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The Crystal Structure of L-Mimosine Sulphate Hydrate

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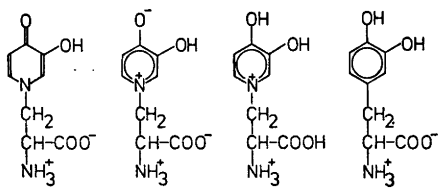
The structure of L-mimosine sulphate hydrate, $C_5H_3(OH)_2NHC_2CH(NH_3)COOH.SO_4.(H_2O)_{1.5}$ has been determined by X-ray methods using 2451 observed reflections collected by counter methods. The crystals are orthorhombic, space group $P2_12_12_1$, with unit cell dimensions $a = 6.42_3$ Å; $b = 13.88_6$ Å; $c = 14.48_7$ Å. The refinements yielded a conventional R-factor of 0.051. The crystal structure is discussed and the bond lengths and angles are compared to those found in the un-protonized mimosine molecules.[1] The conformation of the amino acid is similar to that of L-tyrosine, the α hydrogen atom being in *trans* position relative to the aromatic part.

A previous structure determination [1] showed the anhydrous form of L-mimosine to exist in the crystals as an intermediate between the structures I and II of Fig. 1.



I II III DOPA

Fig. 1.

L-Mimosine forms a dibasic salt with sulphuric acid.[2] The protonized form is assumed to have the structure indicated by III which closely corresponds to the structure of L-DOPA. In order to investigate a molecule of this kind we have studied the sulphate of L-mimosine which is reported to crystallize with 1.5 molecule H_2O per formula unit and to have a melting point nearly 100°C below that of mimosine itself.[2]

A sample of L-mimosine was kindly given to us by Dr. M. P. Hegarty (The Cunningham Laboratory, CSIRO, Australia).

EXPERIMENTAL

Single crystals of the compound were formed by slow evaporation of a solution of L-mimosine in diluted sulphuric acid. A single crystal of approximate dimensions $0.3 \times 0.3 \times 0.17$ mm³ was used in all the X-ray experiments.

Weissenberg photographs indicated orthorhombic symmetry; systematically absent reflections proved the space group to be $P2_12_12_1$. Unit cell dimensions were determined from diffractometer measurements on 15 general reflections using Mo$K(\alpha_1 + \alpha_2)$ radiation ($\lambda = 0.71069$ Å).

The intensity data were recorded with the use of a SYNTEX $P\bar{1}$ diffractometer with graphite crystal monochromated MoK radiation. 3269 independent reflections with $2\theta < 70°$ were measured using the $\omega - 2\theta$ scanning mode with the 2θ scan speed varying from 2 to 12° min^{-1} depending on the intensity. The scan range was from 1° below $2\theta(\alpha_1)$ to 1° above $2\theta(\alpha_2)$ and background counts were taken for half the scan time at each of the scan range limits. Three standard reflections were measured after every 50 reflections; they showed no systematic variation during the experiment.

The estimation of the standard deviation of the intensities was based on counting statistics with 2.5 % addition in order to account for other errors. The 2451 reflections with intensity larger than $2.5\sigma(I)$ were considered to be observed; the remaining data were excluded from the structure refinement procedure.

The structure was determined by the use of the program MULTAN written by P. Main, M. M. Woolfsen and G. Germain. All other computer programs applied are described in Ref. 3. Atomic form factors applied were those of Doyle and Turner [4] for sulphur, oxygen, nitrogen, and carbon atoms and of Stewart, Davidson and Simpson [5] for hydrogen.

CRYSTAL DATA

L-Mimosine sulphate hydrate, $C_8H_{19}N_2O_4.H_2SO_4.1.5H_2O$, m.p. 143 – 143.5°C, with decom-

position.[3] Orthorhombic; $a = 6.423(0.001)$ Å, $b = 13.886(3)$ Å, $c = 14.487(3)$ Å. Figures in parentheses are estimated standard deviations. $V = 1292.1$ Å^3; formula weight 323.29; $F(000) = 676$; $Z = 4$; $D_{calc} = 1.662$ g cm^{-3}. Absent reflections: (h00) for h odd, (0k0) for k odd, (00l) for l odd; space group $P2_12_12_1$.

STRUCTURE DETERMINATION

After being corrected for Lorentz and polarization effects the data were put on an approximate absolute scale by Wilson's statistical method and normalized structure amplitudes were calculated. 472 reflections with E-values greater than 1.25 were used as input in the program assembly MULTAN.[6] Of the solutions obtained the one with the highest absolute figure of merit was used as the basis for an E-map in which all except three of the non-hydrogen atoms were localized. After one Fourier refinement cycle two of the missing heavy atoms appeared in the electron density map. The trial structure was refined by a few least-squares cycles and the approximate positions of the hydrogen atoms bonded to carbon were calculated. A couple of cycles of alternating least-squares refinements and difference Fourier syntheses yielded the positions of the oxygen atom of the "half" water molecule as well as the remaining hydrogen atoms of the mimosine ion and the other water molecule.

In the subsequent full-matrix least-squares refinement the 2451 observed reflections were included; the function minimized was $\sum w(F_o - F_c)^2$, the weight assigned to each reflection was

Table 1. Fractional coordinates and thermal parameters ($\times 10^5$) with estimated standard deviations (in parentheses). The temperature factor is given by exp $-(B11h^2 + B22k^2 + B33l^2 + B12hk + B13hl + B23kl)$.

ATOM	X	Y	Z	B11	B22	B33	B12	B13	B23
S	50974(14)	29430(4)	19360(4)	1603(17)	215(3)	161(2)	-201(15)	-62(13)	18(4)
OS1	48321(60)	39828(16)	24693(17)	4236(100)	238(10)	488(12)	3(67)	-1391(75)	-93(18)
OS2	51624(50)	27049(16)	9461(12)	2686(72)	464(12)	169(7)	-632(64)	154(48)	13(15)
OS3	70037(52)	26244(24)	23968(17)	2359(81)	685(19)	276(11)	886(65)	-91(52)	58(23)
OS4	32973(54)	24479(24)	23313(19)	2748(87)	711(19)	272(18)	-1473(70)	656(56)	-278(24)
O1	19476(46)	22596(15)	39970(14)	2768(75)	226(10)	257(9)	-22(48)	281(46)	-20(15)
O2	18889(41)	22291(16)	58139(14)	2040(62)	327(11)	234(9)	222(48)	184(43)	124(16)
O3	-4467(47)	52435(21)	22453(15)	2516(82)	653(18)	253(9)	-260(61)	377(48)	-295(21)
O4	-31974(41)	51018(17)	31652(15)	2044(63)	482(12)	293(10)	-566(60)	25(46)	-218(18)
OV1	919(99)	33975(32)	9902(29)	2126(126)	381(21)	348(19)	56(121)	125(108)	58(34)
OV2	-15228(50)	52981(20)	2626(19)	2418(78)	465(14)	498(13)	-243(59)	-475(59)	-298(23)
N1	16592(41)	48089(17)	44808(15)	914(52)	211(10)	212(9)	88(42)	-23(39)	22(16)
N2	-18714(48)	62987(17)	44189(16)	1487(65)	232(11)	222(10)	-28(46)	-218(46)	-102(17)
C1	17777(52)	39776(20)	39950(17)	1566(72)	245(12)	178(9)	-63(56)	162(48)	-1(19)
C2	18351(49)	31037(20)	44409(18)	1182(66)	255(13)	229(11)	98(52)	122(48)	-8(19)
C3	17692(49)	30803(21)	54163(18)	1091(64)	301(14)	238(11)	80(55)	102(47)	28(20)
C4	16138(55)	39523(23)	58812(18)	1601(77)	377(16)	193(10)	178(63)	57(51)	-112(22)
C5	15609(56)	47926(22)	54170(19)	1523(75)	286(14)	227(11)	142(57)	-9(51)	-111(21)
C6	17131(56)	57553(20)	39866(20)	1509(76)	222(12)	296(12)	-182(55)	-14(56)	83(21)
C7	-3993(48)	60934(19)	36516(17)	1596(80)	196(11)	211(10)	-50(51)	87(48)	10(18)
C8	-13865(55)	54257(20)	29409(20)	1812(81)	237(12)	235(12)	95(53)	-232(54)	9(20)

Table 2. Fractional coordinates ($\times 10^4$) and the isotropic thermal parameter B for hydrogen atoms. Figures in parentheses are standard deviations.

