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The Structure of Salamander Alkaloids. I. On the Structure of Samandarine-Hydrobromide

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Samandarine $C_{19}H_{31}O_2N$ and the related compounds are the only genuine alkaloids so far known in animals. X-ray analysis shows that the sterol skeleton of samandarine is related to 5β-androstane. The oxazolidine ring as deduced by chemical methods has been confirmed.

The X-ray analysis has been mainly carried out on the hydrobromide with space group $P2_1$,

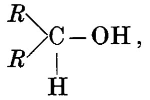
$$a = 12{\cdot}98,\ b = 6{\cdot}28,\ c = 12{\cdot}43\ \text{Å};\ \beta = 95°.$$

There are 2 molecules and 2 methanols in the unit cell. The heavy atom was found from Patterson projections. The heavy-atom technique was used to derive signs, and several 2-dimensional syntheses were calculated until the R_1-factor for the $h0l$ reflections reached 0·28. A 3-dimensional model of the molecule has been found and two 3-dimensional Fourier-syntheses were calculated. The R_1-factor reached 0·25 including unobserved reflections. The least-squares refinement was calculated using the program of Levy & Busing for the IBM 704. For the 3-dimensional intensities the final R_1-factor reached $R_1 = 0{\cdot}17$ including unobserved reflections.

Introduction

The miliary glands of the salamander species 'Salamandra maculosa' and 'Salamandra atra Laur' contain a secretion which has been studied by C. Schöpf and his co-workers. The main part of this secretion consists of proteins and water and only a small fraction of about 10% is a mixture of various alkaloids. Samandarine has been found to be the main alkaloid (60%); in addition Samandaron (10%), Samandaridine (5%), Cyclo-Neosamandion and several others have been isolated. The structures of these compounds are of interest, because they represent the only genuine alkaloids so far known in animals.

The formula of samandarine was determined by Schöpf & Braun (1934) to be $C_{19}H_{31}O_2N$. No double bonds were found. It has been shown that one oxygen belongs to an alcoholic OH-group



$$\begin{array}{l}R\\R\end{array}\!\!>\underset{\substack{|\\ H}}{C}-OH,$$

whereas the other one is an ether–oxygen. It was later confirmed (Schöpf, Blödorn, Klein & Seitz, 1950) that the ether–oxygen and the nitrogen belong to a 5-membered oxazolidin ring system which itself belongs to a 7-membered ring *A* (see Fig. 1).

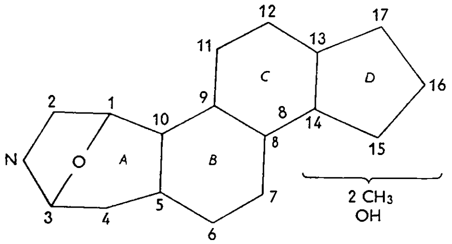


Fig. 1. A sketch of the samandarine molecule. The numbers refer to the carbons and are due to the nomenclature of the steroids.

The carbon skeleton has been elucidated by dehydrogenation of samandarine. A mixture of various derivatives of naphthalene was obtained. A spectroscopical investigation showed that these compounds were substituted in the 1,2,5 and 6-position. From the sum formula a carbon skeleton of two 6-membered rings *B* and *C*, one 5-membered ring *D* and 2 angular CH_3-groups was derived (Schöpf & Klein, 1954).

There was an ambiguity in the attachment of ring *A* to the carbon skeleton of the molecule. One of three possible structures, which has been confirmed by our X-ray structure analysis, is shown in Fig. 1. The chemical analysis made it plausible to try to relate the structure of samandarine to the structure of known steroids e.g. to cholesterol or to 5β-androstane. Since chemical methods did not lead to straightforward results, mainly because only small quantities of these substances were available, it was decided to start an X-ray structure analysis of samandarine and related compounds in addition to further chemical and spectroscopical investigations (Wölfel, Schöpf, Weitz & Habermehl, 1961).

Crystal data

After a few trials, the unstable monoclinic modifications of samandarine-hydrochloride, -hydrobromide, and -hydroiodide, which gave very similar Weissenberg photographs, were found to be the most suitable for the X-ray analysis. It was hoped to be able to use the isomorphous-replacement technique as well as the heavy-atom technique for phase determination. The crystals were grown from methanol solutions. It turned out to be very difficult to grow monoclinic crystals. Often during long periods only triclinic crystals were obtained. The monoclinic crystals were unstable and became triclinic under investigation in the course of a few days. The crystal data of the three salts are collected in Table 1.

Table 1. *Cell dimensions of the halogen salts of samandarine*

	Density g.cm.$^{-3}$	*a* (Å)	*b* (Å)	*c* (Å)	β (°)
Samandarine-HCl	1·25	12·83	6·15	12·47	93
Samandarine-HBr	1·36	12·98	6·28	12·43	95
Samandarine-HJ	1·48	13·10	6·50	12·53	97

From cell dimensions and densities one crystal-methanol per samandarine molecule was deduced, which was later confirmed by the chemical analysis of single crystals. The Laue symmetry was found to be $2/m$ and the space group $P2_1$ was chosen. There are 2 molecules with 2 methanols within the unit cell.

Intensity measurements

In order to have data available for the application of the isomorphous-replacement and the heavy-atom technique for phase determination, X-ray intensity measurements were made on the three salts. For the two-dimensional analysis a first set of structure factors was obtained from equi-inclination Weissenberg photographs using filtered Cu-radiation and the multiple-film technique. The intensities were visually estimated. No correction was made for absorption.

For the 3-dimensional analysis it seemed to be desirable to increase the accuracy of the measured intensities. A new set of integrated equi-inclination Weissenberg photographs was taken for the hydrobromide. Approximately 1400 reflections were obtained from the zero, first, second, and third layer lines. For each photograph a time-calibrated intensity scale was made. The peak intensities were measured using a photometer.

For the intensity measurements a needle-shaped crystal of hydrobromide was used with $a=0{\cdot}11$ mm. and $c=0{\cdot}16$ mm. The absorption ($\mu=30.9$ cm.$^{-1}$) was calculated using a graphical method, but it was later found not to be necessary to correct for absorption. The new set of three-dimensional data was used for the three-dimensional Fourier synthesis of the hydrobromide.

The two-dimensional analysis

The halogen atom parameters for the three salts were

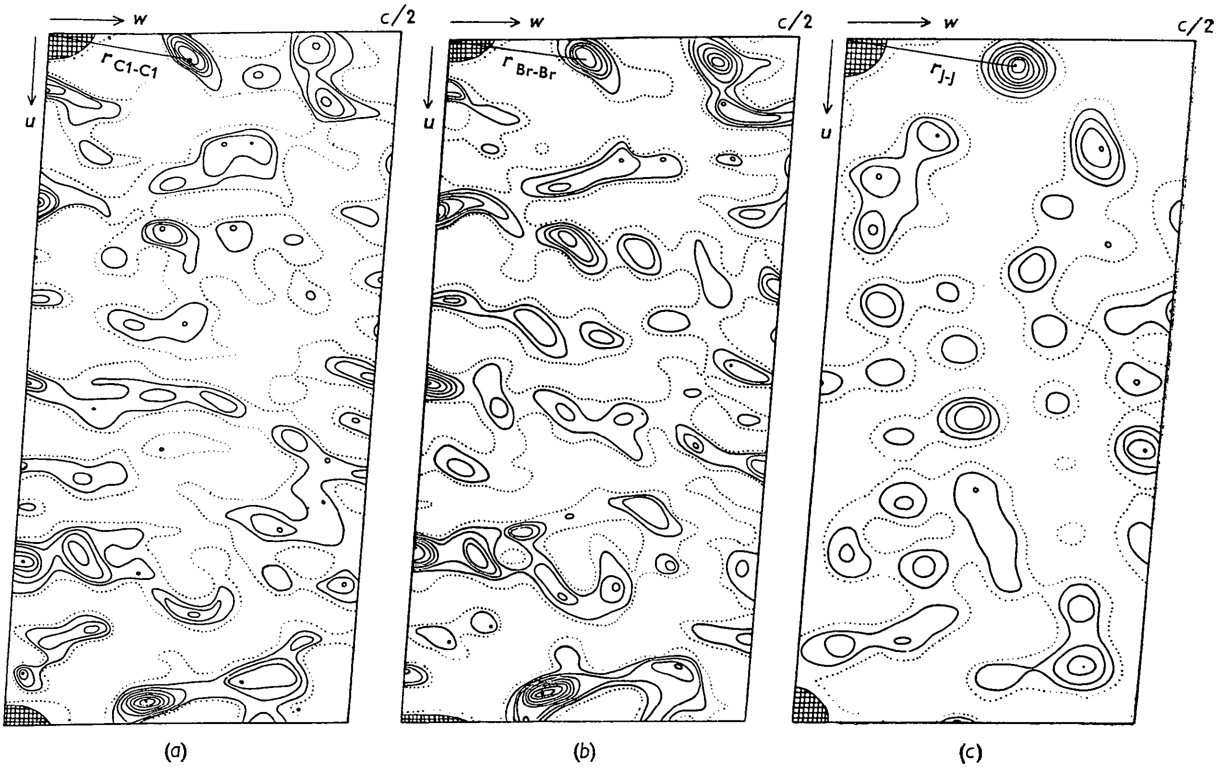


Fig. 2(*a*), (*b*), (*c*). Pattersonsynthesis $P(u, w)$ (*a*) samandarine-hydrochloride, (*b*) samandarine-hydrobromide, and (*c*) samandarine-hydroiodide.

