 | - | 8 |
| 22 | - | 6 |
| 23 | 10 | 17 |
| 24 | 15 | 15 |
| 25 | - | 4 |
| 26 | - | 13 |
| 27 | 13 | 15 |
| **33ℓ** | | |
| 0 | 83 | 69 |
| 1 | 79 | 74 |
| 2 | 64 | 47 |
| 3 | 99 | 57 |
| 4 | 82 | 51 |
| 5 | 68 | 42 |
| 6 | 108 | 68 |
| 7 | 69 | 54 |
| **33ℓ** | | |
| 8 | 23 | 22 |
| 9 | 41 | 35 |
| 10 | 41 | 46 |
| 11 | 45 | 40 |
| 12 | 16 | 18 |
| 13 | 23 | 17 |
| 14 | 43 | 37 |
| 15 | - | 8 |
| 16 | 18 | 16 |
| 17 | 31 | 31 |
| 18 | - | 10 |
| 19 | - | 11 |
| 20 | - | 12 |
| 21 | 11 | 22 |
| 22 | - | 11 |
| 23 | - | 10 |
| 24 | - | 10 |
| 25 | 8 | 14 |
| 26 | 8 | 17 |
| 27 | 15 | 19 |
| **34ℓ** | | |
| 0 | 28 | 44 |
| 1 | 73 | 72 |
| 2 | 27 | 31 |
| 3 | 37 | 31 |
| 4 | 38 | 32 |
| 5 | 48 | 50 |
| 6 | 35 | 31 |
| 7 | 48 | 44 |
| 8 | 41 | 41 |
| 9 | 38 | 28 |
| 10 | 50 | 42 |
| 11 | 9 | 11 |
| 12 | 70 | 61 |
| 13 | 58 | 51 |
| 14 | 27 | 21 |
| 15 | - | 1 |
| 16 | 33 | 32 |
| 17 | 30 | 28 |
| 18 | - | 10 |
| 19 | 29 | 22 |
| 20 | - | 13 |
| 21 | 30 | 32 |
| 22 | 28 | 31 |
| 23 | 13 | 15 |
| 24 | - | 8 |
| 25 | 16 | 18 |
| 26 | 6 | 10 |
| 27 | 8 | 17 |
| **35ℓ** | | |
| 0 | 200 | 163 |
| 1 | 65 | 49 |
| 2 | 42 | 37 |
| 3 | 78 | 58 |
| 4 | 90 | 71 |
| 5 | - | 8 |
| 6 | 55 | 52 |
| 7 | 40 | 33 |
| 8 | - | 8 |
| 9 | - | 7 |
| 10 | 35 | 27 |
| 11 | - | 13 |
| 12 | 37 | 28 |
| 13 | - | 6 |
| 14 | 15 | 17 |
| 15 | 16 | 11 |
| 16 | - | 12 |
| 17 | 22 | 25 |
| 18 | 26 | 20 |
| 19 | - | 10 |
| 20 | 36 | 38 |
| 21 | 9 | 15 |
| 22 | 9 | 13 |
| 23 | - | 5 |
| 24 | 28 | 28 |
| 25 | 7 | 9 |
| 26 | 10 | 14 |
| **36ℓ** | | |
| 0 | - | 2 |
| 1 | 45 | 33 |
| 2 | 61 | 47 |
| 3 | 42 | 40 |
| 4 | 59 | 48 |
| 5 | 70 | 58 |
| 6 | 66 | 51 |
| 7 | 22 | 17 |
| 8 | 86 | 64 |
| 9 | 71 | 56 |
| 10 | 22 | 14 |
| 11 | 38 | 30 |
| 12 | 47 | 41 |
| 13 | - | 4 |
| 14 | 30 | 25 |
| 15 | 47 | 41 |
| 16 | - | 12 |
| 17 | 34 | 24 |
| 18 | 16 | 22 |
| 19 | - | 8 |
| 20 | - | 7 |
| 21 | 15 | 22 |
| **37ℓ** | | |
| 0 | 66 | 52 |
| 1 | 52 | 38 |
| 2 | 18 | 13 |
| 3 | 36 | 28 |
| 4 | 30 | 26 |
| 5 | 46 | 37 |
| 6 | 17 | 16 |
| 7 | 30 | 31 |
| 8 | 31 | 27 |
| 9 | 53 | 50 |
| 10 | 15 | 9 |
| 11 | 50 | 41 |
| 12 | - | 12 |
| 13 | 34 | 31 |
| 14 | - | 1 |
| 15 | 26 | 22 |
| 16 | 30 | 24 |
| 17 | 37 | 31 |
| 18 | 32 | 26 |
| 19 | 14 | 9 |
| 20 | - | 6 |
| 21 | - | 12 |

Table 1 (*cont.*)