ATOM	X	Y	Z	B
HO1	2340(65)	2434(29)	3348(31)	3.3(.8)
HO2	1608(62)	2282(42)	6371(42)	4.9(1.4)
HO4	-3770(84)	4655(39)	2746(36)	4.2(1.0)
H1V2	-1582(87)	5814(40)	259(34)	5.7(1.0)
H2V2	-1127(74)	5205(32)	874(33)	6.0(.9)
H1N2	-2475(58)	5864(27)	4620(22)	2.7(.6)
H2N2	-1435(53)	6546(23)	4746(19)	1.6(.6)
H3N2	-2817(92)	6775(41)	4279(34)	6.3(1.1)
HC1	1887(60)	4051(26)	3330(26)	3.0(.6)
HC4	1582(51)	3888(21)	6592(21)	2.3(.5)
HC5	1496(78)	5446(32)	5686(29)	3.2(.8)
H1C6	2382(31)	6246(14)	4351(13)	1.0(.3)
H2C6	2914(72)	5544(30)	3565(28)	2.5(.8)
HC7	-265(59)	6756(26)	3418(24)	1.2(.7)

Table 3. Observed and calculated structure factors (× 10).

H=	0,K=	0	3	427	448	16	91	95	15	47	43	14	115	123	1	234	218	4	150	148	H=	1,K=	19
2	88	82	4	72	70	18	100	113	H=	0,K=	18	16	87	89	2	35	42	5	198	202	3	136	130
4	151	171	5	249	241	19	49	53	1	158	148	17	82	89	3	430	427	6	132	140	4	48	52
6	1078	1054	6	38	19	20	74	74	2	44	40	18	86	92	5	307	301	7	131	149	5	115	114
8	624	624	7	106	137	H=	0,K=	11	4	138	133	19	123	118	6	204	201	8	82	82	6	50	43
10	411	444	8	85	86	1	264	255	6	49	35	21	75	63	7	236	250	9	182	186	9	56	50
12	145	145	9	164	147	2	123	126	7	63	64	23	54	45	8	176	178	11	99	106	11	41	36
14	191	212	10	244	240	3	399	394	8	98	92	H=	1,K=	3	9	143	146	12	90	85	12	46	43
16	32	24	11	71	71	4	30	28	9	100	105	0	120	113	10	42	48	13	86	89	H=	1,K=	20
18	124	123	12	280	279	5	333	356	10	86	85	1	391	422	11	212	218	14	94	90	0	40	44
20	223	215	14	83	80	6	176	178	11	84	88	2	615	602	12	70	72	15	91	88	1	80	82
22	142	135	16	91	84	7	31	46	12	79	79	3	442	460	13	180	187	16	41	40	2	65	56
H=	0,K=	1	20	120	114	9	57	46	H=	0,K=	19	4	172	156	14	101	96	17	73	74	3	44	45
1	130	168	21	59	56	11	157	162	2	62	61	5	633	606	15	77	70	18	53	50	7	73	67
2	322	384	22	114	118	12	127	134	3	51	54	6	343	329	16	80	78	19	93	98	9	69	63
3	1015	960	H=	0,K=	6	13	151	155	4	50	46	7	303	306	17	98	97	H=	1,K=	13	H=	1,K=	21
4	64	64	0	307	346	14	55	54	5	58	60	8	193	222	18	102	97	0	163	166	2	43	43
5	825	816	1	133	143	15	283	293	6	110	109	9	57	59	19	41	39	1	127	138	4	88	81
6	327	336	2	410	371	16	83	92	7	85	87	10	140	134	21	94	98	2	73	77	5	37	21
7	303	311	3	319	309	19	66	78	8	55	58	11	69	68	H=	1,K=	8	3	144	146	6	101	105
8	119	118	4	331	306	H=	0,K=	12	10	78	77	12	144	148	0	495	492	4	124	124	H=	1,K=	22
9	277	294	6	473	481	0	256	260	H=	0,K=	20	13	135	128	1	183	168	5	85	85	0	43	36
10	272	253	7	97	75	2	34	37	1	64	57	14	71	77	2	192	185	6	121	119	1	99	84
12	65	71	8	395	357	3	45	34	2	139	140	15	91	94	3	40	71	7	88	88	2	44	34
13	127	119	9	298	305	4	65	64	3	43	25	16	50	51	4	226	226	8	38	45	3	44	54
14	149	157	10	270	278	6	110	113	4	45	30	17	63	65	5	121	130	9	32	26	H=	2,K=	0
15	148	148	11	211	212	8	243	248	6	86	90	19	70	76	6	46	47	10	73	73	0	451	482
16	55	46	12	218	220	9	106	113	7	68	55	20	114	111	7	235	229	12	146	146	1	1260	1226
18	41	28	13	103	102	10	120	114	8	49	39	21	79	76	8	227	235	13	82	75	2	893	888
19	99	102	15	119	110	12	148	148	9	64	72	22	103	94	9	74	71	14	97	101	3	221	218
20	77	75	16	124	123	13	70	60	10	70	73	23	47	51	10	245	238	15	85	79	4	117	90
21	117	120	17	242	246	14	67	65	H=	0,K=	21	H=	1,K=	4	11	71	68	16	62	66	5	179	169
22	47	57	18	64	64	15	89	84	3	119	109	0	29	59	12	70	75	H=	1,K=	14	6	451	460
23	117	120	19	74	78	16	97	103	4	51	45	1	328	325	13	107	101	0	104	100	7	365	351
H=	0,K=	2	H=	0,K=	7	17	42	34	5	80	80	2	104	117	14	74	72	1	157	154	8	44	87
0	450	416	1	332	330	18	88	86	6	47	34	3	457	434	15	96	94	2	84	82	10	440	435
1	136	79	2	341	343	19	60	40	H=	0,K=	22	4	453	446	16	95	100	4	56	54	11	99	1
2	349	349	3	395	386	H=	0,K=	13	0	52	63	5	235	234	17	88	88	5	92	100	12	175	169
3	490	555	4	338	341	1	208	210	1	39	24	6	113	118	18	127	127	6	98	98	14	110	107
4	357	337	5	309	293	4	107	110	2	48	38	7	132	121	19	67	60	7	114	118	15	229	239
5	131	144	6	311	273	5	104	97	H=	1,K=	0	8	284	279	20	87	95	8	139	139	16	76	80
6	720	672	7	98	89	6	164	164	1	508	538	9	115	113	H=	1,K=	9	9	65	68	18	168	168
7	35	25	8	26	22	7	134	146	2	43	58	10	217	219	0	266	261	10	64	68	21	65	63
8	88	67	9	84	68	9	97	111	3	578	563	11	149	164	1	305	276	11	68	70	23	51	50
9	349	376	10	165	167	10	56	47	4	280	259	12	106	107	2	101	92	12	66	69	H=	2,K=	1
10	223	199	11	534	544	12	88	87	6	396	394	13	97	102	3	235	217	16	91	88	0	1019	1017
11	105	103	12	203	206	13	158	156	7	284	279	14	102	98	4	261	256	17	84	83	1	957	899
12	244	254	13	77	80	19	51	40	7	284	279	15	106	102	5	127	117	18	56	61	2	733	696
13	39	47	14	237	229	H=	0,K=	14	8	57	60	16	127	125	6	186	185	H=	1,K=	15	3	512	508
14	68	80	15	63	62	1	70	67	9	508	507	17	112	113	7	143	146	0	70	61	4	324	322
15	49	60	17	133	134	2	43	29	10	155	160	18	138	139	9	67	74	1	48	47	5	371	345
16	94	89	20	66	64	3	131	127	11	106	102	19	96	99	10	125	126	2	109	101	6	462	455
17	66	56	22	104	110	4	80	81	12	123	128	20	84	84	11	100	97	3	34	33	7	313	309
18	149	158	H=	0,K=	8	5	73	73	13	115	123	22	46	42	12	147	156	4	114	111	8	356	355
19	39	43	0	414	422	7	96	94	14	55	50	23	51	46	13	112	115	5	115	110	9	191	181
20	101	93	1	599	601	8	131	126	15	90	95	H=	1,K=	5	14	215	211	6	69	73	10	90	87
21	72	67	2	82	71	9	61	59	16	106	114	0	571	561	15	71	70	7	63	63	11	410	409
H=	0,K=	3	3	357	335	10	96	110	17	172	184	1	130	133	16	112	115	8	58	62	12	54	56
1	173	180	5	209	213	11	80	85	19	200	196	2	597	595	17	67	68	9	40	33	13	279	283
2	445	382	6	290	273	12	70	69	20	85	76	3	237	225	21	76	78	11	41	54	14	61	73
3	35	10	7	333	333	13	36	37	22	112	109	4	364	338	H=	1,K=	10	12	51	45	15	164	164
4	754	783	8	173	168	14	69	72	H=	1,K=	1	5	257	258	0	348	348	13	90	86	17	167	171
5	415	432	9	297	290	15	50	45	0	44	48	6	224	229	1	306	302	14	67	74	19	35	18
6	68	87	10	162	158	16	74	82	1	485	504	7	143	137	2	49	55	15	49	49	20	79	65
7	137	129	11	208	211	17	52	62	2	629	636	8	192	179	3	179	183	H=	1,K=	16	21	138	138
8	285	277	12	130	137	H=	0,K=	15	3	242	248	9	221	229	4	48	37	0	33	30	22	74	74
9	176	172	14	62	64	3	77	75	4	678	664	10	125	132	5	83	93	1	44	64	23	60	51
10	231	237	17	101	99	4	196	191	5	84	93	11	203	203	6	77	83	2	94	94	H=	2,K=	2
11	55	60	18	46	56	5	61	49	6	606	584	12	265	279	7	285	279	3	67	60	0	101	98
12	393	403	19	75	72	6	34	38	7	170	172	13	246	257	8	81	92	5	45	37	1	537	515
14	171	170	20	57	54	11	147	158	8	365	363	14	89	95	9	317	319	8	91	89	2	199	163
15	136	141	H=	0,K=	9	12	64	61	9	109	79	15	139	131	10	118	122	9	124	115	3	153	141
16	59	51	1	80	78	13	67	77	10	100	90	16	107	107	11	220	218	10	106	108	4	314	296
18	73	69	2	124	136	14	93	100	11	82	83	18	91	92	12	55	45	12	48	43	5	311	312
19	101	90	3	132	134	15	48	18	12	243	246	20	53	50	13	67	68	13	55	43	6	482	474
20	91	87	4	240	217	16	65	73	13	179	178	21	97	91	14	64	58	14	44	40	7	198	199
21	124	119	5	261	253	H=	0,K=	16	14	120	127	22	51	49	15	41	41	16	72	67	8	409	389
22	81	83	6	174	181	0	138	141	15	127	130	H=	1,K=	6	17	96	108	H=	1,K=	17	9	319	314
23	50	53	8	247	250	1	97	92	16	92	84	0	548	552	18	42	45	0	61	63	10	324	323
H=	0,K=	4	9	59	53	2	42	32	17	95	100	1	448	433	19	89	89	3	103	98	11	182	180
0	1279	1313	11	94	86	3	84	80	18	38	50	2	345	354	20	70	51	5	148	142	12	167	173
1	916	883	12	175	170	4	48	43	19	88	85	3	59	59	H=	1,K=	11	6	38	42	13	102	111
2	450	460	13	175	180	5	79	85	20	107	106	4	122	118	0	471	477	7	111	115	14	164	164
3	87	60	15	57	60	7	97	109	21	102	98	5	538	523	1	117	125	9	39	38	15	84	81
4	688	629	17	79	74	9	65	69	22	141	142	6	147	126	2	259	256	11	137	133	16	101	105
5	116	108	18	85	81	10	166	162	23	69	64	7	153	168	3	75	79	12	44	46	18	146	136
6	256	246	H=	0,K=	10	11	55	52	H=	1,K=	2	8	167	175	4	258	255	13	112	111	19	96	88
7	117	125	0	487	483	13	83	84	0	750	786	9	152	163	6	186	186	15	51	57	20	131	130
8	103	118	2	66	63	16	57	53	2	570	551	10	465	471	8	140	151	H=	1,K=	18	21	53	58
9	362	358	4	99	101	H=	0,K=	17	3	242	230	11	195	199	10	74	74	0	137	140	H=	2,K=	3
10	40	38	5	61	51	2	96	96	4	520	521	12	192	212	11	47	49	2	122	122	0	195	193
11	199	196	6	174	158	4	149	146	5	399	379	13	114	118	12	186	191	3	74	72	1	397	405
12	35	43	7	71	78	5	152	140	6	228	198	14	54	58	14	120	116	4	81	74	2	257	241
14	179	178	8	327	342	6	138	139	7	204	202	15	91	90	16	63	56	5	82	74	3	145	150
17	170	164	9	153	148	8	39	37	8	158	156	16	79	78	20	83	68	6	98	104	4	258	264
18	69	57	10	143	137	9	61	65	9	278	252	17	57	63	H=	1,K=	12	8	125	129	5	266	260
19	109	108	11	37	28	11	161	159	10	214	217	18	140	137	0	37	41	9	103	100	6	196	205
H=	0,K=	5	12	126	124	12	57	56	11	186	192	20	71	66	1	336	349	10	64	67	7	237	227
1	488	489	13	84	73	13	54	54	12	206	206	H=	1,K=	7	2	247	250	11	93	84	8	107	105
2	507	492	14	86	79	14	84	98	13	56	59	0	60	60	3	34	16	12	89	85	9	97	92