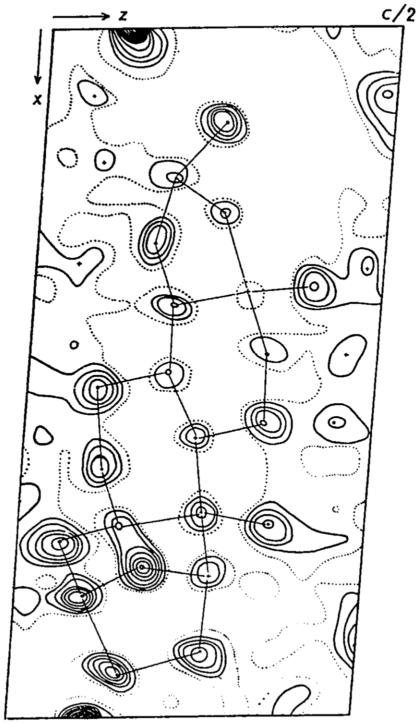


Fig. 3. The first bromine-phased Fourier-projection $\varrho(x, z)$.

determined from Patterson projections which are shown in Fig. 2(*a*), (*b*), (*c*). It can be seen that the halogen–halogen maximum is clearly recognizable, especially in the projection of the hydroiodide. From this projection the x- and z-parameters of the heavy atoms could be derived. Two centrosymmetric Fourier-projections were calculated along the 2_1-axis for the hydrobromide and for the hydroiodide using the signs (1) as derived from the position of the heavy atoms alone and (2) as determined by isomorphous-replacement. It was found that (1) gave better results. 19 maxima could be located in the bromine-phased and the iodine-phased Fourier projections; the former is shown in Fig. 3. After a few trials, it was possible to locate with these positions the ring system *A*, *B*, *C*, and *D* in agreement with the conceptions of the organic chemists.

The halogen salts of the samandarine are isotypic. The electron-density projections $\varrho(x,z)$ of samandarine-hydroiodide is similar to the one of S–HBr with nearly the same atomic positions. After several cycles the reliability factor of the $h0l$ zone reached $R_1 = 0{\cdot}17$ for the samandarine-hydroiodide.

For further investigations the samandarine-hydrobromide was chosen. A new set of $h0l$ structure factors was computed, using the Br-position and the parameters of the 19 maxima. The agreement between the observed and calculated structure factors was promising. A second projection showed the position of all atoms, even those of methanol.

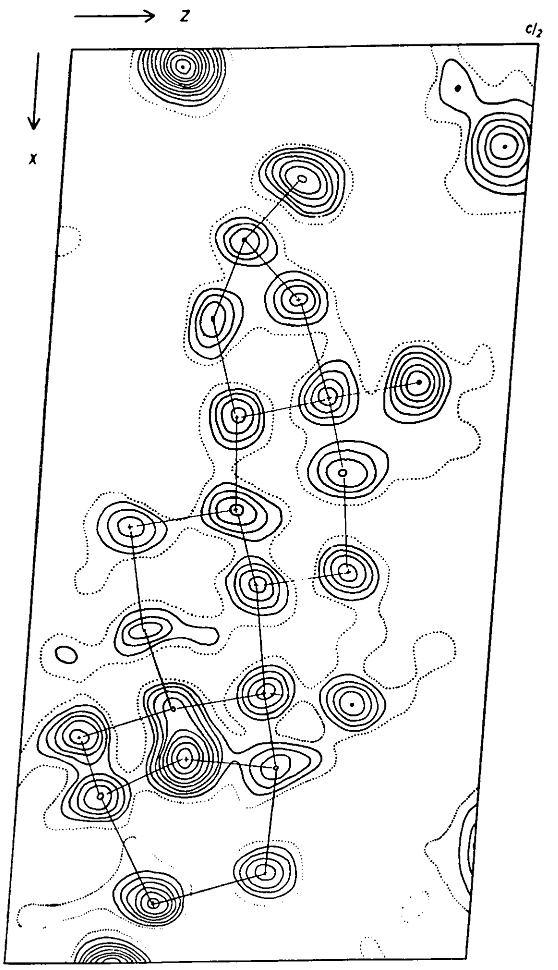


Fig. 4. The final Fourier-projection $\varrho(x, z)$ of samandarine-hydrobromide.

At this stage of the analysis, different atomic scattering factors for the C, N and O atoms were introduced and a Debye–Waller-temperature factor $B = 3{\cdot}0$ for all atoms was chosen to calculate a new set of structure factors. After several cycles, which were calculated in fraction of 1/100, the x- and z-parameters of all atoms were refined. Several difference projections were calculated, which, however, did not lead to any noticeable improvement. Finally no further improvement of agreement between calculated and observed structure factors could be reached. The reliability factor for the $h0l$ reflections was 0·28. Fig. 4 shows the last electron-density projection of the asymmetric unit of samandarine-hydrobromide.

The three-dimensional analysis

From the refined x- and z-parameters and the assumed average C–C-distance of 1·50 Å, a three-dimensional model of the samandarine-molecule was constructed. Because of the uncertainty of the linkage between the molecule and the Br-ion, the latter was shifted towards the molecule, until the best agreement between the calculated and the observed structure factors was reached. Having found the optimal position of Br^-, the phases of all structure factors were calculated. The position of the methanol was not yet known and therefore not considered in these calculations. The agreement between observed and calculated hkl structure factors was promising with $R_1 = 0{\cdot}30$.

Using the phases from these structure factors, a three-dimensional Fourier synthesis was calculated. This synthesis confirmed the chosen position of the atoms, refining them somewhat in respect to their y-parameters. Also the methanol could be located. For the new set of calculated structure factors, the refined atomic positions including methanol were used. The agreement factor dropped to $R_1 = 0{\cdot}26$.

In the meantime the new set of observed structure factors became available. With these values as coefficients and the improved phases, a second three-dimensional Fourier synthesis in fractions of 1/50 was computed, which further refined the y-parameters. For a refinement of x- and z-parameters, a Fourier projection in fractions of 1/100 was calculated. The result of the second three dimensional synthesis in sections with respect to the b-axis is shown in Fig. 5.

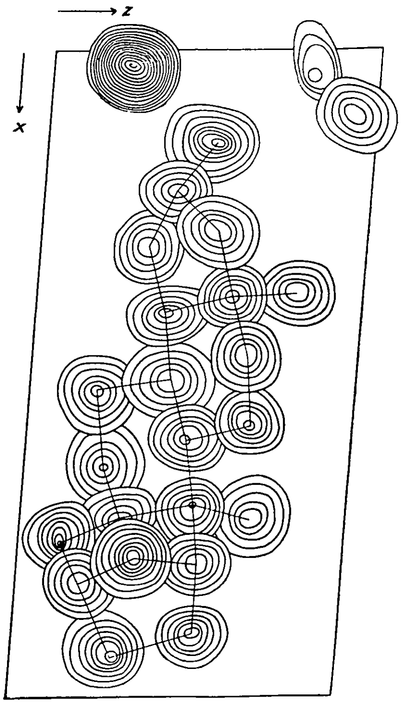


Fig. 5. The Fourier-synthesis in section along [010] due to the three-dimensional Fourier-synthesis.

With the final atomic parameters about 1400 structure factors were calculated. The agreement factor reached 0·25 including unobserved reflections.

