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The Structure of Strychnine Sulfonic Acid Tetrahydrate

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Strychnine sulphonic acid tetrahydrate, $C_{21}H_{22}N_2O_2.SO_3.4H_2O$, crystallizes in space group $P2_12_12_1$ with $a=14{\cdot}007$ (4), $b=20{\cdot}379$ (5), $c=7{\cdot}441$ (3) Å, $Z=4$. The crystal data were collected on a General Electric single-crystal diffractometer. The structure* was solved by direct methods with the cosine values of the structure invariants. Refinement by a block-diagonal least-squares procedure resulted in a final R of 7·9% for 1388 observed reflections. Hydrogen atoms were located in a difference synthesis. The molecules are held together by hydrogen bonds between water molecules and sulfur-oxygens. The strychnine molecule is compared in three of its derivatives.

Introduction

Several isomeric sulfonic acids of strychnine and of various strychnine derivatives have been reported by Leuchs and his collaborators (Leuchs & Weber, 1909; Leuchs & Rauch, 1914; Leuchs & Schwaebel, 1914). Strychnine sulfonic acids are produced by bubbling sulfur dioxide into a suspension of strychnine and manganese dioxide in water (Edward, 1972). The position of the sulfonic acid group in these compounds is not known so far.

The structure of the strychnine molecule was established on chemical grounds by the independent work of Robinson & Stephen (1948) and Woodward & Brehm (1948). The molecular configuration favored by Robinson and Woodward was confirmed by X-ray methods by Bokhoven, Schoone & Bijvoet (1951), and Robertson & Beevers (1950). The first group used the isomorphous replacement method with strychnine sulfate and selenate pentahydrates and the second used strychnine hydrobromide dihydrate but the hydrogen atoms were not located. The structure of strychnine sulfonic acid tetrahydrate was solved by direct methods with structure invariants. The molecular configuration given in Fig. 1 shows the numbering of atoms and ring designations. The hydrogen atoms are omitted from the diagrams but are given the same numbers as the atoms to which they are bonded. Wherever two hydrogen atoms are bonded to the same atom, they are indicated by the atom number followed by *A* or *B*. Oxygen of a water molecule is indicated by O(*W*) and oxygen bonded to sulfur by O(S).

The structure is particularly interesting in that the position of attachment of the sulfonic acid group is at a tertiary rather than the expected secondary carbon atom adjacent to nitrogen. The method of formation of the compound, based on its structure, would seem to be *via* a ring opening followed by a ring closure reaction of the ether ring as is known to occur in the formation of a number of other derivatives of strychnine (Manske, 1965).

Experimental

Crystals of strychnine sulfonic acid tetrahydrate were grown from a methanol/water solution, and are needle-shaped and colorless. A crystal with dimensions of about 0·10 × 0·10 × 0·15 mm was used for data collection. X-ray measurements were carried out on a General Electric single-crystal diffractometer. The crystal was

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* The structure was solved at 'The Workshop on the Use of Structure Invariants in Phase Determination'. Medical Foundation of Buffalo and SUNY/Buffalo, July 10-30, 1972.

mounted with the needle axis (c) parallel to the φ axis of the instrument. The systematic extinctions ($h00$, $h=2n+1$; $0k0$, $k=2n+1$; $00l$, $l=2n+1$) indicated the space group $P2_12_12_1$. The unit-cell dimensions were determined from a least-squares analysis of 60 independent measurements of high-angle reflections. The density was measured by flotation in CCl_4 and kerosene. The crystal data are given in Table 1.

Table 1. *Crystal data for strychnine sulfonic acid tetrahydrate*

$C_{21}H_{22}N_2O_2.SO_3.4H_2O$
F.W. 486·52
Orthorhombic, $P2_12_12_1$
$Z=4$
$F(000)=1032$
$a=14{\cdot}007\ (4)$ Å
$b=20{\cdot}379\ (5)$
$c=\ 7{\cdot}441\ (3)$
$D_m=1{\cdot}51\ \mathrm{g\ cm^{-3}}$
$D_c\ =1{\cdot}52\ \mathrm{g\ cm^{-3}}$
$\lambda(\mathrm{Cu}\ K\alpha_1)=1{\cdot}54051$ Å
$\lambda(\mathrm{Cu}\ K\alpha_2)=1{\cdot}54438$ Å

Intensities were measured for 2258 independent spectra with $2\theta < 140°$ by the stationary-crystal stationary-counter method, with Cu $K\alpha$ radiation, monochromated by balanced nickel and cobalt filters and by pulse-height discrimination. Each reflection was measured for 10 s with each filter. Intensities were corrected for Lorentz and polarization effects, but not for absorption ($\mu=18{\cdot}42\ \mathrm{cm^{-1}}$). Normalized structure-factor amplitudes were derived from the scaled intensities.

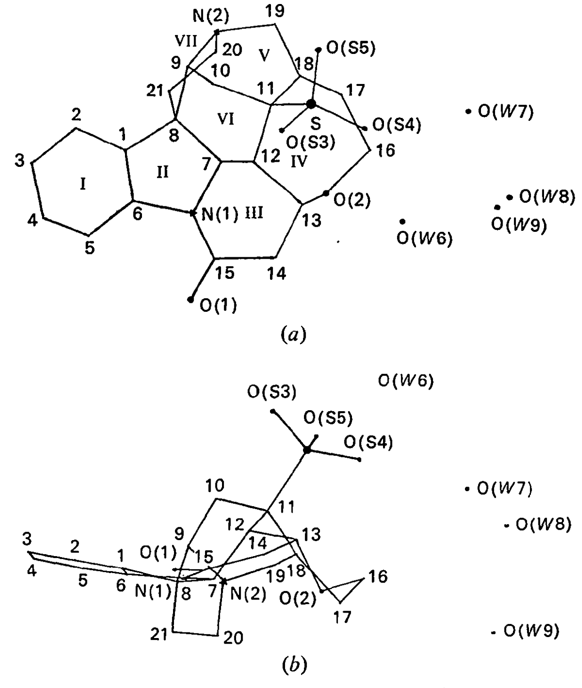

Fig. 1. Strychnine sulfonic acid tetrahydrate. (*a*) View down **c** showing the numbering of atoms and ring designations. (*b*) View down **a** showing the numbering of atoms.

Structure determination

The phases of four reflections with large normalized structure factors, E, and having many interactions with other triplets were arbitrarily specified to fix the origin and enantiomorph (Table 2).

Table 2. *Assignment of origin and enantiomorph*

h			$\lvert E\rvert$	φ	
0	13	3	2·448	$\pi/2$	Origin specification
0	16	1	2·430	0	
7	5	0	2·308	$-\pi/2$	
1	18	0	2·704	$\pi/2$	Enantiomorph

Three phases were obtained by means of the $\sum_1$ relations (Hauptman & Karle, 1953). In addition, pair relations (Hauptman, 1972) proved very useful in deriving several other phases. The remaining phases were derived with the values of the structure invariants. An initial set of 52 phases thus obtained was used as input in the tangent formula of Karle & Hauptman (1956) and the phases of 295 reflections with $E > 1{\cdot}5$ were determined. With these phases an E map was computed from which 28 non-hydrogen atoms out of 33 were obtained. With the positions of these atoms, three cycles of block-diagonal least-squares refinement reduced $R=[\sum\lvert(\lvert F_o\rvert-\lvert F_c\rvert)\rvert/\sum(\lvert F_o\rvert)]$ to 0·40. The remaining non-hydrogen atoms were obtained from a difference map calculated with 1388 observed structure factors. R at this stage was 0·30. Several cycles of full-matrix least-squares refinement with an isotropic thermal parameter of 3·00 Å^2 reduced R to 0·14. The refinement was continued with anisotropic thermal parameters. R converged to 0·10. A difference synthesis computed at this stage revealed the locations of the hydrogen atoms. The alternative positions for the hydrogen atom attached either to the sulfonic acid oxygen or to the nitrogen N(2) are considered in the discussion. The Booth correction (Stout & Jensen, 1968) was applied to fix the positional parameters of the hydrogen atoms. For subsequent refinement, the hydrogens were assigned an isotropic thermal parameter of 5·0 Å^2 and their positions were fixed. Three cycles of block diagonal least-squares refinement were performed. All non-hydrogen atoms were refined anisotropically. All the diffraction data (including unobserved reflections) were used in the refinement except those for which $F_{\mathrm{calc}}/F_{\mathrm{obs}} < 0{\cdot}70$. The principal effect of this cut-off was to eliminate those unobserved reflections that were much lower in intensity than the threshold value assigned. Conversely, those 'unobserved' reflections that were calculated to be larger than the threshold value were allowed to influence the refinement. The inclusion of unobserved data and the cut-off value led to improved geometry. The weighting

Table 3. *Observed and calculated structure factor amplitudes from the refined parameters for this structure*

The values are tabulated on ten times absolute scale.