|  | $F_o$ | $\lvert F_c \rvert$ |
|---|---|---|
| **00ℓ** |  |  |
| 2 | 45 | 92 |
| 4 | 181 | 147 |
| 6 | 286 | 220 |
| 8 | 54 | 26 |
| 10 | 100 | 112 |
| 12 | 116 | 103 |
| 14 | 19 | 17 |
| 16 | 19 | 19 |
| 18 | 34 | 30 |
| 20 | 91 | 80 |
| 22 | 14 | 19 |
| 24 | 50 | 51 |
| 26 | 34 | 35 |
| 28 | 16 | 16 |
| **01ℓ** |  |  |
| 1 | 44 | 48 |
| 2 | 45 | 98 |
| 3 | 8 | 14 |
| 4 | 81 | 59 |
| 5 | 84 | 79 |
| 6 | 69 | 65 |
| 7 | 39 | 33 |
| 8 | 108 | 96 |
| 9 | 36 | 41 |
| 10 | 66 | 42 |
| 11 | 78 | 70 |
| 12 | 124 | 103 |
| 13 | 37 | 36 |
| 14 | 10 | 10 |
| 15 | 24 | 30 |
| 16 | 13 | 19 |
| 17 | - | 1 |
| 18 | 19 | 22 |
| 19 | 28 | 28 |
| 20 | 20 | 17 |
| 21 | 13 | 11 |
| 22 | 26 | 23 |
| 23 | 11 | 8 |
| 24 | 8 | 6 |
| 25 | 17 | 14 |
| 26 | 10 | 8 |
| 27 | 25 | 28 |
| **02ℓ** |  |  |
| 0 | 15 | 24 |
| 1 | 86 | 96 |
| 2 | 9 | 4 |
| 3 | 55 | 57 |
| 4 | 35 | 24 |
| 5 | 56 | 48 |
| 6 | 8 | 17 |
| 7 | 84 | 72 |
| 8 | 34 | 23 |
| 9 | 91 | 84 |
| 10 | 24 | 31 |
| 11 | 36 | 29 |
| 12 | - | 5 |
| 13 | 16 | 20 |
| 14 | - | 3 |
| 15 | 10 | 13 |
| 16 | 11 | 5 |
| 17 | 20 | 19 |
| 18 | 24 | 23 |
| 19 | 10 | 7 |
| 20 | 23 | 18 |
| 21 | 21 | 20 |
| 22 | - | 4 |
| 23 | 30 | 28 |
| 24 | - | 7 |
| 25 | 24 | 20 |
| 26 | 8 | 7 |
| 27 | - | 3 |
| 28 | - | 2 |
| 29 | 15 | 14 |
| **03ℓ** |  |  |
| 1 | 37 | 39 |
| 2 | 23 | 24 |
| 3 | 28 | 13 |
| 4 | 103 | 104 |
| 5 | 82 | 51 |
| 6 | 14 | 18 |
| 7 | - | 3 |
| 8 | 49 | 44 |
| 9 | 106 | 87 |
| 10 | 9 | 7 |
| 11 | 61 | 54 |
| 12 | 8 | 3 |
| 13 | 41 | 38 |
| 14 | 11 | 14 |
| 15 | 51 | 47 |
| 16 | 27 | 27 |
| 17 | - | 2 |
| 18 | 11 | 9 |
| 19 | - | 1 |
| 20 | 12 | 14 |
| 21 | - | 0 |
| 22 | 14 | 13 |
| 23 | 31 | 33 |
| 24 | 22 | 23 |
| 25 | 9 | 7 |
| 26 | 10 | 9 |
| 27 | 8 | 4 |
| 28 | 25 | 23 |
| **04ℓ** |  |  |
| 0 | 183 | 193 |
| 1 | 171 | 142 |
| 2 | 31 | 40 |
| 3 | 183 | 169 |
| 4 | 44 | 33 |
| 5 | 66 | 68 |
| 6 | 27 | 23 |
| 7 | 121 | 102 |
| 8 | 13 | 6 |
| 9 | 66 | 54 |
| 10 | 82 | 69 |
| 11 | - | 4 |
| 12 | - | 2 |
| 13 | 36 | 43 |
| 14 | 25 | 26 |
| 15 | 40 | 34 |
| 16 | 27 | 30 |
| 17 | - | 4 |
| 18 | - | 6 |
| 19 | 45 | 44 |
| 20 | 31 | 31 |
| 21 | 59 | 50 |
| 22 | 11 | 8 |
| 23 | 39 | 40 |
| 24 | 14 | 12 |
| 25 | - | 1 |
| 26 | 16 | 15 |
| 27 | 17 | 16 |
| **05ℓ** |  |  |
| 1 | 73 | 57 |
| 2 | 68 | 78 |
| 3 | 72 | 47 |
| 4 | 80 | 79 |
| 5 | 88 | 55 |
| 6 | 8 | 6 |
| 7 | 22 | 14 |
| 8 | 17 | 14 |
| 9 | 48 | 43 |
| 10 | 15 | 10 |
| 11 | 21 | 30 |
| 12 | 76 | 73 |
| 13 | 9 | 5 |
| 14 | 19 | 14 |
| 15 | 27 | 22 |
| 16 | - | 2 |
| 17 | 26 | 29 |
| 18 | 13 | 12 |
| 19 | 20 | 15 |
| 20 | 16 | 15 |
| 21 | - | 7 |
| 22 | 48 | 45 |
| 23 | - | 7 |
| 24 | - | 8 |
| 25 | - | 1 |
| 26 | - | 1 |
| 27 | 15 | 13 |
| **06ℓ** |  |  |
| 0 | 88 | 70 |
| 1 | 56 | 51 |
| 2 | 6 | 1 |
| 3 | 92 | 65 |
| 4 | 53 | 41 |
| 5 | 13 | 15 |
| 6 | 9 | 17 |
| 7 | 22 | 28 |
| 8 | 12 | 7 |
| 9 | 37 | 31 |
| 10 | 40 | 46 |
| 11 | 15 | 16 |
| 12 | - | 10 |
| 13 | 57 | 52 |
| 14 | 19 | 27 |
| 15 | - | 7 |
| 16 | 17 | 14 |
| 17 | 30 | 25 |
| 18 | 21 | 23 |
| 19 | 30 | 29 |
| 20 | - | 4 |
| 21 | - | 1 |
| 22 | 24 | 25 |
| 23 | - | 2 |
| 24 | 15 | 16 |
| 25 | - | 4 |
| 26 | 9 | 8 |
| **07ℓ** |  |  |
| 1 | 34 | 34 |
| 2 | 24 | 13 |
| 3 | 67 | 51 |
| 4 | 21 | 14 |
| 5 | 62 | 62 |
| 6 | 113 | 92 |
| 7 | 11 | 19 |
| 8 | 72 | 54 |
| 9 | - | 0 |
| 10 | 36 | 39 |
| 11 | 18 | 12 |
| 12 | 90 | 74 |
| 13 | 24 | 23 |
| 14 | 30 | 27 |
| 15 | 27 | 23 |
| 16 | - | 6 |
| 17 | - | 1 |
| 18 | 35 | 27 |
| 19 | 11 | 12 |
| 20 | 21 | 18 |
| 21 | - | 1 |
| 22 | 18 | 17 |
| 23 | 24 | 21 |
| 24 | 9 | 6 |
| 25 | 12 | 10 |
| **08ℓ** |  |  |
| 0 | 120 | 91 |
| 1 | 30 | 27 |
| 2 | 11 | 10 |
| 3 | 14 | 11 |
| 4 | 73 | 57 |
| 5 | 17 | 17 |
| 6 | 75 | 60 |
| 7 | 12 | 5 |
| 8 | 10 | 7 |
| 9 | 22 | 19 |
| 10 | 73 | 63 |
| 11 | 27 | 31 |
| 12 | - | 9 |
| 13 | 20 | 20 |
| 14 | 63 | 51 |
| 15 | - | 2 |
| 16 | - | 3 |
| 17 | - | 6 |
| 18 | 9 | 8 |
| 19 | - | 2 |
| 20 | - | 5 |
| 21 | 27 | 24 |
| 22 | 7 | 12 |
| 23 | 15 | 11 |
| 24 | 4 | 7 |
| **09ℓ** |  |  |
| 1 | 12 | 21 |
| 2 | 73 | 56 |
| 3 | - | 7 |
| 4 | 27 | 25 |
| 5 | 12 | 7 |
| 6 | 20 | 15 |
| 7 | 17 | 14 |
| 8 | - | 6 |
| 9 | - | 1 |
| 10 | - | 4 |
| 11 | 14 | 11 |
| 12 | 30 | 29 |
| 13 | 45 | 43 |
| 14 | - | 2 |
| 15 | 17 | 14 |
| 16 | - | 6 |
| 17 | 11 | 10 |
| 18 | 15 | 14 |
| 19 | 19 | 15 |
| 20 | - | 3 |
| 21 | 9 | 13 |
| 22 | 19 | 19 |
| **0,10,ℓ** |  |  |
| 0 | 39 | 30 |
| 1 | 14 | 12 |
| 2 | 27 | 26 |
| 3 | 50 | 45 |
| 4 | - | 2 |
| 5 | 13 | 9 |
| 6 | - | 1 |
| 7 | 11 | 9 |
| 8 | 15 | 7 |
| 9 | 12 | 9 |
| 10 | 11 | 9 |
| 11 | - | 8 |
| 12 | 18 | 13 |
| 13 | 27 | 24 |
| 14 | - | 2 |
| 15 | - | 7 |
| 16 | 13 | 12 |
| 17 | - | 3 |
| 18 | 20 | 17 |
| 19 | 13 | 13 |
| 20 | 16 | 14 |
| **0,11,ℓ** |  |  |
| 1 | 19 | 13 |
| 2 | - | 3 |
| 3 | 42 | 40 |
| 4 | - | 1 |
| 5 | 24 | 26 |
| 6 | 15 | 11 |
| 7 | 24 | 19 |
| 8 | 21 | 21 |
| 9 | 56 | 44 |
| 10 | 15 | 12 |
| 11 | 38 | 25 |
| 12 | 11 | 9 |
| 13 | - | 2 |
| 14 | 21 | 20 |
| 15 | 47 | 37 |
| 16 | 14 | 11 |
| 17 | 25 | 23 |
| **0,12,ℓ** |  |  |
| 0 | 28 | 26 |
| 1 | 22 | 21 |
| 2 | 21 | 15 |
| 3 | 45 | 40 |
| 4 | 28 | 24 |
| 5 | 12 | 10 |
| 6 | - | 0 |
| 7 | 35 | 34 |
| 8 | 18 | 14 |
| 9 | 39 | 30 |
| 10 | 20 | 16 |
| 11 | 35 | 30 |
| 12 | 7 | 8 |
| 13 | 18 | 19 |
| 14 | 9 | 8 |
| **0,13,ℓ** |  |  |
| 1 | 23 | 19 |
| 2 | - | 1 |
| 3 | 17 | 15 |
| 4 | - | 7 |
| 5 | - | 7 |
| 6 | - | 1 |
| 7 | 16 | 12 |
| **10ℓ** |  |  |
| 1 | 90 | 87 |
| 2 | 73 | 25 |
| 3 | 167 | 127 |
| 4 | 50 | 29 |
| 5 | 14 | 1 |
| 6 | 108 | 65 |
| 7 | 45 | 25 |
| 8 | 154 | 119 |
| 9 | 16 | 21 |
| 10 | 38 | 34 |
| 11 | 31 | 43 |
| 12 | 132 | 94 |
| 13 | 31 | 12 |
| 14 | 46 | 49 |
| 15 | 12 | 12 |
| 16 | 29 | 30 |
| 17 | 15 | 18 |
| 18 | 13 | 12 |
| 19 | 12 | 13 |
| 20 | 45 | 45 |
| 21 | 24 | 20 |
| 22 | - | 8 |
| 23 | 21 | 21 |
| 24 | - | 2 |
| 25 | 17 | 21 |
| 26 | 13 | 12 |
| **11ℓ** |  |  |
| 0 | 15 | 16 |
| 1 | 64 | 110 |
| 2 | 112 | 120 |
| 3 | 51 | 42 |
| 4 | 119 | 110 |
| 5 | 87 | 72 |
| 6 | 50 | 26 |
| 7 | 88 | 79 |
| 8 | 55 | 42 |
| 9 | 174 | 139 |
| 10 | 95 | 78 |
| 11 | 95 | 82 |
| 12 | 9 | 9 |
| 13 | 136 | 108 |
| 14 | 22 | 16 |
| 15 | 36 | 46 |
| 16 | 33 | 35 |
| 17 | 21 | 24 |
| 18 | - | 7 |
| 19 | 34 | 29 |
| 20 | 14 | 19 |
| 21 | 24 | 20 |
| 22 | 17 | 17 |
| 23 | 26 | 20 |
| 24 | 20 | 20 |
| 25 | 21 | 16 |
| 26 | 10 | 8 |
| **12ℓ** |  |  |
| 0 | 40 | 36 |
| 1 | 108 | 116 |
| 2 | 54 | 69 |
| 3 | 103 | 78 |
| 4 | 94 | 69 |
| 5 | 46 | 46 |
| 6 | 30 | 36 |
| 7 | 19 | 23 |
| 8 | 66 | 69 |
| 9 | 26 | 19 |
| 10 | 23 | 32 |
| 11 | 39 | 39 |
| 12 | 66 | 56 |
| 13 | 26 | 34 |
| 14 | 30 | 28 |
| 15 | - | 5 |
| 16 | 17 | 14 |
| 17 | 44 | 39 |
| 18 | 48 | 45 |
| 19 | 21 | 15 |
| 20 | 22 | 19 |