Table 3. Continued.

10	181	184	18	54	53	9	60	42	5	398	388	4	228	213	14	58	53	3	93	93	18	88	83
11	296	306	19	74	74	10	61	57	6	337	318	5	209	193	15	131	125	6	46	36	19	81	70
12	183	189	Hk	2,Kk	9	13	56	55	7	274	242	6	150	138	16	45	51	7	42	53	Hk	4,Kk	5
13	153	151	0	194	180	14	58	58	8	100	108	7	107	104	Hk	3,Kk	12	Hk	3,Kk	21	1	61	57
14	144	151	1	151	145	15	44	45	9	131	131	8	372	381	0	473	489	4	68	75	2	258	250
15	100	96	2	183	170	16	40	37	10	249	263	9	159	162	1	250	253	Hk	4,Kk	0	3	137	136
16	99	100	3	283	285	17	60	53	11	160	170	10	104	106	2	62	64	0	189	208	4	195	192
17	80	56	4	184	174	Hk	2,Kk	15	12	228	235	11	210	215	3	143	152	1	787	759	5	141	142
21	64	61	5	351	355	1	69	69	13	38	47	12	169	170	4	53	56	2	383	370	6	114	117
22	87	79	6	281	286	2	108	106	14	171	179	13	133	142	5	66	31	3	65	67	7	82	85
Hk	2,Kk	4	7	278	266	3	35	30	15	120	123	14	91	82	6	128	133	4	145	136	8	150	154
0	379	340	8	75	75	4	98	98	16	178	186	16	178	176	7	188	183	5	286	280	9	91	93
1	608	606	9	73	72	5	45	47	18	83	66	17	113	111	8	133	144	6	46	46	10	106	100
2	172	167	10	137	142	6	73	79	19	140	136	19	47	46	9	137	140	7	125	128	11	213	213
3	162	170	12	126	124	7	82	84	20	90	83	20	86	86	11	81	85	8	116	118	12	79	74
4	223	229	13	85	83	8	33	34	Hk	3,Kk	2	Hk	3,Kk	7	12	88	77	9	79	76	13	61	64
5	204	180	14	63	71	9	35	26	0	397	394	1	284	250	15	79	80	10	242	253	14	88	86
7	107	78	15	123	120	10	64	58	1	112	130	2	62	52	17	87	87	11	171	163	16	62	63
8	137	129	16	59	57	11	88	82	2	261	263	3	108	131	Hk	3,Kk	13	13	152	160	17	59	49
9	286	273	17	40	46	13	43	41	3	134	122	4	305	282	0	113	110	15	101	100	18	72	63
10	147	153	21	63	60	14	105	99	4	35	39	5	37	37	1	107	113	16	89	85	19	81	79
11	253	265	Hk	2,Kk	10	Hk	2,Kk	16	5	416	403	6	93	94	2	202	204	17	48	52	20	86	79
13	38	36	0	213	220	0	96	96	6	111	97	7	264	259	3	88	73	18	108	107	Hk	4,Kk	6
14	65	65	1	214	214	1	139	144	7	222	230	8	115	114	4	57	62	21	123	119	0	87	74
15	79	78	2	361	369	2	72	74	8	164	169	9	68	67	5	111	114	Hk	4,Kk	1	1	291	297
17	108	101	3	73	67	3	56	50	9	358	361	10	182	189	6	148	145	0	379	341	2	98	97
18	47	43	4	168	171	4	83	82	10	113	112	11	118	116	7	101	99	1	387	379	3	159	154
19	114	107	5	34	51	5	86	83	11	165	166	12	41	47	9	49	58	2	331	303	4	138	135
20	53	49	6	140	149	6	46	35	12	111	112	13	81	81	10	74	70	3	256	261	5	251	245
21	37	22	7	205	203	7	95	96	13	30	26	14	33	29	12	60	57	4	230	249	6	49	55
Hk	2,Kk	5	8	84	80	8	76	65	14	66	67	15	96	97	13	40	40	5	144	149	7	165	162
0	297	318	9	134	134	9	63	66	15	97	100	16	53	58	14	114	113	6	291	281	8	108	108
1	299	313	10	145	140	10	53	38	16	59	65	17	58	64	15	65	61	7	213	211	9	253	257
2	340	337	11	71	69	11	66	61	17	81	85	20	58	55	Hk	3,Kk	14	8	239	235	10	61	69
3	177	177	12	131	131	12	72	72	18	94	93	21	83	81	1	108	111	9	73	62	11	214	216
4	320	323	13	38	38	15	64	56	19	85	83	Hk	3,Kk	8	2	88	75	10	95	101	12	102	98
5	229	216	14	68	67	Hk	2,Kk	17	20	64	68	0	267	278	3	43	37	11	143	144	13	85	96
6	150	153	15	74	71	0	57	52	22	66	57	1	350	349	4	53	56	12	40	52	15	85	88
7	68	56	16	122	123	1	84	81	Hk	3,Kk	3	2	155	154	5	64	65	13	149	161	16	107	100
8	103	99	17	37	25	2	122	122	0	108	115	3	277	273	6	50	41	14	72	70	17	111	109
9	210	209	18	110	109	3	94	94	1	169	167	4	27	24	9	54	48	15	81	83	19	110	102
10	205	198	19	70	63	4	176	172	2	127	123	5	77	74	10	77	88	16	35	27	Hk	4,Kk	7
11	250	260	20	41	41	5	80	81	3	318	307	6	132	141	14	50	45	17	69	68	1	80	86
12	112	112	Hk	2,Kk	11	6	73	75	4	105	103	8	90	92	15	47	41	19	56	47	2	257	261
13	118	117	0	374	377	7	50	43	5	181	171	9	104	100	16	39	25	20	47	46	3	172	170
14	147	145	1	234	232	8	73	69	6	163	150	10	244	246	Hk	3,Kk	15	21	86	85	4	194	188
15	43	48	2	184	185	9	88	92	7	191	197	11	76	78	1	71	60	Hk	4,Kk	2	5	127	127
16	152	144	3	194	199	10	180	164	8	187	185	12	67	61	2	45	50	0	549	536	6	195	193
17	130	139	4	96	97	11	66	67	9	140	141	13	33	39	3	140	130	1	287	290	7	80	103
18	95	86	5	170	169	12	98	84	10	165	160	15	37	32	4	41	37	2	31	20	8	109	114
20	114	110	6	98	108	13	41	29	11	118	124	16	39	33	5	130	134	3	111	105	9	105	99
22	73	63	7	147	148	14	85	75	12	211	215	17	122	112	7	38	54	4	66	40	10	183	184
Hk	2,Kk	6	8	66	70	Hk	2,Kk	18	13	98	91	18	117	123	8	38	42	5	108	102	11	82	80
0	122	117	9	60	67	1	105	107	14	124	123	19	54	47	11	109	96	6	119	115	12	188	195
1	218	218	10	64	67	2	60	57	15	111	112	20	69	63	13	56	61	7	192	197	13	79	68
2	241	227	11	68	71	3	123	111	16	128	133	Hk	3,Kk	9	15	57	40	8	240	243	14	84	80
3	142	138	12	87	91	4	46	39	17	82	68	0	58	65	16	38	28	9	246	249	16	68	67
5	450	405	13	160	157	5	58	50	20	89	73	1	191	191	Hk	3,Kk	16	10	261	252	20	66	60
6	271	286	14	50	36	7	99	93	21	45	55	2	174	176	0	125	129	11	139	138	Hk	4,Kk	8
7	151	159	15	92	95	8	58	51	Hk	3,Kk	4	3	329	327	1	82	77	12	80	85	0	71	73
8	240	232	16	54	62	9	86	87	0	194	193	4	194	194	2	75	76	13	82	85	1	206	202
9	298	302	17	48	56	10	95	88	1	238	236	5	70	79	3	70	66	14	96	97	2	84	57
10	187	186	19	48	43	11	96	90	2	160	163	6	187	192	4	114	110	16	37	33	3	176	182
11	331	336	Hk	2,Kk	12	12	60	61	3	420	388	7	143	145	5	50	46	17	54	52	4	41	38
12	161	167	0	178	180	13	55	50	4	198	203	8	54	56	6	108	95	18	106	94	5	39	32
13	143	148	2	244	251	Hk	2,Kk	19	5	268	259	9	80	81	8	156	158	19	77	80	6	76	73
15	100	108	3	230	232	2	40	46	6	236	223	11	151	155	10	38	32	20	112	109	7	64	60
16	107	108	5	57	62	3	37	38	7	73	75	12	175	173	11	91	85	Hk	4,Kk	3	8	126	124
17	119	117	6	173	172	4	125	119	8	223	215	13	87	99	12	81	79	0	32	57	9	177	179
19	171	169	7	162	166	5	101	98	9	138	132	14	38	54	13	51	52	1	166	147	10	89	95
22	46	35	8	125	126	6	84	84	10	123	116	15	79	84	14	46	38	2	158	165	11	84	86
Hk	2,Kk	7	9	44	38	7	61	50	11	167	175	16	43	39	Hk	3,Kk	17	3	175	182	12	100	103
0	169	191	10	142	144	Hk	2,Kk	20	12	143	145	17	54	55	2	40	31	4	130	118	14	55	47
1	82	90	12	63	53	0	119	121	14	63	72	19	40	39	3	51	61	5	113	112	15	44	50
2	188	205	13	48	40	1	50	55	15	34	33	20	90	88	4	64	67	6	136	140	16	60	60
3	294	269	14	45	47	2	40	34	16	114	106	Hk	3,Kk	10	5	130	136	7	160	151	17	60	72
4	480	451	15	45	28	3	50	56	17	57	45	0	100	104	6	84	94	8	105	109	18	59	45
5	252	241	16	93	89	6	50	35	18	81	82	1	223	232	7	56	42	9	103	103	19	71	66
6	139	142	17	57	63	8	79	68	19	88	90	2	137	134	10	66	59	10	54	48	Hk	4,Kk	9
7	96	90	18	80	81	9	66	62	20	87	84	3	181	177	11	58	51	11	120	117	1	72	77
8	138	138	Hk	2,Kk	13	Hk	2,Kk	21	21	44	27	4	84	77	12	44	41	12	171	174	2	97	108
9	215	211	0	50	51	1	53	51	Hk	3,Kk	5	5	73	78	13	78	79	13	93	90	3	235	241
10	178	184	1	145	147	3	58	65	0	29	45	6	71	68	Hk	3,Kk	18	14	44	52	4	114	117
11	119	125	2	123	128	5	81	68	1	276	274	7	33	29	0	77	83	15	89	86	5	200	199
12	283	283	3	152	153	Hk	2,Kk	22	2	142	166	9	158	156	1	53	39	16	48	46	6	119	117
13	79	86	4	129	128	0	95	95	3	439	418	10	97	94	2	81	80	17	39	35	7	126	123
14	110	115	5	172	179	Hk	3,Kk	0	4	201	191	11	94	100	3	60	51	18	36	20	8	69	65
16	149	142	6	140	147	1	96	116	5	164	155	12	48	60	4	57	47	20	62	53	9	60	60
17	100	94	7	67	67	2	39	38	6	152	126	13	40	36	5	47	42	21	42	34	10	38	44
18	62	68	8	65	62	3	414	411	7	161	166	14	61	71	7	43	36	Hk	4,Kk	4	11	94	94
20	64	71	9	47	47	5	37	24	8	179	178	15	87	86	8	41	36	0	32	22	12	49	58
Hk	2,Kk	8	10	56	67	6	161	154	9	118	123	17	48	45	9	44	41	1	342	314	13	77	68
0	244	222	11	119	118	7	316	282	10	90	87	19	43	46	10	121	110	2	158	154	15	104	102
1	273	272	13	39	49	9	432	440	11	528	525	Hk	3,Kk	11	Hk	3,Kk	19	3	116	105	16	45	44
2	190	216	14	98	94	10	67	70	12	125	129	0	36	26	0	39	26	4	128	124	17	47	40
3	219	220	15	56	49	11	352	361	13	100	97	1	213	212	1	79	82	5	80	73	Hk	4,Kk	10
4	78	82	16	46	49	12	48	50	15	34	21	2	117	126	2	49	47	6	70	71	0	177	183
5	128	120	Hk	2,Kk	14	13	81	81	16	95	85	3	87	98	3	41	46	7	178	181	1	222	225
6	47	50	0	40	45	15	113	122	17	88	86	4	228	229	4	97	87	8	37	31	2	235	243
7	128	120	1	94	93	19	82	87	18	92	87	5	233	239	5	87	85	9	203	210	3	69	72
8	200	204	2	84	84	21	232	225	19	77	73	6	250	256	6	59	62	10	174	176	4	106	110
9	265	269	3	130	126	Hk	3,Kk	1	21	89	80	7	59	59	7	64	68	11	48	53	5	42	37
10	113	113	4	75	71	0	212	190	Hk	3,Kk	6	8	122	121	9	78	71	12	114	110	6	148	153
11	181	181	5	47	55	1	340	320	0	193	142	9	78	76	Hk	3,Kk	20	13	79	80	7	88	90
14	71	66	6	58	55	2	322	330	1	108	108	10	64	62	0	104	102	15	91	87	8	138	137
15	56	58	7	114	117	3	320	319	2	102	134	11	75	81	1	53	49	16	59	58	9	111	110
16	87	81	8	83	94	4	90	92	3	165	181	12	60	58	2	46	52	17	81	83	10	143	142

Table 3. Continued.