H	K	L	FO	FC
0	2	-0	224	219
0	4	-0	22	75
0	6	-0	1100	978
0	8	-0	1115	927
0	10	-0	37	7
0	12	-0	181	217
0	14	-0	173	155
0	16	-0	230	238
0	18	-0	267	253
0	20	-0	57	55
1	1	-0	678	810
1	2	-0	865	1138
1	3	-0	83	24
1	4	-0	830	887
1	5	-0	25	23
1	6	-0	684	652
1	7	-0	497	456
1	8	-0	278	286
1	9	-0	75	32
1	10	-0	65	68
1	11	-0	304	262
1	12	-0	117	103
1	13	-0	150	131
1	14	-0	123	97
1	15	-0	226	231
1	16	-0	140	153
1	17	-0	55	62
1	18	-0	398	388
1	19	-0	57	40
1	20	-0	57	131
2	0	-0	796	807
2	1	-0	429	390
2	2	-0	810	823
2	3	-0	944	975
2	4	-0	384	330
2	5	-0	296	186
2	6	-0	441	351
2	7	-0	83	49
2	8	-0	408	309
2	9	-0	84	69
2	10	-0	470	418
2	11	-0	153	161
2	12	-0	127	121
2	13	-0	243	188
2	14	-0	49	36
2	15	-0	51	8
2	16	-0	491	509
2	17	-0	191	189
2	18	-0	57	19
2	20	-0	113	98
3	1	-0	23	11
3	2	-0	744	741
3	3	-0	268	223
3	4	-0	154	159
3	5	-0	364	350
3	6	-0	940	823
3	7	-0	630	585
3	8	-0	427	353
3	9	-0	802	715
3	10	-0	255	236
3	11	-0	62	38
3	12	-0	202	211
3	13	-0	270	241
3	14	-0	235	190
3	15	-0	191	204
3	16	-0	85	68
3	17	-0	167	166
3	18	-0	127	155
3	19	-0	57	49
3	20	-0	207	177
4	0	-0	744	706
4	1	-0	102	110
4	2	-0	74	10
4	3	-0	409	373
4	4	-0	448	340
4	5	-0	854	703
4	6	-0	259	179
4	7	-0	56	82
4	8	-0	852	772
4	9	-0	147	166
4	10	-0	66	39
4	11	-0	44	46
4	12	-0	134	138
4	13	-0	178	181
4	14	-0	95	87
4	15	-0	215	229
4	16	-0	87	126
4	17	-0	126	102
4	18	-0	57	13
4	19	-0	57	17
4	20	-0	125	110
5	1	-0	451	380
5	2	-0	420	367
5	3	-0	83	70
5	4	-0	506	443
5	5	-0	321	238
5	6	-0	1008	862
5	7	-0	136	214
5	8	-0	198	196
5	9	-0	314	263
5	10	-0	559	578
5	11	-0	112	108
5	12	-0	214	218
5	13	-0	50	47
5	14	-0	174	134
5	15	-0	54	58
5	16	-0	56	40
5	17	-0	90	95
5	18	-0	57	61
5	19	-0	80	98
5	20	-0	55	13
6	0	-0	348	425
6	1	-0	512	510
6	2	-0	34	17
6	3	-0	55	0
6	4	-0	250	264
6	5	-0	529	439
6	6	-0	62	105
6	7	-0	583	564
6	8	-0	99	157
6	9	-0	93	105
6	10	-0	92	121
6	11	-0	59	38
6	12	-0	177	187
6	13	-0	188	181
6	14	-0	54	21
6	15	-0	179	218
6	16	-0	56	36
6	17	-0	285	303
6	18	-0	57	62
6	19	-0	56	24
6	20	-0	164	188
7	0	-0	37	0
7	1	-0	74	51
7	2	-0	568	530
7	3	-0	444	459
7	4	-0	213	220
7	5	-0	701	701
7	6	-0	136	117
7	7	-0	367	283
7	8	-0	101	81
7	9	-0	247	245
7	10	-0	109	108
7	11	-0	87	87
7	12	-0	52	19
7	13	-0	166	171
7	14	-0	146	195
7	15	-0	113	105
7	16	-0	107	102
7	17	-0	57	52
7	18	-0	56	13
7	19	-0	55	80
7	20	-0	54	57
8	0	-0	160	156
8	1	-0	147	151
8	2	-0	41	49
8	3	-0	135	183
8	4	-0	241	201
8	5	-0	287	315
8	6	-0	44	74
8	7	-0	282	293
8	8	-0	68	70
8	9	-0	111	106
8	10	-0	63	42
8	11	-0	306	302
8	12	-0	66	59
8	13	-0	56	26
8	14	-0	107	196
8	15	-0	307	313
8	16	-0	57	86
8	17	-0	56	49
8	18	-0	68	103
8	19	-0	56	2
8	20	-0	82	112
9	1	-0	63	66
9	2	-0	45	0
9	3	-0	71	98
9	4	-0	65	56
9	5	-0	47	8
9	6	-0	264	240
9	7	-0	392	364
9	8	-0	96	128
9	9	-0	118	97
9	10	-0	85	85
9	11	-0	422	434
9	12	-0	324	339
9	13	-0	80	82
9	14	-0	57	95
9	15	-0	57	40
9	16	-0	56	44
9	17	-0	87	74
9	18	-0	66	111
9	19	-0	213	205
9	20	-0	60	86
10	0	-0	266	266
10	1	-0	177	139
10	2	-0	48	28
10	3	-0	49	35
10	4	-0	78	84
10	5	-0	123	121
10	6	-0	51	46
10	7	-0	97	83
10	8	-0	223	183
10	9	-0	55	22
10	10	-0	79	93
10	11	-0	160	126
10	12	-0	57	29
10	13	-0	166	149
10	14	-0	56	30
10	15	-0	205	189
10	16	-0	55	25
10	17	-0	54	23
10	18	-0	52	19
10	19	-0	49	19
10	20	-0	44	6
11	1	-0	163	158
11	2	-0	52	57
11	3	-0	286	313
11	4	-0	220	184
11	5	-0	155	156
11	6	-0	54	38
11	7	-0	133	135
11	8	-0	116	130
11	9	-0	155	166
11	10	-0	133	132
11	11	-0	156	125
11	12	-0	57	19
11	13	-0	56	75
11	14	-0	55	2
11	15	-0	122	131
11	16	-0	136	125
11	17	-0	81	102
11	18	-0	48	25
11	19	-0	43	26
12	0	-0	524	530
12	1	-0	163	146
12	2	-0	196	205
12	3	-0	291	316
12	4	-0	263	288
12	5	-0	220	227
12	6	-0	130	139
12	7	-0	55	20
12	8	-0	212	230
12	9	-0	55	47
12	10	-0	56	42
12	11	-0	56	3
12	12	-0	118	124
12	13	-0	189	150
12	14	-0	54	52
12	15	-0	53	55
12	16	-0	50	16
12	17	-0	92	95
12	18	-0	41	41
2	16	-0	57	8
13	1	-0	56	18
13	2	-0	104	94
13	3	-0	56	57
13	4	-0	56	57
13	5	-0	152	142
13	6	-0	141	161
13	7	-0	55	80
13	8	-0	55	65
13	9	-0	54	60
13	10	-0	54	31
13	11	-0	55	33
13	12	-0	54	52
13	13	-0	106	109
13	14	-0	51	40
13	15	-0	48	14
13	16	-0	43	18
13	17	-0	37	18
14	0	-0	78	86
14	1	-0	95	95
14	2	-0	103	105
14	3	-0	55	102
14	4	-0	55	20
14	5	-0	54	11
14	6	-0	54	32
14	7	-0	54	84
14	8	-0	53	13
14	9	-0	53	14
14	10	-0	198	180
14	11	-0	144	158
14	12	-0	50	11
14	13	-0	47	24
14	14	-0	44	97
14	15	-0	39	12
0	1	1	544	604
0	2	1	314	300
0	3	1	506	538
0	4	1	884	874
0	5	1	474	466
0	6	1	125	74
0	7	1	31	24
0	8	1	67	3
0	9	1	36	19
0	10	1	109	71
0	11	1	329	321
0	12	1	92	98
0	13	1	46	11
0	14	1	49	73
0	15	1	248	250
0	16	1	466	476
0	17	1	305	330
0	18	1	56	65
0	19	1	273	282
0	20	1	345	314
1	0	1	142	188
1	1	1	637	719
1	2	1	812	904
1	3	1	126	81
1	4	1	426	355
1	5	1	630	588
1	6	1	218	246
1	7	1	253	228
1	8	1	257	198
1	9	1	63	55
1	10	1	360	369
1	11	1	291	273
1	12	1	227	208
1	13	1	196	195
1	14	1	331	334
1	15	1	96	115
1	16	1	245	227
1	17	1	87	79
1	18	1	196	186
1	19	1	145	155
1	20	1	98	136
2	0	1	540	553
2	1	1	61	16
2	2	1	183	197
2	3	1	330	300
2	4	1	902	850
2	5	1	217	232
2	6	1	349	300
2	7	1	175	183
2	8	1	722	631
2	9	1	401	365
2	10	1	136	149
2	11	1	205	166
2	12	1	234	247
2	13	1	198	206
2	14	1	197	200
2	15	1	220	208
2	16	1	76	87
2	17	1	162	185
2	18	1	200	199
2	19	1	57	112
2	20	1	195	175
3	0	1	849	837
3	1	1	651	628
3	2	1	907	888
3	3	1	531	473
3	4	1	696	581
3	5	1	168	131
3	6	1	359	279
3	7	1	290	254
3	8	1	109	139
3	9	1	547	543
3	10	1	686	656
3	11	1	43	50
3	12	1	325	279
