

Molecular Arrangements in Sphingolipids. Crystal Structure of *N*-Tetracosanoylphytosphingosine

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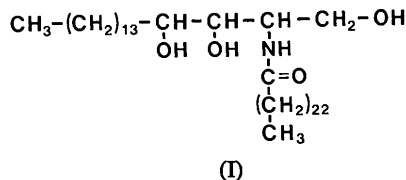
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Tetracosanoylphytosphingosine, which has been studied as a ceramide model compound, is triclinic (*P*1) with $a = 6.181$, $b = 4.929$, $c = 37.278 \text{ \AA}$, $\alpha = 90.96$, $\beta = 91.30$, $\gamma = 105.51^\circ$. The two hydrocarbon chains point in opposite directions from the polar groups. The molecules cannot pack laterally when fully extended due to the space requirements of the polar groups. The chains form an angle of 101° , thereby accommodating the polar groups in the apices of the V-shaped molecules. The molecules are linked together by one intra- and three intermolecular hydrogen bonds. The chain packing is of the common triclinic type (*T*1)

Introduction

Tetracosanoylphytosphingosine (I) belongs to the class of compounds known as ceramides. These consist of a long chain fatty acid bound to the amino-group of a long chain base and constitute the lipophilic part in all natural sphingolipids (Karlsson & Pascher, 1971). Ceramides may exist free in animal and plant tissue but are usually found in glycosidic linkage to carbohydrates (glycosphingolipids) or esterified with phosphorylcholine (sphingomyelin) or phosphonoethylamine (for reviews see Karlsson, 1970; Wiegandt, 1971).



Sphingolipids are important constituents of the outer cell membrane and are thought to participate in transport function (Karlsson, Samuelsson & Steen, 1971) and intercellular recognition phenomena (Roseman, 1970) and exhibit immunological activity (Hakomori, 1970). The knowledge of the phase behaviour and conformation of these lipids is of fundamental importance for the understanding of their function in biological membranes.

Sphingolipids containing a trihydroxy base (phytosphingosine and related substances) were first thought to be specific for plants only, but were later discovered to be also rather abundant in glycosphingolipids and sphingomyelin of human and bovine tissue (Karlsson, 1964; 1970). Recently phytosphingosine was reported to be the only long chain base in a pentaglycosyl ceramide in human adenocarcinoma (Yang & Hakomori, 1971).

Experimental

Tetracosanoylphytosphingosine (D-ribo-1,3,4-trihydroxy-2-tetracosanoylamidooctadecane) was synthesized as a ceramide model compound by selective *N*-acylation of highly purified yeast phytosphingosine (Karlsson, 1966) with tetracosanoic (lignoceric) acid. Both compounds had a purity of more than 99%. Crystals were obtained from a chloroform-methanol solution in a temperature controlled cooling apparatus. They grow as elongated prisms which on heating undergo three phase transitions and finally melt at 121°C (Dahlén & Pascher, 1972).

Crystal data

Molecular formula $\text{C}_{42}\text{H}_{85}\text{NO}_4$
 Unit cell:
 triclinic, $a = 6.181$ (7), $b = 4.929$ (8), $c = 37.278$ (35) \AA
 $\alpha = 90.96$ (9), $\beta = 91.30$ (9), $\gamma = 105.51$ (10)
 $V = 1093.8 \text{ \AA}^3$
 M.W. 668.15
 $Z = 1$
 $D_c = 1.014 \text{ g.cm}^{-3}$
 $D_m = 1.015 \text{ g.cm}^{-3}$
 $\lambda = 1.54051 \text{ \AA}$ (Cu $K\alpha_1$ radiation)
 Space group *P*1

As the unit-cell contains only one asymmetric molecule the space group must be *P*1.

Data were collected on a Picker four circle automatic diffractometer using graphite monochromated Cu $K\alpha$ radiation. A single crystal with dimensions $0.20 \times 0.05 \times 0.02$ mm was mounted along the *b* axis, which corresponds to the longest dimension of the crystal, coinciding with the φ axis of the diffractometer.

The reflexions were measured using the $\theta/2\theta$ scanning mode with a scan rate of $0.5^\circ/\text{min}$ and with 10 sec background count at each side. Intensities were re-

Table 1. Observed and calculated structure factors (x 100)

Table with 16 columns: h, k, l, Fobs, Fcalc, h, k, l, Fobs, Fcalc, h, k, l, Fobs, Fcalc, h, k, l, Fobs, Fcalc. It contains a grid of numerical data representing structure factors for various hkl reflections.