11	47	50	9	91	93	10	114	115	0	174	173	5	138	135	4	65	74	7	87	89	7	55	61
12	110	102	Hm	4,Km	19	11	65	68	1	145	150	6	46	54	5	68	70	9	57	54	8	41	52
13	90	83	3	41	45	12	110	104	2	131	138	7	66	66	6	62	67	10	49	45	11	76	73
14	36	31	4	71	64	13	123	119	3	42	32	8	54	47	7	39	39	12	67	59	14	45	43
15	94	93	5	61	37	15	80	82	4	49	43	9	104	108	8	68	64	13	80	71	Hm	7,Km	10
16	83	81	6	75	78	16	59	55	5	45	53	10	82	86	9	52	66	14	81	79	0	57	56
Hm	4,Km	11	Hm	4,Km	20	17	40	24	6	150	152	11	49	49	11	43	46	16	59	62	1	111	112
0	165	163	0	61	64	18	44	47	7	123	124	12	61	66	12	76	78	17	42	36	3	51	45
1	195	203	2	43	33	Hm	5,Km	6	8	60	63	18	66	54	13	106	107	Hm	7,Km	2	6	65	58
2	228	223	Hm	5,Km	0	0	186	184	9	119	117	Hm	6,Km	3	15	41	35	1	145	155	7	49	53
3	120	128	1	318	312	1	60	53	11	95	90	0	157	149	16	46	44	2	61	66	9	79	77
5	134	146	2	67	68	2	177	171	12	44	48	1	41	38	Hm	6,Km	10	4	103	99	10	70	66
6	153	156	3	352	346	4	113	103	13	39	36	2	130	129	0	186	193	6	72	70	11	70	62
7	95	102	4	151	160	5	154	157	14	73	62	3	78	69	1	32	24	7	86	87	13	48	43
8	69	71	5	208	215	6	33	41	15	46	47	4	167	164	3	58	64	8	47	48	Hm	7,Km	11
9	65	66	7	159	162	7	60	63	Hm	5,Km	13	5	76	76	4	69	78	9	118	111	0	137	135
10	44	46	8	106	113	9	55	53	0	38	40	6	109	108	5	45	43	10	84	85	2	91	101
11	64	52	9	179	192	10	255	254	1	113	117	7	52	60	6	43	40	11	76	75	3	64	58
13	140	134	10	68	67	11	175	185	3	61	61	8	84	79	8	158	158	12	78	78	4	75	69
14	59	54	11	110	109	12	93	90	4	123	116	9	54	58	9	63	54	13	44	36	6	102	97
15	82	86	17	140	139	13	48	42	5	35	24	10	91	88	10	71	72	14	46	41	7	40	37
16	75	69	19	105	97	14	79	69	7	58	61	11	54	46	12	59	59	15	41	44	8	39	52
17	44	45	20	77	71	18	113	113	9	43	46	12	125	120	14	44	42	17	48	41	12	49	48
18	56	62	Hm	5,Km	1	19	39	27	10	57	55	13	39	26	Hm	6,Km	11	Hm	7,Km	3	Hm	7,Km	12
Hm	4,Km	12	0	161	166	Hm	5,Km	7	12	93	90	14	80	84	0	68	68	1	79	77	1	137	144
0	90	98	1	177	173	0	71	73	13	66	62	16	40	24	1	111	111	2	77	71	2	40	45
2	98	103	2	180	175	1	71	65	Hm	5,Km	14	18	41	43	2	34	41	3	69	68	4	95	87
4	31	25	3	84	84	3	200	206	0	34	32	Hm	6,Km	4	3	154	152	4	63	63	5	59	57
6	75	66	4	291	287	4	60	56	1	51	52	0	161	165	4	34	27	5	59	50	7	52	40
7	121	126	5	48	55	5	183	188	2	44	47	1	171	173	5	163	159	6	42	41	9	65	63
8	104	104	6	204	211	6	88	90	5	54	51	2	97	56	6	54	54	7	49	47	Hm	7,Km	13
9	35	43	7	96	91	7	95	95	6	70	72	3	48	47	11	88	93	8	73	73	0	37	40
10	59	73	8	159	155	8	84	80	7	67	68	4	105	115	12	51	48	11	100	101	1	71	69
11	63	50	9	58	62	9	43	48	8	84	87	5	55	49	13	52	50	12	64	58	2	46	45
14	45	38	10	68	68	10	104	105	9	66	61	6	57	43	15	117	113	13	41	38	3	45	44
16	102	96	12	122	126	11	99	102	Hm	5,Km	15	7	50	58	Hm	6,Km	12	15	43	34	5	67	60
Hm	4,Km	13	13	58	59	13	127	130	1	81	73	8	86	85	0	84	81	16	47	51	6	42	46
0	44	36	14	74	72	14	120	117	2	43	43	9	168	166	1	44	43	17	42	43	8	51	42
1	51	47	15	62	67	15	38	33	4	75	70	10	45	44	2	66	65	Hm	7,Km	4	Hm	7,Km	14
2	41	43	16	39	30	16	52	53	5	56	49	11	78	75	3	41	26	0	56	62	0	88	91
3	115	117	20	51	53	17	62	69	6	39	41	12	71	79	4	37	31	1	49	42	1	51	40
4	132	141	Hm	5,Km	2	Hm	5,Km	8	7	79	78	13	42	36	6	61	64	2	73	68	2	45	46
5	120	118	0	134	136	0	311	320	12	52	48	14	42	50	8	107	110	5	82	81	4	47	47
6	103	103	1	251	244	1	88	91	13	66	60	16	38	40	9	37	41	6	65	60	8	39	43
7	61	65	2	151	144	2	111	112	Hm	5,Km	16	17	76	76	10	49	51	7	44	44	Hm	7,Km	15
10	36	30	3	75	83	3	97	102	0	37	39	Hm	6,Km	5	12	61	57	8	96	100	2	42	30
11	81	81	4	126	125	4	58	49	2	65	62	1	101	104	13	58	49	9	40	35	3	43	43
12	52	45	5	130	136	5	58	58	3	55	48	2	106	108	Hm	6,Km	13	11	44	49	5	53	51
13	73	61	6	37	38	7	141	134	7	45	46	3	110	113	0	48	41	12	65	63	6	42	37
14	103	102	7	158	152	8	125	119	8	65	58	4	58	59	1	109	107	13	50	49	Hm	7,Km	16
15	47	47	8	81	90	9	57	57	9	79	70	6	82	71	2	40	36	14	56	48	0	45	41
16	47	47	9	77	76	10	154	155	10	73	77	7	100	94	4	49	46	16	52	43	2	52	51
Hm	4,Km	14	10	63	69	11	64	65	11	73	64	8	39	42	6	44	48	Hm	7,Km	5	Hm	8,Km	0
