Acta Cryst. (1969). B25, 2553

The Crystal Structure of Triacetylsphingosine

BY A. M. O'CONNELL

Crystallography Group, Medical Research Council Unit for Molecular Structure Analysis, University of Göteborg, Göteborg, Sweden

AND I. PASCHER

Institute of Medical Biochemistry, University of Göteborg, Göteborg, Sweden

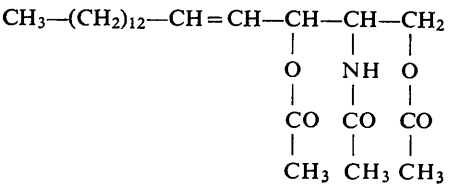
(*Received* 18 *October* 1968)

The crystal structure of triacetylsphingosine (D-erythro-1,3-diacetoxy-2-acetamido-4-*trans*-octadecene, $C_{24}H_{43}O_5N$) has been determined by direct methods. The crystals are orthorhombic, $P2_12_12_1$, with $a=5{\cdot}002$, $b=8{\cdot}709$ and $c=60{\cdot}62$ Å. Positional and isotropic thermal parameters of the non-hydrogen atoms were refined to give a final R index of 0·109. The molecules are arranged head-to-tail in layers within which the carbon chains pack according to the common orthorhombic subcell, $O\perp$. The chain axis forms an angle of 58° with the end group planes. Adjacent layers show opposite tilt of the chains. In spite of the bulky acetyl branches the molecules adopt a very effective packing ($D_m=1{\cdot}07$ g.cm^{-3}). The molecules are connected by a continuous system of N–H---O hydrogen bonds parallel to **a**, and there is also evidence for two weaker C–H---O type interactions.

Introduction

For our investigations on the structure and function of lipids occurring in biological membranes, model compounds of sphingolipids (sphingosines, ceramides, cerebrosides, sulphatides) are prepared in our laboratory for use in biochemical and physicochemical studies. The base molecules in all sphingolipids are sphingosines. These long chain amino alcohols differ in chain length, degree of saturation or number of hydroxyl groups. A brief review of naturally occurring sphingosine species has been given by Karlsson & Holm (1965) and Karlsson, Samuelsson & Steen (1968). The most common of these molecules is the parent base, sphingosine (D-*erythro*-1,3-dihydroxy-2-amino-4-*trans*-octadecene) which was first isolated by Thudichum (1882) from brain lipids.

Though free sphingosines and their simple acetyl derivatives are not present in the membranes their properties, especially with regard to their molecular packing and ability to form hydrogen bonds, are of interest for a comparison with the more complex lipids. Among the acetates of sphingosines the fully acetylated derivatives exhibit good crystallizing properties, sharp melting points and high optical rotation. On account of these properties they are used for purification and characterization of sphingosines (Thomas & Thierfelder, 1912; Klenk & Diebold, 1931; Carter, Norris, Glick, Phillips & Harris, 1947).



(I)

Triacetylsphingosine (I) crystallizes readily from acetone or ether in well-shaped brittle needles. The melting point (104·5°) of this lipid appears to be unexpectedly high when compared with the free sphingosine base (m.p. 83°) or the corresponding *N*-acetyl derivative (m.p. 87·5°). Because of the presence of free amino- and hydroxy groups, both of these latter compounds should be able to form more effective hydrogen bond systems than the fully acylated derivative. As acetylation considerably decreases the polarity of sphingosine and moreover introduces bulky acetyl branches into the molecule these physical properties must then be a molecular packing effect.

The structure analysis of triacetylsphingosine is the first of a series of comparative single-crystal investigations on sphingolipids being made in this laboratory.

Table 1. *Phase assignments for specifying the origin and enantiomorph and from the* Σ_1 *relation*

h	k	l	φ	$\lvert E\rvert$	
2	0	27	$-\pi/2$	2·95	Origin and enantiomorph
0	3	43	$-\pi/2$	2·64	
0	3	44	$-\pi/2$	2·26	
3	6	0	$\pi/2$	1·51	
0	2	8	0	3·35	Σ_1
0	4	40	π	2·49	
0	2	48	π	2·14	

Table 2. *Observed and calculated structure factors* (× 10)

The phase angles are given as fractions of one revolution. Unobserved reflexions (defined as those having a net intensity < 2 e.s.d. are indicated by negative signs on the $|F_o|$' s. They were assigned the smallest observed intensity.