Table 2. *Measured and calculated values of the three dimensional structure factors of samandarine-hydrobromide*

The calculated structure factors are taken from the last least-squares cycle

h00		
1	26,0	33,9
2	31,8	30,1
3	50,3	43,5
4	59,1	49,6
5	39,5	35,5
6	11,0	8,4
7	18,6	21,3
8	25,4	18,7
9	—	0,7
10	22,8	23,1
11	9,8	6,8
12	9,9	4,0
13	9,7	6,3
14	10,9	5,7
15	—	1,0
16	13,0	7,7
h01		
0	43,3	58,0
1	56,4	59,6
2	16,0	17,0
3	4,5	2,4
4	47,5	40,4
5	36,5	33,4
6	19,8	8,3
7	17,0	14,2
8	25,7	19,7
9	25,1	21,5
10	14,5	15,2
11	9,8	9,1
12	—	0,6
13	9,6	7,5
14	10,7	8,5
15	—	0,5
16	13,5	7,5
h02		
0	73,1	89,6
1	62,7	56,0
2	19,8	17,1
3	14,2	7,8
4	36,0	29,2
5	21,2	20,9
6	3,1	1,1
7	24,1	24,5
8	37,4	27,8
9	6,3	1,9
10	51,1	47,1
11	9,9	6,5
12	12,1	9,5
13	15,0	14,1
14	17,1	13,9
15	11,3	9,0
16	7,0	3,4
h03		
0	75,5	63,4
1	29,6	34,8
2	31,5	26,8
3	39,8	42,8
4	42,7	50,5
5	32,9	30,6
6	39,4	40,0
7	13,6	17,2
8	13,6	15,1
9	13,1	13,1
10	26,0	28,5
11	21,2	18,6
12	12,0	9,7
13	11,3	9,0
14	12,9	12,2
15	8,2	3,7
h04		
0	64,8	50,3
1	12,0	18,7
2	50,7	59,3
3	54,3	58,0
4	50,1	51,1
5	40,6	39,5
6	29,6	27,2
7	12,8	15,2
8	6,3	7,8
9	16,3	14,9
10	4,4	4,1
11	22,3	17,5
h05		
0	47,5	42,1
1	47,3	46,9
2	45,3	38,6
3	12,6	14,7
4	10,1	6,1
5	—	1,0
6	11,6	6,6
7	—	0,5
8	5,1	4,5
9	—	2,2
10	12,2	13,8
11	—	0,2
12	—	1,1
13	13,3	11,2
14	13,2	9,9
h06		
0	15,5	15,4
1	—	15,3
2	—	0,3
3	—	0,9
4	14,6	10,2
5	8,2	9,4
6	6,2	5,7
7	6,5	6,3
8	15,3	13,4
9	26,3	25,0
10	14,0	13,9
11	—	8,2
12	6,5	7,5
13	9,5	7,3
14	9,0	6,8
h07		
0	19,8	21,1
1	31,3	29,8
2	29,9	29,8
3	19,6	20,3
4	10,3	15,2
5	16,6	17,2
6	23,7	22,9
7	6,8	10,3
8	9,9	17,2
9	14,1	16,1
10	11,9	14,5
h08		
0	28,0	30,1
1	40,1	32,1
2	44,7	40,2
3	21,4	26,4
4	18,2	16,3
5	18,9	18,1
6	21,7	21,5
7	17,2	15,8
8	—	0,7
9	—	2,2
10	11,4	9,6
11	12,0	8,0
h09		
0	12,7	11,1
1	15,7	15,5
2	16,0	18,3
3	14,9	15,9
4	18,0	13,5
5	18,4	18,6
6	15,7	18,3
7	7,0	6,8
8	6,9	7,5
9	9,3	8,3
10	6,0	7,5
h010		
0	—	3,1
1	—	4,9
2	—	3,8
3	—	0,7
4	—	0,1
5	—	1,7
6	—	1,0
7	11,8	13,7
h011		
0	—	0,3
1	15,7	11,5
2	17,3	17,8
3	17,2	15,7
4	—	8,0
5	16,8	18,6
6	11,5	15,8
7	8,9	4,1
8	18,5	20,0
h012		
0	—	6,5
1	—	8,5
2	16,9	16,7
3	—	8,4
4	16,2	15,8
5	14,2	13,7
6	—	6,1
7	—	1,0
8	12,0	12,5
h013		
0	18,6	17,6
1	6,5	7,4
2	—	5,5
3	—	4,8
4	11,8	9,6
h0$\bar{1}$		
1	14,2	18,2
2	13,0	18,8
3	49,0	55,1
4	51,2	67,7
5	19,5	19,9
6	33,0	43,1
7	28,5	29,5
8	46,0	40,0
9	38,2	36,4
10	23,9	22,6
11	16,0	14,2
12	12,2	16,6
13	11,9	13,1
14	8,9	10,1
15	—	4,3
16	8,4	7,7
h0$\bar{2}$		
1	7,6	8,1
2	40,3	37,6
3	17,4	17,8
4	31,2	27,8
5	23,9	25,5
6	31,0	31,1
7	25,3	30,8
8	45,2	38,7
9	15,1	14,6
10	22,8	26,1
11	20,7	24,9
12	31,6	30,3
13	11,8	12,3
14	—	0,6
15	9,4	9,9
16	16,3	15,8
h0$\bar{3}$		
1	66,6	72,2
2	18,5	15,3
3	6,3	3,4
4	—	3,5
5	4,5	4,8
6	15,0	11,2
7	19,3	17,8
8	—	4,5
9	—	4,8
10	11,6	11,4
11	24,0	27,2
12	12,2	11,3
13	11,8	11,0
14	8,8	9,6
15	10,7	10,2
16	9,1	8,4
h0$\bar{4}$		
1	65,5	57,0
2	66,1	89,4
3	80,4	68,6
4	54,1	48,6
5	43,4	36,6
6	31,8	28,3
7	7,9	6,9
8	13,5	12,7
9	—	1,0
10	—	4,1
11	10,0	12,5
12	—	0,7
13	—	4,8
14	—	1,8
15	10,3	7,8
h0$\bar{5}$		
1	38,7	33,8
2	35,8	31,0
3	22,5	23,2
4	24,1	22,0
5	29,3	26,2
6	47,7	38,1
h0$\bar{5}$		
7	42,8	38,9
8	21,5	18,5
9	16,1	13,7
10	15,5	11,2
11	24,4	30,3
12	9,8	5,7
13	25,4	21,4
h0$\bar{6}$		
1	14,3	17,0
2	20,0	14,7
3	7,0	6,8
4	17,0	16,3
5	30,1	23,6
6	32,2	30,9
7	32,2	26,6
8	41,7	41,4
9	22,2	18,1
10	18,7	18,3
11	9,9	14,4
12	25,6	21,6
13	16,8	15,5
h0$\bar{7}$		
1	37,8	25,7
2	—	0,0
3	33,2	14,9
4	11,3	4,1
5	11,8	7,4
6	11,3	9,0
7	6,5	6,6
8	18,7	13,7
9	20,1	17,0
10	19,4	15,5
11	9,8	12,1
12	27,3	25,9
13	—	—
14	2,3	3,6
15	11,2	9,7
h0$\bar{8}$		
1	34,2	31,1
2	16,9	22,0
3	31,3	24,8
4	—	4,7
5	—	4,8
6	18,9	13,3
7	28,6	24,2
8	17,7	17,1
h0$\bar{9}$		
1	9,0	5,5
2	67,7	60,1
3	9,1	5,6
4	18,9	12,8
5	25,4	21,3
6	24,8	23,9
7	27,4	23,2
8	9,9	9,2
9	20,1	16,5
10	16,6	11,6
11	—	1,2
12	11,6	11,3
h0$\overline{10}$		
1	9,6	10,2
2	25,6	21,8
3	—	1,4
4	9,8	8,8
5	40,7	36,4
6	41,2	28,1
7	—	0,5
8	15,6	13,1
9	13,5	12,1
10	15,7	11,8
11	11,8	13,8
12	7,3	7,8
13	9,4	7,7
h0$\overline{11}$		
1	14,0	10,3
2	21,6	20,5
3	—	6,5
4	8,3	8,5
5	8,3	10,0
6	9,9	6,7
7	—	2,1
8	7,8	5,8
9	—	2,3
10	16,5	15,8
11	9,0	5,9
12	8,6	5,4
h0$\overline{12}$		
1	15,6	13,7
2	14,0	12,1
3	13,9	10,7
4	—	3,9
5	5,2	6,2
6	11,5	7,9