0	116	125	11	41	37	13	96	91	Hm	5,Km	17	9	77	75	7	65	67	0	58	45	0	105	111
1	45	60	12	42	47	14	60	68	1	37	30	10	51	55	8	58	56	1	67	68	1	74	86
2	43	53	14	33	21	15	67	66	3	78	78	11	44	41	9	46	52	2	128	127	2	120	120
3	94	98	16	63	72	16	49	49	5	73	67	12	159	164	12	40	42	3	93	94	3	86	97
5	64	64	17	46	55	17	43	32	7	42	40	13	54	48	13	66	73	4	69	68	6	116	118
6	51	45	18	53	52	18	78	73	Hm	5,Km	18	14	51	59	Hm	6,Km	14	5	86	88	7	47	44
7	86	87	19	96	90	Hm	5,Km	9	0	33	38	17	54	57	1	50	52	7	68	68	10	104	108
8	82	88	20	39	31	0	129	126	2	52	48	18	56	51	2	49	38	9	47	50	11	62	66
9	77	75	Hm	5,Km	3	1	66	72	5	56	49	Hm	6,Km	6	3	71	68	10	196	193	Hm	8,Km	1
10	82	80	0	60	60	2	64	63	6	78	75	1	97	99	4	42	40	12	97	93	0	72	85
11	79	81	1	186	190	3	109	109	8	84	78	2	139	139	5	68	68	13	82	79	1	95	102
13	54	50	2	160	162	4	83	88	Hm	5,Km	19	3	30	32	6	42	40	15	49	47	2	87	83
14	46	42	3	159	159	5	111	102	1	39	23	4	115	109	7	73	66	16	84	37	3	46	45
Hm	4,Km	15	4	80	76	6	83	83	2	45	40	6	115	117	8	56	40	Hm	7,Km	6	4	48	38
1	56	51	5	241	229	7	68	66	3	75	64	7	75	63	9	42	37	0	100	98	7	79	80
2	59	59	6	133	137	10	94	96	5	40	42	8	139	140	10	48	48	2	80	85	8	48	52
3	34	29	7	176	183	12	69	70	Hm	6,Km	0	9	160	160	Hm	6,Km	15	3	46	37	10	51	49
4	64	62	8	92	100	13	57	61	0	724	752	10	119	112	2	51	53	5	119	111	11	76	62
5	81	81	9	74	76	14	114	112	2	54	53	11	43	49	3	61	59	6	70	72	12	47	37
6	50	47	10	92	95	15	37	33	6	130	128	12	93	92	4	98	90	8	82	80	13	65	69
7	52	60	12	51	46	16	55	58	7	112	103	13	50	53	6	59	49	9	79	74	Hm	8,Km	2
8	51	49	13	111	118	18	43	44	8	242	251	14	52	45	10	63	56	10	107	103	0	36	30
10	62	57	14	44	41	Hm	5,Km	10	9	64	49	16	46	51	11	69	68	12	108	104	1	95	104
12	56	48	15	75	73	0	191	192	10	114	106	17	81	83	Hm	6,Km	16	13	66	75	2	60	65
13	85	74	18	75	74	1	110	115	12	69	72	Hm	6,Km	7	1	46	44	16	46	41	6	65	65
14	45	62	Hm	5,Km	4	3	38	39	13	36	40	0	85	86	3	68	50	Hm	7,Km	7	7	47	54
Hm	4,Km	16	0	209	210	5	50	55	14	116	118	1	101	92	4	39	42	1	57	59	8	55	51
0	36	19	1	252	255	6	94	99	15	43	43	2	88	86	5	38	35	3	87	87	10	79	72
1	71	74	2	229	223	7	177	181	18	47	49	3	160	161	7	49	51	5	52	45	12	52	42
2	45	40	3	144	139	8	76	68	19	59	47	4	141	129	9	45	43	7	60	57	13	45	45
5	77	81	4	182	182	9	138	144	Hm	6,Km	1	6	134	136	Hm	6,Km	17	9	45	43	Hm	8,Km	3
7	96	84	5	104	104	10	56	52	0	252	266	8	57	45	2	50	30	10	40	44	1	70	73
9	46	37	6	29	26	11	94	100	2	50	50	9	100	106	4	67	71	11	101	96	2	67	62
10	39	33	7	126	126	12	69	64	3	199	205	10	65	62	6	59	58	13	66	59	3	39	38
11	81	74	8	155	150	15	55	54	4	46	47	11	165	170	Hm	6,Km	18	Hm	7,Km	8	6	54	56
12	71	66	9	94	96	17	77	76	5	169	174	12	64	64	0	46	51	0	39	52	8	67	69
Hm	4,Km	17	10	195	201	Hm	5,Km	11	6	86	92	14	110	102	1	71	66	1	39	37	9	45	45
1	40	33	11	43	43	0	123	130	7	92	92	15	48	28	Hm	7,Km	0	2	70	67	10	53	45
2	90	96	13	47	39	1	80	86	8	56	56	17	56	62	1	90	94	3	71	73	11	41	45
3	44	48	16	45	46	2	144	144	9	89	97	Hm	6,Km	8	7	73	75	6	52	46	13	49	40
4	118	116	17	56	44	4	117	114	10	42	39	1	134	127	8	76	72	7	50	52	14	43	36
6	84	75	18	99	93	5	60	61	11	89	89	3	65	71	9	98	97	8	91	91	Hm	8,Km	4
8	65	69	20	57	55	6	103	102	12	35	44	5	37	42	11	46	42	9	47	52	1	59	65
10	149	145	Hm	5,Km	5	7	68	76	13	87	81	6	66	72	12	72	61	10	80	41	3	45	55
12	100	97	0	45	25	8	71	71	14	48	53	7	111	117	15	43	32	12	82	49	4	49	48
Hm	4,Km	18	1	93	90	9	75	73	15	63	66	8	74	71	16	49	40	14	48	35	7	69	59
0	37	44	2	125	129	10	55	66	16	57	57	9	103	101	Hm	7,Km	1	Hm	7,Km	9	9	61	61
1	83	85	3	37	23	12	130	128	19	56	44	10	80	73	0	33	35	0	92	92	11	107	115
2	52	52	4	189	185	13	37	26	Hm	6,Km	2	11	101	104	1	48	59	1	87	92	14	48	44
3	93	86	5	236	230	14	90	88	0	97	96	12	87	83	2	111	117	2	34	46	Hm	8,Km	5
4	60	61	6	93	89	15	61	66	1	86	85	17	64	61	3	52	58	3	35	33	1	61	50
5	57	45	7	66	67	16	42	31	2	145	146	Hm	6,Km	9	4	88	96	4	120	118	4	79	70
7	71	74	8	144	144	17	45	45	3	161	158	2	42	40	5	44	37	5	40	45	6	83	78
8	49	35	9	92	85	Hm	5,Km	12	4	71	77	3	49	48	6	108	113	6	63	56	7	37	34