3	13	1	76	78
3	14	1	269	283
3	15	1	147	192
3	16	1	244	233
3	17	1	56	57
3	18	1	220	226
3	19	1	57	72
3	20	1	56	41
4	0	1	201	252
4	1	1	343	237
4	2	1	525	492
4	3	1	254	256
4	4	1	355	283
4	5	1	487	401
4	6	1	178	196
4	7	1	108	86
4	8	1	578	511
4	9	1	212	202
4	10	1	123	114
4	11	1	70	82
4	12	1	289	272
4	13	1	115	138
4	14	1	63	59
4	15	1	85	91
4	16	1	253	245
4	17	1	56	45
4	18	1	180	170
4	19	1	150	141
4	20	1	172	157
5	0	1	118	140
5	1	1	558	495
5	2	1	396	352
5	3	1	271	193
5	4	1	817	721
5	5	1	380	402
5	6	1	145	129
5	7	1	347	278
5	8	1	151	149
5	9	1	189	192
5	10	1	544	499
5	11	1	139	174
5	12	1	138	168
5	13	1	102	110
5	14	1	75	86
5	15	1	164	162
5	16	1	228	232
5	17	1	254	250
5	18	1	57	74
5	19	1	56	31
5	20	1	55	78
6	0	1	323	328
6	1	1	743	707
6	2	1	389	390
6	3	1	203	208
6	4	1	260	227
6	5	1	255	238
6	6	1	293	296
6	7	1	221	177
6	8	1	272	272
6	9	1	71	75
6	10	1	181	155
6	11	1	49	140
6	12	1	152	189
6	13	1	118	103
6	14	1	305	302
6	15	1	208	193
6	16	1	106	112
6	17	1	189	178
6	18	1	178	166
6	19	1	56	63
6	20	1	54	58
7	0	1	97	94
7	1	1	161	115
7	2	1	434	387
7	3	1	452	405
7	4	1	164	144
7	5	1	104	76
7	6	1	105	89
7	7	1	174	161
7	8	1	278	290
7	9	1	190	207
7	10	1	60	67
7	11	1	237	208
7	12	1	158	150
7	13	1	227	226
7	14	1	167	152
7	15	1	283	295
7	16	1	189	188
7	17	1	69	87
7	18	1	56	51
7	19	1	55	72
7	20	1	54	31
8	0	1	302	260
8	1	1	125	130
8	2	1	42	51
8	3	1	124	129
8	4	1	197	209
8	5	1	513	532
8	6	1	64	63
8	7	1	187	179
8	8	1	219	210
8	9	1	138	164
8	10	1	116	117
8	11	1	275	281
8	12	1	416	420
8	13	1	163	189
8	14	1	98	108
8	15	1	114	157
8	16	1	80	76
8	17	1	56	86
8	18	1	55	18
8	19	1	85	88
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0	2	7	140	111
0	3	7	57	74
0	4	7	57	8
0	5	7	231	214
0	6	7	57	10
0	7	7	56	57
0	8	7	143	145
0	9	7	56	20
0	10	7	55	70
0	11	7	54	35
0	12	7	100	77
0	13	7	52	8
0	14	7	70	87
0	15	7	46	3
0	16	7	42	34
1	0	7	56	48
1	1	7	107	111
1	2	7	90	84
1	3	7	127	103
1	4	7	57	66
1	5	7	57	96
1	6	7	80	85
1	7	7	56	64
1	8	7	56	38
1	9	7	55	65
1	10	7	95	109
1	11	7	54	10
1	12	7	53	57
1	13	7	116	93
1	14	7	49	57
1	15	7	46	52
1	16	7	41	53
2	0	7	130	135
2	1	7	96	109
2	2	7	175	164
2	3	7	57	37
2	4	7	170	162
2	5	7	89	79
2	6	7	98	79
2	7	7	56	22
2	8	7	112	95
2	9	7	55	24
2	10	7	55	105
2	11	7	54	36
2	12	7	53	26
2	13	7	51	42
2	14	7	49	27
2	15	7	45	44
2	16	7	40	31
3	0	7	55	4
3	1	7	96	97
3	2	7	136	111
3	3	7	57	37
3	4	7	89	78
3	5	7	80	72
3	6	7	89	69
3	7	7	56	22
3	8	7	55	57
3	9	7	55	66
3	10	7	109	65
3	11	7	54	51
3	12	7	91	79
3	13	7	50	54
3	14	7	58	53
3	15	7	44	59
3	16	7	38	37
4	0	7	55	26
4	1	7	55	72
4	2	7	117	117
4	3	7	55	76
4	4	7	56	48
4	5	7	97	103
4	15	7	41	23
4	6	7	88	56
4	7	7	162	150
4	8	7	165	137
4	9	7	55	66
4	10	7	56	30
4	11	7	53	54
4	12	7	51	44
4	13	7	92	81
4	14	7	46	26
5	0	7	55	6
5	1	7	95	97
5	2	7	55	22
5	3	7	55	64
5	4	7	56	50
5	5	7	152	149
5	6	7	68	55
5	7	7	109	101
5	8	7	54	12
5	9	7	132	121
5	10	7	53	22
5	11	7	155	118
5	12	7	50	56
5	13	7	47	52
5	14	7	43	41
5	15	7	38	51
6	0	7	54	51
6	1	7	54	46
6	2	7	54	55
6	3	7	54	54
6	4	7	54	51
6	5	7	122	142
6	6	7	55	22
6	7	7	77	135
6	8	7	54	65
6	9	7	53	27
6	10	7	51	16
6	11	7	61	77
6	12	7	81	91
6	13	7	61	49
6	14	7	39	34
7	0	7	53	7
7	1	7	53	28
7	2	7	53	55
7	3	7	53	54
7	4	7	53	79
7	5	7	106	112
7	6	7	101	104
7	7	7	53	57
7	8	7	52	84
7	9	7	190	174
7	10	7	186	149
7	11	7	65	71
7	12	7	43	61
7	13	7	90	85
8	0	7	53	61
8	1	7	53	23
8	2	7	52	61
8	3	7	54	56
8	4	7	52	55
8	5	7	81	98
8	6	7	51	49
8	7	7	160	124
8	8	7	49	40
8	9	7	67	74
8	10	7	45	31
8	11	7	59	64
8	12	7	53	36
9	0	7	51	21
9	1	7	94	109
9	2	7	50	26
9	3	7	106	111
9	4	7	49	26
9	5	7	76	91
9	6	7	47	47
9	7	7	46	63
9	8	7	45	21
9	9	7	67	69
9	10	7	39	21
10	0	7	47	30
10	1	7	47	42
10	2	7	46	25
10	3	7	102	90
10	4	7	45	35
10	5	7	62	59
10	6	7	59	66
10	7	7	89	100
10	8	7	38	52
11	0	7	41	39
11	1	7	70	82
11	2	7	40	41
11	3	7	55	50
11	4	7	38	40
11	5	7	80	89
0	0	8	77	76
0	1	8	55	21
0	2	8	109	102
0	3	8	122	91
0	4	8	54	10
0	5	8	54	35
0	6	8	53	59
0	7	8	53	44
0	8	8	51	25
0	9	8	50	8
0	10	8	48	41
0	11	8	71	70
0	12	8	42	4
0	13	8	37	21
1	0	8	53	57
1	1	8	54	28
1	2	8	54	90
1	3	8	54	61
1	4	8	209	167
1	5	8	54	51
1	6	8	84	91
1	7	8	52	72
1	8	8	51	48
1	9	8	50	43
1	10	8	48	79
1	11	8	45	36
1	12	8	41	2
1	13	8	36	41
2	0	8	75	76
2	1	8	53	31
2	2	8	54	60
2	3	8	54	37
2	4	8	54	58
2	5	8	53	46
2	6	8	65	79
2	7	8	52	36
2	8	8	51	47
2	9	8	49	29
2	10	8	94	93
2	11	8	44	34
2	12	8	57	77
3	0	8	53	18
3	1	8	53	38
3	2	8	53	60
3	3	8	54	42
3	4	8	53	59
3	5	8	75	86
3	6	8	52	51
3	7	8	72	83
3	8	8	70	95
3	9	8	48	46
3	10	8	45	56
3	11	8	42	44
3	12	8	38	53
4	0	8	52	58
4	1	8	52	72
4	2	8	52	14
4	3	8	52	40
4	4	8	53	30
4	5	8	52	31
4	6	8	108	101
4	7	8	50	61
4	8	8	48	29
4	9	8	46	58
4	10	8	86	95
4	11	8	40	19
5	0	8	51	0
5	1	8	51	50
5	2	8	51	35
5	3	8	50	69
5	4	8	50	55
5	5	8	50	72
5	6	8	49	47
5	7	8	82	88
5	8	8	72	88
5	9	8	63	19
5	10	8	63	81
6	0	8	49	24
6	1	8	49	48
6	2	8	49	76
6	3	8	84	85
6	4	8	48	45
6	5	8	48	15
6	6	8	46	36
6	7	8	44	11
6	9	8	62	77
7	0	8	46	46
7	1	8	46	9
7	2	8	46	50
7	3	8	45	58
7	4	8	44	20
7	5	8	43	30
7	6	8	85	88
7	7	8	75	74
7	8	8	37	22
8	0	8	42	25
8	1	8	66	82
8	2	8	41	27
8	3	8	76	64
8	4	8	39	39
8	5	8	38	46
8	6	8	35	53
9	0	8	35	17
0	1	9	44	43
0	2	9	44	37
0	3	9	43	91
0	4	9	42	4
0	5	9	40	43
0	6	9	93	94
1	0	9	74	76
1	1	9	44	50
1	2	9	61	72
1	3	9	42	25
1	4	9	41	23
1	5	9	40	43
1	6	9	37	42
2	0	9	42	7
2	1	9	42	35
2	2	9	42	25
2	3	9	41	32
2	4	9	49	60
2	5	9	38	10
2	6	9	57	89
3	0	9	40	52
3	1	9	40	51
3	2	9	39	63
3	3	9	39	44
3	4	9	66	76
3	5	9	36	41
4	0	9	37	16
4	1	9	37	27
4	2	9	37	65
4	3	9	35	26