H	K	L	Fobs	Fcalc	PI
0	0	2	643	641	0.500
0	0	4	343	392	1.000
0	0	6	786	804	1.000
0	0	8	1049	1171	0.500
0	0	10	216	215	0.500
0	0	12	1296	1277	1.000
0	0	14	1090	997	0.500
0	0	16	345	315	1.000
0	0	18	-35	61	1.000
0	0	20	136	46	1.000
0	0	22	391	382	0.500
0	0	24	816	792	1.000
0	0	26	-36	30	0.500
0	0	28	1074	969	1.000
0	0	30	279	278	1.000
0	0	32	300	260	1.000
0	0	34	373	300	0.500
0	0	36	148	139	1.000
0	0	38	97	121	0.500
0	0	40	100	87	1.000
0	0	42	-45	25	1.000
0	0	44	98	102	0.500
0	0	46	-47	47	1.000
0	0	48	88	116	1.000
0	0	50	118	145	0.500
0	0	52	-53	54	1.000
0	0	54	-53	25	0.500
0	0	56	339	351	0.500
0	1	1	272	256	0.250
0	1	2	399	381	0.250
0	1	3	553	533	0.750
0	1	4	96	126	0.750
0	1	5	357	371	0.250
0	1	6	237	283	0.750
0	1	7	89	148	0.750
0	1	8	-31	15	0.251
0	1	9	-31	58	0.250
0	1	10	89	98	0.750
0	1	11	285	270	0.750
0	1	12	749	770	0.250
0	1	13	438	438	0.250
0	1	14	833	781	0.750
0	1	15	547	462	0.750
0	1	16	146	117	0.250
0	1	17	387	277	0.250
0	1	18	378	312	0.250
0	1	19	73	37	0.250
0	1	20	434	396	0.750
0	1	21	403	367	0.750
0	1	22	272	295	0.250
0	1	23	409	368	0.250
0	1	24	86	83	0.250
0	1	25	57	24	0.250
0	1	26	269	298	0.750
0	1	27	132	157	0.750
0	1	28	387	321	0.250
0	1	29	217	186	0.250
0	1	30	73	39	0.750
0	1	31	193	156	0.750
0	1	32	-32	17	0.250
0	1	33	-33	39	0.750
0	1	34	113	140	0.250
0	1	35	96	117	0.750
0	1	36	-36	79	0.750
0	1	37	127	138	0.250
0	1	38	-37	1	0.250
0	1	39	142	137	0.750
0	1	40	180	168	0.250
0	1	41	-48	86	0.250
0	1	42	166	151	0.750
0	1	43	-47	27	0.750
0	1	44	-47	14	0.250
0	1	45	-47	34	0.250
0	1	46	-48	30	0.250
0	1	47	-48	33	0.750
0	1	48	-50	64	0.250
0	1	49	-51	24	0.750
0	1	50	151	166	0.750
0	1	51	97	107	0.750
0	1	52	91	69	0.750
0	1	53	-52	7	0.250
0	1	54	91	88	0.250
0	1	55	-53	46	0.750
0	1	56	-54	124	0.750
0	1	57	-53	21	0.250
0	2	0	184	160	1.000
0	2	1	1208	1225	1.000
0	2	2	62	58	1.000
0	2	3	394	448	0.500
0	2	4	565	544	0.500
0	2	5	61	39	0.500
0	2	6	656	670	1.000
0	2	7	704	666	1.000
0	2	8	1557	1486	1.000
0	2	9	1149	1095	0.500
0	2	10	-32	56	1.000
0	2	11	922	965	0.500
0	2	12	756	767	1.000
0	2	13	920	894	1.000
0	2	14	219	180	0.500
0	2	15	422	376	0.500
0	2	16	122	190	0.500
0	2	17	229	203	0.500
0	2	18	144	109	0.500
0	2	19	374	329	1.000
0	2	20	130	133	1.000
0	2	21	247	225	0.500
0	2	22	-32	68	0.500
0	2	23	123	155	0.500
0	2	24	188	139	0.500
0	2	25	299	301	1.000
0	2	26	178	210	1.000
0	2	27	215	201	0.500
0	2	28	75	75	0.500
0	2	29	49	15	0.500
0	2	30	62	72	0.500
0	2	31	52	59	1.000
0	2	32	109	138	1.000
0	2	33	138	127	1.000
0	2	34	-34	24	0.500
0	2	35	484	500	0.500
0	2	36	234	264	1.000
0	2	37	-33	34	1.000
0	2	38	186	181	1.000
0	2	39	152	155	0.500
0	2	40	92	109	1.000
0	2	41	142	148	0.500
0	2	42	-47	18	0.500
0	2	43	197	193	1.000
0	2	44	140	132	0.500
0	2	45	75	131	0.500
0	2	46	-50	55	0.500
0	2	47	246	219	0.500
0	2	48	209	208	0.500
0	2	49	125	112	0.500
0	2	50	127	127	0.500
0	2	51	-53	3	0.999
0	2	52	89	63	1.000
0	2	53	-54	59	0.500
0	2	54	-53	25	0.500
0	2	55	103	56	1.000
0	2	56	-53	37	1.000
0	3	1	247	269	0.250
0	3	2	320	322	0.250
0	3	3	306	342	0.750
0	3	4	316	275	0.750
0	3	5	107	106	0.750
0	3	6	114	66	0.250
0	3	7	281	342	0.250
0	3	8	100	82	0.750
0	3	9	164	195	0.750
0	3	10	353	385	0.250
0	3	11	121	158	0.750
0	3	12	302	313	0.750
0	3	13	378	387	0.250
0	3	14	89	100	0.250
0	3	15	622	646	0.750
0	3	16	186	176	0.750
0	3	17	298	321	0.250
0	3	18	-33	12	0.749
0	3	19	131	104	0.250
0	3	20	220	198	0.250
0	3	21	435	463	0.750
0	3	22	81	103	0.750
0	3	23	288	250	0.250
0	3	24	135	90	0.750
0	3	25	112	127	0.250
0	3	26	149	125	0.250
0	3	27	371	367	0.750
0	3	28	74	91	0.750
0	3	29	332	309	0.250
0	3	30	61	71	0.250
0	3	31	-34	11	0.750
0	3	32	-33	11	0.750
0	3	33	200	197	0.750
0	3	34	75	65	0.750
0	3	35	147	167	0.250
0	3	36	-46	26	0.250
0	3	37	-45	23	0.250
0	3	38	134	146	0.250
0	3	39	134	154	0.750
0	3	40	120	136	0.750
0	3	41	47	16	0.750
0	3	42	90	65	0.250
0	3	43	286	287	0.750
0	3	44	234	226	0.750
0	3	45	-51	66	0.250
0	3	46	83	88	0.250
0	3	47	-52	77	0.750
0	3	48	-51	6	0.250
0	3	49	97	49	0.750
0	3	50	-52	27	0.750
0	3	51	-53	98	0.250
0	3	52	-53	21	0.750
0	3	53	-52	61	0.750
0	3	54	-52	42	0.250
0	4	0	403	392	0.500
0	4	1	193	207	0.500
0	4	2	245	258	1.000
0	4	3	-34	38	1.000
0	4	4	87	59	1.000
0	4	5	233	203	1.000
0	4	6	189	149	0.500
0	4	7	-33	28	0.500
0	4	8	82	62	0.500
0	4	9	653	617	0.500
0	4	10	131	135	0.500
0	4	11	121	97	1.000
0	4	12	744	733	0.500
0	4	13	335	290	0.500
0	4	14	305	280	1.000
0	4	15	345	361	0.500
0	4	16	401	440	1.000
0	4	17	90	125	0.500
0	4	18	76	87	0.500
0	4	19	327	324	0.500
0	4	20	496	517	1.000
0	4	21	-34	33	1.000
0	4	22	150	150	0.500
0	4	23	-33	34	1.000
0	4	24	144	166	0.500
0	4	25	127	128	0.500
0	4	26	169	204	1.000
0	4	27	212	218	1.000
0	4	28	-45	46	0.500
0	4	29	202	208	0.500
0	4	30	66	114	0.500
0	4	31	75	74	1.000
0	4	32	106	119	1.000
0	4	33	76	93	1.000
0	4	34	-46	34	1.000
0	4	35	86	135	0.500
0	4	36	213	237	0.500
0	4	37	206	228	0.500
0	4	38	-50	43	0.500
0	4	39	-49	13	1.000
0	4	40	258	264	0.500
0	4	41	358	374	0.500
0	4	42	108	123	0.500
0	4	43	-53	68	0.500
0	4	44	299	298	1.000
0	4	45	-53	8	0.500
0	4	46	-52	37	1.000
0	4	47	213	252	0.500
0	4	48	139	154	1.000
0	4	49	-53	11	0.500
0	4	50	-53	45	0.500
0	5	1	98	118	0.250
0	5	2	191	223	0.250
0	5	3	66	56	0.750
0	5	4	181	179	0.750
0	5	5	143	179	0.750
0	5	6	62	86	0.750
0	5	7	100	78	0.250
0	5	8	81	63	0.250
0	5	9	118	64	0.750
0	5	10	116	72	0.750
0	5	11	99	66	0.250
0	5	12	-34	12	0.749
0	5	13	97	97	0.750
0	5	14	167	139	0.250
0	5	15	78	77	0.250
0	5	16	159	149	0.750
0	5	17	94	87	0.750
0	5	18	98	88	0.250
0	5	19	-45	26	0.250
0	5	20	-45	10	0.250
0	5	21	-45	10	0.750
0	5	22	-45	55	0.250
0	5	23	-45	48	0.750
0	5	24	102	123	0.750
0	5	25	-46	81	0.250
0	5	26	-47	42	0.250
0	5	27	-47	69	0.750
0	5	28	-46	75	0.250
0	5	29	-46	78	0.250
0	5	30	-47	14	0.750
0	5	31	-49	59	0.750
0	5	32	97	74	0.750
0	5	33	-48	56	0.750
0	5	34	-50	31	0.750
0	5	35	-51	116	0.750
0	5	36	187	183	0.750
0	5	37	87	51	0.750
0	5	38	114	103	0.250
0	5	39	111	123	0.250
0	5	40	102	41	0.750
0	5	41	160	157	0.750
0	5	42	-53	33	0.750
0	5	43	109	110	0.250
0	5	44	95	64	0.250
0	5	45	-52	20	0.750
0	5	46	-53	10	0.750
0	6	0	259	277	0.500
0	6	1	383	421	0.500
0	6	2	272	292	0.500
0	6	3	101	115	0.500
0	6	4	45	28	1.000
0	6	5	-45	16	0.500
0	6	6	107	168	0.500
0	6	7	-46	90	0.500
0	6	8	-46	108	1.000
0	6	9	-45	38	0.500
0	6	10	-45	0	0.999
0	6	11	88	128	1.000
0	6	12	-46	10	1.000
0	6	13	-45	59	0.500
0	6	14	87	84	0.500
0	6	15	-47	37	0.500
0	6	16	-47	87	1.000
0	6	17	-47	76	1.000
0	6	18	-46	24	0.500
0	6	19	-46	31	0.500
0	6	20	-48	55	0.500
0	6	21	-47	20	0.500
0	6	22	-49	47	1.000
0	6	23	-48	2	0.999
0	6	24	-49	76	1.000
0	6	25	100	126	0.500
0	6	26	-49	1	0.504
0	6	27	-49	37	1.000
0	6	28	-49	30	1.000
0	6	29	144	155	0.500
0	6	30	188	212	0.500
0	6	31	138	122	0.500
0	6	32	-52	26	0.500
0	6	33	-52	50	0.500
0	6	34	-53	119	0.500
0	6	35	-52	40	0.500
0	6	36	-52	120	1.000
0	6	37	-52	9	1.000
0	6	38	-52	79	0.500
0	6	39	-51	40	1.000
0	6	40	-52	54	0.500
0	7	1	-49	61	0.750
0	7	2	-49	23	0.750
0	7	3	97	80	0.250
0	7	4	93	177	0.250
0	7	5	138	161	0.750
0	7	6	-46	109	0.750
0	7	7	89	89	0.250
0	7	8	-49	23	0.750
0	7	9	73	72	0.250
0	7	10	-50	40	0.250
0	7	11	102	97	0.750
0	7	12	-50	49	0.750
0	7	13	-50	42	0.250
0	7	14	-49	7	0.250
0	7	15	-48	4	0.251
0	7	16	-50	68	0.250
0	7	17	75	34	0.750
0	7	18	-51	100	0.750
0	7	19	87	51	0.250
0	7	20	75	42	0.250
0	7	21	-50	6	0.750
0	7	22	-50	99	0.250
0	7	23	-50	29	0.750
0	7	24	124	164	0.750
0	7	25	82	75	0.750
0	7	26	-50	34	0.250
0	7	27	-51	20	0.250
0	7	28	-50	28	0.750
0	7	29	78	71	0.750
0	7	30	-49	13	0.750
0	7	31	-51	35	0.250
0	8	0	-50	11	1.000
0	8	1	136	131	1.000
0	8	2	-51	33	0.500
0	8	3	-51	28	0.500
0	8	4	-50	11	0.500
0	8	5	77	90	1.000
0	8	6	187	217	0.500
0	8	7	234	246	1.000
0	8	8	-51	70	0.500
0	8	9	89	77	0.500
0	8	10	-50	34	0.500
0	8	11	89	61	1.000
0	8	12	-53	7	0.500
0	8	13	-52	15	1.000
0	8	14	-52	7	0.500
0	8	15	-53	86	0.500
0	8	16	-52	0	0.507
0	8	17	118	181	0.750
1	0	1	1188	1148	0.500
1	0	2	360	401	0.750
1	0	3	1070	1013	1.000
1	0	4	373	380	0.250
1	0	5	141	163	0.500
1	0	6	130	129	0.250
1	0	7	408	452	1.000
1	0	8	675	664	0.750
1	0	9	347	338	0.500
1	0	10	525	434	0.250
1	0	11	88	126	0.500
1	0	12	73	66	0.250
1	0	13	286	297	1.000
1	0	14	481	471	0.750
1	0	15	119	77	0.500
1	0	16	455	499	0.250
1	0	17	80	109	0.500
1	0	18	202	217	0.750
1	0	19	215	225	1.000
1	0	20	-32	41	0.750
1	0	21	263	331	0.500
1	0	22	-33	27	0.250
1	0	23	-33	47	1.000
1	0	24	125	107	0.250
1	0	25	573	582	1.000
1	0	26	603	558	0.750
1	0	27	106	77	1.000
1	0	28	377	357	0.750
1	0	29	156	185	1.000
1	0	30	-33	34	0.250
1	0	31	243	250	1.000
1	0	32	-34	95	0.750
1	0	33	212	230	0.500
1	0	34	71	112	0.250
1	0	35	135	137	1.000
1	0	36	-33	44	0.750
1	0	37	-33	44	0.500
1	0	38	106	77	1.000
1	0	39	-46	21	0.750
1	0	40	-46	20	0.500
1	0	41	-46	19	0.250
1	0	42	-46	27	0.500
1	0	43	-47	2	0.748
1	0	44	106	114	1.000
1	0	45	81	29	0.250
1	0	46	-49	43	0.500
1	0	47	73	51	0.750
1	0	48	82	56	0.500
1	0	49	-50	19	0.250
1	0	50	91	64	1.000
1	0	51	-52	24	0.750
1	0	52	-52	40	1.000
1	0	53	-52	5	0.750
1	0	54	167	152	0.500
1	0	55	91	96	0.750
1	0	56	-52	24	1.000
1	1	0	155	175	0.250
1	1	1	450	461	0.877
1	1	2	297	298	0.728
1	1	3	1458	1435	0.267
1	1	4	1839	1808	0.656
1	1	5	1202	1193	0.123
1	1	6	157	144	0.672
1	1	7	543	569	0.074
1	1	8	602	619	0.740
1	1	9	487	435	0.492
1	1	10	467	456	0.348
1	1	11	83	112	0.931
1	1	12	384	375	0.609
1	1	13	181	162	0.861
1	1	14	149	96	0.609
1	1	15	135	143	0.367
1	1	16	156	168	0.457
1	1	17	82	79	0.155
1	1	18	113	132	0.892
1	1	19	252	260	0.734
1	1	20	-36	28	0.088
1	1	21	249	246	0.261
1	1	22	66	78	0.088
1	1	23	444	403	0.945
1	1	24	363	352	0.851
1	1	25	343	393	0.717
1	1	26	66	90	0.229
1	1	27	197	212	0.198
1	1	28	183	198	0.839
1	1	29	137	158	0.788
1	1	30	290	272	0.688
1	1	31	355	322	0.136
1	1	32	114	104	0.746
1	1	33	209	229	0.222
1	1	34	312	308	0.667
1	1	35	114	170	0.017
1	1	36	83	79	0.620
1	1	37	69	19	0.233
1	1	38	192	172	0.178
1	1	39	-46	61	0.480
1	1	40	-47	95	0.713
1	1	41	-46	74	0.851
1	1	42	-46	46	0.312
1	1	43	-47	28	0.965
1	1	44	-48	39	0.993
1	1	45	85	90	0.416
1	1	46	86	52	0.726
1	1	47	-51	197	0.862
1	1	48	-50	86	0.294
1	1	49	-52	87	0.312
1	1	50	-51	17	0.616
1	1	51	115	116	0.306
1	1	52	173	153	0.282
1	1	53	-53	70	0.299
1	1	54	-52	52	0.406
1	1	55	-52	16	0.038
1	1	56	-52	36	0.948
1	2	0	270	251	0.750
1	2	1	690	659	0.692
1	2	2	296	296	0.412
1	2	3	414	366	0.097
1	2	4	50	52	0.863
1	2	5	111	141	0.101
1	2	6	439	378	0.007
1	2	7	485	473	0.436
1	2	8	598	544	0.598
1	2	9	596	575	0.975
1	2	10	-34	21	0.695
1	2	11	377	380	0.324
1	2	12	248	223	0.749
1	2	13	-35	18	0.553
1	2	14	341	342	0.270
1	2	15	82	76	0.778
1	2	16	430	454	0.811
1	2	17	264	253	0.848
1	2	18	127	142	0.271
1	2	19	94	79	0.675
1	2	20	686	653	0.814
1	2	21	705	727	0.825
1	2	22	111	140	0.709
1	2	23	288	282	0.273
1	2	24	199	208	0.181