| 21 | 27 | 27 |
| 22 | 23 | 21 |
| 23 | - | 8 |
| 24 | 31 | 33 |
| **13ℓ** |  |  |
| 0 | 10 | 10 |
| 1 | 129 | 121 |
| 2 | 75 | 58 |
| 3 | 158 | 139 |
| 4 | 79 | 66 |
| 5 | 42 | 52 |
| 6 | 71 | 41 |
| 7 | 28 | 13 |
| 8 | 85 | 59 |
| 9 | 37 | 47 |
| 10 | 105 | 82 |
| 11 | 34 | 32 |
| 12 | 69 | 66 |
| 13 | - | 4 |
| 14 | 21 | 24 |
| 15 | 26 | 22 |
| 16 | 71 | 63 |
| 17 | 30 | 30 |
| 18 | 22 | 18 |
| 19 | 38 | 32 |
| 20 | 24 | 22 |
| 21 | 12 | 13 |
| 22 | 25 | 18 |
| 23 | 21 | 23 |
| 24 | - | 4 |
| 25 | 15 | 17 |
| 26 | 15 | 12 |
| **14ℓ** |  |  |
| 0 | 86 | 67 |
| 1 | 82 | 64 |
| 2 | 23 | 30 |
| 3 | 53 | 48 |
| 4 | 92 | 60 |
| 5 | 94 | 66 |
| 6 | 39 | 27 |
| 7 | 14 | 17 |
| 8 | 33 | 28 |
| 9 | 122 | 94 |
| 10 | 22 | 16 |
| 11 | 75 | 64 |
| 12 | 19 | 17 |
| 13 | 21 | 16 |
| 14 | - | 8 |
| 15 | 82 | 68 |
| 16 | - | 6 |
| 17 | 39 | 34 |
| 18 | 18 | 13 |
| 19 | 30 | 25 |
| 20 | 20 | 13 |
| 21 | 12 | 14 |
| 22 | 23 | 21 |
| 23 | - | 10 |
| 24 | - | 9 |
| 25 | 23 | 21 |
| **15ℓ** |  |  |
| 0 | 74 | 72 |
| 1 | 100 | 79 |
| 2 | 19 | 3 |
| 3 | 23 | 25 |
| 4 | 31 | 31 |
| 5 | 59 | 51 |
| 6 | 65 | 50 |
| 7 | 53 | 46 |
| 8 | 53 | 43 |
| 9 | 62 | 62 |
| 10 | 38 | 38 |
| 11 | 40 | 45 |
| 12 | 59 | 59 |
| 13 | 78 | 71 |
| 14 | 49 | 51 |
| 15 | 32 | 34 |
| 16 | 35 | 37 |
| 17 | 14 | 16 |
| 18 | 12 | 14 |
| 19 | 24 | 21 |
| 20 | 12 | 9 |
| 21 | 14 | 10 |
| 22 | 25 | 22 |
| 23 | 19 | 17 |
| 24 | 10 | 8 |
| **16ℓ** |  |  |
| 0 | 24 | 20 |
| 1 | 79 | 61 |
| 2 | 40 | 42 |
| 3 | 119 | 96 |
| 4 | 34 | 20 |
| 5 | 11 | 10 |
| 6 | 36 | 20 |
| 7 | 27 | 25 |
| 8 | 15 | 18 |
| 9 | 21 | 27 |
| 10 | 27 | 27 |
| 11 | 21 | 22 |
| 12 | 13 | 9 |
| 13 | 47 | 48 |
| 14 | 36 | 32 |
| 15 | 37 | 31 |
| 16 | 19 | 24 |
| 17 | - | 3 |
| 18 | 17 | 16 |
| 19 | 15 | 18 |
| 20 | - | 9 |
| 21 | 22 | 23 |
| 22 | - | 0 |
| 23 | 19 | 21 |
| 24 | 12 | 11 |
| **17ℓ** |  |  |
| 0 | 54 | 51 |
| 1 | 38 | 35 |
| 2 | 80 | 72 |
| 3 | 51 | 52 |
| 4 | 40 | 37 |
| 5 | 52 | 41 |
| 6 | 63 | 60 |
| 7 | 10 | 4 |
| 8 | 15 | 17 |
| 9 | 49 | 51 |
| 10 | 19 | 15 |
| 11 | 27 | 31 |
| 12 | 18 | 18 |
| 13 | 22 | 20 |
| 14 | - | 4 |
| 15 | 39 | 37 |
| 16 | - | 7 |
| 17 | 29 | 26 |
| 18 | 34 | 31 |
| 19 | 18 | 20 |
| 20 | 14 | 13 |
| 21 | - | 8 |
| 22 | 10 | 13 |
| 23 | 13 | 12 |
| 24 | 14 | 14 |
| **18ℓ** |  |  |
| 0 | 41 | 40 |
| 1 | 62 | 57 |
| 2 | 45 | 44 |
| 3 | 24 | 21 |
| 4 | 23 | 24 |
| 5 | 28 | 26 |
| 6 | 40 | 36 |
| 7 | 29 | 27 |
| 8 | 46 | 45 |
| 9 | 26 | 27 |
| 10 | 11 | 12 |
| 11 | - | 7 |
| 12 | 37 | 33 |
| 13 | 16 | 15 |
| 14 | 21 | 22 |
| 15 | 27 | 25 |
| 16 | - | 4 |
| 17 | - | 6 |
| 18 | 22 | 18 |
| 19 | 22 | 20 |
| 20 | 10 | 9 |
| 21 | 17 | 19 |
| **19ℓ** |  |  |
| 0 | 34 | 26 |
| 1 | 19 | 19 |
| 2 | - | 4 |
| 3 | 21 | 18 |
| 4 | 11 | 12 |
| 5 | 41 | 37 |
| 6 | 33 | 30 |
| 7 | 30 | 29 |
| 8 | 24 | 21 |
| 9 | 27 | 28 |
| 10 | 37 | 29 |
| 11 | 10 | 9 |
| 12 | 39 | 34 |
| 13 | 18 | 19 |
| 14 | 22 | 20 |
| 15 | - | 1 |
| 16 | 10 | 8 |
| 17 | 24 | 20 |
| 18 | - | 8 |
| 19 | - | 8 |
| 20 | - | 5 |
| 21 | - | 7 |
| 22 | 13 | 14 |
| **1,10,ℓ** |  |  |
| 0 | 57 | 48 |
| 1 | 10 | 12 |
| 2 | 31 | 29 |
| 3 | 28 | 27 |
| 4 | 30 | 30 |
| 5 | 10 | 11 |
| 6 | 30 | 25 |
| 7 | 18 | 18 |
| 8 | 15 | 16 |
| 9 | 21 | 17 |
| 10 | 12 | 14 |
| 11 | 23 | 22 |
| 12 | 11 | 11 |
| 13 | 30 | 27 |
| 14 | - | 3 |
| 15 | - | 9 |
| 16 | 15 | 12 |
| 17 | - | 6 |
| 18 | 17 | 18 |
| **1,11,ℓ** |  |  |
| 0 | - | 8 |
| 1 | 22 | 23 |
| 2 | 42 | 42 |
| 3 | 40 | 39 |
| 4 | 11 | 10 |
| 5 | 16 | 14 |
| 6 | 31 | 33 |
| 7 | 13 | 15 |
| 8 | - | 10 |
| 9 | 20 | 18 |
| 10 | 13 | 14 |
| 11 | 15 | 14 |
| 12 | 15 | 14 |
| 13 | 12 | 10 |
| 14 | 15 | 11 |
| 15 | 18 | 14 |
| 16 | - | 8 |
| 17 | 13 | 14 |
| **1,12,ℓ** |  |  |
| 0 | 14 | 14 |
| 1 | 33 | 34 |
| 2 | 27 | 21 |
| 3 | 13 | 11 |
| 4 | 13 | 11 |
| 5 | 36 | 34 |
| 6 | 40 | 36 |
| 7 | - | 8 |
| 8 | - | 6 |
| 9 | - | 7 |
| 10 | 17 | 14 |
| 11 | 11 | 11 |
| 12 | - | 6 |
| 13 | - | 2 |
| 14 | 8 | 12 |
| **1,13,ℓ** |  |  |
| 0 | - | 3 |
| 1 | - | 3 |
| 2 | 20 | 20 |
| 3 | 17 | 18 |
| 4 | 13 | 10 |
| 5 | 11 | 12 |
| 6 | 9 | 11 |
| 7 | 19 | 21 |
| **20ℓ** |  |  |
| 0 | 36 | 32 |
| 1 | 45 | 75 |
| 2 | 20 | 8 |
| 3 | 9 | 5 |
| 4 | 26 | 3 |
| 5 | 105 | 84 |
| 6 | 32 | 21 |
| 7 | 56 | 54 |
| 8 | 88 | 88 |
| 9 | 71 | 69 |
| 10 | 76 | 80 |
| 11 | 21 | 16 |
| 12 | 10 | 2 |
| 13 | 24 | 24 |
| 14 | 64 | 52 |
| 15 | 21 | 23 |
| 16 | 23 | 17 |
| 17 | 31 | 28 |
| 18 | - | 5 |
| 19 | - | 4 |
| 20 | 8 | 8 |
| 21 | 9 | 8 |
| 22 | 30 | 26 |
| 23 | 19 | 19 |
| 24 | - | 1 |
| 25 | - | 1 |
| 26 | 12 | 7 |
| 27 | 24 | 20 |
| **21ℓ** |  |  |
| 0 | 79 | 111 |
| 1 | 51 | 43 |
| 2 | 72 | 92 |
| 3 | 177 | 161 |
| 4 | 41 | 36 |
| 5 | 83 | 82 |
| 6 | 22 | 20 |
| 7 | 7 | 25 |
| 8 | 30 | 31 |
| 9 | 73 | 73 |
| 10 | 22 | 16 |
| 11 | 52 | 52 |
| 12 | 61 | 52 |
| 13 | 27 | 32 |
| 14 | - | 11 |
| 15 | 60 | 52 |
| 16 | 16 | 14 |
| 17 | 34 | 34 |
| 18 | 22 | 19 |
| 19 | 31 | 29 |
| 20 | 22 | 21 |
| 21 | 41 | 40 |
| 22 | - | 8 |
| 23 | 23 | 22 |
| 24 | - | 7 |
| 25 | - | 7 |
| 26 | 13 | 12 |
| 27 | 13 | 13 |
| 28 | 12 | 11 |
| 29 | 6 | 4 |
| **22ℓ** |  |  |
| 0 | 130 | 112 |
| 1 | 135 | 149 |
| 2 | 86 | 76 |
| 3 | 125 | 131 |
| 4 | 72 | 83 |
| 5 | 58 | 42 |
| 6 | 92 | 83 |
| 7 | 7 | 10 |
| 8 | 80 | 87 |
| 9 | 68 | 59 |
| 10 | 63 | 56 |
| 11 | 42 | 51 |
| 12 | 107 | 102 |
| 13 | 24 | 18 |
| 14 | 38 | 41 |
| 15 | 28 | 28 |
| 16 | 20 | 19 |
| 17 | 21 | 21 |
| 18 | - | 8 |
| 19 | 21 | 17 |
| 20 | 27 | 27 |
| 21 | 21 | 19 |
| 22 | 30 | 24 |
| 23 | 32 | 30 |
| 24 | 26 | 22 |
| 25 | 12 | 9 |
| 26 | 14 | 16 |
| 27 | 7 | 8 |
| 28 | 8 | 6 |
| **23ℓ** |  |  |
| 0 | 163 | 163 |
| 1 | 79 | 79 |
| 2 | 70 | 68 |
| 3 | 22 | 27 |
| 4 | 102 | 105 |
| 5 | 44 | 60 |
| 6 | 75 | 73 |
| 7 | 24 | 19 |
| 8 | 44 | 43 |
| 9 | 30 | 29 |
| 10 | 29 | 35 |
| 11 | 29 | 32 |
| 12 | 18 | 10 |
| 13 | 18 | 17 |
| 14 | 36 | 34 |
| 15 | 20 | 18 |
| 16 | 9 | 6 |
| 17 | 17 | 19 |
| 18 | 33 | 34 |
| 19 | 18 | 16 |
| 20 | 19 | 17 |
| 21 | 28 | 23 |
| 22 | 7 | 8 |
| 23 | 28 | 25 |
| 24 | 23 | 22 |
| 25 | 18 | 18 |
| 26 | - | 5 |
| 27 | - | 3 |
| 28 | 5 | 7 |
| **24ℓ** |  |  |
| 0 | 25 | 37 |
| 1 | 32 | 29 |
| 2 | 23 | 24 |
| 3 | 36 | 33 |
| 4 | 80 | 66 |
| 5 | 17 | 22 |
| 6 | 59 | 47 |
| 7 | 36 | 41 |
| 8 | 41 | 46 |
| 9 | 36 | 39 |
| 10 | 30 | 22 |
| 11 | 39 | 38 |
| 12 | 44 | 46 |
| 13 | 34 | 32 |
| 14 | 26 | 27 |
| 15 | 11 | 7 |
| 16 | 30 | 30 |
| 17 | 27 | 26 |
| 18 | 16 | 13 |
| 19 | 17 | 18 |
| 20 | 17 | 17 |
| 21 | 16 | 15 |
| 22 | 14 | 12 |
| 23 | 12 | 9 |
| 24 | 13 | 10 |
| 25 | 10 | 10 |
| 26 | 12 | 10 |
| 27 | 13 | 13 |
| 28 | 7 | 10 |
| **25ℓ** |  |  |
| 0 | 118 | 101 |
| 1 | 23 | 13 |
| 2 | 62 | 51 |
| 3 | 59 | 40 |
| 4 | 77 | 66 |
| 5 | 17 | 17 |