scheme used in the final refinement was $1/\omega=\{[(|F_o|-20)/20]^2+1\}^{1/2}$ in which the constants were selected so that the quantity minimized, $\sum\omega(|F_o|-|F_c|)^2$ remained invariant with $|F_o|$. The refinement was terminated when shifts of positional parameters were less than 25% of their estimated standard deviations. The final R with 1388 observed reflections was 7·9% and with all 2258 reflections was 12%. The observed and calculated structure factors are given in Table 3. The positional and thermal parameters of the non-hydrogen atoms are presented in Tables 4 and 5, and the positional parameters of the hydrogen atoms in Table 6.

Table 4. *Positional parameters and standard deviations of the nonhydrogen atoms* ($\times 10^5$)

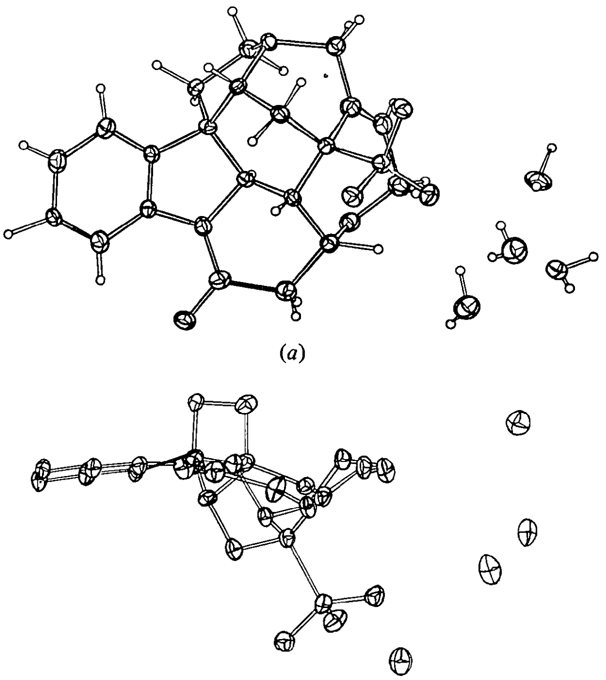
	x	y	z
S	2880 (16)	28906 (11)	18809 (33)
C(1)	8647 (63)	51914 (41)	58856 (143)
C(2)	4690 (73)	57991 (48)	55915 (162)
C(3)	10734 (82)	63303 (48)	52981 (164)
C(4)	20541 (66)	62626 (66)	54035 (153)
C(5)	24633 (71)	56454 (71)	57687 (151)
C(6)	18443 (65)	51222 (65)	59675 (139)
C(7)	11972 (57)	40423 (57)	62384 (135)
C(8)	3620 (59)	45532 (59)	63347 (129)
C(9)	−4860 (61)	43908 (61)	50834 (122)
C(10)	−2550 (64)	40141 (64)	34524 (135)
C(11)	2803 (63)	33769 (63)	39419 (126)
C(12)	12776 (59)	36125 (59)	45850 (131)
C(13)	20484 (67)	30861 (67)	50002 (148)
C(14)	29911 (66)	34478 (66)	55007 (179)
C(15)	29503 (74)	41844 (74)	59498 (163)
C(16)	10716 (73)	22492 (73)	63823 (171)
C(17)	837 (78)	25496 (78)	64382 (165)
C(18)	−2717 (71)	30175 (71)	53846 (134)
C(19)	−12505 (63)	32705 (63)	56787 (119)
C(20)	−8157 (70)	40354 (70)	82195 (150)
C(21)	−975 (62)	45972 (62)	81831 (131)
N(1)	20785 (54)	44506 (54)	62094 (113)
N(2)	−11721 (52)	39885 (52)	63178 (107)
O(1)	36837 (43)	45108 (43)	60063 (110)
O(2)	18289 (45)	27295 (45)	66412 (103)
O(*S*3)	7656 (49)	32925 (49)	5618 (100)
O(*S*4)	7922 (53)	22747 (53)	22493 (98)
O(*S*5)	−7239 (48)	27894 (48)	15002 (104)
O(*W*6)	24337 (56)	18412 (56)	2268 (133)
O(*W*7)	4923 (44)	9641 (44)	34115 (133)
O(*W*8)	20993 (46)	4892 (46)	47122 (118)
O(*W*9)	22114 (62)	6817 (62)	82716 (138)

Structure description

The strychnine molecule contains seven fused rings and the sulfonic acid group is attached to a tertiary carbon, C(11) (Fig. 1). Bond lengths and angles are given in Tables 7 and 8. Table 9 gives the hydrogen–nonhydrogen bond distances. For comparison, the bond lengths and bond angles in strychnine hydrobromide dihydrate and strychnine sulfate pentahydrate are presented in Tables 7 and 8. The accuracy is about ±0·008 for x and y, and about ±0·001 for z in strychnine hydrobromide dihydrate (Robertson & Beevers, 1950). The averaged error in atomic positions is ±0·08 Å in strychnine sulfate pentahydrate (Bokhoven, Schoone & Bijvoet, 1951). Some of the bond lengths in (ii) and (iii) of Tables 7 and 8 are high. The molecular configuration of the strychnine molecule remains the same in all structures. The differences in bond lengths and angles are probably due to the different crystallographic environment.

The equations of the least-squares planes through portions of the molecule, and the atomic deviations and interplanar angles are listed in Table 10(*a*), (*b*), and (*c*). A study of Table 10(*b*) and (*c*) reveals the total nonplanarity of the molecule. Benzene ring I is flat. Four atoms C(1), C(6), C(8) and N(1) of plane *PB* in ring II lie in the same plane but the fifth C(7) projects at a distance of 0·200 Å. The bond C(7)–C(12) makes an angle of 65·2° with the plane *PB*. Four atoms C(20), C(21), C(9), and N(2) of plane *PD* lie in the plane and the fifth C(8) projects at a distance of 0·557 Å. The atoms are approximately tetrahedrally coordinated around C(8). The plane *PE* makes an angle of 143·9° with plane *PD*. Similar 5-ring nonplanarities have been found in the structures of sucrose (Beevers, McDonald, Robertson & Stern, 1952), benzylpenicillin (Geoffrey, 1952) and many other molecules.