Table 2 (*cont.*)

H	K	L	Fobs	Fcalc	FI
1	2	25	141	116	0.415
1	2	26	57	66	0.826
1	2	27	127	140	0.958
1	2	28	176	162	0.918
1	2	29	133	126	0.799
1	2	30	197	197	0.214
1	2	31	-37	57	0.173
1	2	32	176	159	0.737
1	2	33	57	58	0.034
1	2	34	84	96	0.095
1	2	35	184	207	0.558
1	2	36	156	145	0.153
1	2	37	95	89	0.813
1	2	38	-46	-5	0.030
1	2	39	117	143	0.482
1	2	40	77	55	0.976
1	2	41	116	121	0.899
1	2	42	-46	25	0.391
1	2	43	-50	111	0.363
1	2	44	-50	43	0.890
1	2	45	-51	95	0.745
1	2	46	-50	68	0.561
1	2	47	-52	82	0.537
1	2	48	177	166	0.666
1	2	49	100	85	0.739
1	2	50	82	96	0.077
1	2	51	-52	22	0.252
1	2	52	-52	66	0.497
1	2	53	-52	24	0.490
1	2	54	-52	22	0.592
1	3	0	478	454	0.250
1	3	1	108	116	0.454
1	3	2	339	316	0.760
1	3	3	202	196	0.055
1	3	4	66	76	0.441
1	3	5	126	125	0.653
1	3	6	217	208	0.160
1	3	7	146	140	0.284
1	3	8	139	118	0.752
1	3	9	327	373	0.782
1	3	10	233	194	0.438
1	3	11	437	490	0.238
1	3	12	211	239	0.616
1	3	13	523	479	0.213
1	3	14	100	103	0.551
1	3	15	440	409	0.156
1	3	16	140	178	0.455
1	3	17	336	306	0.350
1	3	18	238	224	0.296
1	3	19	152	157	0.673
1	3	20	243	226	0.883
1	3	21	168	134	0.085
1	3	22	141	141	0.371
1	3	23	122	110	0.457
1	3	24	-34	45	0.614
1	3	25	173	179	0.871
1	3	26	101	105	0.908
1	3	27	132	154	0.379
1	3	28	-37	76	0.297
1	3	29	60	48	0.992
1	3	30	88	77	0.583
1	3	31	92	67	0.758
1	3	32	146	76	0.956
1	3	33	113	115	0.249
1	3	34	45	25	0.215
1	3	35	47	93	0.747
1	3	36	46	73	0.448
1	3	37	47	32	0.800
1	3	38	134	125	0.795
1	3	39	206	227	0.189
1	3	40	116	118	0.469
1	3	41	115	95	0.254
1	3	42	205	214	0.518
1	3	43	278	286	0.247
1	3	44	51	39	0.402
1	3	45	239	242	0.285
1	3	46	176	209	0.275
1	3	47	183	186	0.718
1	3	48	82	88	0.696
1	3	49	80	120	0.207
1	3	50	52	38	0.050
1	3	51	53	43	0.702
1	3	52	52	23	0.246
1	4	0	34	25	0.250
1	4	1	149	178	0.635
1	4	2	177	174	0.576
1	4	3	96	111	0.090
1	4	4	167	148	0.114
1	4	5	193	206	0.987
1	4	6	101	85	0.107
1	4	7	236	226	0.443
1	4	8	223	210	0.686
1	4	9	297	284	0.766
1	4	10	297	320	0.852
1	4	11	229	224	0.976
1	4	12	129	112	0.486
1	4	13	401	413	0.667
1	4	14	449	430	0.823
1	4	15	362	371	0.159
1	4	16	216	191	0.409
1	4	17	89	85	0.909
1	4	18	83	83	0.810
1	4	19	210	234	0.338
1	4	20	221	213	0.666
1	4	21	189	212	0.968
1	4	22	34	28	0.397
1	4	23	156	161	0.505
1	4	24	185	182	0.128
1	4	25	87	73	0.022
1	4	26	146	127	0.671
1	4	27	44	42	0.278
1	4	28	46	30	0.520
1	4	29	127	123	0.669
1	4	30	46	72	0.103
1	4	31	113	117	0.158
1	4	32	46	26	0.415
1	4	33	48	84	0.877
1	4	34	74	85	0.798
1	4	35	137	110	0.464
1	4	36	49	70	0.324
1	4	37	72	56	0.846
1	4	38	105	98	0.651
1	4	39	137	117	0.513
1	4	40	167	182	0.694
1	4	41	116	114	0.555
1	4	42	166	173	0.031
1	4	43	123	88	0.035
1	4	44	93	90	0.446
1	4	45	169	138	0.518
1	4	46	93	110	0.919
1	4	47	53	23	0.442
1	4	48	42	43	0.176
1	4	49	53	73	0.956
1	4	50	86	109	0.750
1	4	51	168	146	0.249
1	4	52	112	102	0.520
1	4	53	132	169	0.933
1	4	54	206	181	0.197
1	4	55	259	264	0.332
1	4	56	171	177	0.291
1	5	7	251	220	0.325
1	5	8	206	210	0.268
1	5	9	-34	21	0.151
1	5	10	86	73	0.340
1	5	11	-35	-3	0.394
1	5	12	111	110	0.732
1	5	13	52	48	0.308
1	5	14	-46	57	0.137
1	5	15	117	103	0.799
1	5	16	-46	67	0.300
1	5	17	-46	4	0.171
1	5	18	97	131	0.742
1	5	19	171	156	0.262
1	5	20	82	58	0.614
1	5	21	93	77	0.984
1	5	22	49	55	0.743
1	5	23	161	186	0.184
1	5	24	217	215	0.640
1	5	25	48	50	0.519
1	5	26	91	142	0.141
1	5	27	48	47	0.864
1	5	28	48	22	0.838
1	5	29	48	67	0.293
1	5	30	84	80	0.650
1	5	31	49	27	0.680
1	5	32	142	122	0.279
1	5	33	131	151	0.317
1	5	34	132	132	0.331
1	5	35	115	94	0.624
1	5	36	115	120	0.448
1	5	37	166	184	0.290
1	5	38	139	137	0.218
1	5	39	52	83	0.772
1	5	40	114	88	0.758
1	5	41	51	13	0.682
1	5	42	52	39	0.393
1	5	43	52	48	0.211
1	5	44	51	16	0.064
1	6	0	152	172	0.750
1	6	1	48	69	0.542
1	6	2	91	68	0.835
1	6	3	137	142	0.906
1	6	4	80	76	0.524
1	6	5	145	127	0.760
1	6	6	47	68	0.832
1	6	7	102	77	0.206
1	6	8	47	57	0.013
1	6	9	98	84	0.405
1	6	10	47	63	0.398
1	6	11	128	124	0.866
1	6	12	48	32	0.867
1	6	13	49	65	0.387
1	6	14	48	39	0.554
1	6	15	49	10	0.954
1	6	16	48	32	0.142
1	6	17	48	26	0.219
1	6	18	48	37	0.895
1	6	19	49	48	0.702
1	6	20	49	61	0.495
1	6	21	48	36	0.317
1	6	22	73	83	0.913
1	6	23	88	46	0.149
1	6	24	50	51	0.465
1	6	25	50	72	0.047
1	6	26	52	101	0.766
1	6	27	91	118	0.274
1	6	28	137	133	0.572
1	6	29	52	57	0.489
1	6	30	51	60	0.274
1	6	31	52	21	0.801
1	6	32	89	109	0.556
1	6	33	88	94	0.449
1	6	34	50	49	0.047
1	6	35	50	26	0.927
1	6	36	49	4	0.165
1	6	37	49	28	0.958
1	6	38	50	25	0.466
1	7	0	50	21	0.750
1	7	1	100	105	0.554
1	7	2	269	298	0.199
1	7	3	183	208	0.710
1	7	4	92	68	0.300
1	7	5	50	21	0.977
1	7	6	87	87	0.887
1	7	7	49	86	0.522
1	7	8	49	86	0.288
1	7	9	50	64	0.896
1	7	10	50	53	0.988
1	7	11	51	78	0.185
1	7	12	50	57	0.837
1	7	13	50	56	0.522
1	7	14	50	80	0.305
1	7	15	50	64	0.839
1	7	16	82	40	0.775
1	7	17	76	85	0.246
1	7	18	50	16	0.737
1	7	19	79	66	0.699
1	7	20	94	91	0.226
1	7	21	51	18	0.168
1	7	22	85	65	0.728
1	7	23	50	32	0.225
1	7	24	50	56	0.372
1	7	25	97	98	0.443
1	7	26	111	112	0.318
1	7	27	52	58	0.291
1	7	28	51	35	0.667
1	8	0	89	45	0.750
1	8	1	53	43	0.986
1	8	2	85	49	0.135
1	8	3	54	93	0.444
1	8	4	53	48	0.527
1	8	5	101	107	0.956
1	8	6	90	51	0.711
1	8	7	85	93	0.402
1	8	8	79	91	0.986
1	8	9	53	50	0.439
1	8	10	107	55	0.460
2	0	0	1109	1009	0.500
2	0	1	923	887	0.750
2	0	2	94	103	0.500
2	0	3	218	222	0.750
2	0	4	67	62	1.000
2	0	5	148	170	0.250
2	0	6	355	306	0.500
2	0	7	92	105	0.750
2	0	8	484	443	1.000
2	0	9	122	143	0.250
2	0	10	222	173	0.500
2	0	11	38	34	0.250
2	0	12	33	74	0.500
2	0	13	261	271	0.750
2	0	14	95	96	1.000
2	0	15	266	291	0.250
2	0	16	33	21	1.000
2	0	17	71	83	0.750
2	0	18	251	278	0.500
2	0	19	131	122	0.750
2	0	20	30	50	1.000
2	0	21	133	144	0.250