| 6 | 76 | 69 |
| 7 | 20 | 24 |
| 8 | 66 | 55 |
| 9 | 13 | 16 |
| 10 | 8 | 7 |
| 11 | 12 | 12 |
| 12 | 77 | 67 |
| 13 | 20 | 19 |
| 14 | 19 | 21 |
| 15 | 25 | 24 |
| 16 | 32 | 29 |
| 17 | 30 | 29 |
| 18 | 41 | 38 |
| 19 | 22 | 20 |
| 20 | 19 | 15 |
| 21 | 21 | 18 |
| 22 | 10 | 9 |
| 23 | - | 4 |
| 24 | 25 | 25 |
| 25 | 20 | 19 |
| 26 | 15 | 17 |
| **26ℓ** |  |  |
| 0 | 77 | 71 |
| 1 | 30 | 18 |
| 2 | 83 | 74 |
| 3 | 73 | 63 |
| 4 | 69 | 54 |
| 5 | 30 | 26 |
| 6 | 34 | 30 |
| 7 | 40 | 35 |
| 8 | 33 | 29 |
| 9 | 108 | 96 |
| 10 | 14 | 18 |
| 11 | 72 | 54 |
| 12 | 18 | 16 |
| 13 | 33 | 37 |
| 14 | - | 1 |
| 15 | 40 | 45 |
| 16 | 22 | 19 |
| 17 | 25 | 20 |
| 18 | 22 | 21 |
| 19 | 27 | 23 |
| 20 | 29 | 31 |
| 21 | - | 5 |
| 22 | - | 8 |
| 23 | 20 | 16 |
| 24 | 26 | 22 |
| 25 | 17 | 14 |
| 26 | 9 | 11 |
| **27ℓ** |  |  |
| 0 | 35 | 44 |
| 1 | 43 | 46 |
| 2 | 18 | 23 |
| 3 | 33 | 24 |
| 4 | 31 | 31 |
| 5 | 60 | 55 |
| 6 | 22 | 17 |
| 7 | 35 | 28 |
| 8 | 18 | 18 |
| 9 | 13 | 10 |
| 10 | 24 | 23 |
| 11 | 25 | 18 |
| 12 | 26 | 21 |
| 13 | 22 | 17 |
| 14 | 27 | 27 |
| 15 | 25 | 21 |
| 16 | 11 | 9 |
| 17 | 26 | 22 |
| 18 | 16 | 17 |
| 19 | 20 | 20 |
| 20 | 22 | 18 |
| 21 | 46 | 14 |
| 22 | 21 | 16 |
| 23 | - | 4 |
| 24 | 10 | 11 |
| 25 | 10 | 13 |
| **28ℓ** |  |  |
| 0 | 18 | 15 |
| 1 | 34 | 32 |
| 2 | 15 | 15 |
| 3 | 27 | 28 |
| 4 | 20 | 24 |
| 5 | 34 | 34 |
| 6 | 32 | 29 |
| 7 | 22 | 20 |
| 8 | 34 | 23 |
| 9 | 37 | 35 |
| 10 | 35 | 33 |
| 11 | 9 | 16 |
| 12 | 19 | 17 |
| 13 | - | 3 |
| 14 | 24 | 18 |
| 15 | 18 | 17 |
| 16 | 28 | 29 |
| 17 | 16 | 15 |
| 18 | 29 | 27 |
| 19 | 6 | 6 |
| 20 | 16 | 15 |
| 21 | 11 | 13 |
| 22 | 9 | 11 |
| **29ℓ** |  |  |
| 0 | 46 | 50 |
| 1 | 36 | 30 |
| 2 | 25 | 23 |
| 3 | 41 | 38 |
| 4 | 47 | 43 |
| 5 | 52 | 51 |
| 6 | 11 | 12 |
| 7 | 20 | 19 |
| 8 | - | 5 |
| 9 | 43 | 36 |
| 10 | 23 | 20 |
| 11 | 18 | 16 |
| 12 | - | 2 |
| 13 | - | 6 |
| 14 | 22 | 21 |
| 15 | 36 | 34 |
| 16 | 7 | 5 |
| 17 | 8 | 12 |
| 18 | 19 | 16 |
| 19 | 12 | 11 |
| 20 | 14 | 12 |
| **2,10,ℓ** |  |  |
| 0 | 30 | 33 |
| 1 | 24 | 24 |
| 2 | 14 | 14 |
| 3 | 45 | 41 |
| 4 | 10 | 14 |
| 5 | 13 | 14 |
| 6 | 29 | 28 |
| 7 | - | 4 |
| 8 | 35 | 33 |
| 9 | 33 | 30 |
| 10 | 34 | 33 |
| 11 | 13 | 11 |
| 12 | 34 | 36 |
| 13 | 7 | 8 |
| 14 | 30 | 27 |
| 15 | 6 | 2 |
| 16 | 13 | 12 |
| 17 | 10 | 11 |
| 18 | 4 | 4 |
| 19 | 11 | 10 |
| 20 | 9 | 11 |
| **2,11,ℓ** |  |  |
| 0 | 15 | 18 |
| 1 | 11 | 12 |
| 2 | 21 | 21 |
| 3 | 7 | 9 |
| 4 | 29 | 27 |
| 5 | 6 | 7 |
| 6 | 27 | 23 |
| 7 | 12 | 10 |
| 8 | 12 | 15 |
| 9 | - | 4 |
| 10 | 22 | 22 |
| 11 | - | 6 |
| 12 | 11 | 9 |
| 13 | 8 | 5 |
| 14 | 21 | 19 |
| 15 | - | 4 |
| 16 | 11 | 11 |
| 17 | 4 | 6 |
| **2,12,ℓ** |  |  |
| 0 | 11 | 12 |
| 1 | 13 | 12 |
| 2 | 36 | 36 |
| 3 | 8 | 7 |
| 4 | 10 | 10 |
| 5 | 14 | 13 |
| 6 | 35 | 35 |
| 7 | 12 | 13 |
| 8 | 5 | 4 |
| 9 | - | 3 |
| 10 | 7 | 12 |
| 11 | - | 3 |
| 12 | 7 | 7 |
| 13 | 11 | 13 |
| 14 | 9 | 18 |
| **2,13,ℓ** |  |  |
| 0 | - | 5 |
| 1 | 10 | 13 |
| 2 | 8 | 10 |
| 3 | 24 | 25 |
| 4 | - | 5 |
| 5 | 16 | 16 |
| 6 | 21 | 22 |
| 7 | 10 | 11 |
| 8 | 9 | 16 |
| **30ℓ** |  |  |
| 1 | - | 5 |
| 2 | 75 | 90 |
| 3 | - | 6 |
| 4 | 70 | 71 |
| 5 | 90 | 62 |
| 6 | 75 | 38 |
| 7 | 78 | 66 |
| 8 | 34 | 15 |
| 9 | 16 | 17 |
| 10 | 61 | 46 |
| 11 | 53 | 42 |
| 12 | 61 | 49 |
| 13 | 33 | 32 |
| 14 | - | 1 |
| 15 | 21 | 23 |
| 16 | - | 1 |
| 17 | - | 9 |
| 18 | 33 | 35 |
| 19 | 15 | 15 |
| 20 | - | 8 |
| 21 | 25 | 21 |
| 22 | 50 | 46 |
| 23 | 10 | 11 |
| 24 | 20 | 21 |
| 25 | - | 3 |
| 26 | - | 5 |
| 27 | - | 7 |
| 28 | 12 | 17 |
| **31ℓ** |  |  |
| 0 | 209 | 186 |
| 1 | 146 | 141 |
| 2 | 80 | 60 |
| 3 | 127 | 105 |
| 4 | 73 | 56 |
| 5 | 5 | 23 |
| 6 | 44 | 34 |
| 7 | 73 | 62 |
| 8 | 23 | 19 |
| 9 | 25 | 21 |
| 10 | 41 | 36 |
| 11 | 33 | 41 |
| 12 | 37 | 36 |
| 13 | 31 | 24 |
| 14 | - | 7 |
| 15 | 20 | 23 |
| 16 | - | 4 |
| 17 | - | 12 |
| 18 | 33 | 30 |
| 19 | 22 | 25 |
| 20 | 17 | 25 |
| 21 | 36 | 33 |
| 22 | 18 | 19 |
| 23 | 18 | 20 |
| 24 | 20 | 24 |
| 25 | - | 8 |
| 26 | - | 3 |
| 27 | 11 | 16 |
| **32ℓ** |  |  |
| 0 | 125 | 106 |
| 1 | 70 | 43 |
| 2 | 50 | 55 |
| 3 | 91 | 76 |
| 4 | 81 | 66 |
| 5 | 107 | 88 |
| 6 | 87 | 63 |
| 7 | 65 | 42 |
| 8 | 139 | 101 |
| 9 | 69 | 57 |
| 10 | 51 | 49 |
| 11 | 68 | 63 |
| 12 | 46 | 46 |
| 13 | 66 | 60 |
| 14 | 48 | 51 |
| 15 | 37 | 31 |
| 16 | 67 | 56 |
| 17 | 11 | 19 |
| 18 | 32 | 31 |
| 19 | 19 | 16 |
| 20 | 10 | 9 |
| 21 | - | 8 |
| 22 | - | 6 |
| 23 | 10 | 17 |
| 24 | 15 | 15 |
| 25 | - | 4 |
| 26 | - | 13 |
| 27 | 13 | 15 |
| **33ℓ** |  |  |
| 0 | 83 | 69 |
| 1 | 79 | 74 |
| 2 | 64 | 47 |
| 3 | 99 | 57 |
| 4 | 82 | 51 |
| 5 | 68 | 42 |
| 6 | 108 | 68 |
| 7 | 69 | 54 |
| 8 | 23 | 22 |
| 9 | 41 | 35 |
| 10 | 41 | 46 |
| 11 | 45 | 40 |
| 12 | 16 | 18 |
| 13 | 23 | 17 |
| 14 | 43 | 37 |
| 15 | - | 8 |
| 16 | 18 | 16 |
| 17 | 31 | 31 |
| 18 | - | 10 |
| 19 | - | 13 |
| 20 | - | 12 |
| 21 | 11 | 22 |
| 22 | - | 11 |
| 23 | - | 10 |
| 24 | - | 10 |
| 25 | 8 | 14 |
| 26 | 8 | 17 |
| 27 | 15 | 19 |
| **34ℓ** |  |  |
| 0 | 28 | 44 |
| 1 | 73 | 72 |
| 2 | 27 | 31 |
| 3 | 37 | 31 |
| 4 | 38 | 32 |
| 5 | 48 | 50 |
| 6 | 35 | 31 |
| 7 | 48 | 44 |
| 8 | 41 | 41 |
| 9 | 38 | 28 |
| 10 | 50 | 42 |
| 11 | 9 | 11 |
| 12 | 70 | 61 |
| 13 | 58 | 51 |
| 14 | 27 | 21 |
| 15 | - | 1 |
| 16 | 33 | 32 |
| 17 | 30 | 28 |
| 18 | - | 10 |
| 19 | 29 | 22 |
| 20 | - | 13 |
| 21 | 30 | 32 |
| 22 | 28 | 31 |
| 23 | 13 | 15 |
| 24 | - | 8 |
| 25 | 16 | 18 |
| 26 | 6 | 10 |
| 27 | 8 | 17 |
| **35ℓ** |  |  |
| 0 | 200 | 163 |
| 1 | 65 | 49 |
| 2 | 42 | 37 |
| 3 | 78 | 58 |
| 4 | 90 | 71 |
| 5 | - | 8 |
| 6 | 55 | 52 |
| 7 | 40 | 33 |
| 8 | - | 8 |
| 9 | - | 7 |
| 10 | 35 | 27 |
| 11 | - | 13 |
| 12 | 37 | 28 |
| 13 | - | 6 |
| 14 | 15 | 17 |
| 15 | 16 | 11 |
| 16 | - | 12 |
| 17 | 22 | 25 |
| 18 | 26 | 20 |
| 19 | - | 10 |
| 20 | 36 | 38 |
| 21 | 9 | 15 |
| 22 | 9 | 13 |
| 23 | - | 5 |
| 24 | 28 | 28 |
| 25 | 7 | 9 |
| 26 | 10 | 14 |
| **36ℓ** |  |  |
| 0 | - | 2 |
| 1 | 45 | 33 |
| 2 | 61 | 47 |
| 3 | 42 | 40 |
| 4 | 59 | 48 |
| 5 | 70 | 58 |
| 6 | 66 | 51 |
| 7 | 22 | 17 |
| 8 | 86 | 64 |
| 9 | 71 | 56 |
| 10 | 22 | 14 |
| 11 | 38 | 30 |
| 12 | 47 | 41 |
| 13 | - | 4 |
| 14 | 30 | 25 |
| 15 | 47 | 41 |
| 16 | - | 12 |
| 17 | 34 | 24 |
| 18 | 16 | 22 |
| 19 | - | 8 |
| 20 | - | 7 |
| 21 | 15 | 22 |
| **37ℓ** |  |  |
| 0 | 66 | 52 |
| 1 | 52 | 38 |
| 2 | 18 | 13 |
| 3 | 36 | 28 |
| 4 | 30 | 26 |
| 5 | 46 | 37 |
| 6 | 17 | 16 |
| 7 | 30 | 31 |
| 8 | 31 | 27 |
| 9 | 53 | 50 |
| 10 | 15 | 9 |
| 11 | 50 | 41 |
| 12 | - | 12 |
| 13 | 34 | 31 |
| 14 | - | 1 |
| 15 | 26 | 22 |
| 16 | 30 | 24 |
| 17 | 37 | 31 |
| 18 | 32 | 26 |
| 19 | 14 | 9 |
| 20 | - | 6 |
| 21 | - | 12 |