Table 3. Continued.

9	60	58	H=	8,K=	7	10	59	56	5	44	34	5	74	68	H=	9,K=	5	1	48	40	4	46	24
10	66	64	1	59	64	11	48	44	7	70	67	6	45	40	0	43	34	H=	9,K=	9	5	42	35
12	46	49	4	102	94	H=	8,K=	9	H=	8,K=	12	7	38	34	3	99	99	2	51	54	H=	10,K=	2
13	39	28	5	64	61	1	59	62	0	60	58	9	41	50	4	42	42	3	43	38	0	99	92
14	40	44	7	51	53	2	69	74	2	75	75	H=	9,K=	2	8	60	47	5	39	31	1	51	38
H=	8,K=	6	8	65	58	5	61	55	3	64	70	0	41	53	9	53	60	6	53	51	H=	10,K=	3
1	54	58	9	44	50	6	51	54	H=	8,K=	13	2	51	32	H=	9,K=	6	H=	9,K=	10	1	42	36
2	52	49	10	40	45	7	68	64	2	60	58	3	64	62	0	93	91	0	58	44	3	45	39
3	42	53	11	75	77	9	49	48	3	61	57	7	40	31	5	44	33	1	50	54	4	41	39
4	45	52	12	67	58	H=	8,K=	10	5	65	58	8	49	49	7	46	49	4	40	43	H=	10,K=	4
5	40	55	H=	8,K=	8	1	39	36	H=	9,K=	0	9	52	56	8	52	65	H=	9,K=	11	2	49	42
6	53	45	0	80	75	2	78	76	1	68	68	H=	9,K=	3	H=	9,K=	7	1	47	45	H=	10,K=	6
8	61	62	2	79	79	4	49	42	6	52	45	6	55	53	0	66	59	2	48	51	1	43	39
9	72	72	3	36	17	6	57	39	10	42	31	11	40	40	2	41	22	H=	10,K=	0	H=	1,K=	2
10	51	61	5	50	42	7	40	39	H=	9,K=	1	H=	9,K=	4	5	49	41	1	86	98	1	1105	1104
11	90	87	6	42	30	H=	8,K=	11	1	72	76	0	70	65	8	48	45	H=	10,K=	1	H=	9,K=	11
12	40	47	7	51	56	0	110	120	2	55	53	2	44	45	H=	9,K=	8	2	55	58	1	47	45
13	51	50	8	53	41	1	46	54	3	44	41	9	38	34									

Table 4. R.m.s. amplitudes of vibration $(\overline{u^2})^{1/2}$ and B-values (Å^2) along the principal axes of vibration given by the components of a unit vector **e** in fractional coordinates ($\times 10^4$).

	$(\overline{u^2})^{1/2}$	B	e_x	e_y	e_z		$(\overline{u^2})^{1/2}$	B	e_x	e_y	e_z
	,187	2,77	-1474	224	65		,152	1,82	187	352	597
S	,140	1,54	501	674	103	N1	,147	1,71	933	475	- 315
	,130	1,33	64	- 123	680		,132	1,38	1233	- 413	148
	,328	8,51	1341	22	- 351		,184	2,68	1308	144	- 349
OS1	,185	2,70	755	- 253	554	N2	,163	2,10	736	- 524	345
	,147	1,71	240	675	218		,130	1,33	416	474	487
	,257	5,22	1283	- 407	38		,184	2,67	1499	- 102	161
OS2	,189	2,83	861	592	99	C1	,154	1,87	200	713	48
	,132	1,38	195	64	- 683		,131	1,35	375	27	- 670
	,283	6,32	850	604	14		,168	2,22	1143	317	358
OS3	,194	2,96	-1220	362	254	C2	,159	1,99	58	- 567	425
	,168	2,22	465	- 155	642		,144	1,64	-1057	312	410
	,321	8,14	974	- 528	187		,175	2,42	480	644	227
OS4	,175	2,41	1025	491	223	C3	,158	1,98	717	- 318	532
	,149	1,75	654	17	- 627		,145	1,66	-1297	63	378
	,243	4,66	1524	- 15	142		,201	3,18	695	625	- 155
O1	,162	2,06	318	159	- 659	C4	,180	2,55	1370	- 273	199
	,148	1,73	- 42	703	152		,135	1,45	- 257	234	643
	,216	3,68	1336	304	203		,186	2,75	1095	446	- 242
O2	,178	2,51	- 795	555	266	C5	,171	2,32	1086	- 359	357
	,145	1,67	101	346	- 605		,141	1,56	- 227	438	540
	,270	5,75	624	- 609	245		,186	2,73	- 992	301	448
O3	,224	3,96	1392	321	37	C6	,177	2,46	1112	2	484
	,142	1,59	- 315	213	645		,138	1,50	454	655	- 207
	,238	4,46	1015	- 497	220		,184	2,67	1530	- 52	121
O4	,190	2,84	1041	233	- 463	C7	,149	1,75	- 242	157	666
	,144	1,63	560	468	463		,137	1,49	167	701	- 141
	,214	3,62	1408	180	240		,200	3,17	1456	80	- 233
OV1	,196	3,03	- 625	559	338	C8	,155	1,90	256	511	474
	,183	2,64	230	419	- 553		,148	1,72	490	- 503	445
	,258	5,26	611	337	- 547						
OV2	,232	4,26	1248	- 430	31						
	,166	2,17	704	470	421						

taken as the inverse of the variance of the observed structure factor. The parameters refined were the scale factor, 105 positional parameters, 189 anisotropic thermal parameters for the heavy atoms, and 14 isotropic thermal parameters for the hydrogen atoms.