2	0	22	362	330	0.500
2	0	23	33	50	0.750
2	0	24	110	56	1.000
2	0	25	34	21	0.250
2	0	26	125	125	1.000
2	0	27	555	548	0.750
2	0	28	101	106	0.500
2	0	29	34	51	0.750
2	0	30	166	179	0.500
2	0	31	138	155	0.750
2	0	32	67	100	1.000
2	0	33	46	8	0.749
2	0	34	47	21	0.500
2	0	35	46	32	0.250
2	0	36	47	22	1.000
2	0	37	47	37	0.250
2	0	38	47	16	0.500
2	0	39	47	12	0.750
2	0	40	49	39	1.000
2	0	41	49	51	0.750
2	0	42	99	88	0.500
2	0	43	83	86	0.250
2	0	44	121	134	1.000
2	0	45	53	52	0.750
2	0	46	126	128	0.500
2	0	47	53	24	0.750
2	0	48	53	50	1.000
2	0	49	53	24	0.250
2	0	50	52	4	0.999
2	0	51	53	33	0.750
2	0	52	52	18	0.500
2	1	0	37	33	1.000
2	1	1	302	274	0.643
2	1	2	191	182	0.713
2	1	3	458	416	0.160
2	1	4	227	214	0.293
2	1	5	504	495	0.747
2	1	6	276	268	0.313
2	1	7	38	47	0.103
2	1	8	146	158	0.625
2	1	9	116	113	0.159
2	1	10	218	230	0.015
2	1	11	75	54	0.677
2	1	12	207	205	0.593
2	1	13	66	21	0.552
2	1	14	177	159	0.184
2	1	15	107	69	0.227
2	1	16	139	146	0.732
2	1	17	106	71	0.649
2	1	18	123	143	0.250
2	1	19	55	59	0.119
2	1	20	68	31	0.509
2	1	21	72	57	0.812
2	1	22	404	358	0.761
2	1	23	469	437	0.651
2	1	24	429	369	0.569
2	1	25	221	203	0.630
2	1	26	115	94	0.913
2	1	27	123	122	0.862
2	1	28	146	185	0.686
2	1	29	58	73	0.468
2	1	30	34	23	0.232
2	1	31	207	211	0.211
2	1	32	245	230	0.897
2	1	33	180	174	0.402
2	1	34	187	172	0.660
2	1	35	47	41	0.137
2	1	36	73	53	0.030
2	1	37	47	52	0.414
2	1	38	47	42	0.222
2	1	39	87	82	0.008
2	1	40	81	87	0.095
2	1	41	50	52	0.696
2	1	42	84	61	0.207
2	1	43	50	53	0.431
2	1	44	52	26	0.766
2	1	45	52	35	0.997
2	1	46	52	3	0.125
2	1	47	53	38	0.819
2	1	48	54	47	0.578
2	1	49	53	52	0.433
2	1	50	53	11	0.001
2	1	51	53	34	0.446
2	1	52	102	88	0.529
2	2	0	32	12	0.501
2	2	1	262	245	0.515
2	2	2	137	135	0.828
2	2	3	59	46	0.109
2	2	4	129	149	0.298
2	2	5	135	127	0.079
2	2	6	100	109	0.626
2	2	7	210	176	0.741
2	2	8	328	320	0.295
2	2	9	439	392	0.840
2	2	10	217	193	0.381
2	2	11	104	88	0.066
2	2	12	87	58	0.248
2	2	13	127	112	0.813
2	2	14	96	90	0.817
2	2	15	98	86	0.589
2	2	16	136	151	0.408
2	2	17	381	374	0.124
2	2	18	291	275	0.284
2	2	19	355	345	0.689
2	2	20	143	157	0.773
2	2	21	167	139	0.049
2	2	22	306	298	0.281
2	2	23	156	161	0.290
2	2	24	247	250	0.781
2	2	25	128	142	0.716
2	2	26	34	61	0.359
2	2	27	33	46	0.180
2	2	28	103	126	0.189
2	2	29	44	37	0.913
2	2	30	118	116	0.708
2	2	31	130	135	0.417
2	2	32	46	23	0.765
2	2	33	126	119	0.905
2	2	34	177	165	0.222
2	2	35	117	103	0.761
2	2	36	48	35	0.500
2	2	37	48	35	0.592
2	2	38	131	116	0.329
2	2	39	173	189	0.837
2	2	40	77	65	0.285
2	2	41	50	52	0.221
2	2	42	107	86	0.756
2	2	43	124	120	0.488
2	2	44	81	94	0.173
2	2	45	143	148	0.027
2	2	46	52	8	0.967
2	2	47	52	55	0.275
2	2	48	116	104	0.082
2	2	49	111	71	0.118
2	2	50	101	69	0.186
2	3	0	33	39	1.000
2	3	1	123	127	0.596
2	3	2	286	267	0.756
2	3	3	83	113	0.107
2	3	4	292	283	0.250
2	3	5	87	69	0.298
2	3	6	119	128	0.618
2	3	7	134	148	0.697
2	3	8	146	122	0.806
2	3	9	32	51	0.188
2	3	10	197	208	0.176
2	3	11	222	199	0.009
2	3	12	285	268	0.473
2	3	13	566	541	0.684
2	3	14	195	197	0.697
2	3	15	177	185	0.889
2	3	16	294	284	0.503
2	3	17	415	424	0.608
2	3	18	197	195	0.728
2	3	19	133	133	0.985
2	3	20	88	87	0.921
2	3	21	124	118	0.348
2	3	22	121	110	0.292
2	3	23	117	96	0.907
2	3	24	46	80	0.712
2	3	25	98	95	0.485
2	3	26	46	61	0.187
2	3	27	70	70	0.141
2	3	28	46	46	0.699
2	3	29	112	123	0.772
2	3	30	77	53	0.255
2	3	31	122	117	0.000
2	3	32	47	74	0.868
2	3	33	47	34	0.738
2	3	34	77	71	0.382
2	3	35	111	99	0.771
2	3	36	74	72	0.619
2	3	37	83	85	0.250
2	3	38	103	112	0.831
2	3	39	50	51	0.232
2	3	40	51	58	0.431
2	3	41	92	58	0.573
2	3	42	52	74	0.681
2	3	43	164	189	0.284
2	3	44	52	22	0.638
2	3	45	115	106	0.624
2	3	46	51	66	0.405
2	3	47	53	72	0.937
2	3	48	75	66	0.762
2	4	0	149	144	1.000
2	4	1	52	56	0.491
2	4	2	170	147	0.357
2	4	3	115	108	0.902
2	4	4	165	165	0.779
2	4	5	193	190	0.399
2	4	6	69	73	0.227
2	4	7	133	131	0.852
2	4	8	89	93	0.099
2	4	9	243	188	0.153
2	4	10	81	102	0.228
2	4	11	56	69	0.080
2	4	12	237	239	0.991
2	4	13	85	89	0.201
2	4	14	142	120	0.352
2	4	15	196	201	0.004
2	4	16	176	201	0.398
2	4	17	234	239	0.591
2	4	18	141	159	0.341
2	4	19	205	230	0.992
2	4	20	196	192	0.407
2	4	21	79	109	0.638
2	4	22	48	23	0.365
2	4	23	143	148	0.357
2	4	24	96	142	0.918
2	4	25	156	162	0.974
2	4	26	86	119	0.514
2	4	27	48	72	0.579
2	4	28	86	82	0.178
2	4	29	93	101	0.428
2	4	30	80	83	0.937
2	4	31	139	145	0.974
2	4	32	87	122	0.546
2	4	33	75	79	0.519
2	4	34	50	46	0.069
2	4	35	51	38	0.220
2	4	36	90	101	0.125
2	4	37	111	84	0.101
2	4	38	52	73	0.392
2	4	39	52	89	0.287
2	4	40	136	142	0.079
2	4	41	112	116	0.093
2	4	42	110	96	0.206
2	4	43	53	59	0.732
2	4	44	102	103	0.463
2	5	0	45	14	1.000
2	5	1	83	79	0.039
2	5	2	45	56	0.891
2	5	3	113	132	0.779
2	5	4	94	118	0.877
2	5	5	151	183	0.416
2	5	6	142	146	0.701
2	5	7	149	159	0.749
2	5	8	89	75	0.571
2	5	9	184	183	0.625
2	5	10	48	70	0.615
2	5	11	132	114	0.176
2	5	12	132	93	0.990
2	5	13	69	58	0.877
2	5	14	103	109	0.489
2	5	15	49	68	0.717
2	5	16	86	88	0.037
2	5	17	124	105	0.289
2	5	18	79	82	0.939
2	5	19	105	109	0.856
2	5	20	86	116	0.249
2	5	21	148	154	0.793
2	5	22	98	128	0.383
2	5	23	103	101	0.271
2	5	24	132	122	0.366
2	5	25	50	73	0.695
2	5	26	83	86	0.905
2	5	27	50	6	0.940
2	5	28	51	43	0.446
2	5	29	50	34	0.801
2	5	30	52	41	0.775
2	5	31	84	99	0.231
2	5	32	84	99	0.231
2	5	33	52	55	0.169
2	5	34	52	55	0.169
2	5	35	52	54	0.593
2	5	36	51	54	0.593
2	5	37	52	54	0.593
2	5	38	51	66	0.401
2	5	39	51	66	0.401
2	5	40	53	60	0.211
2	5	41	53	60	0.211
2	5	42	51	62	0.267
2	5	43	51	62	0.267
2	5	44	52	84	0.297
2	5	45	52	84	0.297
2	5	46	51	84	0.922
2	5	47	51	84	0.922
2	5	48	81	94	0.736
2	5	49	81	94	0.736
2	6	0	181	155	1.000
2	6	1	161	154	0.066
2	6	2	133	123	0.255