correct choice and also to assist, if possible, in the extraction of the S and Cl positions from the vector maps. The S atoms were located with reasonable certainty in this manner and, moreover, the $\Delta\varrho$ distribution confirmed clearly the deficiency of the $CH_2Br_2$, indicating a content of only 65% in the crystal used for the analysis, the effective *Z* being then 23. However, the Cl position remained indeterminate and a three-dimensional Fourier synthesis was calculated with phase angles based on the contributions of two 0·65 Br and two S atoms. Although the agreement for this set was only moderate ($R=0{\cdot}45$) it was possible to locate in the distribution what was most probably the Cl atom (the peak height in this first $\varrho_0(x, y, z)$ corresponded only to 0·25 of that expected for a Cl atom). With the aid of $\varrho_0$ and $\Delta\varrho$ projections down the *a* and *b* axes (signed with $2\times0{\cdot}65$ Br+2S+Cl), the locations of about 12 atoms were extracted also from the first $\varrho_0(x, y, z)$.

The second three-dimensional distribution was calculated with phases determined by the contributions of ($2\times0{\cdot}65$ Br+2S+Cl) and from this distribution (with back-reference to the first three-dimensional distribution), and *a*- and *b*-axis $\varrho_0$ and $\Delta\varrho$ projections, signed with progressively increasing number of light atoms (assumed provisionally as carbon), the molecular skeleton was gradually extracted and built up on a ball-on-spike model with due regard to stereochemical detail. The stereochemistry and bond length considerations and also the gradual improvement of the $\varrho_0$ and $\Delta\varrho$ projections allowed the light atoms to be differentiated into C, N and O and in this way 28 light atoms could be fitted in the skeletal model with reasonable certainty (the agreement for the *h*0*l* and 0*kl* projections improving to $R=0{\cdot}28$ and 0·23) except for one atom site which was less well-defined in the electron density distributions. With this dubious atom placed as end-carbon in an *N*-ethyl group, the provisional structure was communicated to the New Zealand team, who raised doubt as to the existence of an *N*-ethyl group on the basis of their nuclear magnetic resonance data. In view of this objection, the existing data were reexamined more closely revealing an alternative location for the atom more satisfactory in respect of packing considerations, changing it from the *N*-ethyl end-position to a *C*-methyl group (*cf.* Fridrichsons & Mathieson, (1962*a*). The correctness of this allocation was evident from the next two-dimensional projections and the three-dimensional structure factors improved to $R=0{\cdot}22$. The composite electron-density map of the resultant Fourier synthesis from sections through atom centres projected down [100] is shown in Fig. 1 with a superimposed diagram of the molecule.