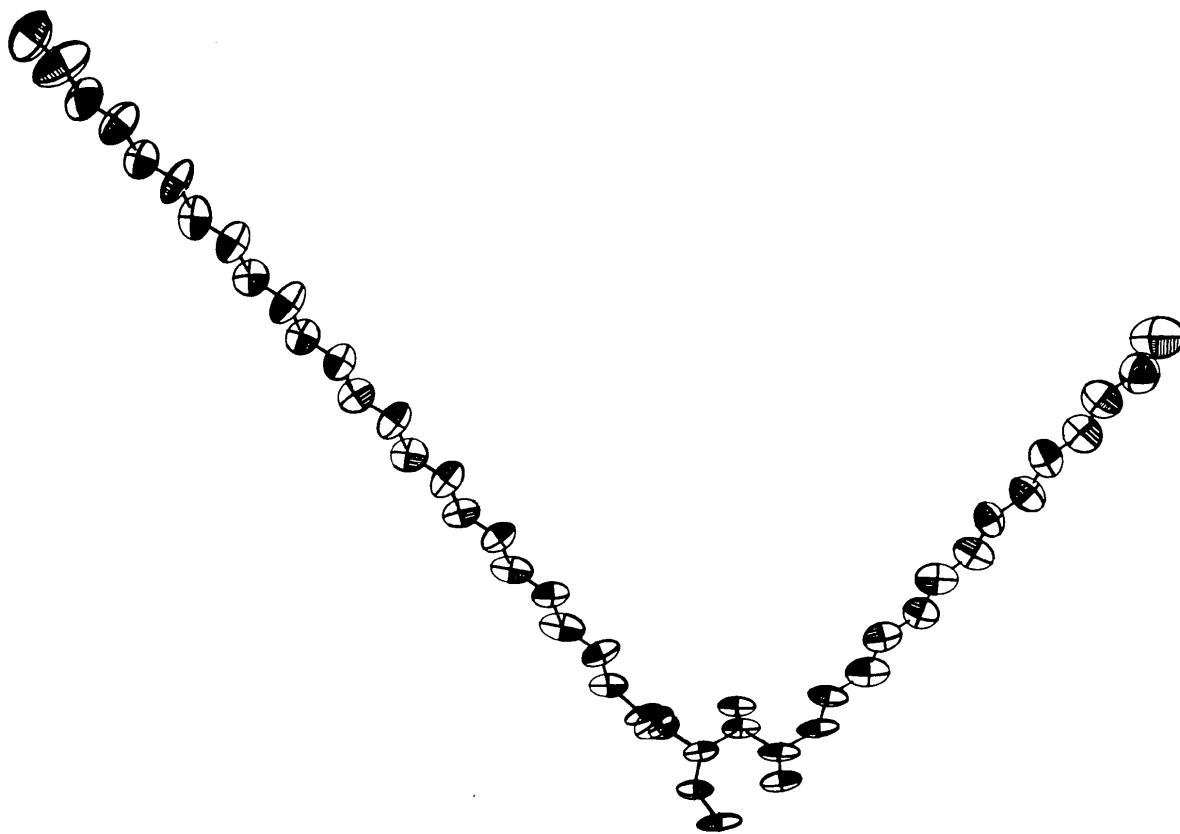


Fig.2. The molecule seen along the b axis showing the ellipsoids of thermal motion with a probability of 50%, drawn using *ORTEP* (Johnson, 1965).