Table 2 (*cont.*)

H	K	L	Fobs	Fcalc	FI
2	6	3	178	147	0.192
2	6	4	79	115	0.985
2	6	5	<50	59	0.689
2	6	6	<50	76	0.409
2	6	7	<50	70	0.149
2	6	8	<49	33	0.251
2	6	9	<50	30	0.861
2	6	10	<50	30	0.794
2	6	11	<52	95	0.537
2	6	12	<50	18	0.903
2	6	13	<51	65	0.040
2	6	14	<52	85	0.461
2	6	15	<51	29	0.187
2	6	15	<51	29	0.187
2	6	16	124	147	0.976
2	6	16	124	147	0.976
2	6	17	88	96	0.579
2	6	17	88	96	0.579
2	6	18	96	120	0.484
2	6	18	96	120	0.484
2	6	19	110	99	0.986
2	6	19	110	99	0.986
2	6	20	<52	58	0.962
2	6	20	<52	58	0.962
2	6	21	108	102	0.312
2	6	21	108	102	0.312
2	6	22	<52	31	0.380
2	6	22	<52	31	0.380
2	6	23	88	107	0.736
2	6	23	88	107	0.736
2	6	24	<51	17	0.482
2	6	24	<51	17	0.482
2	6	25	<53	103	0.048
2	6	25	<53	103	0.048
2	6	26	<52	58	0.687
2	6	26	<52	58	0.687
2	6	27	<52	53	0.399
2	6	27	<52	53	0.399
2	6	28	130	159	0.220
2	6	28	130	159	0.220
2	6	29	<52	19	0.512
2	6	29	<52	19	0.512
2	6	30	<52	24	0.456
2	6	30	<52	24	0.456
2	6	31	90	112	0.146
2	6	31	90	112	0.146
2	6	32	<52	35	0.095
2	6	32	<52	35	0.095
2	7	0	<52	29	1.000
2	7	0	<52	29	1.000
2	7	1	<52	42	0.721
2	7	1	<52	42	0.721
2	7	2	165	189	0.326
2	7	2	165	189	0.326
2	7	3	<53	105	0.932
2	7	3	<53	105	0.932
2	7	4	129	177	0.730
2	7	5	<52	60	0.344
2	7	6	<52	80	0.169
2	7	7	<52	40	0.790
2	7	8	86	83	0.317
2	7	9	<51	16	0.702
2	7	10	<53	92	0.811
2	7	11	<52	30	0.335
2	7	12	<51	54	0.344
2	7	13	<52	23	0.957
2	7	14	<51	33	0.162
2	7	15	<52	29	0.712
2	7	16	75	58	0.691
2	7	17	<51	39	0.308
2	7	18	<51	25	0.122
2	7	19	<51	40	0.770
3	0	1	77	69	0.250
3	0	2	107	109	1.000
3	0	3	90	83	0.750
3	0	4	56	44	0.500
3	0	5	103	86	0.250
3	0	6	60	44	1.000
3	0	7	134	140	0.750
3	0	8	98	89	0.500
3	0	9	76	82	0.250
3	0	10	52	37	0.500
3	0	11	<34	11	0.750
3	0	12	82	113	1.000
3	0	13	<34	2	0.748
3	0	14	<34	23	0.500
3	0	15	<44	19	0.749
3	0	16	127	139	0.500
3	0	17	<45	17	0.750
3	0	18	168	206	1.000
3	0	19	<46	35	0.250
3	0	20	148	142	0.500
3	0	21	<46	7	0.749
3	0	22	<47	56	1.000
3	0	23	<47	45	0.250
3	0	24	<47	28	1.000
3	0	25	104	96	0.750
3	0	26	271	289	0.500
3	0	27	<48	21	0.250
3	0	28	388	344	0.500
3	0	29	141	102	0.250
3	0	30	182	160	0.500
3	0	31	130	154	0.750
3	0	32	75	78	0.500
3	0	33	178	102	0.250
3	0	34	<52	74	1.000
3	0	35	<51	93	0.750
3	0	36	<49	45	0.500
3	0	37	82	57	0.250
3	0	38	<49	34	1.000
3	0	39	<50	18	0.750
3	0	40	<50	29	0.500
3	0	41	<50	20	0.250
3	0	42	<50	34	1.000
3	0	43	<50	28	0.750
3	0	44	<49	31	0.500
3	0	45	<49	9	0.750
3	1	0	216	208	0.750
3	1	1	81	106	0.342
3	1	2	117	149	0.211
3	1	3	78	85	0.671
3	1	4	325	281	0.031
3	1	5	335	304	0.521
3	1	6	177	170	0.850
3	1	7	<34	83	0.155
3	1	8	<33	30	0.216
3	1	9	54	80	0.668
3	1	10	140	112	0.232
3	1	11	82	74	0.360
3	1	12	108	90	0.728
3	1	13	119	97	0.918
3	1	14	101	99	0.487
3	1	15	<44	19	0.096
3	1	16	145	132	0.945
3	1	17	153	123	0.499
3	1	18	94	138	0.324
3	1	19	125	106	0.942
3	1	20	71	98	0.767
3	1	21	57	76	0.796
3	1	22	<44	12	0.728
3	1	23	209	210	0.495
3	1	24	114	138	0.590
3	1	25	126	125	0.980
3	1	26	82	62	0.023
3	1	27	<45	10	0.823
3	1	28	84	79	0.540
3	1	29	118	99	0.437
3	1	30	<48	55	0.019
3	1	31	48	41	0.325
3	1	32	82	100	0.802
3	1	33	<48	31	0.718
3	1	34	<50	70	0.165
3	1	35	<51	105	0.384
3	1	36	<50	52	0.894
3	1	37	<50	38	0.831
3	1	38	<50	48	0.409
3	1	39	<51	50	0.973
3	1	40	<52	64	0.919
3	1	41	80	78	0.448
3	1	42	<51	77	0.458
3	1	43	98	51	0.012
3	1	44	<50	43	0.941
3	2	0	118	124	0.750
3	2	1	115	117	0.710
3	2	2	115	135	0.252
3	2	3	73	95	0.146
3	2	4	105	129	0.718
3	2	5	80	71	0.444
3	2	6	92	126	0.063
3	2	7	147	114	0.697
3	2	8	<48	46	0.025
3	2	9	223	212	0.462
3	2	10	187	160	0.017
3	2	11	<44	79	0.482
3	2	12	<45	107	0.026
3	2	13	112	119	0.755
3	2	14	<44	72	0.560
3	2	15	108	123	0.219
3	2	16	<46	68	0.443
3	2	17	142	129	0.615
3	2	18	181	154	0.544
3	2	19	206	201	0.488
3	2	20	303	294	0.433
3	2	21	299	270	0.428
3	2	22	120	85	0.592
3	2	23	122	107	0.747
3	2	24	80	66	0.646
3	2	25	<49	43	0.147
3	2	26	148	125	0.150
3	2	27	<50	4	0.575
3	2	28	101	116	0.694
3	2	29	<50	35	0.514
3	2	30	<52	55	0.203
3	2	31	51	70	0.128
3	2	32	<51	15	0.091
3	2	33	106	97	0.706
3	2	34	<48	34	0.509
3	2	35	101	98	0.139
3	2	36	114	121	0.567
3	2	37	125	116	0.935
3	2	38	<52	102	0.307
3	2	39	<51	14	0.864
3	2	40	119	82	0.688
3	2	41	82	49	0.401
3	2	42	<51	23	0.232
3	3	0	<47	65	0.750
3	3	1	85	60	0.017
3	3	2	72	67	0.345
3	3	3	133	97	0.480
3	3	4	<47	48	0.888
3	3	5	104	51	0.076
3	3	6	<47	58	0.555
3	3	7	88	95	0.754
3	3	8	88	50	0.034
3	3	9	126	149	0.235
3	3	10	95	86	0.333
3	3	11	137	160	0.617
3	3	12	122	133	0.942
3	3	13	136	128	0.932
3	3	14	116	116	0.948
3	3	15	178	141	0.502
3	3	16	86	88	0.702
3	3	17	<49	46	0.876
3	3	18	124	134	0.046
3	3	19	150	154	0.976
3	3	20	<50	65	0.431
3	3	21	134	149	0.501
3	3	22	93	85	0.639
3	3	23	86	86	0.054
3	3	24	<50	38	0.087
3	3	25	<50	29	0.379
3	3	26	<51	26	0.153
3	3	27	143	65	0.684
3	3	28	<51	44	0.623
3	3	29	91	59	0.086
3	3	30	<51	37	0.191
3	3	31	<51	34	0.470
3	3	32	78	43	0.844
3	3	33	<52	51	0.716
3	3	34	<52	39	0.456
3	3	35	<53	83	0.155
3	3	36	<52	16	0.577
3	3	37	<53	49	0.533
3	3	38	<53	48	0.015
3	3	39	<53	37	0.612
3	3	40	<53	52	0.902
3	4	0	116	138	0.250
3	4	1	72	87	0.725
3	4	2	104	96	0.764
3	4	3	83	96	0.241
3	4	4	<48	27	0.321
3	4	5	92	65	0.787
3	4	6	<48	26	0.682
3	4	7	<49	23	0.569
3	4	8	71	27	0.361
3	4	9	122	113	0.434
3	4	10	211	157	0.485
3	4	11	119	126	0.522
3	4	12	83	118	0.479
3	4	13	123	123	0.398
3	4	14	81	53	0.402
3	4	15	153	126	0.571
3	4	16	130	146	0.963
3	4	17	80	93	0.488
3	4	18	117	123	0.019
3	4	19	85	55	0.582
3	4	20	89	87	0.127
3	4	21	163	157	0.485
3	4	22	97	65	0.799
3	4	23	106	130	0.435
3	4	24	<51	34	0.487
3	4	25	<52	63	0.784
3	4	26	<52	54	0.280
3	4	27	115	94	0.427
3	4	28	<53	51	0.879
3	4	29	88	73	0.976
3	4	30	<52	74	0.561
3	4	31	<52	16	0.533
3	4	32	<52	72	0.195
3	4	33	<53	75	0.541
3	4	34	85	86	0.783
3	4	35	<53	83	0.064
3	5	0	<49	26	0.750
3	5	1	<49	13	0.097
3	5	2	77	86	0.170
3	5	3	<49	31	0.425
3	5	4	99	116	0.722
3	5	5	109	65	0.929
3	5	6	93	113	0.095
3	5	7	76	80	0.830
3	5	8	<51	64	0.730
3	5	9	<51	73	0.253
3	5	10	<50	43	0.905
3	5	11	<51	78	0.909
3	5	12	<51	51	0.504
3	5	13	<51	32	0.513
3	5	14	<51	77	0.685
3	5	15	<51	48	0.903
3	5	16	106	98	0.620
3	5	17	<51	48	0.963
3	5	18	93	97	0.245
3	5	19	79	85	0.335
3	5	20	125	143	0.946
3	5	21	<51	35	0.333
3	5	22	162	133	0.479
3	5	23	<52	14	0.776
3	5	24	129	117	0.986
3	5	25	<52	62	0.454
3	5	26	<51	43	0.059
3	5	27	<50	48	0.900
3	5	28	126	132	0.515
3	6	0	104	124	0.250
3	6	1	142	162	0.320
3	6	2	<53	70	0.667
3	6	3	<52	58	0.521
3	6	4	85	82	0.527
3	6	5	<53	53	0.503
3	6	6	<52	75	0.330
3	6	7	<52	36	0.309
3	6	8	<53	79	0.966
3	6	9	<53	34	0.837
3	6	10	<53	13	0.395
3	6	11	<53	10	0.535
3	6	12	<53	12	0.379
3	6	13	<54	28	0.168
3	6	14	<54	46	0.890
3	6	15	<53	23	0.504
3	6	16	<53	8	0.144
3	6	17	<53	57	0.895
3	7	0	150	102	1.000
3	7	1	<50	48	0.250
3	7	2	124	105	0.500
3	7	3	<49	43	0.250
3	7	4	76	35	0.500
3	7	5	<49	38	0.250
3	7	6	139	108	1.000
3	7	7	<49	71	0.750
3	7	8	72	54	0.500
3	7	9	<48	21	0.250
3	7	10	<50	67	0.500
3	7	11	<48	24	0.750
3	7	12	139	130	1.000
3	7	13	<49	23	0.250
3	7	14	106	108	0.500
3	7	15	<50	3	0.749
3	7	16	<51	75	1.000
3	7	17	<51	31	0.250
3	7	18	<50	15	0.500
4	0	19	<51	26	0.750
4	0	20	<51	29	0.500
4	0	21	<51	9	0.750
4	0	22	<51	51	1.000
4	0	23	<51	10	0.250
4	0	24	<51	10	0.500
4	0	25	77	30	0.750
4	0	26	93	84	0.500
4	0	27	<53	56	0.250
4	0	28	111	98	0.500
4	0	29	<53	74	0.750
4	0	30	77	36	1.000
4	0	31	75	21	0.250
4	1	0	102	56	0.500
4	1	1	<49	38	0.146
4	1	2	117	71	0.784
4	1	3	<50	39	0.614
4	1	4	<50	36	0.512
4	1	5	100	97	0.166
4	1	6	<50	30	0.710
4	1	7	<52	110	0.162
4	1	8	99	93	0.693
4	1	9	132	136	0.597
4	1	10	<52	62	0.149
4	1	11	84	86	0.046
4	1	12	<51	60	0.326
4	1	13	77	33	0.318
4	1	14	146	118	0.794
4	1	15	108	96	0.670
4	1	16	121	88	0.257
4	1	17	<52	62	0.188
4	1	18	<51	17	0.823
4	1	19	<52	70	0.957
4	1	20	<51	36	0.744
4	1	21	137	156	0.456
4	1	22	170	180	0.358
4	1	23	156	150	0.253
4	1	24	176	156	0.230
4	1	25	180	155	0.249
4	1	26	<52	88	0.505
4	1	27	86	82	0.544
4	1	28	90	94	0.305
4	1	29	<51	35	0.385
4	1	30	110	109	0.984
4	1	31	75	99	0.771
4	2	0	<51	11	1.000
4	2	1	153	143	0.933
4	2	2	<51	43	0.336
4	2	3	93	106	0.382
4	2	4	<51	53	0.772
4	2	5	80	80	0.675
4	2	6	<50	44	0.080
4	2	7	74	54	0.077
4	2	8	<50	43	0.541
4	2	9	83	68	0.237
4	2	10	<52	7	0.604
4	2	11	94	95	0.630
4	2	12	<50	51	0.678
4	2	13	148	136	0.069
4	2	14	75	76	0.105
4	2	15	<52	69	0.504
4	2	16	<52	55	0.632
4	2	17	112	90	0.676
4	2	18	<51	39	0.423
4	2	19	82	69	0.308
4	2	20	<52	48	0.445
4	2	21	97	66	0.797
4	2	22	89	99	0.766
4	2	23	<53	57	0.539
4	2	24	85	82	0.197
4	2	25	79	65	0.177
4	2	26	86	53	0.696
4	2	27	<52	51	0.733
4	2	28	<52	29	0.487
4	3	0	<51	44	0.500
4	3	1	<52	77	0.455
4	3	2	<51	31	0.096
4	3	3	94	63	0.897
4	3	4	<50	27	0.695
4	3	5	<53	53	0.333
4	3	6	<52	17	0.058
4	3	7	<52	72	0.033
4	3	8	<52	36	0.332
4	3	9	<52	67	0.578
4	3	10	87	83	0.677
4	3	11	80	80	0.129
4	3	12	<53	27	0.783
4	3	13	212	218	0.240
4	3	14	192	188	0.451
4	3	15	156	154	0.340
4	3	16	<52	37	0.272
4	3	17	155	151	0.314
4	3	18	89	97	0.249
4	3	19	85	92	0.369
4	3	20	<53	88	0.470
4	3	21	<53	87	0.951
4	3	22	88	80	0.902
4	3	23	<53	63	0.037
4	4	0	109	102	0.500
4	4	1	<53	33	0.040
4	4	2	<53	65	1.000
4	4	3	<53	8	0.242
4	4	4	<52	16	0.202
4	4	5	<54	36	0.774
4	4	6	<54	25	0.574
4	4	7	<54	49	0.190
4	4	8	<53	29	0.358
4	4	9	<54	64	0.722
4	4	10	<53	30	0.727
4	4	11	<54	50	0.454
4	4	12	82	74	0.568
4	4	13	<54	18	0.936
4	4	14	<53	75	0.930
4	4	15	84	82	0.761