C(11) projects 0·722 Å from plane *PF* in ring VI. The plane *PG* consisting of atoms C(10), C(11) and C(12) makes an angle of 126·8° with plane *PF*. Ring V has a boat-like configuration with atoms C(10) and C(19) above the plane at distances 0·672 and 0·666 Å, respectively. The plane *PH* makes angles 130·9° and 128·2° with planes *PI* and *PJ*, respectively. Ring III


(*a*)

(*b*)

Fig. 2. Strychnine sulfonic acid tetrahydrate showing two different views of the thermal vibration ellipsoids. The hydrogen atoms are not shown in (*b*).

Table 5. *Thermal parameters* ($\times 10^4$) *of the nonhydrogen atoms in the form*: $\exp\{-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)\}$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	370 (10)	319 (10)	439 (10)	−1 (10)	−24 (11)	−18 (10)
C(1)	328 (48)	197 (44)	549 (61)	−47 (35)	14 (46)	22 (42)
C(2)	439 (58)	368 (50)	573 (06)	42 (42)	10 (54)	−11 (49)
C(3)	668 (70)	286 (50)	585 (70)	−4 (49)	59 (61)	3 (51)
C(4)	350 (48)	284 (48)	644 (68)	−69 (38)	−35 (50)	14 (48)
C(5)	437 (55)	307 (50)	546 (62)	−58 (40)	−10 (51)	−6 (46)
C(6)	379 (52)	258 (46)	460 (55)	10 (37)	21 (45)	33 (41)
C(7)	174 (39)	351 (48)	492 (54)	−5 (34)	−10 (38)	3 (44)
C(8)	198 (41)	368 (48)	447 (51)	15 (35)	−16 (39)	−54 (41)
C(9)	311 (47)	345 (48)	346 (45)	34 (36)	4 (39)	−39 (38)
C(10)	277 (45)	347 (48)	514 (56)	15 (40)	−62 (45)	107 (42)
C(11)	287 (43)	286 (44)	406 (47)	10 (37)	34 (43)	0 (38)
C(12)	282 (44)	254 (44)	431 (51)	−0 (34)	−64 (40)	65 (41)
C(13)	319 (48)	361 (50)	595 (62)	60 (39)	−27 (48)	95 (46)
C(14)	278 (48)	422 (54)	803 (82)	49 (41)	−95 (53)	−127 (56)
C(15)	376 (54)	443 (56)	578 (68)	53 (44)	36 (53)	−0 (51)
C(16)	414 (56)	454 (63)	670 (73)	−48 (44)	−105 (54)	−138 (57)
C(17)	581 (66)	317 (52)	610 (68)	−112 (44)	37 (56)	43 (48)
C(18)	417 (53)	347 (50)	474 (54)	−13 (44)	98 (50)	−23 (42)
C(19)	360 (47)	376 (50)	341 (41)	−11 (39)	23 (38)	−30 (39)
C(20)	378 (51)	513 (61)	452 (55)	−46 (46)	63 (48)	−91 (53)
C(21)	339 (48)	307 (46)	430 (47)	36 (35)	16 (44)	−48 (41)
N(1)	328 (39)	292 (39)	486 (47)	−28 (32)	−81 (38)	52 (36)
N(2)	348 (39)	302 (37)	393 (42)	−76 (31)	13 (34)	−35 (34)
O(1)	227 (32)	528 (42)	685 (50)	−55 (29)	−44 (34)	48 (40)
O(2)	370 (35)	380 (35)	551 (42)	34 (28)	−40 (33)	34 (34)
O(S3)	464 (38)	511 (42)	476 (41)	−109 (33)	24 (35)	23 (36)
O(S4)	566 (42)	349 (35)	516 (42)	100 (31)	−58 (36)	−38 (33)
O(S5)	366 (35)	507 (42)	584 (44)	−90 (31)	−53 (35)	−123 (38)
O(*W*6)	593 (48)	557 (48)	886 (65)	128 (39)	−41 (49)	26 (50)
O(*W*7)	245 (34)	618 (46)	1003 (65)	−2 (31)	−114 (40)	196 (50)
O(*W*8)	290 (34)	441 (37)	822 (57)	−68 (29)	31 (38)	−13 (41)
O(*W*9)	632 (51)	626 (52)	824 (63)	59 (41)	−87 (53)	−21 (51)

Table 6. *Positional parameters of the hydrogen atoms* ($\times 10^4$)

	x	*y*	*z*
H(2)	−221	5941	5436
H(3)	805	6788	4901
H(4)	2414	6773	5320
H(5)	3028	5654	4977
H(7)	1185	3718	7500
H(9)	4204	145	5500
H(10*A*)	−893	3885	2725
H(10*B*)	200	4334	2850
H(12)	1439	3890	3590
H(13)	2000	2708	3956
H(14*A*)	3288	3205	6688
H(14*B*)	3312	3394	4479
H(16*A*)	1034	2241	5150
H(16*B*)	1114	1890	7470
H(17)	4556	2543	2541
H(19*A*)	−1700	3250	4750
H(19*B*)	−1623	2964	6704
H(20*A*)	−455	3583	8576
H(20*B*)	3547	688	1323
H(21*A*)	4382	5	1595
H(21*B*)	246	4493	9194
H(*W*6*A*)	1876	1951	737
H(*W*6*B*)	2649	2098	−760
H(*W*7*A*)	21	797	4327
H(*W*7*B*)	313	1125	2483
H(*W*8*A*)	2305	424	3696
H(*W*8*B*)	2071	143	5365
H(*W*9*A*)	2260	987	9130
H(*W*9*B*)	1740	687	9091

also has a boat-like configuration with C(12) and C(15) raised above the plane *PK*. The plane *PK* makes angles 119·8° and 174·3° with planes *PL* and *PM*, respectively. In ring IV, the deviations of the atoms from the mean plane are quite large. Atoms C(10), C(12), C(18), and C(11) form a convex surface with C(11) at its vertex where the sulfonic acid group is attached. Rings III, IV, V, VI, and VII form a 'hill shape' structure with atoms in ring I and II lying in the plane. The thermal vibrational ellipsoids in two different views are shown in Fig. 2(*a*) and (*b*).

Hydrogen bonding

The molecular packing diagrams given in Fig. 3(*a*) and (*b*) show the projection down **c** and **a**, respectively. The hydrogen-bond distances and angles are given in Table 11(*a*). Other intermolecular approaches less than 3·6 Å are in Table 11(*b*). Water molecules fill the space between the molecules and are involved in hydrogen bonding. The molecules are linked by a three-dimensional network of O–H···O and C–H···O hydrogen bonds. The bonds are of complex zigzag configuration. The O···O and C···O bond distances have normal values. The shortest O–H···O hydrogen bond is 2·682 Å. The range of hydrogen bond angles found here is greater than that typical for the class of O–H···O

Table 7. *Bond lengths* (Å) *and their standard deviations in strychnine sulfonic acid tetrahydrate* (i) *and bond lengths in strychnine hydrobromide dihydrate* (ii) *and strychnine sulfate pentahydrate* (iii)

	(i)	(ii)	(iii)
C(1)—C(6)	1·379 (13)	1·40	1·505
C(6)—C(5)	1·380 (13)	1·31	1·385
C(5)—C(4)	1·406 (13)	1·34	1·379
C(4)—C(3)	1·381 (15)	1·29	1·456
C(3)—C(2)	1·389 (15)	1·30	1·382
C(2)—C(1)	1·372 (13)	1·30	1·424
C(1)—C(8)	1·514 (12)	1·59	1·416
C(8)—C(21)	1·519 (13)	1·53	1·579
C(21)-C(20)	1·522 (13)	1·54	1·445
C(20)-N(2)	1·501 (14)	1·44	1·340
N(2)—C(19)	1·540 (12)	1·55	1·539
C(19)-C(18)	1·479 (13)	1·65	1·570
C(18)-C(11)	1·510 (13)	1·58	1·566
C(18)-C(17)	1·329 (14)	1·16	1·391
C(17)-C(16)	1·512 (15)	1·54	1·533
C(16)-O(2)	1·454 (12)	1·45	1·401
O(2)—C(13)	1·451 (13)	1·43	1·395
C(13)-C(12)	1·551 (13)	1·36	1·480
C(12)-C(11)	1·551 (12)	1·51	1·611
C(11)-C(10)	1·541 (12)	1·56	1·566
C(10)-C(9)	1·469 (13)	1·64	1·558
C(9)—N(2)	1·559 (12)	1·59	1·586
C(9)—C(8)	1·543 (12)	1·41	1·551
C(12)-C(7)	1·512 (13)	1·55	1·473
C(7)—C(8)	1·565 (12)	1·49	1·519
C(7)—N(1)	1·487 (11)	1·46	1·312
N(1)—C(6)	1·416 (11)	1·37	1·332
N(1)—C(15)	1·348 (13)	1·50	1·541
C(15)-O(1)	1·223 (12)	1·15	1·331
C(15)-C(14)	1·536 (15)	1·49	1·481
C(14)-C(13)	1·555 (14)	1·56	1·502
S——C(11)	1·822 (9)		
S——O(*S*3)	1·440 (8)		
S——O(*S*4)	1·464 (7)		
S——O(*S*5)	1·458 (7)		