h0$\overline{13}$		
1	9,3	8,3
2	9,3	7,7
3	6,5	5,0
4	6,4	5,7
5	14,0	12,7
6	14,7	10,7
7	11,4	6,1
8	9,1	7,7
9	—	4,1
10	7,7	10,7
h0$\overline{14}$		
1	—	3,7
2	9,4	6,1
3	9,2	5,9
4	—	1,2
5	15,2	10,5
6	12,4	9,5
7	9,3	6,7
8	9,5	8,3
9	8,2	9,4
h10		
1	21,1	17,8
2	73,2	71,4
3	31,9	28,2
4	40,6	41,2
5	70,5	63,8
6	35,4	36,4
7	31,4	28,4
8	15,9	19,8
9	12,4	16,6
10	30,0	29,4
11	14,6	12,0
12	15,4	15,0
13	18,4	15,4
14	7,8	7,7
15	6,6	8,1
16	4,2	4,0
h11		
0	74,1	69,9
h11		
1	74,4	76,5
2	86,8	82,9
3	63,6	64,3
4	66,0	66,6
5	56,4	49,4
6	69,3	72,0
7	36,9	40,0
8	28,8	31,8
9	31,2	38,6
10	2,7	2,8
11	15,4	16,3
12	6,2	8,7
13	2,6	4,8
14	3,8	4,6
15	—	1,5
16	8,0	6,4
h12		
0	54,1	54,2
1	53,6	50,1
2	61,3	62,9
3	48,7	50,4
4	34,9	33,5
5	38,0	36,1
6	43,0	33,9
7	21,5	31,5
8	32,3	31,3
9	31,8	21,3
10	12,2	12,3
11	2,8	5,3
12	5,6	6,0
13	—	0,2
14	2,3	2,2
15	4,3	5,2
h13		
0	84,9	93,8
1	69,1	62,0
2	38,3	33,5
3	31,5	29,4
4	4,4	7,0
5	16,2	21,8
6	9,8	11,6
7	5,1	5,5
8	12,4	10,3
9	12,6	6,3
10	16,4	11,6
11	12,6	8,8
12	10,7	8,0
13	8,5	3,9
14	2,2	3,6
15	2,8	3,5
16	0,8	9,4
h14		
0	23,3	24,1
1	26,4	27,4
2	26,8	23,8
3	12,4	11,7
4	11,2	10,1
5	24,2	20,0
6	17,9	22,2
7	28,3	29,3
8	30,3	26,1
9	21,5	24,0
10	14,0	12,2
11	2,8	8,4
12	6,6	10,8
13	2,4	7,4
14	—	2,5
15	2,5	4,4
h15		
0	57,1	52,7
1	41,3	44,8
2	21,8	26,8
3	32,1	36,1
4	24,6	28,6
5	36,9	34,9
6	34,5	34,9
7	26,2	28,4
8	31,4	29,6
9	8,8	9,8
10	19,9	17,0
11	—	10,1
12	4,1	5,4
13	2,3	6,9
h16		
0	42,7	41,6
1	29,4	29,9
2	32,4	31,2
3	25,4	29,6
4	32,7	33,1
5	34,5	34,7
6	19,3	22,1
7	13,2	16,2
8	19,0	20,8
9	12,6	12,1
10	8,8	10,2
11	6,0	4,2
12	—	2,3
13	2,1	2,4
h17		
0	33,5	30,5
1	21,9	25,1
2	13,9	20,3
3	19,9	20,5
4	13,8	16,1
5	5,7	7,0
6	1,8	4,0
7	9,7	7,8
8	10,9	9,6
9	12,6	10,1
10	8,6	5,7
11	8,0	3,7
h18		
0	16,2	14,8
1	11,2	10,1
2	2,4	3,7
3	8,0	11,1
4	9,2	10,9
5	15,4	15,6
6	12,4	14,2
7	8,9	11,4
8	10,9	10,2
9	4,3	2,8
10	9,1	7,6
h19		
0	11,9	15,3
1	—	2,5
2	9,3	10,2
3	15,7	14,9
4	11,2	12,1
5	14,7	16,6
6	10,9	11,5
7	9,9	10,2
8	21,2	20,8
9	10,0	9,8
10	7,5	6,4
h110		
0	35,9	27,6
1	12,7	14,6
2	15,7	20,8
3	12,9	15,0
4	16,9	14,9
5	8,9	9,3
6	—	4,9
7	19,1	16,6
8	9,0	7,1
9	9,1	10,7
10	3,2	4,9
h111		
0	17,9	20,9
1	17,2	18,1
2	17,7	14,3
3	15,8	13,9
4	10,7	7,5
5	—	2,1
6	5,8	6,0
7	3,9	5,3
8	2,8	2,4
h112		
0	1,3	3,6
1	2,7	5,2
2	1,9	4,1
3	7,3	6,1
4	3,7	4,1
5	2,5	5,2
6	1,6	3,9
7	6,8	6,5
8	3,0	1,7
9	5,9	7,9
h113		
0	4,1	4,9
1	—	1,4
2	2,5	3,7
3	5,9	6,3
4	—	1,2
5	3,0	9,8
6	4,3	5,9
7	5,9	8,2
h114		
0	—	3,0
1	7,0	6,9
2	5,2	6,5
3	7,1	7,4
4	—	3,6
5	2,6	4,2
6	4,2	6,3
h115		
0	5,6	6,3
1	3,4	5,5
2	3,8	4,7
3	2,2	4,2
h1$\bar{1}$		
1	47,8	43,4
2	49,3	47,1
3	58,3	57,8
4	35,5	31,2
5	44,0	37,0
6	29,9	32,7
7	3,3	6,2
8	5,6	6,9
9	5,0	6,9
10	19,8	18,3
11	—	2,7
12	10,9	11,4
13	14,9	17,6
14	12,4	12,7
15	4,7	6,3
16	3,5	3,3
h1$\bar{2}$		
1	56,0	56,1
2	75,4	79,0
3	73,0	81,8
4	32,7	34,1
5	60,4	58,0
6	44,4	40,0
7	27,8	28,9
8	18,7	17,1
9	2,5	3,5
10	11,2	12,6
11	12,5	13,0
12	3,4	8,9
13	—	2,5
14	—	0,9
15	—	3,6
16	2,5	2,9
h1$\bar{3}$		
1	47,5	46,0
2	76,1	74,3
3	59,0	67,7
4	66,0	65,2
5	48,7	51,6
6	46,5	47,4
7	43,6	45,0
8	41,0	35,4
9	31,0	31,0
10	19,8	23,1
11	15,7	16,1
12	9,9	12,8
13	8,5	9,7
14	12,2	12,0
15	2,0	3,3
h1$\bar{4}$		
1	15,5	13,7
2	65,2	59,8
3	33,6	28,8
4	24,0	22,0
5	38,4	35,7
6	25,7	25,2
7	30,8	25,6
8	34,2	30,1
9	31,2	26,3
10	28,4	29,2
11	—	4,6
12	16,5	14,3
13	16,8	15,5
14	14,6	11,3
15	11,9	9,4
16	7,1	6,1
h1$\bar{5}$		
1	13,2	13,0
2	45,5	50,2
3	27,5	31,9
4	15,8	16,5
5	—	3,4
6	7,1	10,4
7	—	3,5
8	9,0	10,8
9	6,5	6,6
10	18,9	12,5
11	18,4	18,6
h1$\bar{6}$		
1	12,4	13,8
2	45,7	46,2
3	41,9	45,8
4	40,2	36,5
5	33,0	31,3
6	15,5	20,2
7	13,0	13,7
8	14,9	15,9
9	12,7	12,8
10	2,8	6,1
11	11,7	12,6
12	2,7	5,4
13	7,9	10,5
14	2,1	3,4
h1$\bar{7}$		
1	40,7	36,5
2	56,7	43,8
3	51,1	46,1
4	50,5	46,5
5	46,1	44,5
6	32,7	29,5
7	21,1	19,8
8	15,4	15,6
9	16,6	13,0
10	16,9	14,3
11	13,8	11,4
12	13,7	11,7
13	12,4	7,2
14	5,5	5,6
15	5,2	7,1
h1$\bar{8}$		
1	25,3	21,7
2	12,7	11,1
3	32,5	31,4
4	14,2	14,9
5	16,9	16,4
6	23,0	20,3
7	17,9	14,3
8	24,2	23,0
9	15,9	7,7
10	22,3	15,6
11	28,7	25,9
12	2,4	1,3
13	16,9	15,2
14	9,7	9,0
h1$\bar{9}$		
1	8,1	11,0
2	9,5	12,8
3	2,6	6,2
4	3,7	6,2
5	12,7	16,1
6	—	4,7
7	22,5	22,8
8	12,4	16,6
9	10,0	10,3
10	8,5	10,1
11	11,3	11,6
12	17,0	15,5
13	9,2	8,5