Experimental

Sphingosine (D-*erytho*-1,3-dihydroxy-2-amino-4-*trans*-octadecene) was prepared from brain sphingomyelin by enzymatic and alkaline degradation in collaboration with Karlsson (1968). The crude sphingosine, which still contained about 13% homologues, was converted into the triacetyl derivative and purified by slow crystallization in a programmed cryostate. After 6 recrystallizations from diethyl ether the impurities (consisting of the triacetyl derivatives of mainly dihydrosphingosine and to a less extent of C_{20}-sphingosine) had fallen below 1%.

Crystal data

$C_{24}H_{43}O_5N$, D-*erythro*-1,3-Diacetoxy-2-acetamido-4-*trans*-octadecene.

Molecular weight: 425·3,
Melting point: 104·0–104·5 °C (corr.);
Optical rotation: $[\alpha]_D^{20} = -14{\cdot}0 \pm 0{\cdot}1°$ ($c = 1$ in chloroform);
Orthorhombic: $a = 5{\cdot}002 \pm 5$, $b = 8{\cdot}709 \pm 8$, $c = 60{\cdot}62 \pm 6$ Å ($\lambda = 1{\cdot}5418$),
Space group: $P2_12_12_1$;
Absent spectra: $h00$, h odd; $0k0$, k odd; $00l$, l odd;
Density $D_m = 1{\cdot}07$ g.cm^{-3} (by flotation)
$D_x = 1{\cdot}07$ g.cm^{-3},
$Z = 4$.
$\mu = 6{\cdot}38$ cm^{-1} for $\lambda = 1{\cdot}5418$ Å.

The data collection was carried out on a Hilger and Watts four circle automatic diffractometer with a crystal having dimensions $0{\cdot}30 \times 0{\cdot}20 \times 0{\cdot}15$ mm. Intensity measurements were made by step scanning on $\omega/2\theta$ using Ni-filtered Cu $K\alpha$ radiation. A total of 1412 reflexions having $2\theta < 95°$ were measured. Of these 930 had net intensities exceeding twice the estimated standard deviation and were coded 'observed'. The other reflexions were not included in the subsequent refinement and R index calculations.

Solution and refinement

The phase determination was carried out by application of the Σ_1, Σ_2 and tangent formulae [see Karle & Karle (1966) for a recent review of these techniques]. Normalized structure factors $|E_h|$, were evaluated with use of the formula

$$|E_{\mathbf{h}}|^2 = |F_{\mathbf{h}}|^2/\varepsilon \sum_{j=1}^{N} f_j^2(\mathbf{h}) \qquad (1)$$

where the $|F_{\mathbf{h}}|$ are the structure factor magnitudes on an absolute scale and are corrected for vibrational motion, f_j is the atomic scattering factor for the jth atom in a unit cell containing N atoms and ε is a constant which corrects for the space-group extinctions.

In order to initiate the phase determination procedure the signs of four reflexions were assigned to fix the origin and enantiomorph. Three more phases were evaluated with the Σ_1 relation:

$$s\Sigma(0,2k,2l) = s\Sigma(-1)^{h+k}(|E_{hkl}|^2 - 1) \qquad (2)$$

where s means 'sign of' and similar expressions apply for the $2h,0,2l$ and $2h,2k,0$ data (Karle & Hauptman, 1956). Phases calculated in this way were accepted if their associated $|E|$ values exceeded 2·0 and if their sign probability,

$$P+(2\mathbf{h}) = \tfrac{1}{2} + \tfrac{1}{2} \tanh (\sigma_3 |E_{2\mathbf{h}}| \Sigma_1 / 2\sigma_2^{3/2}) ,$$

was greater than 0·80. In this formula $\sigma_n = \sum_{j=1}^{N} Z_j^N$, where Z_j is the atomic number of the jth atom.

The list of 7 known phases (Table 1) was extended and refined by use of the Σ_2 and tangent relations

Table 3. *Atomic parameters and (in parentheses) their standard deviations*

The e.s.d.'s in the positions have been multiplied by 10^4 and in the B values by 10.

	X/a	Y/b	Z/c	B
C(1)	0·1661 (36) Å	1·2422 (19) Å	0·2077 (3) Å	4·5 (4)
C(2)	0·3043 (36)	1·2164 (18)	0·1865 (3)	4·1 (4)
C(3)	0·1868 (32)	1·0811 (18)	0·1742 (2)	3·8 (4)
C(4)	0·3321 (38)	1 0452 (19)	0 1539 (3)	5·1 (4)
C(5)	0·2362 (50)	1·0470 (23)	0·1342 (3)	7·6 (5)
C(6)	0·3765 (43)	1·0175 (23)	0·1121 (3)	6·7 (5)
C(7)	0·2470 (46)	0·8861 (22)	0·0992 (3)	6·6 (5)
C(8)	0·3845 (45)	0·8647 (23)	0·0765 (3)	6·9 (5)
C(9)	0·2682 (39)	0·7351 (19)	0·0632 (3)	4·8 (4)
C(10)	0·3926 (39)	0·7145 (20)	0·0411 (3)	5·2 (4)
C(11)	0·2685 (42)	0·5859 (20)	0·0276 (3)	5·6 (4)
C(12)	0·3935 (39)	0·5615 (19)	0·0050 (3)	5·0 (4)
C(13)	0·2683 (40)	0·4327 (19)	−0·0079 (3)	5·1 (4)
C(14)	0·3890 (39)	0·4092 (20)	−0·0308 (3)	5·3 (4)
C(15)	0·2721 (41)	0·2767 (19)	−0·0437 (3)	5·3 (4)
C(16)	0·3862 (43)	0·2526 (21)	−0·0662 (3)	6·0 (5)
C(17)	0·2747 (50)	0·1152 (24)	−0·0787 (3)	7·8 (5)
C(18)	0·3925 (45)	0·0876 (25)	−0·1012 (3)	7·5 (6)
C(19)	0·2379 (42)	1·3965 (22)	0·2405 (3)	5·3 (4)
C(20)	0·4158 (39)	1·5053 (23)	0·2519 (3)	5·8 (5)
C(21)	0·4902 (43)	1·4258 (21)	0·1636 (3)	5·2 (4)
C(22)	0·4374 (38)	1·5654 (20)	0·1501 (3)	5·3 (4)
C(23)	0·0232 (47)	0·8420 (25)	0·1878 (3)	6·7 (5)
C(24)	0·0793 (48)	0·7023 (25)	0·2025 (3)	7·8 (6)
O(1)	0·3245 (23)	1·3512 (12)	0·2203 (2)	4·8 (3)
O(2)	0·2076 (26)	0·9499 (13)	0·1891 (2)	5·4 (3)
O(3)	0·0364 (38)	1·3392 (18)	0·2475 (2)	8·4 (4)
O(4)	−0·1461 (38)	0·8394 (19)	0·1730 (3)	10·9 (5)
O(5)	0·7266 (29)	1·3811 (14)	0·1674 (2)	6·4 (3)
N(1)	0·2810 (27)	1·3546 (14)	0·1728 (2)	3·8 (3)

$$\varphi_{\mathbf{h}} = < \varphi_{\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}} > , \quad (3)$$

$$\tan \varphi_{\mathbf{h}} = \frac{\sum_{\mathbf{k}} |E_{\mathbf{k}} . E_{\mathbf{h}-\mathbf{k}}| \sin (\varphi_{\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}})}{\sum_{\mathbf{h}} |E_{\mathbf{k}} . E_{\mathbf{h}-\mathbf{k}}| \cos (\varphi_{\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}})} \quad (4)$$

Initially only terms with $|E_{\mathbf{h}}| > 2{\cdot}0$ were used in (3). Phases were rejected if their variance (Karle & Karle, 1966) exceeded 0·5 radian. The accepted phases were then refined with (4). If, after several tangent cycles, the shift in the phases calculated by (4) were large or tended to oscillate these terms were rejected. Terms were also rejected if their calculated $|E|$ value, $|E_{\mathbf{h}}|_{\text{calc}}$, determined from the numerator and denominator of (4), was less than a minimum specified value, initially set at 0·8. The tangent iteration was terminated when all shifts were less than 5°. The minimum $|E|$ value was then decreased by 0·2 and the procedure was repeated using the refined phases as input for (3).