Table 8. *Bond angles and their standard deviations in strychnine sulfonic acid tetrahydrate* (i) *and bond angles in strychnine hydrobromide dihydrate* (ii) *and strychnine sulfate pentahydrate* (iii)

	(i)	(ii)	(iii)
N(1)—C(15)-C(14)	117·2 (9)	118·1	116·1
N(1)—C(15)-O(1)	122·4 (8)	123·7	111·6
C(14)-C(15)-O(1)	120·4 (10)	117·3	131·8
C(15)-N(1)—C(6)	125·4 (8)	115·3	119·9
C(15)-N(1)—C(7)	121·8 (7)	115·0	114·7
C(6)—N(1)—C(7)	110·4 (6)	119·8	118·2
N(1)—C(6)—C(5)	127·8 (9)	140·2	145·7
N(1)—C(6)—C(1)	109·5 (7)	102·5	92·0
C(5)—C(6)—C(1)	122·7 (8)	117·1	117·1
C(6)—C(5)—C(4)	117·0 (9)	125·6	127·4
C(5)—C(4)—C(3)	120·3 (8)	112·7	111·7
C(4)—C(3)—C(2)	121·2 (9)	126·8	117·3
C(3)—C(2)—C(1)	118·7 (11)	120·7	126·4
C(6)—C(1)—C(2)	120·0 (8)	116·0	109·6
C(6)—C(1)—C(8)	111·4 (7)	110·3	124·6
C(2)—C(1)—C(8)	128·3 (11)	133·3	125·7
C(1)—C(8)—C(7)	102·3 (7)	104·6	88·8
C(1)—C(8)—C(9)	114·1 (6)	110·8	122·9
C(1)—C(8)—C(21)	110·2 (6)	108·7	113·2
C(7)—C(8)—C(9)	113·8 (6)	120·3	116·3
C(7)—C(8)—C(21)	113·4 (7)	109·4	112·6
C(9)—C(8)—C(21)	103·4 (6)	102·7	103·2

Table 8 (*cont.*)

	(i)	(ii)	(iii)
N(1)—C(7)—C(8)	104·4 (6)	99·3	112·9
N(1)—C(7)—C(12)	104·5 (7)	108·1	113·0
C(8)—C(7)—C(12)	118·5 (8)	122·4	115·2
C(7)—C(12)-C(13)	106·8 (8)	111·2	116·3
C(7)—C(12)-C(11)	111·2 (7)	111·6	119·5
C(13)-C(12)-C(11)	118·3 (6)	123·8	112·3
C(12)-C(13)-C(14)	108·1 (8)	117·1	110·5
C(12)-C(13)-O(2)	111·4 (7)	111·6	113·3
C(14)-C(13)-O(2)	102·4 (7)	110·6	97·8
C(15)-C(14)-C(13)	118·8 (8)	111·4	115·5
C(13)-O(2)—C(16)	112·3 (7)	120·7	125·7
O(2)—C(16)-C(17)	113·0 (8)	112·9	126·4
C(16)-C(17)-C(18)	128·0 (9)	115·2	107·6
C(17)-C(18)-C(11)	125·0 (9)	129·8	136·3
C(17)-C(18)-C(19)	120·6 (7)	119·5	94·1
C(11)-C(18)-C(19)	114·2 (6)	110·7	122·0
C(12)-C(11)-C(18)	113·0 (6)	108·7	116·0
C(12)-C(11)-C(10)	104·5 (7)	106·4	112·6
C(12)-C(11)-S	114·9 (7)		
C(18)-C(11)-C(10)	109·0 (9)	109·0	109·6
C(18)-C(11)-S	109·7 (5)		
C(10)-C(11)-S	105·2 (6)		
C(11)-C(10)-C(9)	110·6 (7)	116·7	99·3
C(8)—C(9)—C(10)	116·1 (9)	110·7	124·9
C(8)—C(9)—N(2)	103·4 (6)	108·3	107·4
C(10)-C(9)—N(2)	110·3 (7)	102·4	104·5
C(8)—C(21)-C(20)	104·6 (6)	100·2	95·9
C(21)-C(20)-N(2)	104·5 (6)	110·4	129·5
C(9)—N(2)—C(20)	108·4 (8)	102·2	95·2
C(9)—N(2)—C(19)	111·1 (7)	115·5	126·0
C(20)-N(2)—C(19)	112·0 (9)	109·6	110·0
N(2)—C(19)-C(18)	108·0 (6)	115·4	107·2
C(11)-S-O(*S*4)	108·1 (6)		
C(11)-S-O(*S*5)	103·5 (5)		
C(11)-S-O(*S*3)	105·4 (6)		
O(*S*4)-S-O(*S*5)	112·5 (4)		
O(*S*4)-S-O(*S*3)	112·9 (6)		
O(*S*5)-S-O(*S*3)	113·5 (4)		

Table 9. *Hydrogen–nonhydrogen distances* (Å)

C(2)——H(2)	1·015
C(3)——H(3)	1·049
C(4)——H(4)	1·158
C(5)——H(5)	0·987
C(7)——H(7)	1·149
C(9)——H(9)	1·130
C(10)—H(10*A*)	1·078
C(10)—H(10*B*)	1·016
C(12)—H(12)	0·960
C(13)—H(13)	1·097
C(14)—H(14*A*)	1·095
C(14)—H(14*B*)	0·890
C(16)—H(16*A*)	0·919
C(16)—H(16*B*)	1·093
C(17)—H(17)	1·076
C(19)—H(19*A*)	0·936
C(19)—H(19*B*)	1·116
C(20)—H(20*A*)	1·084
C(20)—H(20*B*)	1·111
C(21)—H(21*A*)	1·104
C(21)—H(21*B*)	0·917
O(*W*6)-H(*W*6*A*)	0·898
O(*W*6)-H(*W*6*B*)	0·951
O(*W*7)-H(*W*7*A*)	1·008
O(*W*7)-H(*W*7*B*)	0·805
O(*W*8)-H(*W*8*A*)	0·821
O(*W*8)-H(*W*8*B*)	0·858
O(*W*9)-H(*W*9*A*)	0·896
O(*W*9)-H(*W*9*B*)	0·899

hydrogen bonds. All H_2O molecules have hydrogen bonds to one another or to oxygens of the sulfonic acid

The grouping of the water molecules gives the oxygen atoms an approximately tetrahedral arrangement. The oxygen atoms are connected by hydrogen atoms lying approximately along the inter-oxygen vectors. The equilibrium positions of the hydrogen atoms are not on the O–O lines, though O–H···O linearity is not a necessary criterion for the formation of a hydrogen bond (Chidambaram, 1961, 1962). It seems that the hydrogen bonding adapts itself to the fixed geometry of the water-oxygens and to the arrangement of the molecules in the crystal. The intermolecular arrangement makes it apparent that there are indeed C–H···O hydrogen bonds. Similar 'short' intermolecular distances between a carbon atom with at least one hydrogen atom attached to it and an oxygen atom have been observed (Sutor, 1962), mainly in crystal structures of heterocyclic molecules with which strychnine

Table 10. *Equations of and deviations from least-squares planes and interplanar angles*

(*a*) Equations of least-squares planes

The equations are of the form $lx+my+nz=p$ where x, y and z are in Å.

Plane	Atoms in plane	Equation of plane
PA	C(1), C(2), C(3), C(4), C(5), C(6)	$-0{\cdot}02742x+0{\cdot}18472y+0{\cdot}98241z=6{\cdot}2310$
PB	C(1), C(6), N(1), C(8)	$0{\cdot}03476x+0{\cdot}18521y+0{\cdot}98208z=6{\cdot}3425$
LC	C(7), C(12)	$0{\cdot}0000\ x+0{\cdot}81447y-0{\cdot}58021z=4{\cdot}0146$
PD	C(9), C(21), C(20), N(2)	$0{\cdot}68639x+0{\cdot}72336y+0{\cdot}07503z=7{\cdot}2745$
PE	C(8), C(9), C(21)	$-0{\cdot}16339x+0{\cdot}97658y-0{\cdot}13999z=8{\cdot}3186$
PF	C(10), C(9), C(8), C(7), C(12)	$0{\cdot}44412x+0{\cdot}72574y-0{\cdot}52542z=4{\cdot}3482$
PG	C(10), C(11), C(12)	$-0{\cdot}34363x+0{\cdot}06417y+0{\cdot}93691z=3{\cdot}0545$
PH	C(9), C(11), C(18), N(2)	$0{\cdot}69447x+0{\cdot}13031y+0{\cdot}70763z=3{\cdot}3080$
PI	C(18), C(19), N(2)	$0{\cdot}03451x-0{\cdot}31122y+0{\cdot}94971z=1{\cdot}8785$
PJ	C(9), C(10), C(11)	$0{\cdot}87274x+0{\cdot}48282y-0{\cdot}07215z=3{\cdot}4525$
PK	C(7), C(13), C(14), N(1)	$0{\cdot}05598x-0{\cdot}30968y+0{\cdot}94919z=1{\cdot}8446$
PL	C(7), C(12), C(13)	$0{\cdot}70606x+0{\cdot}60558y-0{\cdot}36708z=4{\cdot}4681$
PM	C(14), C(15), N(1)	$0{\cdot}05918x-0{\cdot}21462y+0{\cdot}97490z=2{\cdot}7305$
PN	C(13), C(16), C(17), C(18), C(11)	$0{\cdot}04948x+0{\cdot}64000y+0{\cdot}76628z=6{\cdot}8680$
PP	C(8), C(7), N(1)	$0{\cdot}03623x-0{\cdot}02784y+0{\cdot}99896z=4{\cdot}4687$
PO	C(10), C(12), C(18)	$-0{\cdot}09924x+0{\cdot}57551y+0{\cdot}81175z=6{\cdot}8285$

(*b*) Deviations (Å) from the least-squares planes

Deviations in parentheses are not included in the least-squares calculations.