L-Mimosine sulphate was reported to contain 1.5 molecules of water per formula unit.[3] The X-ray crystallographic study revealed the position of one water molecule which is firmly hydrogen bonded to mimosine ions and for which the hydrogen positions were determined. Another position was found for an additional water molecule where only weak interactions with the surrounding molecules are possible; the occupancy for this water molecule is probably less than one per position. When allowed to vary during the least-squares refinement the occupancy factor for the oxygen atom of this water molecule (OV1) refined to 0.6. The thermal parameters associated with the atom were rather large, however, and highly correlated with the occupancy factor. When fixing the occupancy factor at 0.5 the thermal parameters refined to values comparable to those of the other water molecule (*cf.* Table 4). Because of the correlation we cannot decide whether this is correct or if the molecule has larger fractional population and thermal parameters.

The refinement converged with a final conventional R-factor of 0.051 ($R_w = 0.050$). The corresponding atomic parameters are listed in Tables 1 and 2. A comparison of observed and calculated structure factors is given in Table 3.

Magnitudes and directions of the principal axes of vibration for the heavy atoms are given in Table 4. As may be seen from these values the amplitudes of thermal vibration along the main axes for the oxygen atoms of the sulphate ion are quite large. A rigid-body analysis showed that the thermal motion of the ion could to a good approximation be interpreted in terms of translational and librational oscillations. A corresponding analysis for the entire mimosine ion was far less satisfactory; omitting the alanine part of the ion in the analysis seemed to give adequate agreement between observed and calculated U-values.

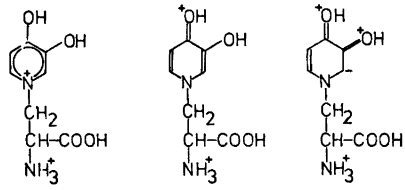
Bond lengths and angles, and some intermolecular distances are given in Table 5. Bond lengths corrected for thermal librations are given where such corrections seem to be justified.

Standard deviations in distances and angles were calculated from the correlation matrix.

DISCUSSION OF THE STRUCTURE

A drawing of the protonized form of L-mimosine as found in the crystals of the sulphate is presented in Fig. 2 where also the numbering of the atoms is indicated. The bond lengths and angles arrived at in the present analysis are indicated in this figure and may also be found in Table 5. The standard deviations in the bond lengths are 0.003 Å for S–O bonds, 0.004–0.005 for bonds between C, N, and O atoms, and 0.04–0.05 Å for bonds involving hydrogen atoms. The standard deviations in angles are 0.2–0.3°.

The six-membered ring of the hydroxypyridyl part of the molecule is planar. The distances from various atoms to a least-squares plane through the ring atoms are indicated in Fig. 2c. O1 and O2 are situated slightly out of the plane and the N1–C6 bond is bent out from the C3–N1 direction. The two C–N bonds in the pyridyl ring are of equal lengths (1.354 Å and 1.358 Å) and comparable to the mean value (1.356 Å) of the corresponding bonds in mimosine.[1] For the latter structure it was concluded that the contributions from the two resonance structures I and II of Fig. 1 are about equal. If an analogous simple valence bond picture is applied to the doubly protonized form the contributions from the structures IV–VI seem to be of importance.

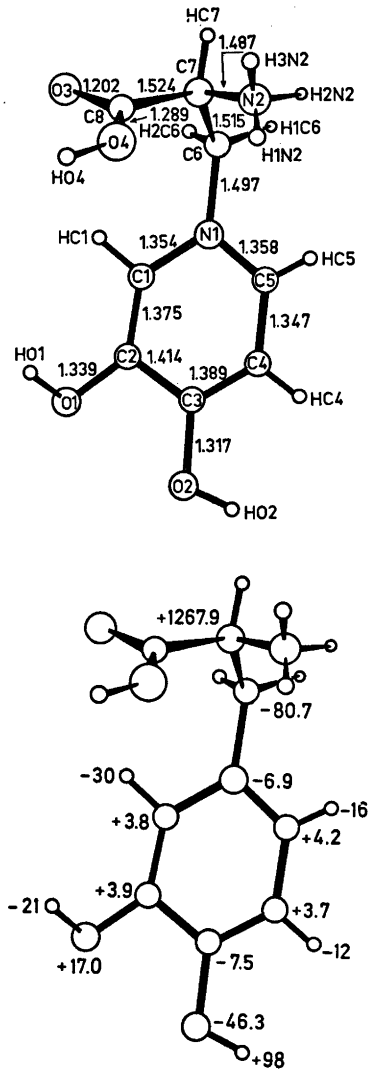


IV V VI

The contribution from VI explains the rather short C–O bonds (1.339 Å and 1.317 Å, as compared to the C–O bonds in phenols, 1.36–1.38 Å) and also that C4–C5 (1.347 Å) is shorther than C1–C2 (1.375 Å). The difference between the C–O bond lengths may be explained by the contribution from V, which also

Table 5. Bond lengths (Å), bond angles (°) and some intermolecular distances in mimosine sulphate hydrate. Distances given in parentheses are corrected for thermal libration.

Bond		Corr.	Angle		Hydrogen bonds		
S–OS1	1.467	(1.485)	OS1–S–OS2	110.7	OS1···HO4–O4	(1+x, y, z)	2.557
S–OS2	1.472	(1.483)	OS1–S–OS3	109.6	OS2···H2N2–N2	(½−x, 1−y, −½+z)	2.831
S–OS3	1.463	(1.479)	OS1–S–OS4	108.6	OS2···H3N2–N2	(−x, −½+y, ½−z)	2.926
S–OS4	1.462	(1.480)	OS2–S–OS3	110.7	OS3···HO2–O2	(½+x, ½−y, 1−z)	2.601
N1–C1	1.354	(1.359)	OS2–S–OS4	107.4	OS4···HO1–O1	(x, y, z)	2.577
C1–C2	1.375	(1.378)	OS3–S–OS4	109.9	O1···H1V2–OV2	(−x, −½+y, ½−z)	2.940
C2–C3	1.414	(1.421)	N1–C1–C2	120.6	O3···H2V2–OV2	(x, y, z)	2.955
C3–C4	1.389	(1.393)	C1–C2–C3	119.3	OV2···H1N2–N2	(−½−x, 1−y, −½+z)	2.734
C4–C5	1.347	(1.350)	C2–C3–C4	117.8			
C5–N1	1.358	(1.364)	C3–C4–C5	121.0	Distances involving the half		
C2–O1	1.339	(1.342)	C4–C5–N1	120·8	water molecule (less than 3.2 Å)		
C3–O2	1.317	(1.319)	C5–N1–C1	120.5	OV1···OS3	(−1+x, y, z)	3.040
N1–C6	1.497	(1.499)	C1–C2–O1	123.3	OV1···OS4	(x, y, z)	3.123
C6–C7	1.515		O1–C2–C3	117.5	OV1···O3	(x, y, z)	3.162
C7–N2	1.487		C2–C3–O2	117.1	OV1···OV2	(x, y, z)	3.025
C7–C8	1.524		O2–C3–C4	125.1	OV1···OS2	(−½+x, ½−y, −z)	3.196
C8–O3	1.202		C5–N1–C6	119.6	OV1···N2	(−½−x, 1−y, −½+z)	3.104
C8–O4	1.289		C1–N1–C6	119.9	OV1···N2	(−x, −½+y, ½−z)	3.186
O1–HO1	1.00		N1–C6–C7	113.9	OV1···HC7	(−x, −½+y, ½−z)	2.438
O2–HO2	0.83		C6–C7–N2	1129			
O4–HO4	0.94		C6–C7–C8	113.6			
OV2–H1V2	0.72		C8–C7–N2	110.9			
OV2–H2V2	0.93		C7–C8–O3	119.1			
N2–H1N2	0.77		C7–C8–O4	114.7			
N2–H2N2	0.65		O3–C8–O4	126.3			
N2–H3N2	0.92						
C1–HC1	0.97						
C4–HC4	1.03						
C5–HC5	0.99						
C6–H1C6	0.96						
C6–H2C6	1.03						
C7–HC7	0.98						



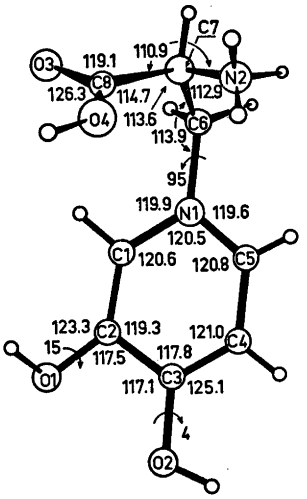


Fig. 2. a. Bond lengths (Å) and *b.* bond angles (°) in the mimosine ion. *c.* Deviations ($\times 10^3$ Å) from the best plane through the pyridine ring.

accounts for the shortness of the C1 – C2 and the C4 – C5 bonds relative to the aromatic C – C bond as found in pyridine. In accordance with the resulting charge distribution the two phenolic oxygen atoms act as hydrogen donors in fairly short hydrogen bonds (2.601 Å and 2.577 Å to oxygen atoms of the sulphate ion).