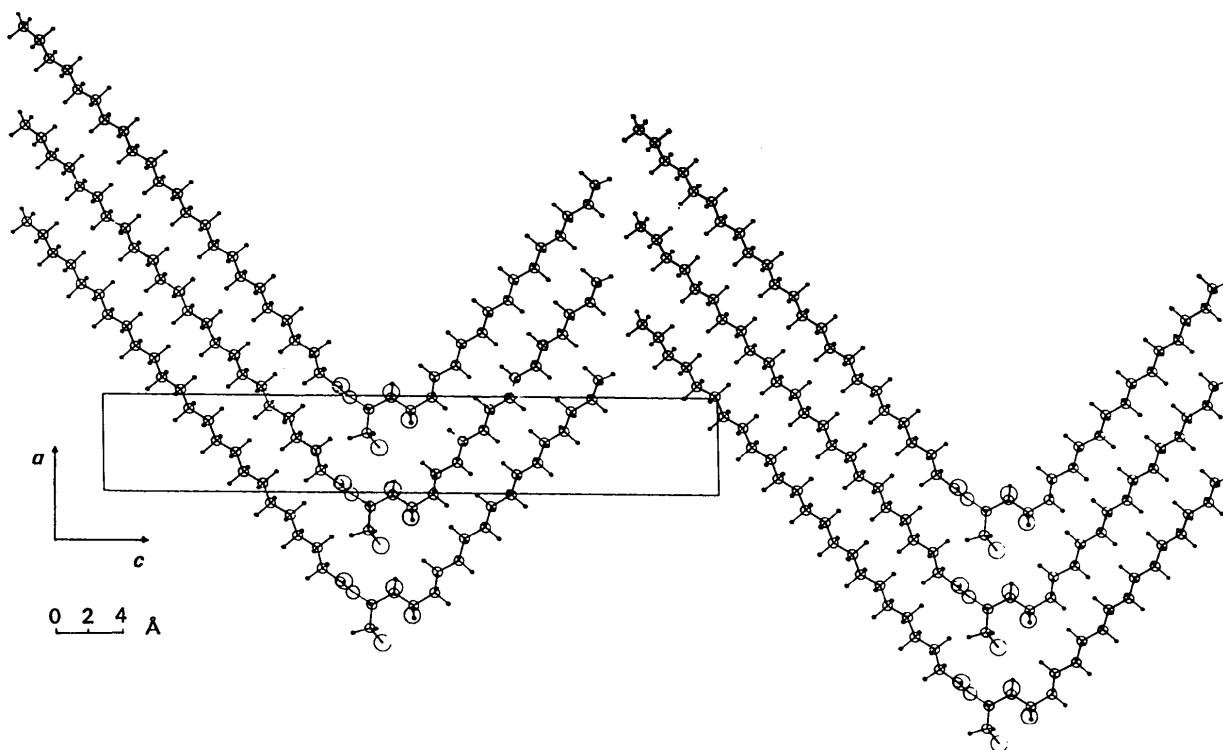


Fig.3. Molecular packing projected on the (010) plane.

Table 2. Fractional atomic coordinates with standard deviations (in parentheses) for the non-hydrogen atoms

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	-0.3877 (19)	-0.4697 (21)	0.4290 (3)
C(2)	-0.1424 (17)	-0.2825 (17)	0.4328 (3)
C(3)	-0.0231 (16)	-0.2932 (17)	0.4685 (3)
C(4)	-0.1469 (19)	-0.2705 (20)	0.5006 (5)
C(5)	-0.0169 (19)	-0.2555 (20)	0.5346 (4)
C(6)	0.1993 (19)	-0.0232 (22)	0.5399 (4)
C(7)	0.3163 (24)	-0.0445 (23)	0.5752 (5)
C(8)	0.5390 (22)	-0.1700 (21)	0.5845 (4)
C(9)	0.6523 (24)	0.1235 (26)	0.6189 (4)
C(10)	0.8661 (24)	0.3313 (24)	0.6288 (5)
C(11)	0.9851 (26)	0.2689 (27)	0.6623 (5)
C(12)	1.1976 (24)	0.4757 (24)	0.6715 (4)
C(13)	1.3169 (26)	0.4247 (27)	0.7056 (4)
C(14)	1.5296 (27)	0.6296 (27)	0.7171 (4)
C(15)	1.6457 (29)	0.5662 (30)	0.7500 (5)
C(16)	1.8489 (30)	0.7728 (32)	0.7616 (5)
C(17)	1.9736 (38)	0.7163 (40)	0.7957 (5)
C(18)	2.1759 (41)	0.8976 (57)	0.8062 (8)
O(1)	-0.5396 (13)	-0.3563 (14)	0.4481 (3)
O(2)	0.0354 (13)	-0.5586 (16)	0.4690 (3)
O(3)	-0.2494 (11)	0.0290 (12)	0.4975 (2)
N(1)	-0.0219 (15)	-0.3307 (15)	0.4017 (3)
C(1')	0.0904 (19)	-0.1268 (29)	0.3814 (4)
C(2')	0.2262 (17)	-0.2078 (16)	0.3531 (3)
C(3')	0.4367 (20)	0.0055 (21)	0.3455 (4)
C(4')	0.5578 (18)	-0.0784 (18)	0.3134 (4)
C(5')	0.7665 (18)	0.1412 (20)	0.3024 (4)
C(6')	0.8839 (18)	0.0528 (19)	0.2702 (4)
C(7')	1.0913 (19)	0.2753 (21)	0.2585 (3)
C(8')	1.2051 (17)	0.1848 (18)	0.2274 (3)
C(9')	1.4101 (21)	0.3980 (22)	0.2153 (4)
C(10')	1.5244 (22)	0.3054 (21)	0.1837 (4)
C(11')	1.7326 (24)	0.5201 (24)	0.1716 (4)
C(12')	1.8497 (22)	0.4302 (22)	0.1399 (4)
C(13')	2.0531 (22)	0.6463 (22)	0.1272 (4)
C(14')	2.1708 (21)	0.5510 (21)	0.0962 (4)
C(15')	2.3724 (26)	0.7722 (23)	0.0850 (4)
C(16')	2.4912 (23)	0.6821 (21)	0.0543 (4)
C(17')	2.6944 (24)	0.8987 (24)	0.0412 (4)
C(18')	2.8090 (28)	0.8028 (24)	0.0094 (4)
C(19')	3.0128 (26)	1.0267 (24)	-0.0033 (4)
C(20')	3.1152 (24)	0.9202 (25)	-0.0332 (4)
C(21')	3.3148 (30)	1.1378 (30)	-0.0494 (4)
C(22')	3.4310 (31)	1.0440 (35)	-0.0785 (5)
C(23')	3.6184 (36)	1.2613 (41)	-0.0946 (8)
C(24')	3.7518 (41)	1.1774 (51)	-0.1204 (6)
O(1')	0.0983 (13)	0.1315 (14)	0.3881 (2)