	PA	*PB*	*PD*	*PF*	*PH*	*PK*	*PN*
C(1)	−0·0077	−0·0402					
C(2)	0·0214						
C(3)	−0·0161						
C(4)	−0·0026						
C(5)	0·0163						
C(6)	−0·0113	0·0414					
C(7)		(−0·1997)		−0·0646		0·1046	
C(8)		0·0207	(−0·5572)	0·1342			
C(9)			−0·0520	−0·1452	0·0617		
C(10)				0·0801	(−0·6723)		
C(11)				(−0·7219)	−0·0638		−0·1940
C(12)				−0·0047		(−0·7854)	
C(13)						−0·0998	0·1538
C(14)						0·0995	
C(15)							
C(16)							−0·2185
C(17)							−0·1366
C(18)					0·0647		0·1220
C(19)					(−0·6656)		
C(20)			−0·0839				
C(21)			0·0522				
S							
N(1)		−0·0240				−0·1043	
N(2)			0·0838		−0·0626		
O(1)							
O(2)							
O(S3)							
O(S4)							
O(S5)							

Table 10 (*cont.*)

(*c*) Interplanar angles

Plane 1	Plane 2	Angle
PA	*PB*	176·44°
PB	*LC*	65·23
PD	*PE*	143·91
PG	*PF*	126·75
PH	*PI*	130·95
PH	*PJ*	128·17
PK	*PL*	119·76
PK	*PM*	174·35
PA	*PD*	76·93
PA	*PF*	66·78
PA	*PH*	134·44
PA	*PN*	150·43
PA	*PK*	150·90
PA	*PO*	155·03
PA	*PP*	167·22

derivatives can be grouped (Kitaigorodskii, 1961). The hydrogen atom is located between the two electronegative atoms and Hamilton & Ibers (1968) have also shown that the bond formed by these is not necessarily linear. The 'short' C···O contact distances observed in various organic molecules vary from 3·00 to 3·24 Å, H···O distances vary from 2·07 to 2·76 Å, and C–H···O angles vary from 109·1 to 173·3° (Sutor, 1962). The contact distances and bond angles in the present study are within the accepted limits. A hydrogen atom was initially assigned to the oxygen of the SO_3 group. However, Professor J. T. Edward, in a private communication, pointed out that the hydrogen was more likely to be located on nitrogen N(2). Examination of the difference map revealed a possible hydrogen position near N(2), and the data for this are presented in Table 12. Typical hydrogen atom heights in this compound are 130–200 units. Consequently, this hydrogen atom cannot be unambiguously assigned from the diffraction data, whereas the chemical evidence is in favor of its being attached to N(2).

Table 11. *Intermolecular distances*

(*a*) Hydrogen bonding

X–H···Y	Distance (Å) X–H	Distance (Å) X···Y	Distance (Å) H···Y	Angle (°)
O(*W*7)–H(*W*7*A*)···O(1)	1·008	2·747	1·992	129·7
O(*W*7)–H(*W*7*B*)···O(S4)	0·805	2·838	2·443	111·5
O(*W*6)–H(*W*6*A*)···O(S4)	0·898	2·886	2·000	168·9
O(*W*6)–H(*W*6*B*)···O(S5)	0·951	2·982	2·358	112·8
O(*W*9)–H(*W*9*A*)···O(*W*6)	0·896	2·794	1·938	159·3
O(*W*8)–H(*W*8*A*)···O(*W*9)	0·821	2·682	2·373	112·2
O(*W*8)–H(*W*8*B*)···O(*W*9)	0·858	2·788	2·502	100·4
C(4)—H(4)·······O(S3)	1·158	3·190	2·560	112·6
C(20)—H(20*A*)····O(S3)	1·084	3·190	2·336	135·3

Table 11 (*cont.*)

(*b*) Other close approaches less than 3·6 Å

'Neqv' and 'cell' specify the atom N with respect to atom M Neqv = 1, 2, 3 and 4 refers to the equivalent positions x,y,z; $\frac{1}{2}-x,-y,\frac{1}{2}+z$; $\frac{1}{2}+x,\frac{1}{2}-y,-z$; $-x,\frac{1}{2}+y,\frac{1}{2}-z$ respectively. 'cell' refers to the unit translations along the crystallographic axes.

M···N	Neqv/cell	Distance Å X···Y
C(2)····O(*W*7)	(4/000)	3·286
C(3)····O(S5)	(4/000)	3·298
C(3)····O(*W*7)	(4/000)	3·603
C(4)····C(15)	(2/01$\bar{1}$)	3·437
C(4)····O(S3)	(2/010)	3·190
C(5)····N(1)	(2/01$\bar{1}$)	3·459
C(5)····O(S3)	(2/010)	3·299
C(15)···O(*W*7)	(3/001)	3·605
O(1)····C(21)	(2/01$\bar{1}$)	3·413
O(2)····O(*W*6)	(1/001)	3·334
C(16)···O(*W*6)	(1/001)	3·538
C(16)···O(*W*7)	(1/000)	3·522
C(17)···O(S3)	(1/001)	3·553
C(9)····O(*W*8)	(3/$\bar{1}$01)	3·396
C(19)···O(*W*6)	(3/$\bar{1}$01)	3·571
C(19)···O(*W*8)	(3/$\bar{1}$01)	3·440
N(2)····O(*W*8)	(3/$\bar{1}$01)	2·755
C(20)···O(S3)	(1/001)	3·190
C(20)···O(S5)	(1/001)	3·526
C(20)···O(*W*6)	(3/$\bar{1}$01)	3·248
C(21)···O(S3)	(1/001)	3·416
C(21)···O(1)	(2/010)	3·416
C(21)···O(*W*8)	(4/001)	3·691