14	9,0	7,4
h1$\overline{10}$		
1	35,3	38,8
2	—	1,2
3	24,9	26,6
4	15,7	16,8
5	13,0	16,3
6	13,0	14,1
7	6,3	9,7
8	3,9	4,3
9	—	3,0
10	3,5	5,2
11	3,2	5,4
12	8,4	7,9
h1$\overline{11}$		
1	14,8	18,6
2	17,5	21,3
3	18,4	22,1
4	18,4	19,5
5	15,9	15,0
6	5,5	7,7
7	20,9	19,6
8	11,3	14,2
9	10,4	8,1
10	7,2	7,5
11	—	3,5
12	3,3	4,8
h1$\overline{12}$		
1	1,9	5,3
2	17,5	19,3
3	9,8	12,4
4	9,7	11,4
5	8,5	7,2
6	4,1	5,6
7	10,1	11,0
8	14,3	11,3
9	9,2	8,1
10	6,1	4,7
11	6,2	6,3
h1$\overline{13}$		
1	—	4,3
2	—	2,0
3	3,1	5,4
4	10,2	11,6
5	—	2,4
6	4,7	3,7
7	4,4	2,9
8	6,4	4,4
9	6,3	6,0
10	6,0	6,4
h1$\overline{14}$		
1	4,8	8,0
2	8,3	12,4
3	8,2	11,2
4	5,3	7,9
5	2,0	5,4
6	5,3	6,4
7	—	1,4
8	3,7	3,1
h1$\overline{15}$		
1	4,0	7,0
2	8,4	10,7
3	2,7	5,0
4	8,8	10,4
5	5,9	6,9
6	3,9	2,4
h20		
1	86,5	75,4
2	78,0	67,2
3	69,9	66,8
4	4,5	9,4
5	82,0	87,2
6	10,3	20,7
7	15,8	21,3
8	16,3	17,6
9	11,4	11,5
10	18,3	12,5
11	8,3	7,8
12	9,3	8,6
13	5,8	4,7
14	1,6	2,7
15	3,8	1,7
h21		
0	47,4	47,7
1	78,2	55,5
2	48,7	45,2
3	43,7	39,7
4	44,4	44,8
5	—	3,6
6	25,2	12,7
7	3,6	2,7
8	9,2	8,5
9	14,9	12,8
10	17,4	14,7
11	14,8	9,1
12	6,1	6,8
13	3,6	5,4
14	2,2	3,3
h22		
0	10,8	13,7
1	25,4	18,5
2	30,7	26,0
3	13,1	11,1
4	35,5	38,3
5	56,6	41,7
6	20,4	21,9
7	25,9	24,0
8	12,4	12,9
9	23,9	26,6
10	27,2	27,8
11	17,5	14,9
12	10,6	10,2
13	14,1	10,6
14	3,1	3,8
15	14,1	8,7
h23		
0	40,8	26,5
1	44,5	39,9
2	53,0	46,7
3	45,5	45,3
4	37,3	41,5
5	37,1	34,1
6	8,4	27,8
7	25,8	31,3
8	17,9	22,3
9	13,3	16,2
10	15,8	10,0
11	19,8	16,8
12	17,1	11,3
13	9,9	7,7
14	3,3	4,7
15	6,0	6,2
h24		
0	44,2	37,6
1	51,2	48,0
2	56,7	51,7
3	58,6	59,3
4	59,4	40,3
5	14,9	21,8
6	21,3	23,3
7	14,3	18,2
8	16,8	22,3
9	7,6	9,4
10	—	1,3
11	1,9	2,8
12	5,8	4,7
13	—	1,8
14	5,2	4,9
h25		
0	42,7	44,7
1	11,3	11,8
2	14,2	16,9
3	28,1	27,5
4	18,8	26,1
5	22,3	17,0
6	10,0	8,6
7	5,9	8,4
8	10,9	10,2
9	7,7	9,8
10	—	3,7
11	6,6	7,3
12	9,6	6,3
13	4,8	3,5
h26		
0	36,7	21,5
1	15,1	10,5
2	5,5	4,9
3	5,2	6,2
4	4,8	4,8
5	5,0	5,6
6	7,4	12,1
7	10,9	12,3
8	13,6	18,1
9	13,6	17,8
10	—	4,1
11	4,0	6,1
12	9,7	9,1
13	8,7	7,0
h27		
0	25,1	23,6
1	11,5	16,1
2	22,6	29,1
3	23,2	26,6
4	19,1	26,2
5	10,6	18,5
6	10,9	12,3
7	15,7	20,0
8	13,0	12,6
9	17,4	21,9
10	8,3	9,1
11	6,6	8,4
12	—	5,3
13	5,2	7,3
h28		
0	24,7	29,0
1	26,9	32,7
2	23,1	30,1
3	18,2	24,1
4	15,2	24,5
5	17,4	24,2
6	11,1	13,9
7	6,3	8,1
8	—	5,2
9	5,3	4,7
10	6,7	6,5
11	5,4	5,5
h29		
0	15,2	18,4
1	21,6	26,7
2	2,7	3,0
3	23,3	30,0
4	3,9	6,2
5	11,2	11,7
6	10,9	11,4
7	2,7	3,8
8	2,6	2,4
9	4,9	4,9
h210		
0	6,2	8,1
1	3,9	2,9
2	3,5	13,4
3	1,9	1,2
4	1,9	5,3
5	—	2,5
6	1,9	3,4
7	—	0,6
8	—	3,5
9	3,4	4,2
10	2,9	5,5
h211		
0	6,9	10,0
1	6,2	8,8
2	—	4,3
3	19,4	18,5
4	4,5	6,9
5	11,7	11,9
6	7,9	7,5
h212		
0	12,4	12,1
1	9,5	10,9
2	5,9	7,9
3	11,5	10,5
4	7,8	7,9
5	11,8	11,1
6	2,1	6,6
7	3,1	5,7
h213		
0	6,0	7,6
1	5,4	7,5
2	4,7	7,1
3	1,6	3,8
4	5,8	6,2
h2$\bar{1}$		
1	58,5	61,5
2	39,0	32,9
3	30,8	25,6
4	22,2	20,5
5	42,7	44,7
6	42,3	39,1
7	33,1	34,6
8	27,9	29,3
9	28,7	28,5
10	22,0	21,9
11	17,8	21,3
12	12,4	13,6
13	7,2	5,1
14	1,6	2,6
15	7,5	6,8
h2$\bar{2}$		
1	11,8	13,6
2	17,2	10,9
3	18,8	18,6
4	31,4	32,9
5	30,7	30,8
6	35,0	34,8
7	35,8	29,1
8	15,7	15,5
9	24,7	24,1
10	17,4	16,6
11	26,4	26,8
12	12,4	10,3
13	13,1	9,6
14	4,6	6,0
15	9,6	9,0
h2$\bar{3}$		
1	32,2	28,3
2	57,5	51,6
3	10,2	15,1
4	13,3	10,8
5	2,5	0,8
6	3,5	2,3
7	4,4	6,2
8	15,9	19,3
9	10,6	12,8
10	15,7	21,8
11	15,9	17,3
12	8,7	8,1
13	7,1	8,6
14	5,1	6,7
15	5,1	5,3
h2$\bar{4}$		
1	100,7	94,7
2	70,4	59,7
3	24,4	27,9
4	19,8	20,2
5	40,8	29,2
6	38,8	26,8
7	16,9	16,4
8	5,8	9,3
9	7,4	11,2
10	—	1,1
11	7,7	9,2
12	6,7	6,7
13	1,7	2,7
h2$\bar{5}$		
1	70,5	79,0
2	26,7	30,9
3	24,9	29,7
4	37,2	36,6
5	38,5	39,1
6	31,3	29,1
7	10,1	8,6
8	35,2	28,9
9	15,6	15,5
10	17,8	17,8
11	15,8	16,1
12	10,7	11,8
13	1,7	3,9
h2$\bar{6}$		
1	8,6	3,7
2	13,8	2,4
3	16,7	12,9
4	27,7	23,8
5	23,5	21,5
6	14,2	15,4
7	31,4	31,6
8	26,6	25,5
9	28,5	27,3
10	17,8	20,4
11	13,4	12,9
12	10,9	7,0
13	13,2	12,1
14	6,3	6,0
h2$\bar{7}$		
1	28,0	26,6
2	13,3	15,7
3	9,6	6,7
4	9,8	8,9
5	12,4	14,2
6	7,4	8,0
7	23,0	28,2
8	6,2	7,8
9	17,8	17,8
10	5,5	6,7
11	5,7	4,6
12	7,8	7,7
13	6,4	6,1
14	5,6	4,7
h2$\bar{8}$		
1	20,1	22,7
2	20,3	22,3
3	14,5	19,3
4	14,8	12,4
5	10,7	11,9
6	13,4	14,8
7	7,9	6,6
8	7,9	9,9
9	11,1	12,8
10	4,3	4,6
11	—	1,2