After a number of these cycles 294 phases with $|E| > 1{\cdot}0$ were evaluated. During the later stages the minimum $|E|_{\text{calc}}$ value was reduced to 0·4 and the iteration convergence criterion relaxed to 10° to limit the computer time required. An E map based on these phases revealed the positions of 10 atoms in alternative positions along the straight part of the chain. Several other peaks which were possible atomic sites were of about the same height as a number of spurious peaks in the map and were not included at this stage. The R index based on these 10 atoms was 0·59.

The remainder of the structure was obtained by the method of Karle (1968) when a 'partial structure' is known. The phases of 99 reflexions having $|F_c| \geq 0{\cdot}35$. $|F_o|$ and $|E| \geq 1{\cdot}5$ were used as starting phases in (3) and (4). This set was refined and extended to 158 phases with $|E| \geq 1{\cdot}3$. An E map based on these values gave the positions of 8 more atoms and reduced R to 0·49. After another cycle, in which 189 phases with $|E| \geq 1{\cdot}3$ were determined, a further 7 atoms were located, giving $R = 0{\cdot}31$. The remaining 5 atoms were placed from a difference map, resulting in an R index of 0·21.

Refinement by full-matrix least-squares with isotropic thermal coefficient reduced R to 0·14. The 30 sterically positioned hydrogen atoms were placed at their expected sites assuming a C–H bond length of 1·0 Å. The inclusion of these atoms with thermal coefficients equal to those of the parent carbon atoms, reduced R to 0·127. Further refinement during which the hydrogen atom parameters were included in the structure factor calculations, but were not refined in the least squares, gave a final R value of 0·109.

A difference Fourier was evaluated at this stage; however none of the 13 hydrogen atoms belonging to the amide and methyl groups could be positively identified. Although the hydrocarbon chain and most of the atoms in the polar groups are probably vibrating anisotropically the introduction of additional parameters into the least squares was not considered justified in view of the limited number of observed reflexions available.

Scattering factors for carbon, nitrogen and oxygen were taken from *International Tables for X-ray Crystallography* (1962), while for hydrogen the values given by Stewart, Davidson & Simpson (1965) were used. Reflexion weights were initially calculated from the counting statistics according to Evans (1961), however in the final stages of refinement somewhat better results were obtained by use of the function

$$w = 1 \text{ for } |F_o| < 27,$$
$$w = 27/|F_o| \text{ for } |F_o| > 27.$$

The observed and calculated structure factors are listed in Table 2 and the final positional and isotropic thermal parameters in Table 3. The calculated hydrogen atom positions are given in Table 4.

Table 4. *Calculated hydrogen atom coordinates*

	X/a	*Y/b*	*Z/c*
H(11)	−0·0227 Å	1·2811 Å	0·2054 Å
H(12)	0·1469	1·469	0·2164
H(21)	0·4973	1·1935	0·1895
H(31)	−0·0051	1·1058	0·1704
H(41)	0·5290	1·0111	0·1547
H(51)	0·0315	1·0708	0·1329
H(61)	0·5705	0·9950	0·1145
H(62)	0·3697	1·1152	0·1022
H(71)	0·0524	0·9088	0·0968
H(72)	0·2643	0·7898	0·1081
H(81)	0·5782	0·8442	0·0800
H(82)	0·3695	0·9655	0·0688
H(91)	0·0708	0·7596	0·0611
H(92)	0·2838	0·6390	0·0719
H(101)	0·5841	0·6916	0·0434
H(102)	0·3698	0·8114	0·0326
H(111)	0·0685	0·6014	0·0261
H(112)	0·2905	0·4830	0·0361
H(121)	0·5844	0·5459	0·0064
H(122)	0·3563	0·6598	−0·0038
H(131)	0·0707	0·4475	−0·0091
H(132)	0·2993	0·3338	0·0010
H(141)	0·5867	0·3958	−0·0291
H(142)	0·3555	0·5075	−0·0393
H(151)	0·0720	0·2900	−0·0450
H(152)	0·3005	0·1778	−0·0345
H(161)	0·5931	0·2412	−0·0643
H(162)	0·3617	0·3511	−0·0749
H(171)	0·0739	0·1286	−0·0802
H(172)	0·3002	0·0178	−0·0691

Discussion

The molecular geometry and atom numbering are illustrated in Fig. 1. The structure of the molecule is in agreement with the formula D-*erythro*-1,3-diacetoxy-2-acetamido-4-*trans*-octadecene and confirms the configuration established by Carter & Fujino (1956.) The hydrocarbon chain is bent at the *trans* double bond and the acetoxy group attached at C(1) forms a continuation of the zigzag backbone. Atoms C(5) to C(18) and C(4) to C(20) form two approximately parallel planar groups, the perpendicular distance between

which is 0·6 Å. The equations of the best planes through these two sets of atoms are

$$-0{\cdot}1304X+0{\cdot}2198Y-0{\cdot}9668Z-0{\cdot}0671=0,$$

and

$$0{\cdot}0798X+0{\cdot}2221Y-0{\cdot}9718Z-0{\cdot}0588=0.$$

The only large out of plane deviation is for C(2) which is displaced 0·17 Å towards the amide group. The remaining acetoxy group and the acetamido group form two planar sets with the carbon atoms to which they are attached. The equations of the best planes through C(2)–N(1)–C(21)–C(22)–O(5) and C(3)–O(2)–C(23)–C(24)–O(4) are

$$0{\cdot}0058X+0{\cdot}1020Y+0{\cdot}9948Z-0{\cdot}3114=0$$

and

$$0{\cdot}0730X-0{\cdot}0958Y-0{\cdot}9927Z+0{\cdot}2634=0\,.$$

The bond lengths and angles are shown in Fig. 2. The mean C–C distance in the regular part of the chain C(5)–C(18) is 1·516 Å while the mean C–C–C angle in this region is 113·9°. These values are in agreement with those previously reported for hydrocarbon chains

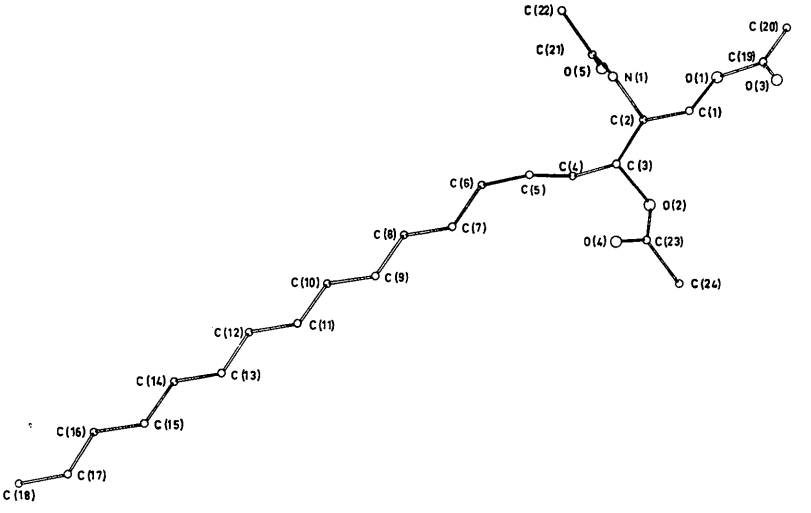


Fig. 1. The molecular geometry (viewed down **a**) and atomic numbering of the triacetylsphingosine molecule.

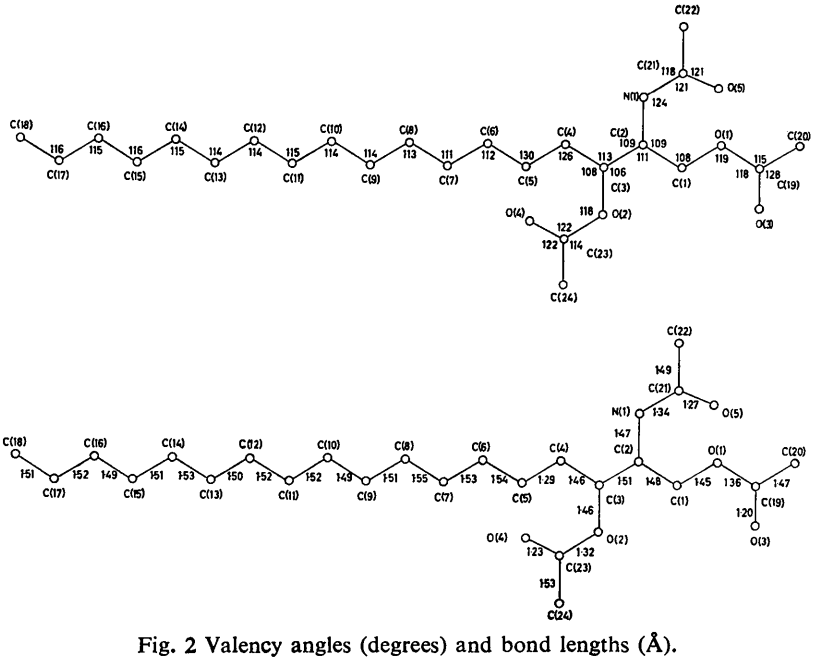


Fig. 2 Valency angles (degrees) and bond lengths (Å).

(*e.g.* Jensen & Mabis, 1966; O'Connell, 1968). The deviations from the expected sp^3–sp^3 bond length and the tetrahedral angle are probably a result of thermal anisotropy and rotary oscillations of the chains about their long axes. The bond lengths and angles in the amide configuration C(2), N(1), C(21), C(22), O(5) are in agreement with those reported in similar groups, *e.g.* in *N*-acetylglycine (Carpenter & Donohue, 1950; Donohue & Marsh, 1962) and acetanilide (Brown & Corbridge, 1954). There are no significant differences in the equivalent bond lengths in the remaining two acetyl groups. The C(19)–C(20) distance (1·47 Å) is short; however, because of the rather large standard deviations and the uncertainty in the thermal corrections it is not possible to say if this is a real effect.