the block-diagonal least-squares technique varying the positional parameters and isotropic temperature factors of all the atoms. As one could expect rather large anisotropic thermal vibrations in the chains, the structure was then refined using the full matrix varying the parameters of only one third of the atoms at a time because of the large number of parameters.

All hydrogen atoms attached to carbons were placed at their expected sites assuming a C-H bond length of 1.09 Å and the same thermal coefficient as the isotropic temperature factors corresponding to those of the parent atom. The hydrogen atom parameters were included in the structure factor calculations but were not refined. The 13 largest *F* values showed poor agreement and were omitted from the refinement but included in the final structure factor calculations. The

hydrogen atom parameters were recalculated at intervals. The final *R* value is 0.082.

A difference map calculated at the end of the refinement was very flat but showed extended positives area

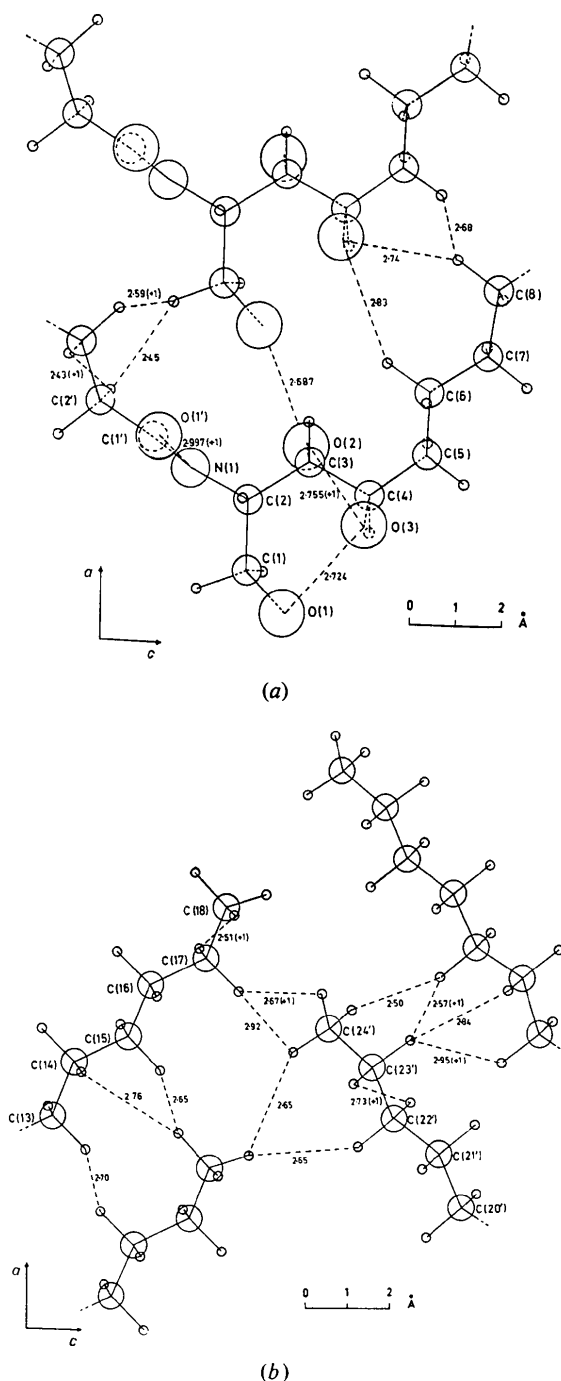


Fig. 4. (a) The shorter contacts in the polar group region of the structure viewed along the *b* axis. (b) The shorter hydrogen contacts in the methyl group contact planes viewed along the *b* axis.