12	9,0	7,5
h2$\bar{9}$		
1	10,7	12,7
2	10,7	9,8
3	13,2	18,2
4	20,5	24,8
5	23,5	24,1
6	8,9	6,5
7	26,3	28,6
8	15,7	16,0
9	13,2	13,3
10	7,3	7,7
11	5,3	7,1
12	12,7	7,8
h2$\overline{10}$		
1	7,9	8,3
2	6,2	7,0
3	15,8	18,7
4	15,9	18,2
5	17,8	16,2
6	13,7	13,2
7	17,5	18,5
8	15,2	13,1
9	10,2	8,4
10	9,5	8,9
11	17,9	10,2
12	9,2	6,4
h2$\overline{11}$		
1	1,9	4,8
2	1,9	2,0
3	—	1,2
4	2,8	5,4
5	3,9	4,5
6	8,6	8,3
7	2,6	3,3
8	—	2,1
9	7,4	6,8
10	5,7	6,0
11	9,9	7,3
h2$\overline{12}$		
1	10,5	10,7
	6,0	7,2
3	9,5	8,7
4	15,7	16,2
5	1,8	3,3
6	3,0	5,4
h2$\overline{13}$		
1	14,1	11,6
2	2,4	3,4
3	12,2	11,8
4	9,2	7,8
5	10,3	8,2
6	3,8	4,4
7	7,9	7,3
8	7,9	8,8
9	5,4	5,3
h2$\overline{14}$		
1	—	2,9
2	4,7	5,4
3	15,6	13,5
4	7,0	6,0
5	7,3	6,2
6	13,0	10,3
7	11,3	10,4
h30		
1	15,6	16,3
2	19,4	15,6
3	26,2	24,7
4	40,0	24,3
5	11,1	12,2
6	13,6	10,6
7	16,1	16,0
8	16,9	17,0
9	12,0	13,6
10	9,2	9,3
11	11,6	8,9
12	10,1	7,1
13	9,6	7,2
14	9,8	7,3
15	5,2	4,7
h31		
0	42,7	33,1
1	31,9	20,7
2	18,6	16,1
3	37,5	31,2
4	47,4	35,3
5	18,0	28,8
6	31,5	32,8
7	32,1	32,1
8	19,1	18,6
9	11,1	11,1
10	9,2	9,4
11	6,4	6,8
12	5,3	4,4
13	7,8	4,5
14	7,3	6,1
h32		
0	34,7	31,2
1	32,9	25,8
2	23,8	22,9
3	27,2	22,3
4	22,9	28,8
5	21,6	27,8
6	27,1	27,6
7	14,1	17,1
8	7,7	8,9
9	7,9	8,4
h32		
10	12,3	8,1
11	1,9	3,9
12	1,2	0,7
13	—	2,8
14	9,1	5,3
h33		
0	28,0	27,1
1	30,8	26,8
2	23,8	22,6
3	9,5	11,1
4	7,5	5,6
5	18,5	16,8
6	—	5,5
7	5,4	6,5
8	6,0	4,1
9	5,7	4,1
10	—	0,8
11	4,4	2,5
12	1,7	1,2
13	2,5	4,4
14	9,1	7,2
h34		
0	7,8	3,8
1	5,0	5,8
2	8,9	4,8
3	6,5	5,2
4	16,6	18,6
5	16,4	23,0
6	19,6	19,8
7	12,6	13,8
8	6,5	7,6
9	11,3	12,7
10	10,1	10,1
11	11,1	7,7
12	—	3,7
13	3,0	4,6
14	6,7	5,1
h35		
0	18,5	11,7
1	21,1	17,0
2	26,4	21,9
3	22,1	24,1
4	14,8	16,5
5	28,0	33,1
6	14,0	14,2
7	12,0	13,7
8	7,9	7,5
9	15,2	16,9
10	14,2	12,1
11	5,9	6,3
12	3,7	4,7
13	2,7	3,1
h36		
0	15,9	21,5
1	27,6	29,2
2	11,5	16,3
3	24,0	27,8
4	11,4	12,7
5	22,6	24,4
6	14,3	20,0
7	11,2	13,1
8	7,9	9,7
9	4,1	5,2
10	3,8	5,2
11	2,7	4,5
h37		
0	12,1	12,8
1	15,5	11,4
2	13,8	11,9
3	17,2	14,2
4	16,4	14,0
5	—	6,7
6	1,9	6,2
7	4,6	6,9
8	7,9	5,0
9	3,9	5,8
10	2,8	3,2
h38		
0	3,1	3,9
1	5,5	4,1
2	8,5	6,6
3	16,0	9,9
4	6,6	4,4
5	7,4	6,2
6	8,0	9,3
7	3,2	5,8
8	1,8	5,1
9	2,3	4,5
10	2,5	4,1
11	2,7	4,1
h39		
0	5,7	6,2
1	3,2	3,1
2	2,6	4,5
3	5,7	5,9
4	9,9	9,1
5	9,0	9,0
6	10,1	11,2
7	6,1	11,1
8	9,0	6,1
h310		
0	9,1	7,4
1	7,3	7,1
2	11,4	12,5
3	2,9	4,5
4	9,0	10,4
5	4,4	7,2
6	2,9	4,8
7	2,7	4,3
8	3,5	5,1
9	2,8	5,5
10	4,1	3,3
h311		
0	5,8	5,5
1	10,0	9,3
2	9,4	10,4
3	3,9	4,2
4	4,2	7,0
5	1,7	2,8
h312		
0	2,9	3,9
1	5,8	3,6
2	3,9	0,9
h313		
0	—	1,1
1	—	1,5
2	—	6,3
3	6,1	1,6
4	—	5,6
5	4,9	2,8
h314		
0	2,3	7,0
1	6,1	5,4
h3$\bar{1}$		
1	27,7	20,9
2	20,3	23,6
3	8,8	11,1
4	17,5	11,0
5	5,2	8,1
6	14,1	12,2
7	7,1	9,1
8	4,4	3,7
9	9,0	9,2
10	7,9	8,3
11	7,9	8,4
12	6,1	6,8
13	10,1	8,0
14	4,8	3,1
15	8,0	6,8
h3$\bar{2}$		
1	49,3	46,2
2	35,9	25,7
3	40,6	35,6
4	38,8	33,3
5	17,7	21,6
6	21,3	19,7
7	10,2	11,3
8	8,7	15,7
9	9,0	9,1
10	6,5	5,3
11	5,6	7,4
12	—	1,1
13	—	1,6
14	—	1,8
15	5,0	3,8
h3$\bar{3}$		
1	32,4	28,2
2	33,9	29,6
3	49,4	44,9
4	33,4	39,2
5	34,6	33,1
6	12,7	13,8
7	26,9	25,9
8	20,8	22,2
9	16,5	15,9
10	15,3	16,7
11	4,6	5,6
12	10,6	8,6
13	7,6	6,9
14	1,4	2,4
15	1,7	1,9
h3$\bar{4}$		
1	15,2	7,8
2	10,1	13,8
3	12,7	17,7
4	18,3	18,7
5	21,0	25,1
6	14,9	16,1
7	27,4	28,8
8	7,7	9,0
9	15,2	13,9
10	15,9	15,2
11	18,2	14,7
12	10,5	10,2
13	8,4	5,0
14	10,3	6,9
15	9,9	5,5
h3$\bar{5}$		
1	4,6	3,9
2	10,7	6,0
3	9,4	10,3
4	7,9	8,3
5	4,1	5,9
6	12,1	14,4
7	23,5	24,2
8	7,8	6,0
9	10,3	9,7
10	—	3,3
11	17,8	12,1
12	5,8	5,0
13	8,1	5,4
14	8,9	5,9
h3$\bar{6}$		
1	13,6	18,1
2	15,0	15,6
3	19,1	19,6
4	28,4	27,7
5	18,2	17,0
6	7,6	8,4
7	26,8	23,6
8	4,6	4,0
9	—	2,8
10	4,5	5,3
11	—	2,0
12	4,8	3,3
13	2,4	2,5
14	3,2	0,3
h3$\bar{7}$		
1	36,0	34,5
2	16,4	24,1
3	23,9	25,0
4	22,7	21,3
5	18,9	21,6
6	18,7	21,1
7	19,6	16,4
8	11,3	10,2
9	6,5	5,9
10	7,0	4,5
11	8,2	6,6
h3$\bar{8}$		
1	14,9	18,9
2	16,2	21,7
3	10,9	8,9
4	6,5	4,1
5	11,2	12,5
6	17,8	15,2
7	3,3	3,9
8	9,0	9,1
9	11,6	11,5
10	9,3	8,9
11	11,7	9,3
12	9,3	8,3
13	6,2	4,7
h3$\bar{9}$		
1	9,3	8,7
2	1,9	3,9
3	1,9	4,5
4	1,9	2,4
5	4,6	6,0
6	8,0	12,1
7	2,9	2,0
8	2,8	4,7
9	8,4	8,2
10	7,3	7,5
11	6,5	6,3
12	7,1	6,6
h3$\overline{10}$		
1	15,9	18,2
2	16,4	20,2