The molecular structure and stereochemical composition being thus established, the analysis was refined by full-matrix least-squares calculations. The first cycle with atomic parameters and individual isotropic temperature factors as variables reduced *R* to 0·20 and the next two cycles, with anisotropic temperature factors for Br, S and Cl and then for N and O, improved it further to 0·162 (0·144)[*] (Table 1).

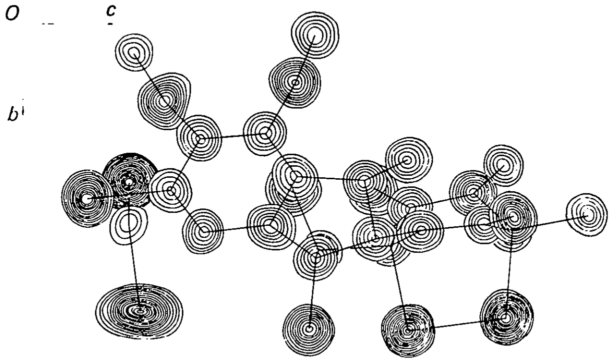


Fig. 1. Electron-density map of the structure, composed of sections through atomic centres parallel to plane *c*.

Table 2. *Atomic parameters*

| Atom | *x*/*a* | *y*/*b* | *z*/*c* | Atom | *x*/*a* | *y*/*b* | *z*/*c* |
|---|---|---|---|---|---|---|---|
| Br(1) | 0·250 | 0·309 | 0·096 | C(3) | 0·745 | 0·423 | 0·323 |
| Br(2) | 0·409 | 0·567 | 0·106 | C(4) | 0·503 | 0·441 | 0·331 |
| C(19) | 0·423 | 0·387 | 0·097 | C(5) | 0·375 | 0·358 | 0·350 |
| S(1) | 0·436 | 0·578 | 0·440 | C(6) | 0·541 | 0·442 | 0·266 |
| S(2) | 0·429 | 0·601 | 0·351 | C(7) | 0·688 | 0·468 | 0·264 |
| Cl | 0·859 | 0·344 | 0·057 | C(8) | 0·763 | 0·398 | 0·224 |
| O(1) | 0·724 | 0·384 | 0·446 | C(9) | 0·832 | 0·300 | 0·250 |
| O(2) | 0·282 | 0·319 | 0·316 | C(10) | 0·915 | 0·214 | 0·218 |
| O(3) | 0·511 | 0·319 | 0·242 | C(11) | 0·925 | 0·232 | 0·159 |
| O(4) | 0·701 | 0·603 | 0·259 | C(12) | 0·852 | 0·325 | 0·132 |
| O(5) | 0·979 | 0·118 | 0·244 | C(13) | 0·767 | 0·412 | 0·163 |
| O(6) | 1·005 | 0·153 | 0·127 | C(14) | 0·257 | 0·267 | 0·433 |
| N(1) | 0·374 | 0·333 | 0·406 | C(15) | 0·479 | 0·368 | 0·504 |
| N(2) | 0·619 | 0·406 | 0·359 | C(16) | 0·929 | 0·266 | 0·348 |
| N(3) | 0·813 | 0·302 | 0·310 | C(17) | 0·893 | 0·021 | 0·265 |
| C(1) | 0·482 | 0·403 | 0·442 | C(18) | 0·936 | 0·056 | 0·094 |
| C(2) | 0·621 | 0·393 | 0·418 | | | | |

---

[*] The value 0·162 corresponds to the weighting of the $F_o$ and $F_c$ values used in the least-squares refinement. The weighting scheme used is aimed at producing best values of atomic and thermal parameters (which are more sensitive in high $\sin\theta$ regions). On the other hand the scale value, $kF_o=F_c$, is largely independent of atomic and thermal parameters on the low $\sin\theta$ region but very sensitively coupled to these in high $\sin\theta$ regions. So far as scale is concerned, the $F_o$ and $F_c$ values were therefore brought to a common scale with respect to low angle terms and the resulting *R* was then 0·144.

At this stage it was decided, partly because of the location of the computer and because it had not the scope to refine all variables simultaneously, that the refinement had proceeded far enough to establish the correctness of the structure, the determination of which was the main object of this work, and the analysis was terminated, although further refinement which would lead to more precise thermal parameters with small improvements in atomic positions is still possible.

The atomic parameters resulting from the last least-squares cycle are given in Table 2 with the corresponding bond lengths and bond angles in Table 3, and also in Fig. 2. Although the values do not pretend to a high degree of accuracy the deviations of some of the bonds from normal values seem to be real and caused by sterical strains in the rather asymmetric structure.

## Discussion

The analysis was initiated and carried to the penultimate stage without reference to chemical evidence on the structure (even the empirical formula being not quite definite). Apart from the guiding comment by our New Zealand colleagues regarding the non-existence of the ethyl group proposed at the penultimate stage, the structure represented in Fig. 3 was based solely on the X-ray diffraction data, with critical assessment of bond-length limitations, bond angles and evident planarity of certain atom groups.

Difficulties in the first stages of the analysis were caused by the reduction of the effective scattering power of the Br atoms, resulting in the lack of definition in the vector maps and also by the coincidental

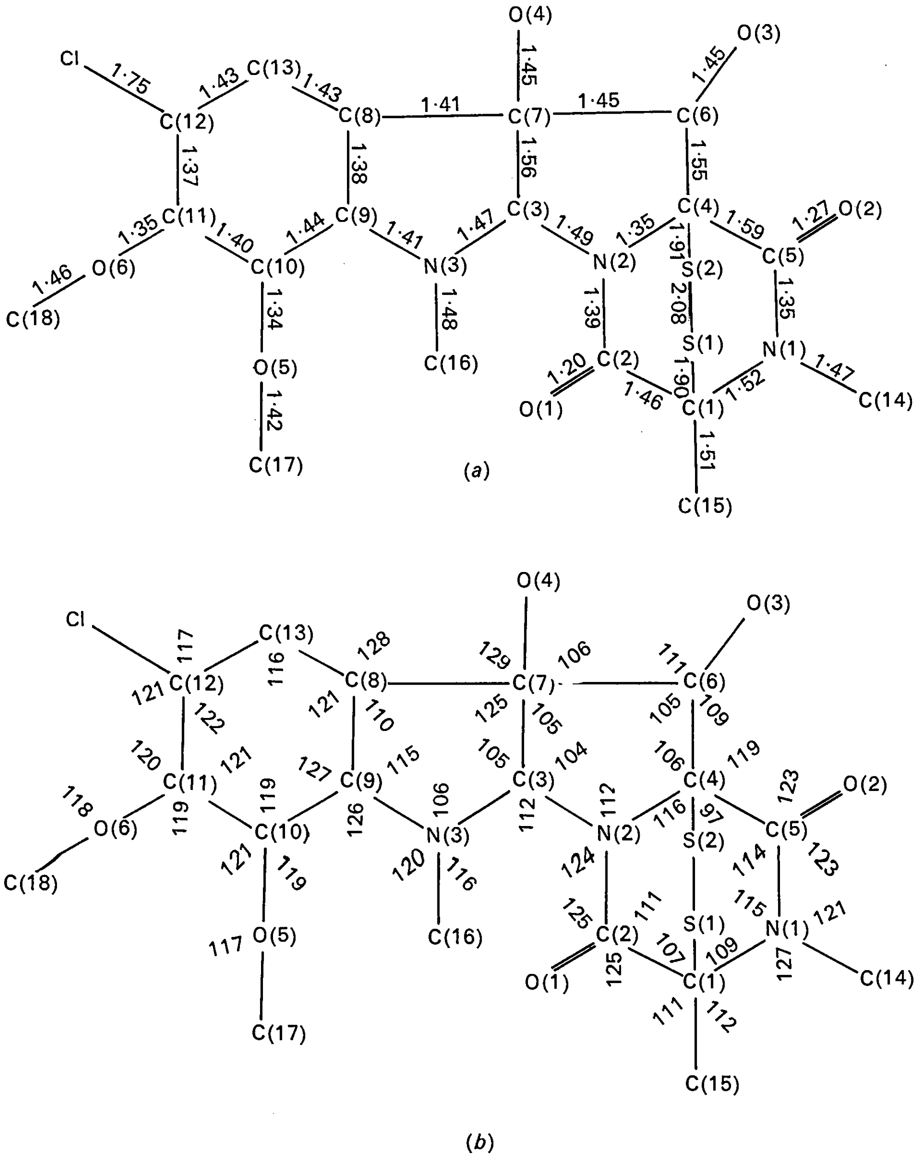


Fig. 2. (*a*) Bond lengths. (*b*) Bond angles.

closeness of Br $z$ parameters introducing ambiguity in the choice of the heavy-atom positions. Once these difficulties were resolved, the analysis proceeded normally and the S and Cl atoms also assisted in the deduction of the molecular skeleton. It is to be noted that in the first 3-D distribution (phased with $2 \times 0{\cdot}65$ Br+2S) the Cl peak only appeared at 25% of its final value, which could not be regarded as highly decisive. The low value may have been due to the near-symmetry of the group 2Br+2S (Fig. 9) and provides further evidence of difficulties of deciding which peaks are real and which artifact (*e.g.* Fridrichsons, Mathieson & Sutor, 1963).

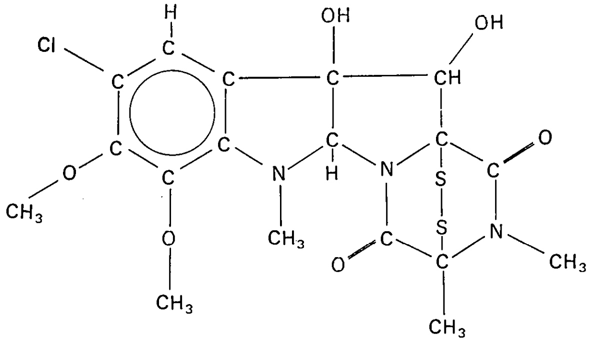


Fig. 3. Structural formula of sporidesmin.

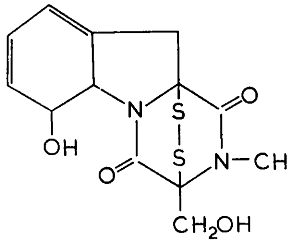


Fig. 4. Proposed structural formula of gliotoxin.