between the hydroxyl oxygens at a maximum height of about 0.2 e.Å^{-3} , but attempts to locate these hydrogen atoms or the hydrogen atom attached to the nitrogen atom were unsuccessful.

All calculations were performed on a Datasaab D21 computer with the program system written by Abrahamsson, Aleby, Larsson, Nilsson, Selin & Westerdahl, 1965. The form factors were those given in the *International Tables for X-ray Crystallography* (1962) for carbon, oxygen and nitrogen while for hydrogen the values given by Stewart, Davidson & Simpson (1965) were used.

The weight assigned to each observation in the least-squares refinement was (Mills & Rollett, 1961)

$$\omega = 1 / \left[1 + \left(\frac{|F_o| - 5.4 |F_{\min}|}{2.7 |F_{\min}|} \right)^2 \right]$$

Description of the structure

Observed and calculated structure factors are given in Table 1. The final atomic parameters are listed in Tables 2, 3 and 4 and the interatomic distances and angles are given in Fig. 1 and with their estimated standard deviations in Tables 5 and 6. As the structure was refined in three parts the standard deviations calculated from the least-squares matrix are somewhat underestimated.

Table 3. *Anisotropic thermal parameters* $\times 10^4$

The temperature factor takes the form $\exp[-2\pi^2(h^2a^2U_{11} + k^2b^2U_{22} + l^2c^2U_{33} + 2klb^*c^*U_{23} + 2lha^*c^*U_{31} + 2hka^*b^*U_{12})]$.