The three-dimensional Fourier syntheses were calculated using the IBM 650. The calculations were made in sections $x, 0, z$; $x, 1/50, z$; $x, 2/50, z$; etc. .... After having transformed the structure factors by multiplying them with the phase factor of the desired section, the usual program for two-dimensional Fourier series could be used. The routines for preparing the structure factors for the different sections and for the partial summations of the Fourier coefficients were written by S. Göttlicher.

Least-squares refinement

A further refinement of the three-dimensional data was based on the method of least-squares using the least-squares program of Levy & Busing for the IBM 704. For the first two cycles the x, y, z-parameters of all 25 atoms of the asymmetric unit, the scale factors for each layer-line and the overall temperature factor, starting with $B=3{\cdot}0$, were varied. The reliability factor dropped then from $R_1=0{\cdot}25$ to $R_1=0{\cdot}19$. The x, y, z-parameters did not change essentially after the second cycle and therefore the individualtemperature factors for each atom were varied in the following two cycles. The scale factors and the overall temperature factor were held constant in these cycles. The temperature-factors of the methanol atoms became 7·76 for the C-atom and 10·13 for oxygen whereas the temperature-factors of all the other atoms remained in the range between $B=3$–4. (See Table 3.)

In the following fifth cycle the temperature-factors of the methanol-atoms were held constant. Since the x, y, z-parameters of the atoms did not show noticeable deviations from those of the previous cycle, they were held constant during the sixth and last cycle in which only the scale-factors were varied.

After the third cycle with $R_1=0{\cdot}18_0$ the R_1-factor dropped to $R_1=0{\cdot}17_2$ in the fourth cycle, to $R_1=0{\cdot}16_7$ in the fifth cycle and remained constant in the last cycle.

Table 2 shows the complete set of structure factors on the final scale of the last least-squares cycle. The parameters of all atoms in the asymmetric unit, with which the least-squares refinement was started and the final parameters together with the final individual temperature-factor of each atom are given in Table 3.

Table 3. *The final x, y, z-parameters and individual temperature factor of samandarine-hydrobromide*

	Atom	x	y	z	Temperature-factor
Cycle 1	Br	0·019	0·135	0·119	
Cycle 6		0·019	0·135	0·120	4·67
Cycle 1	C1	0·789	0·680	0·276	
Cycle 6		0·787	0·699	0·274	3·18
Cycle 1	C2	0·906	0·622	0·275	
Cycle 6		0·907	0·632	0·270	3·18
Cycle 1	C3	0·822	0·718	0·088	
Cycle 6		0·825	0·740	0·098	3·29
Cycle 1	C4	0·752	0·540	0·063	
Cycle 6		0·748	0·539	0·062	3·09
Cycle 1	C5	0·724	0·425	0·158	
Cycle 6		0·723	0·406	0·156	3·53
Cycle 1	C6	0·637	0·277	0·121	
Cycle 6		0·635	0·235	0·122	2·71
Cycle 1	C7	0·525	0·362	0·100	
Cycle 6		0·526	0·365	0·108	3·67
Cycle 1	C8	0·507	0·446	0·211	
Cycle 6		0·507	0·469	0·215	2·93
Cycle 1	C9	0·589	0·618	0·241	
Cycle 6		0·599	0·630	0·245	2·37
Cycle 1	C10	0·708	0·522	0·259	
Cycle 6		0·705	0·528	0·256	2·30
Cycle 1	C11	0·575	0·779	0·339	
Cycle 6		0·579	0·774	0·347	3·54
Cycle 1	C12	0·468	0·855	0·329	
Cycle 6		0·467	0·878	0·329	3·41
Cycle 1	C13	0·384	0·699	0·313	
Cycle 6		0·382	0·704	0·306	3·50
Cycle 1	C14	0·404	0·594	0·205	
Cycle 6		0·408	0·582	0·202	2·72
Cycle 1	C15	0·296	0·459	0·172	
Cycle 6		0·308	0·455	0·168	3·30
Cycle 1	C16	0·211	0·630	0·199	
Cycle 6		0·216	0·597	0·199	3·29
Cycle 1	C17	0·276	0·817	0·264	
Cycle 6		0·277	0·820	0·274	3·68
Cycle 1	C18	0·371	0·548	0·398	
Cycle 6		0·377	0·548	0·407	3·02
Cycle 1	C19	0·722	0·372	0·352	
Cycle 6		0·718	0·369	0·359	3·36
Cycle 1	N	0·938	0·677	0·156	
Cycle 6		0·923	0·665	0·150	2·68
Cycle 1	$\mathrm{O^H}$	0·144	0·513	0·258	
Cycle 6		0·146	0·501	0·259	4·16
Cycle 1	O^x	0·780	0·827	0·178	
Cycle 6		0·783	0·846	0·181	2·98
Cycle 1	O^M	0·112	0·293	0·471	
Cycle 6		0·110	0·398	0·478	10·13
Cycle 1	C^M	0·048	0·111	0·416	
Cycle 6		0·006	0·087	0·400	7·76

$\mathrm{O^H}$ refers to the oxygen of the OH-group (C16).
O^x refers to the oxygen of the ether bridge of the oxazolidine ring.
O^M refers to the oxygen of methanol.
C^M refers to the carbon of methanol.

The structure of samandarine-hydrobromide is drawn schematically in Fig. 6, showing the bond lengths and bond angles. The values of the bond lengths and bond angles which were calculated from the final parameters are listed in Table 4.

Discussion of structure

The structure analysis confirmed the sterol skeleton

Table 4. *Bond lengths and bond angles of samandarine-hydrobromide*

	d		Angle
C_1-C_2	1·61 Å	C_1-C_2-N	91°
C_2-N	1·55	C_2-N-C_3	107
$N-C_3$	1·46	$N-C_3-C_4$	111
C_3-C_4	1·65	$C_3-C_4-C_5$	113
C_4-C_5	1·49	$C_4-C_5-C_{10}$	115
C_5-C_{10}	1·50	$C_5-C_{10}-C_1$	109
$C_{10}-C_1$	1·52	$C_5-C_6-C_7$	108
C_5-C_6	1·57	$C_6-C_7-C_8$	110
C_6-C_7	1·59	$C_7-C_8-C_9$	108
C_7-C_8	1·54	$C_8-C_9-C_{10}$	114
C_8-C_9	1·59	$C_9-C_{10}-C_5$	110
C_9-C_{10}	1·52	$C_9-C_{11}-C_{12}$	110
C_9-C_{11}	1·60	$C_{11}-C_{12}-C_{13}$	111
$C_{11}-C_{12}$	1·59	$C_{12}-C_{13}-C_{14}$	108
$C_{12}-C_{13}$	1·58	$C_{13}-C_{14}-C_8$	113
$C_{13}-C_{14}$	1·56	$C_{14}-C_8-C_9$	111
$C_{14}-C_8$	1·48	$C_8-C_9-C_{11}$	120
$C_{14}-C_{15}$	1·54	$C_{13}-C_{14}-C_{15}$	105
$C_{15}-C_{16}$	1·56	$C_{14}-C_{15}-C_{16}$	106
$C_{16}-C_{17}$	1·82	$C_{15}-C_{16}-C_{17}$	105
$C_{17}-C_{13}$	1·57	$C_{16}-C_{17}-C_{13}$	96
$C_{13}-C_{18}$	1·60	$C_{17}-C_{13}-C_{14}$	105
$C_{10}-C_{19}$	1·65	$C_{17}-C_{13}-C_{18}$	113
$C_{16}-O$	1·36	$C_{17}-C_{16}-C_{20}$	110

of the molecule of samandarine and the oxazolidine-ring system as derived by chemical methods (Fig. 6).