The distance between the two S atoms being just over 2 Å, it was clear that they formed a disulphide group and the vicinity of two planar groups of four atoms led to the recognition of a bicyclic ring system, which after differentiation of the constituent atoms proved to be formed of a diketopiperazine ring system, bridged by the disulphide link. The chlorine atom, linked to another planar group of atoms revealed the other end of the molecule, consisting of a benzene ring with two adjacent methoxy groups. The bicyclic ring system and the substituted benzene ring are joined by two linked five-membered rings of pyrrolidine type and the remaining atoms form two hydroxyl, two *N*-methyl and one *C*-methyl side group. From this skeleton, after identification of atom and bond types, the location and correct number of hydrogen atoms could also be deduced, establishing for the compound the formula $C_{18}H_{20}O_6N_3S_2Cl$.

The chemical evidence subsequently published (Hodges, Ronaldson, Taylor & White, 1963*a*, *b*, *c*; Hodges, Ronaldson, Shannon, Taylor & White, 1963) interpreted in accord with the structure derived by the X-ray method, is in agreement in regard to nuclear magnetic resonance spectra and analytical and synthetic results so far obtained.

On inspection of the skeletal structure of sporidesmin some close similarities between it and the structure proposed for gliotoxin (Fig. 4) — $C_{13}H_{14}O_4N_2S_2$ (Bell, Johnson, Wyldi & Woodward, 1958) — were immediately apparent. The cage-like ring system, apart from the end-carbon side group, is identical in both compounds, even to the extent of the linked pyrrolidine ring. The six-membered ring is also present in both

Table 3

(*a*) Bond lengths (Å)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C(1)C(2) | 1·46 | N(1)C(14) | 1·47 | C(7)O(4) | 1·45 | C(12)C(13) | 1·43 |
| C(1)N(1) | 1·52 | C(1)S(1) | 1·90 | N(3)C(16) | 1·48 | C(13)C(8) | 1·43 |
| N(2)C(2) | 1·39 | S(1)S(2) | 2·08 | N(3)C(3) | 1·47 | C(10)O(5) | 1·34 |
| N(2)C(4) | 1·35 | S(2)C(4) | 1·91 | N(3)C(9) | 1·41 | O(5)C(17) | 1·42 |
| C(4)C(5) | 1·59 | C(4)C(6) | 1·55 | C(8)C(9) | 1·38 | C(11)O(6) | 1·35 |
| C(5)N(1) | 1·35 | C(6)C(7) | 1·45 | C(8)C(7) | 1·41 | O(6)C(18) | 1·46 |
| C(2)O(1) | 1·20 | C(3)N(2) | 1·49 | C(9)C(10) | 1·44 | C(12)Cl | 1·75 |
| C(5)O(2) | 1·27 | C(7)C(3) | 1·56 | C(10)C(11) | 1·40 | Br(1)C(19) | 1·87 |
| C(1)C(15) | 1·51 | C(6)O(3) | 1·45 | C(11)C(12) | 1·37 | C(19)Br(2) | 1·93 |

(*b*) Bond angles

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| N(1)C(1)C(2) | 114·0° | C(4)N(2)C(2) | 121·7° | C(6)C(7)C(3) | 105·0° | C(8)C(13)C(12) | 116·5° |
| N(1)C(1)S(1) | 109·3 | C(3)N(2)C(4) | 112·0 | C(6)C(7)O(4) | 106·2 | C(13)C(12)C(11) | 122·0 |
| C(2)C(1)S(1) | 106·9 | C(3)N(2)C(2) | 124·1 | O(4)C(7)C(8) | 129·2 | C(13)C(12)Cl | 117·3 |
| C(15)C(1)S(1) | 105·3 | C(5)C(4)N(2) | 110·5 | C(8)C(7)C(3) | 124·9 | C(11)C(12)Cl | 121·1 |
| C(15)C(1)N(1) | 112·3 | C(5)C(4)C(6) | 118·5 | O(4)C(7)C(3) | 110·8 | C(12)C(11)C(10) | 121·1 |
| C(15)C(1)C(2) | 110·7 | C(6)C(4)N(2) | 106·5 | C(8)C(7)C(6) | 129·0 | C(12)C(11)O(6) | 119·7 |
| C(1)C(2)N(2) | 111·0 | C(5)C(4)S(2) | 97·0 | C(7)C(8)C(9) | 110·0 | C(10)C(11)O(6) | 119·3 |
| N(2)C(2)O(1) | 124·7 | N(2)C(4)S(2) | 115·9 | C(7)C(8)C(13) | 128·5 | C(11)C(10)C(9) | 119·2 |
| C(1)C(2)O(1) | 125·4 | C(6)C(4)S(2) | 109·0 | C(9)C(8)C(13) | 121·1 | C(11)C(10)O(5) | 121·5 |
| C(1)N(1)C(5) | 115·1 | C(7)C(6)C(4) | 105·3 | C(8)C(9)N(3) | 114·8 | C(9)C(10)O(5) | 119·3 |
| C(1)N(1)C(14) | 127·4 | C(7)C(6)O(3) | 110·5 | C(8)C(9)C(10) | 127·4 | C(10)O(5)C(17) | 116·7 |
| C(5)N(1)C(14) | 121·1 | C(4)C(6)O(3) | 109·3 | C(10)C(9)N(3) | 125·9 | C(11)O(6)C(18) | 117·8 |
| N(1)C(5)C(4) | 113·5 | N(2)C(3)N(3) | 112·3 | C(9)N(3)C(3) | 105·9 | C(1)S(1)S(2) | 98·7 |
| N(1)C(5)O(2) | 122·8 | N(2)C(3)C(7) | 104·0 | C(9)N(3)C(16) | 119·6 | C(4)S(2)S(1) | 97·3 |
| C(4)C(5)O(2) | 123·2 | N(3)C(3)C(7) | 104·6 | C(3)N(3)C(16) | 116·4 | Br(1)C(19)Br(2) | 112·0 |

compounds and, on the whole, disregarding the side-groups (and chlorine), the molecular skeletons differ only by the additional pyrrolidine ring in sporidesmin and the nature of the six-membered ring. The lack of the expected basic properties in both substances is also notable. In view of this, a closer parallel investigation of the biological characteristics of both compounds would be of interest as it might lead to the recognition of the functional groups responsible for their toxic and antibiotic properties. An X-ray analysis of gliotoxin is currently being undertaken.

A feature of possible crystallographic interest disclosed in the course of this analysis is the large thermal anisotropy of one Br atom, even at a temperature of −150 °C. The considerable contraction of the *c* dimension (0·52 Å) on cooling from room temperature to −150 °C, larger than is to be expected for normal thermal contraction, with the simultaneous slight *expansion* in the other two directions (0·04 and 0·05 Å) leads to the suggestion that the $CH_2Br_2$ group at room temperature occupies a different position (or more correctly orientation). Support for this is lent by the markedly different intensity distribution in the room temperature patterns, even in the low-$\theta$ range. Subsequent more detailed examination of this change was prevented by failure to obtain further supplies of this particular crystalline form of the compound; the new supply by Dr White proving to be a different polymorph. For the same reason, the intended determination of the absolute configuration of the structure could not be carried out.

### Conformation and configuration

The general sterical aspects of the structure can be seen in Figs. 5 and 6, the latter representing the sterical disposition of one molecule viewed down the *c* axis. In the ring system *A* the diketopiperazine type ring is forced out of its normal planar shape (Corey, 1938; Vainshtein, 1955) by the disulphide bridge C(1)S(1)S(2) C(4) and assumes the 'boat' form, the dihedral angles C(4)C(1)S(1)/C(4)C(1)N(1) and C(4)C(1)S(1)/C(4)C(1) C(2) being 113° and 114°. Because of the fusion to the five membered ring *B*, the planarity of the group C(1)C(2)N(2)C(4) is slightly distorted, N(2) being twisted out of the plane C(4)C(1)C(2) by 0·09 Å (4·3°) with a corresponding shift of C(5) out of plane C(4) C(1)N(1) by 0·11 Å (4·4°). The configuration of ring system *A*, as seen along the line C(1)C(4) is shown in Fig. 7, the linked five-membered ring being indicated by dashed lines. One unexpected feature of this configuration is the deviation of S(2) from the plane C(1)C(4)S(1) by 0·25 Å (1·5°) in direction opposite to that to be expected from the displacements of N(2) and C(5). A possible explanation of this could be sterical hindrance from the hydroxyl oxygen atom O(4). In the present structure the intramolecular distance O(4)S(2) is 3·40 Å and would be too short with S(2) in planar disposition or twisted correspondingly with N(2) and C(5).

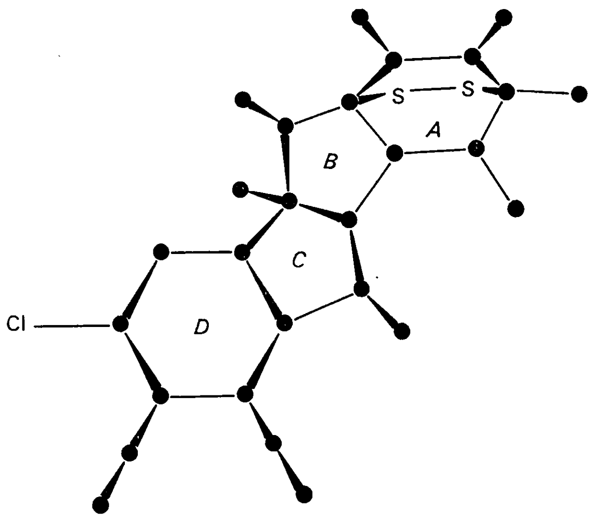


Fig. 5. Sterical diagram of sporidesmin molecule.