Fig. 3 shows the molecular packing projected on to the (100) plane. The molecules are arranged in a zigzag pattern with their chain axes at an angle of 58° to the (001) plane. Regions of chain packing alternate with regions of acetyl branched polar groups of comparable thickness. The straight portions of the hydrocarbon chains are arranged with the orthorhombic subcell packing $O\perp$ (Abrahamsson, 1959). Fig. 4 illustrates the idealized subcell, which has dimensions $a_s=5{\cdot}00$, $b_s=7{\cdot}41$, $c_s=2{\cdot}54$ Å. Alternate molecules in the y axis direction are arranged head to tail and the C(18) methyl group packs into the space between the chains of the four adjacent molecules. Thus layers of only methyl end group contacts with weak van der Waals forces, as common in other lipid crystals, do not exist in this molecular packing. The alternating tilt of the chains and the crosslike arrangement of the branches allow the two acetoxy groups to project into the apices formed by two acetyl branches of neighbouring molecules. The acetamido group is accommodated in the space between an acetoxy group and a methyl chain end. This represents a very effective molecular packing as shown by the fairly high density ($D=1{\cdot}07$ g.cm^{-3}) of the crystals. The good crystallinity and the high melting point of triacetylsphingosine are no doubt a result of this exceptionally good packing and the favourable intermolecular forces which are associated with the bulky acetyl branches.

There are eight intermolecular contacts $<3{\cdot}50$ Å (Table 5), all associated with the polar region of the structure. The molecules are connected by a continuous system of N–H...O hydrogen bonds parallel to **a** between N(1) $[x,y,z]$ and O(5) $[x-1,y,z]$. The N...O distance is 2·80 Å. The existence of this intermolecular bond is confirmed by the solid state infrared spectra. The N–H and C=O streching frequencies, which in solution (chloroform) are 3460 and 1680 cm^{-1} respectively, are shifted to the lower values of 3300 and 1650 cm^{-1}. A corresponding reverse shift of the C–N streching absorption from 1500 to 1540 cm^{-1} also occurs.

Table 5. *Intermolecular contacts* $\leq 3{\cdot}5$ Å

C(1)—O(5)	[−1, 0, 0] I	3·50 Å
C(2)—O(5)	[−1, 0, 0] I	3·43
C(3)—O(5)	[−1, 0, 0] I	3·50
C(4)—O(4)	[1, 0, 0] I	3·37
C(22)–O(4)	[1, 1, 0] I	3·46
C(24)–O(1)	[0, −1, 0] I	3·47
C(24)–O(3)	[0, −1, 0] II	3·31
O(5)—N(1)	[1, 0, 0] I	2·80

I and II refer the equivalent positions x, y, z and $\bar{x}$, $\frac{1}{2}+y$, $\frac{1}{2}-z$. The numbers in square brackets indicate the translations, in multiples of a, b and c in the directions **a**, **b** and **c**.

The shortest C...O contact (3·31 Å), between C(24) and O(3), may be a C–H...O hydrogen bond of the type described by Sutor (1963). The angles C(23–C(24) ...O(3) and C(19)–O(3)...C(24), 102 and 128° respectively, are favourable for such a contact; however, since

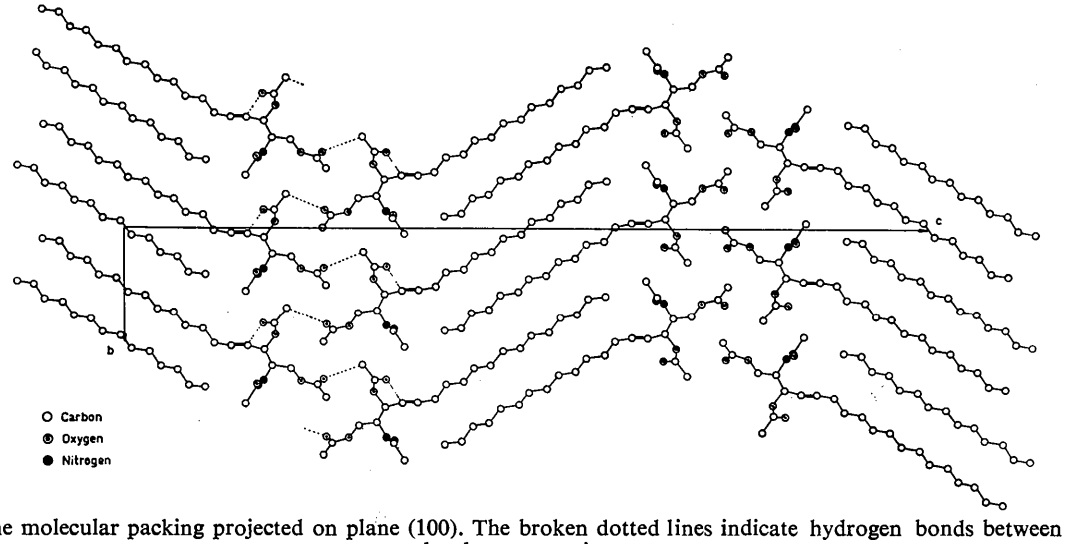


Fig. 3. The molecular packing projected on plane (100). The broken dotted lines indicate hydrogen bonds between atoms in molecules one a axis apart.

the methyl hydrogen atoms were not located the evidence is not conclusive.

There is another short intermolecular contact of this type from the carbonyl oxygen atom O(4) to the carbon atom C(4) of the *trans* double bond. The infrared spectrum shows an interesting separation of the =C–H bending absorption at 970 and 980 cm^{-1} indicating that one hydrogen atom of the allylic double bond is engaged in fairly strong lattice forces in the crystalline state (only one absorption at 960 cm^{-1} in solution). The relevant distances and angles are C(4)...O(4)= 3·37 Å, H(41)...O(4)=2·47 Å, ∠C(23)–O(4)...H(41) =140° and ∠C(4)–H(41)...O(4)=145°, where the position of H(41) has been calculated assuming a C–H distance of 1·00 Å and an ideal trigonal arrangement around C(4).

At present single-crystal investigations on sphingosine hydrochloride and *N*-acetylsphingosine are in progress. In addition to these studies a comparative discussion of the infrared spectra of these sphingosine derivatives will be published.

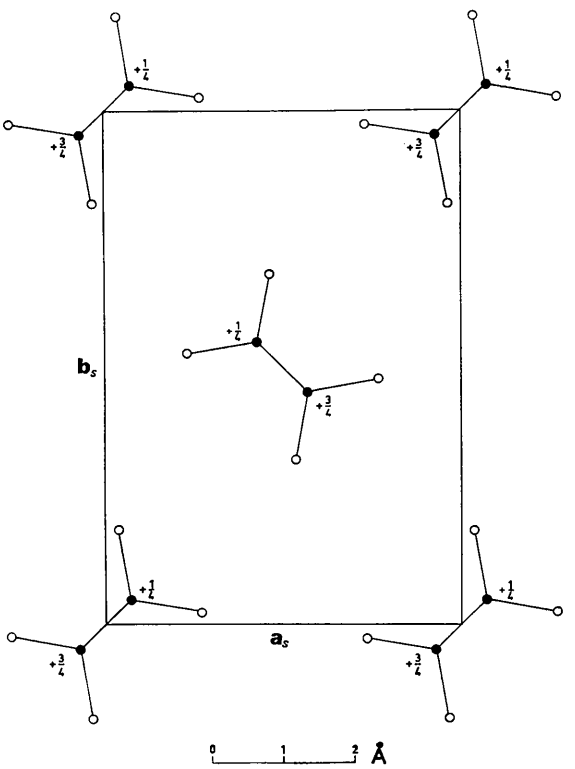


Fig. 4. The idealized subcell, viewed down c_s.

The normalized structure factors were calculated with a program devised by Dr S.R.Hall at the National Research Council, Canada. The tangent formula calculations were made with a routine based largely on a program written by Dr Yow Lam Oh at the University of Western Australia. These sources are gratefully acknowledged. The remaining calculations were made with programs written by Abrahamsson, Aleby, Larsson, Nilsson, Selin & Westerdahl (1965) and additional routines written by one of us (A.O'C.). We would like to thank Hilger and Watts Ltd for generously allowing us to make the intensity measurements at their London laboratory. Financial support was obtained from the Swedish Medical Research Council, the Swedish National Science Research Council, the U.S. Public Health Service (GM–11653) and from the Tri-Centennial Fund of the Bank of Sweden.

References

ABRAHAMSSON, S. (1959). *Ark. Kemi,* **14**, 65.
ABRAHAMSSON, S., ALEBY, S., LARSSON, K., NILSSON, B., SELIN, K. & WESTERDAHL, A. (1965). *Acta Chem. Scand.* **19**, 758.
BROWN, C. J. & CORBRIDGE, D. E. C. (1954). *Acta Cryst.* **7**, 711.
CARPENTER, G. B. & DONOHUE, J. (1950). *J. Amer. Chem. Soc.* **72**, 2315.
CARTER, H. E. & FUJINO, Y. (1956). *J. Biol. Chem.* **221**, 879.
CARTER, H. E., NORRIS, W. P., GLICK, F. J., PHILLIPS, E. G. & HARRIS, R. (1947). *J. Biol. Chem.* **170**, 269.
DONOHUE, J. & MARSH, R. E. (1962). *Acta Cryst.* **15**, 941.
EVANS, H. T. (1961). *Acta Cryst.* **14**, 689.
International Tables for X-ray Crystallography (1962). Vol. III, p. 202. Birmingham: Kynoch Press.
JENSEN, L. H. & MABIS, A. J.. (1966). *Acta Cryst.* **21**, 770.
KARLE, J. (1968). *Acta Cryst.* B**24**, 182.
KARLE, J. & HAUPTMAN, H. (1956). *Acta Cryst.* **9**, 635.
KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849.
KARLSSON, K-A. & HOLM, G. L. A. (1965). *Acta Chem. Scand.* **19**, 2423.
KARLSSON, K-A., SAMUELSSON, B. E. & STEEN, G. O. (1968). *Acta Chem. Scand.* **22**, 1361.
KARLSSON, K-A. (1968). *Acta Chem. Scand.* **22**, 3050.
KLENK, E. & DIEBOLD, W. (1931). *Z. Physiol. Chem.* **198**, 25
O'CONNELL, A. M. (1968). *Acta Cryst.* B**24**, 1399.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.
SUTOR, D. J. (1963). *J. Chem. Soc.* **204**, 1105.
THOMAS, K. & THIERFELDER, H. (1912). *Z. Physiol. Chem.* **77**, 511.
THUDICHUM, J. L. W. (1882). *J. Prakt. Chem.* **25**, 19.