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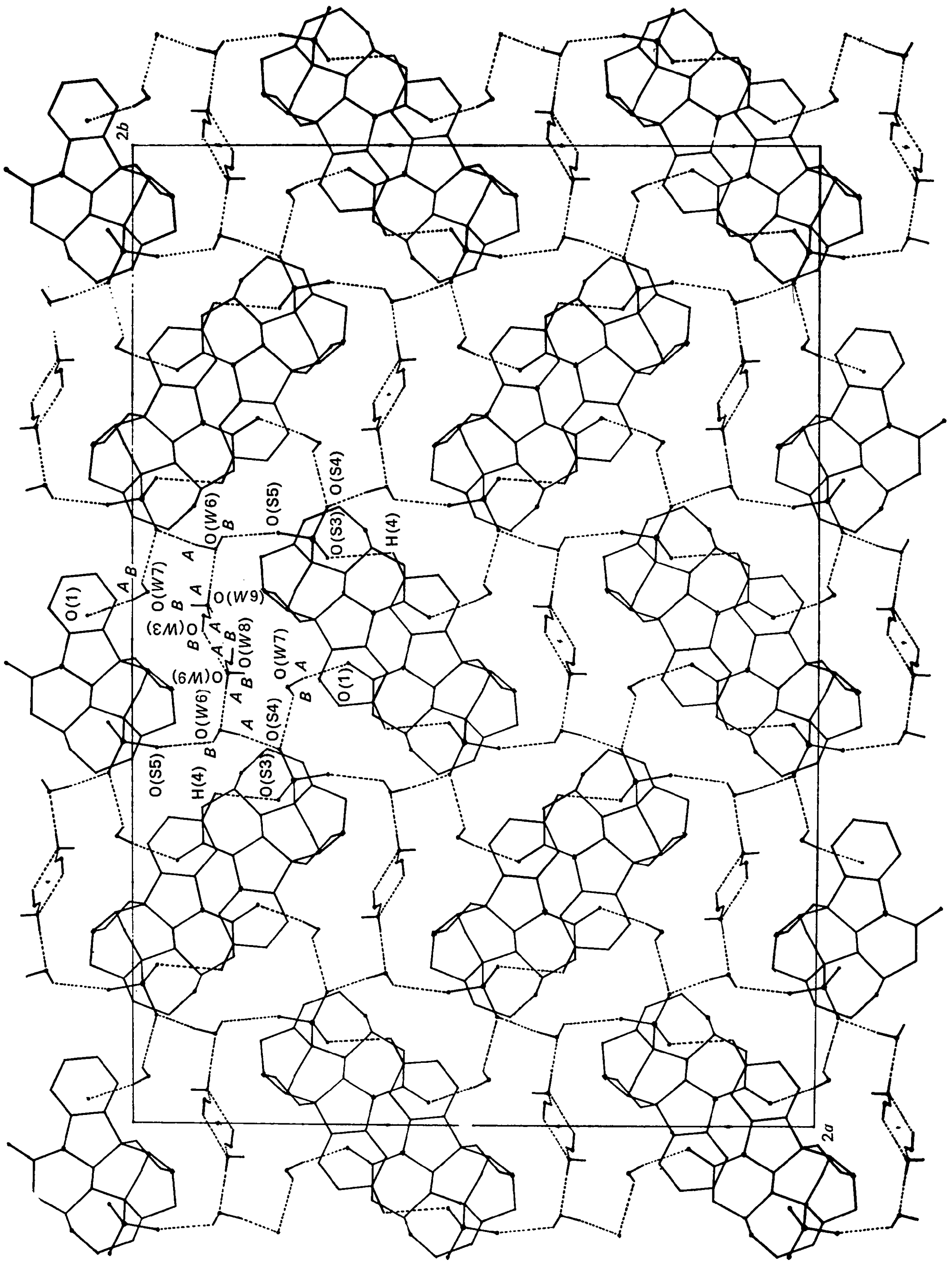
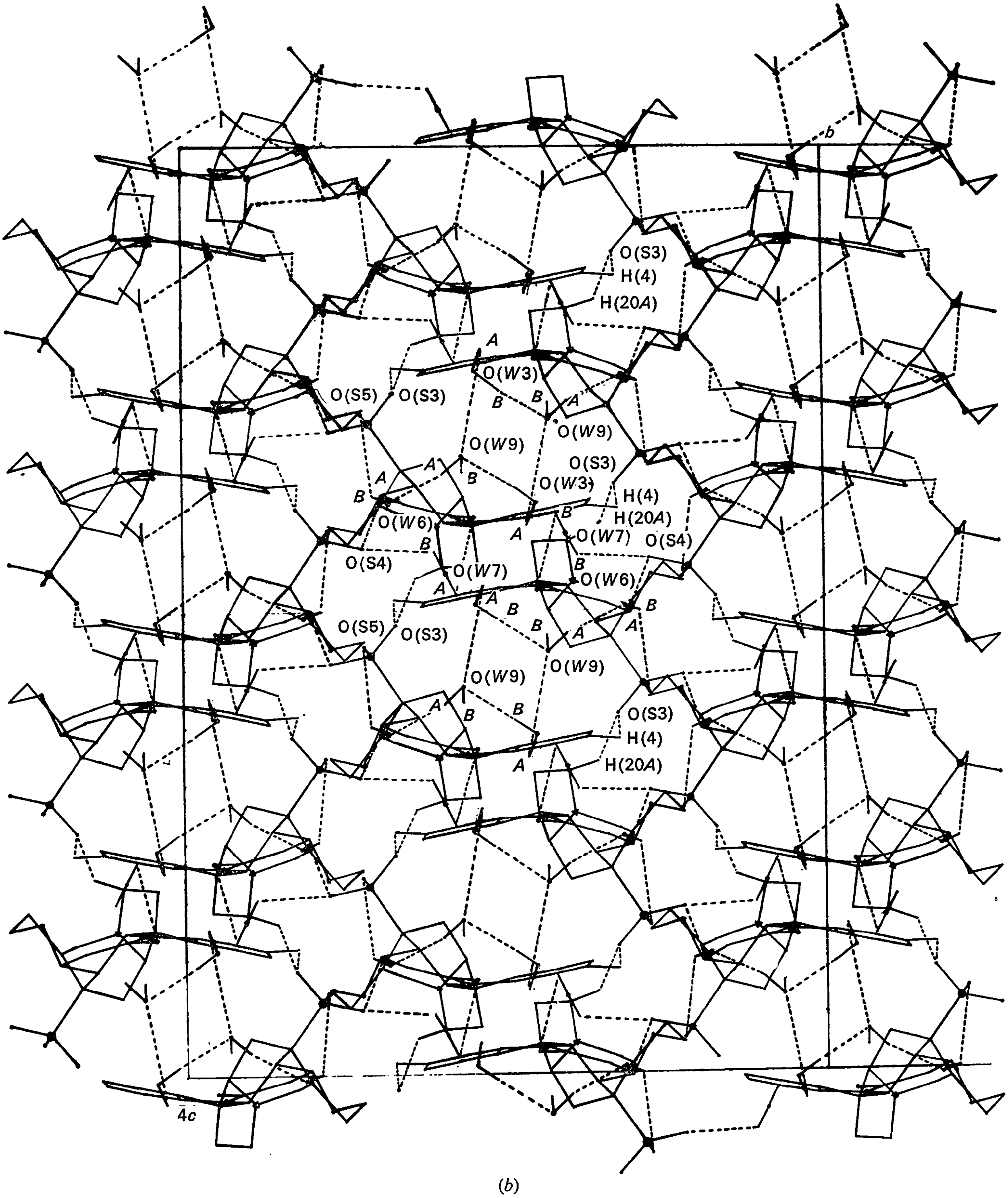


(a)

Fig. 3. (a) Strychnine sulfonic acid tetrahydrate. Molecular packing diagram. View down **c**.



(b)

Fig. 3. (cont.) (b) View down a.

Table 12. *Alternate hydrogen positions*

H attached to	*x*	*y*	*z*	X–H distance	Peak height (arbitrary units)
SO_3	0·0500	0·3000	0·0005	0·815 Å	113
N(2)	0·3680	0·1267	0·4200	0·698	114

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The Crystal and Molecular Structure of an Aldotriouronic Acid Trihydrate: *O*-(4-*O*-Methyl-α-D-Glucopyranosyluronic Acid)-(1-2)-*O*-β-D-xylopyranosyl-(1-4)-D-xylopyranose Trihydrate

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The crystal structure of an aldotriouronic acid trihydrate [*O*-(4-*O*-methyl-α-D-glucopyranosyluronic acid)-(1-2)-*O*-β-D-xylopyranosyl-(1-4)-D-xylopyranose trihydrate] has been determined from three-dimensional X-ray data obtained from crystals maintained at a temperature of approximately −193°C. The structure was solved by a combination of direct acentric phasing methods and Patterson search methods, and the anisotropic refinement was terminated at a final *R* index of 0·066 for 2232 observations. One trisaccharide molecule and three water molecules of crystallization ($C_{17}H_{28}O_{15}.3H_2O$) comprise the asymmetric unit in a monoclinic unit cell with the low-temperature cell parameters of $a = 10{\cdot}136$ (3), $b = 10{\cdot}925$ (8), $c = 10{\cdot}120$ (3) Å, $\beta = 91{\cdot}66$ (3)°, and space group $P2_1$. All three rings in the trisaccharide molecule were found to have the *C*1 chair conformation with all the substituents, except C(1″)–O(2), in an equatorial position. The trisaccharide molecule has no intramolecular hydrogen bonds. The xylose rings in the xylobiose residue are arranged in a left-handed helical conformation with a glycosidic oxygen angle of 113·8° between the two rings. The glycosidic oxygen angle between the two rings linked α-1,2 in the aldobiouronic acid residue is 116·0°. Orientation of the trisaccharide in the crystal is such that the xylobiose residue extends along the *b* axis and the aldobiouronic acid residue extends along the *c* axis. The three water molecules are clustered between the trisaccharide molecules and participate in 10 of the 15 unique hydrogen bonds in the crystal structure.

Introduction

The aldotriouronic acid trisaccharide is a segment of the naturally occurring 4-*O*-methylglucuronoxylans found in hardwood hemicelluloses. The acid trisaccharide contains two different disaccharides: xylobiose (two xylose units connected by a β-1,4-linkage) and an aldobiouronic acid (a 4-*O*-methyl-D-glucuronic acid ring attached to the nonreducing xylose ring by an α-1,2-linkage), neither of which have been studied crystallographically. The conformation of the xylobiose residue of the trisaccharide was of interest because it

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