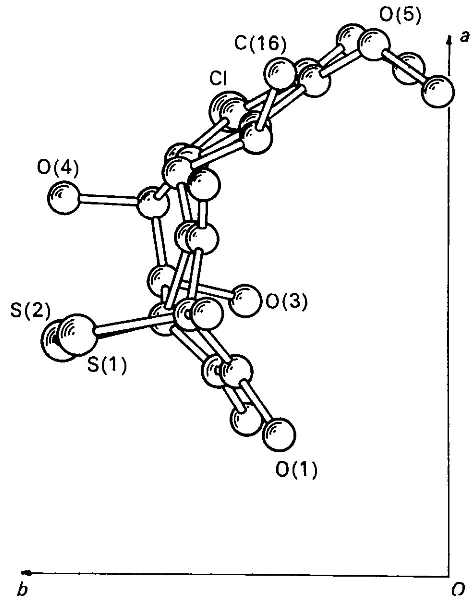


Fig. 6. View of the molecule down the *c* axis.

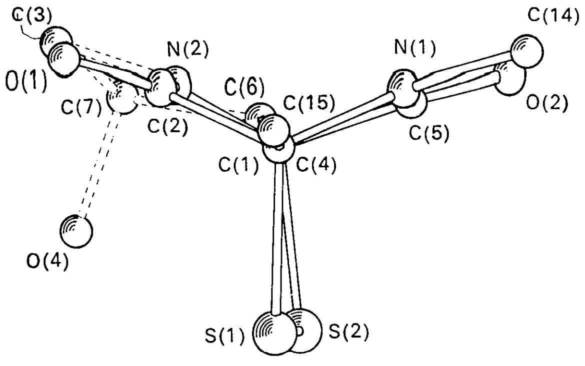


Fig. 7. Configuration of cage structure viewed along line C(1)C(4).

The observed S–S distance (2·08 Å) is longer than reported in non-cyclic disulphides (*e.g.* 2·04 Å in formamidinium disulphide ion — Foss, Johnsen & Tverdten, 1958) but agrees well with values found in five-membered cyclic disulphides (*e.g.* in thiuret hydroiodide and dithiolanecarboxylic acid, 2·09 and 2·10, Foss & Tjmosland, 1958*a*, *b*). The mean value of the angles SSC (98°), as could be expected, is intermediate between the angles found in non-cyclic disulphides (dimethyl disulphide, 107°, Stevenson & Beach, 1938; bistrifluoromethyl disulphide, 105°, Bowen, 1954; formamidinium disulphide ion, 104°, Foss *et al.*, 1958) and those in five-membered cyclic disulphides (*e.g.* 92° in thiuret disulphide ion).

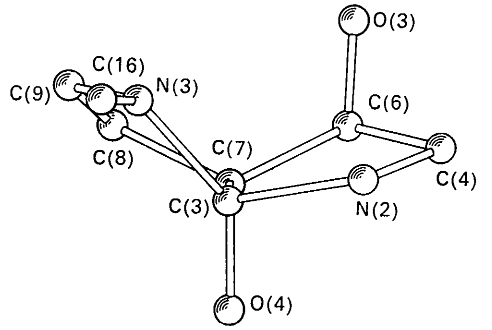


Fig. 8. Configuration of the two five-membered rings viewed nearly along line C(3)C(7).

The keto-oxygen atoms O(1) and O(2) are slightly out of the respective planes C(1)C(4)C(2) and C(1)C(4)C(5) (by 0·15 Å and 0·08 Å) and the short distance between O(2) and O(3) (2·82 Å) indicates an internal hydrogen bond.

The sterical configuration in the two fused five-membered rings *B* and *C*, viewed nearly along the common bond C(3)C(7), is shown in Fig. 8. In ring *B* the group N(2)C(4)C(3)C(7) is approximately planar; C(6) deviates from this mean plane by *ca.* 0·3 Å and the hyd-

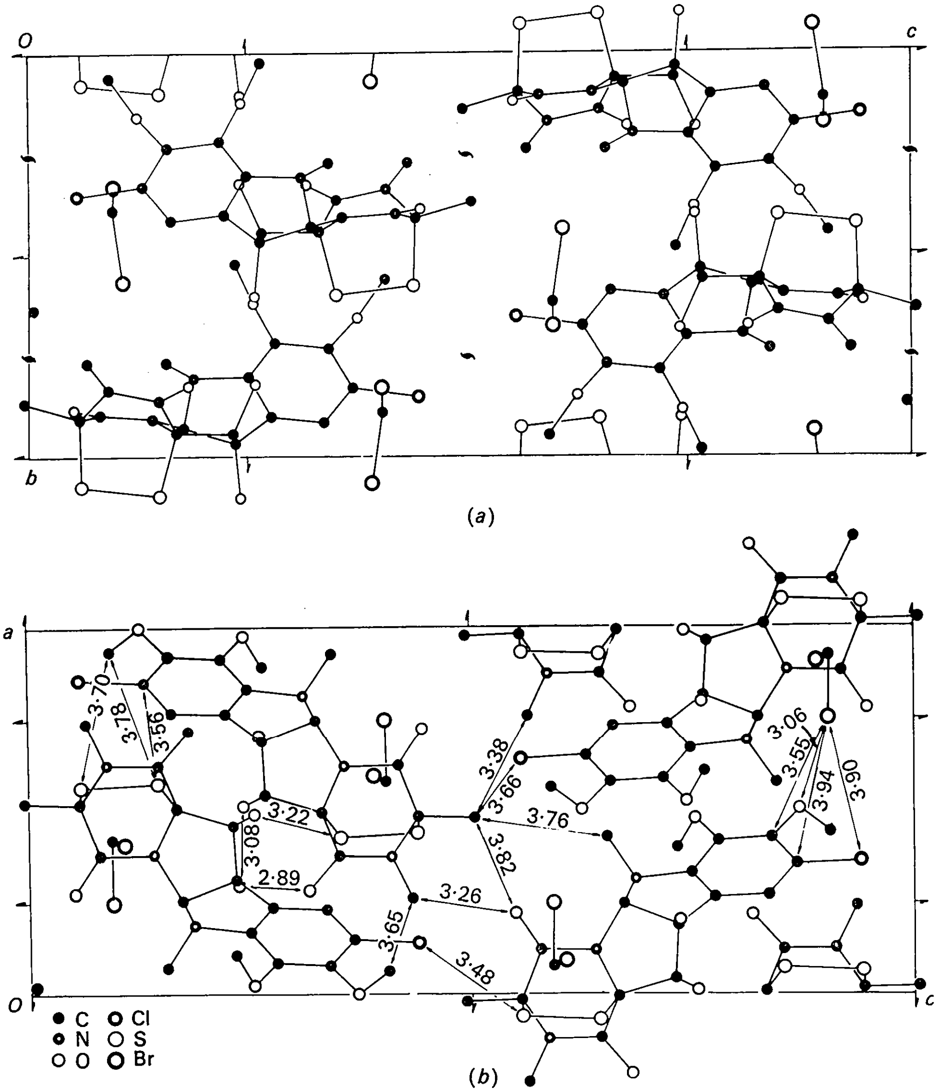


Fig. 9. (*a*) and (*b*) Packing of molecules in one unit cell.

Table 4. *Closest approach distances of adjacent molecules*

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O(4)O(2′) | 2·89 Å | C(14)O(1′) | 3·26 Å | Br(1)C(11′) | 3·55 Å | C(15)C(16′) | 3·76 Å |
| O(4)O(3′) | 3·08 | C(14)C(15′) | 3·38 | C(14)C(18′) | 3·65 | C(15)O(1′) | 3·82 |
| Br(1)O(6′) | 3·06 | S(1)Cl′ | 3·48 | C(15)Cl′ | 3·66 | Br(1)Cl′ | 3·90 |
| O(5)O(4′) | 3·09 | Br(2)C(2′) | 3·52 | C(18)S(1′) | 3·70 | Br(1)C(12′) | 3·94 |
| O(3)S(2′) | 3·22 | S(2)C(12′) | 3·56 | C(18)S(2′) | 3·78 | S(1)Cl′ | 4·01 |

roxyl oxygen atoms O(3) and O(4) are in *trans* positions. In ring *C*, because of fusion to the planar aromatic ring *D*, the nearly planar group is N(3)C(9)C(8) C(7) with C(3) out of the plane by *ca.* 0·3 Å and O(4) and C(16) in *cis* positions.

The six-membered ring *D* is planar, the deviation from the mean plane not exceeding 0·025 Å for the ring carbons. The linked Cl, O(5) and O(6) atoms deviate from the ring plane by 0·09, 0·07 and −0·05 Å respectively. The planes of the methoxyl groups C(10) O(5)C(17) and C(11)O(6)C(18) form with the plane of the ring angles of 71° and 69°, with C(17) and C(18) in *cis* positions. A planar disposition of the two adjacent methoxyl groups, as in cryptopleurine methiodide (Fridrichsons & Mathieson, 1954) is prevented here by steric hindrance of Cl and C(16) and a *trans* configuration of the carbons C(17) and C(18) is precluded by packing considerations.

### Packing

The packing arrangement of the molecules in the unit cell is shown in Fig. 9, representing the contents of one whole cell. The shortest approach distance of 2·89 Å is between O(2) and the hydroxyl oxygen O(4′), suggesting a hydrogen bond. The next shortest distances, 3·08 and 3·06 Å are between the hydroxyl oxygen atoms O(3) and O(4′) and between Br(1) and O(6′), the latter being probably responsible for the more rigid disposition of this bromine atom in comparison with Br (2). Other approach distances are given in Table 4 and shown also in Fig. 9(*b*).

We particularly wish to express special appreciation for the aid we received from Professor G. A. Barclay of the University of New South Wales in arranging for the calculation of the three-dimensional Fourier synthesis on UTECOM. Also to Dr J. A. Wunderlich for his aid and guidance in carrying out the full-matrix least-squares refinement on the IBM 7090 computer at Weapon Research Establishment, Salisbury, South Australia. Finally we are grateful to Dr White for his persistence in preparation of a variety of samples of crystals of the $CCl_4$ and $CH_2Br_2$ adducts of sporidesmin in the search for suitable specimens.

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