The external angles at the carbon atoms carrying the hydroxyl groups exhibit the characteristics commonly found in hydrogen bonded phenols and catechols: the angles "*cis*" to the hydrogen atoms are greater than 120° (123.3° and 125.1° for O1 and O2, respectively) whereas the angles "*trans*" are less than 120° (117.5° and 117.1°), even if the consequence is a rather small O – O nonbonded separation. The phenolic hydrogen atoms are close to the plane of the pyridyl ring, the dihedral angles C – C – O – H being 15° (O1) and 4° (O2).

The N1 – C6 bond connecting the hydroxypyridyl ring to the alanine moiety is found to be somewhat longer (1.497 Å) than in mimosine (1.478 Å). The bond lengths found within the alanine part of the ion correspond closely to

those given by Sundaralingam and Putkey [7] as the mean values for a number of protonized amino acids. As for the bond angles the agreement is also good with the exception of the two C – C – O angles which show a significant difference. Their figures are based on amino acids having the normal conformation, however, with the nitrogen atom situated close to plane of the carboxyl group and in the *anti* position relative to the hydroxyl oxygen atom. In the present structure the conformation is *syn*, resulting in a 3.5° opening of the C – C – OH angle and a corresponding decrease in the C – C = O angle relative to the values given in the paper referred to; the O – C – O angle remains unchanged. The nitrogen atom is situated close to the plane through $C_\alpha - CO_2$ (0.13 Å); the dihedral angle O(H) – C – C – N is 5.6°. The conformation about the C – N bond is staggered.

The conformation of the mimosine ion with respect to the $C_\alpha - C_\beta$ bond is different from that found for L-mimosine but is the same as that reported for L-tyrosine.[8] The carboxyl and the amino groups are both in *gauche* positions relative to the pyridyl-ring with torsional angles N1 – C6 – C7 – N2 and N1 – C6 – C7 – C8 equal to 64.6° and – 62.8°, respectively. The angle between the ring plane and the plane through N1, C6, and C7 is 85.0° in good agreement with the corresponding angles in several phenylalanine derivatives with this specific conformation (83 – 86°).

The oxygen atoms of the sulphate ion are tetrahedrally arranged around the sulphur atom with O – S – O bond angles in the range 107.4° to 110.7°. The S – O bond lengths are equal, mean value 1.466 Å (1.482 Å corrected for thermal motion). This agrees well with the average S – O bond length of 1.473 Å (1.486 Å corrected) as given by Taesler and Olovsson from a number of structure determinations of the sulphate ion.[9]

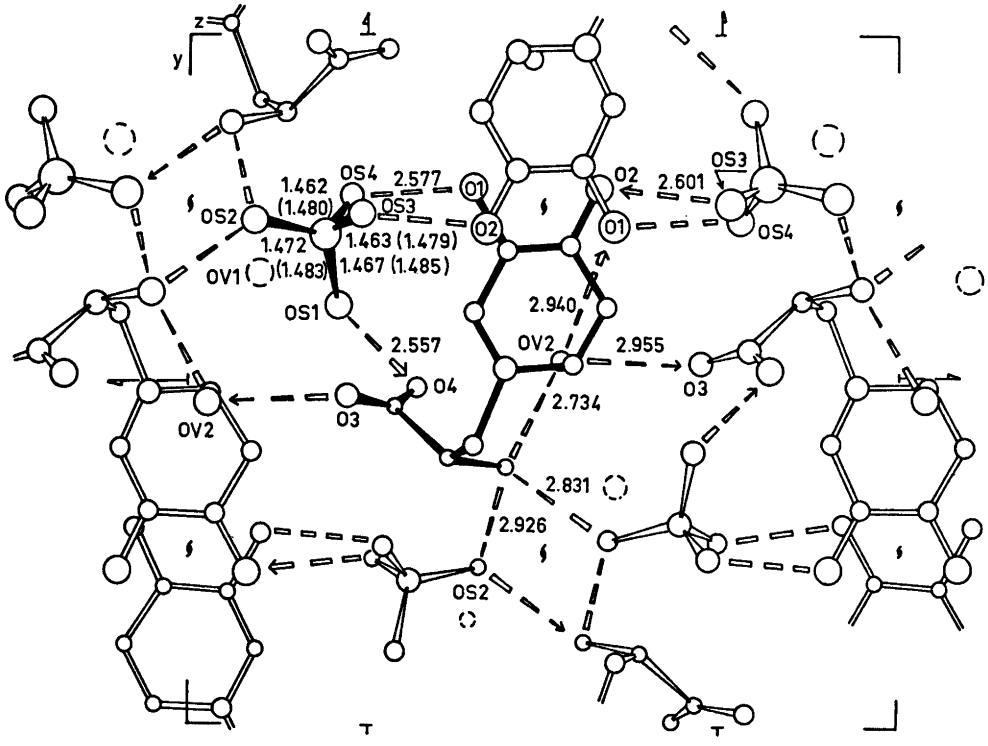


Fig. 3. The crystal structure of mimosine sulphate hydrate as seen down the *a* axis. Hydrogen bonds are indicated by broken lines, arrows indicate hydrogen bonds to atoms in another unit cell.

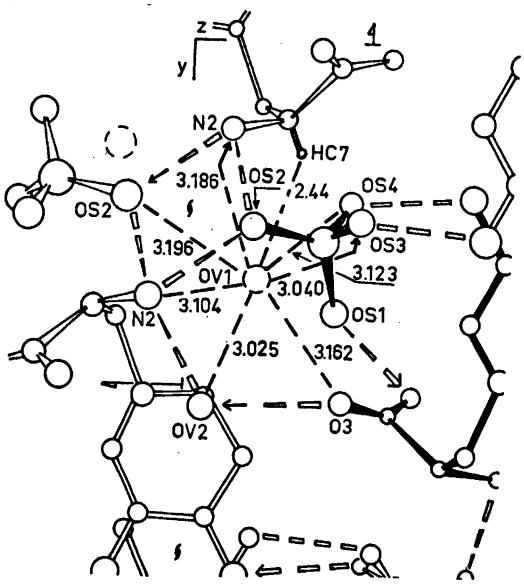


Fig. 4. The cavity containing the "half" water molecule.

The positions of the water molecules may be seen from Fig. 3. OV2 is involved in three hydrogen bonds; two as a hydrogen donor and one (to an ammonium nitrogen atom) as an acceptor. Fig. 4 illustrates the cavity containing the "half" water molecule. The molecule is surrounded by three sulphate ions, two ammonium groups, one water molecule and a carboxyl oxygen atom; there are eight oxygen or nitrogen atoms in distances between 3.0 and 3.2 Å from the OV1 atom. Four of these have lone pairs available for hydrogen bond formation. Since we were not able to localize the hydrogen atoms in this water molecule we are unable to determine which of the hydrogen bonds are established, and there may indeed exist different bonds in different unit cells in a statistical disordered way.

The crystal structure, packing and hydrogen bonding is illustrated in Fig. 3. From this drawing it may be seen that each mimosine ion is coordinated to five sulphate ions in a distorted trigonal bipyramidal arrangement. Each sulphate ion is surrounded by and hydrogen bonded to five mimosine residues. There is no direct contact between mimosine ions.

The molecular units are tied together in the crystal in an extensive three-dimensional hydrogen bond network, with the possible exception of the "half" water molecule. All hydrogen atoms bonded to hetero atoms are engaged in hydrogen bonds. The strongest of these occur between the oxygen atoms of the sulphate ion and the three hydroxyl groups in the mimosine ion, 2.557 Å (OS1 – O4), 2.577 Å (OS4 – O1) and 2.601 Å (OS3 – O2). The carbonyl oxygen atom is rather weakly hydrogen bonded to the water molecule (2.955 Å). The other hydrogen atom of this water molecule is engaged in a weak hydrogen bond to the phenolic oxygen atom O1 (2.940 Å). The N2 atom is involved as a hydrogen donor in three hydrogen bonds, one of 2.940 Å to one sulphate oxygen atom, one of 2.831 Å to another and a third of 2.734 Å to the oxygen atom of the water molecule.

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