From the atomic parameters the junctions of the rings to each other and the configuration of the ring system can be deduced. Using the nomenclature of the steroids, it can be shown from Fig. 7 that the junction between the rings *B* and *C* is 'trans' as in all steroids, whereas the junction between the rings *A* and *B* is 'cis' and the junctions between rings *C* and *D* is 'trans' again. Therefore samandarine can be related to 5β-androstane, which has the same cis–trans–trans junction between the four rings. As shown in Fig. 8, both rings *B* and *C* have the usual chair confirmation.

The connection of the molecules to each other is

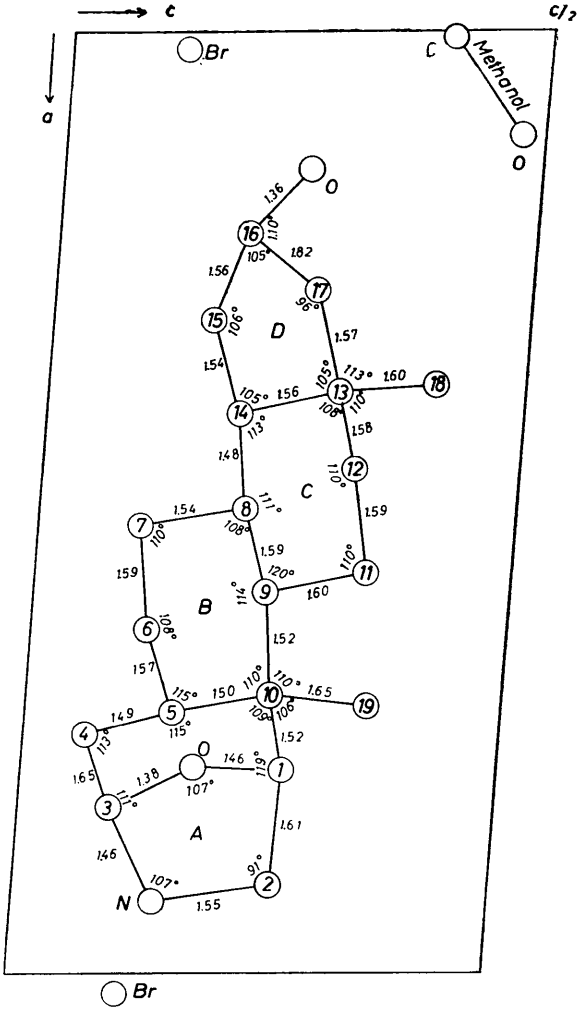


Fig. 6. The structure of samandarine-hydrobromide showing bond length and bond angles.

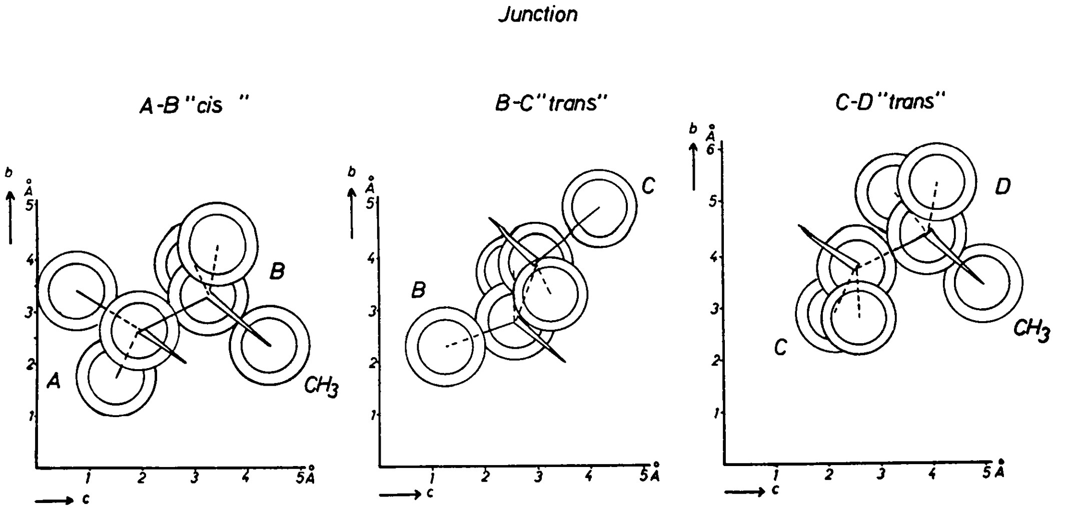


Fig. 7. Junction between the rings *A–B*, *B–C*, *C–D*.

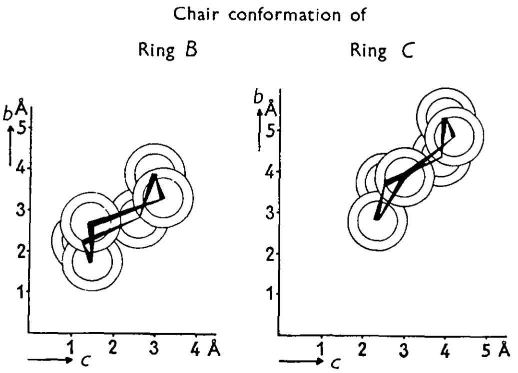


Fig. 8. Chairconfiguration of ring B and C.

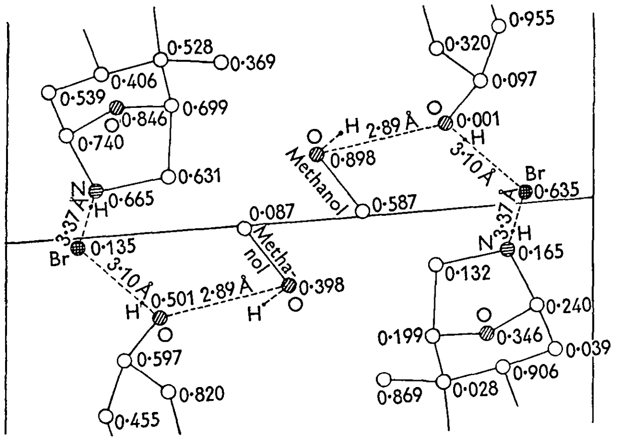


Fig. 9. Connection of the molecules to each other in the structure of samandarine.

shown in Fig. 9. There is a hydrogen bridge of 3·37 Å between the nitrogen of the oxazolidine ring and Br^- and another hydrogen bridge of 3·10 Å between Br^- and the oxygen atom of the ring D of the neighbouring molecule. This shows that the molecules are linked together via hydrogen bridges. The linkage of the methanol to the OH-group is schematically shown in Fig. 9, the O–O distance being 2·89 Å.

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A Reinvestigation of the Crystal Structure of Thortveitite $Sc_2Si_2O_7$

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With 252 $F_o(hkl)$, least-squares solutions for the structure of $Sc_2Si_2O_7$ have been found in each of the space groups *Cm*, *C*2 and *C*2/*m*. After discussion, the correct space group is concluded to be *C*2/*m* and the Si–O–Si angle is therefore 180° [in agreement with Zachariasen (1930)]. The Si–O distances are all close to 1·62 Å; the Sc–O distances average 2·13 Å.

1. Introduction

Following some preliminary work by Gossner & Mussgnug (1929), the crystal structure of thortveitite, $Sc_2Si_2O_7$, was investigated by Zachariasen (1930), who derived a structure in the space group *C*2/*m* with a linear Si–O–Si link in the Si_2O_7 pyrosilicate group. Barclay, Cox & Lynton (1956) called attention to the wide range from 131° to 180° in the reported Si–O–Si angles for the pyrosilicate groups in various minerals and suggested that reinvestigations were needed, particularly of those structures in which 180° angles had

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