Standard deviations are given in parentheses.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{31}	U_{12}
C(1)	546 (80)	597 (68)	1387 (111)	177 (69)	5 (67)	345 (70)
C(2)	441 (69)	279 (57)	1228 (104)	247 (55)	212 (68)	126 (54)
C(3)	501 (59)	186 (51)	1544 (109)	108 (58)	36 (74)	319 (47)
C(4)	475 (70)	423 (70)	1911 (150)	-29 (76)	-34 (97)	351 (57)
C(5)	453 (73)	440 (66)	1877 (146)	54 (72)	128 (80)	293 (66)
C(6)	558 (79)	547 (72)	1644 (132)	182 (70)	-146 (75)	272 (69)
C(7)	945 (98)	519 (76)	2038 (172)	65 (86)	50 (105)	299 (81)
C(8)	974 (96)	419 (67)	1527 (136)	16 (76)	163 (88)	271 (76)
C(9)	1132 (107)	730 (85)	1235 (126)	195 (80)	-56 (88)	401 (89)
C(10)	981 (100)	558 (76)	1771 (150)	196 (84)	20 (97)	170 (83)
C(11)	1145 (109)	750 (86)	1598 (145)	175 (90)	-244 (102)	210 (90)
C(12)	1254 (110)	729 (81)	925 (107)	-74 (73)	-220 (86)	305 (87)
C(13)	1263 (111)	837 (91)	1306 (136)	-57 (88)	-301 (101)	211 (89)
C(14)	1562 (132)	851 (91)	1118 (124)	-48 (86)	-281 (103)	507 (101)
C(15)	1403 (128)	934 (101)	1384 (145)	242 (98)	-98 (111)	171 (103)
C(16)	1509 (141)	1129 (119)	1509 (156)	334 (109)	-168 (120)	432 (115)
C(17)	1842 (178)	1655 (172)	1480 (179)	152 (132)	-23 (154)	655 (151)
C(18)	1776 (198)	2519 (270)	2754 (291)	431 (225)	139 (203)	649 (191)
O(1)	558 (44)	780 (55)	2179 (94)	26 (56)	212 (52)	467 (44)
O(2)	543 (38)	236 (33)	1555 (67)	103 (37)	-9 (40)	332 (30)
O(3)	630 (42)	357 (38)	1691 (74)	270 (41)	252 (44)	321 (33)
N(1)	581 (52)	280 (51)	964 (69)	291 (50)	270 (52)	78 (47)
C(1')	714 (83)	892 (116)	1352 (120)	186 (94)	448 (83)	579 (79)
C(2')	534 (65)	35 (45)	1476 (106)	396 (58)	132 (67)	-58 (53)
C(3')	992 (97)	577 (77)	1508 (118)	-77 (72)	372 (84)	579 (83)
C(4')	685 (78)	102 (50)	2128 (147)	411 (72)	-131 (83)	-155 (59)
C(5')	746 (77)	489 (70)	1486 (116)	-169 (69)	58 (75)	266 (69)
C(6')	746 (79)	288 (57)	1853 (137)	355 (72)	-100 (80)	44 (62)
C(7')	991 (87)	568 (70)	1211 (105)	54 (67)	346 (79)	288 (72)
C(8')	828 (75)	364 (55)	1363 (112)	310 (62)	241 (76)	96 (56)
C(9')	1393 (108)	612 (72)	1174 (112)	234 (73)	504 (94)	427 (77)
C(10')	1031 (90)	387 (61)	1424 (125)	384 (76)	126 (85)	-89 (69)
C(11')	1480 (114)	612 (79)	1199 (114)	17 (74)	481 (95)	436 (88)
C(12')	1160 (96)	426 (65)	1328 (121)	196 (73)	188 (88)	31 (75)
C(13')	1261 (103)	446 (67)	1055 (105)	-143 (70)	206 (85)	-5 (76)
C(14')	1117 (94)	388 (67)	1198 (115)	165 (73)	186 (86)	-112 (73)
C(15')	1769 (134)	549 (77)	1327 (129)	-139 (76)	710 (110)	321 (92)
C(16')	1238 (101)	320 (64)	1314 (123)	269 (72)	142 (91)	-147 (72)
C(17')	1540 (121)	570 (77)	1113 (112)	-92 (75)	405 (97)	204 (88)
C(18')	1867 (144)	609 (83)	1105 (118)	204 (84)	154 (110)	280 (96)
C(19')	1832 (138)	602 (85)	1079 (119)	132 (81)	822 (111)	187 (89)
C(20')	1373 (118)	691 (82)	1211 (119)	188 (83)	187 (97)	76 (90)
C(21')	1675 (143)	962 (105)	1556 (153)	14 (104)	685 (131)	214 (110)
C(22')	1590 (160)	1389 (149)	1362 (160)	483 (125)	430 (132)	-171 (128)
C(23')	1955 (207)	1563 (183)	3055 (291)	-461 (186)	1188 (210)	587 (160)
C(24')	2201 (221)	2226 (229)	1950 (219)	876 (186)	740 (190)	160 (196)
O(1')	1249 (64)	188 (38)	1570 (76)	301 (42)	550 (54)	368 (39)

Table 4. Fractional atomic coordinates and isotropic temperature factors for the hydrogen atoms

The first appended number refers to that of the parent atom.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
H(11)	-0.438	-0.490	0.401	6.4
H(12)	-0.392	-0.676	0.439	6.4
H(21)	-0.138	-0.060	0.432	4.3
H(31)	0.122	-0.109	0.471	4.3
H(41)	-0.276	-0.470	0.501	5.8
H(51)	-0.127	-0.231	0.556	5.7
H(52)	0.026	-0.454	0.537	5.7
H(61)	0.312	-0.037	0.518	6.4
H(62)	0.161	0.180	0.539	6.4
H(71)	0.201	-0.030	0.596	7.9
H(72)	0.348	-0.252	0.575	7.9
H(81)	0.653	0.166	0.563	6.9
H(82)	0.507	0.377	0.586	6.9
H(91)	0.538	0.125	0.640	8.0
H(92)	0.687	-0.081	0.617	8.0
H(101)	0.980	0.342	0.607	7.9
H(102)	0.833	0.535	0.633	7.9
H(111)	0.873	0.260	0.685	8.8
H(112)	1.019	0.065	0.658	8.8
H(121)	1.311	0.480	0.650	7.5
H(122)	1.164	0.681	0.675	7.5
H(131)	1.201	0.416	0.727	8.8
H(132)	1.354	0.222	0.702	8.8
H(141)	1.647	0.647	0.695	9.2
H(142)	1.495	0.833	0.722	9.2
H(151)	1.528	0.541	0.772	9.8
H(152)	1.688	0.368	0.745	9.8
H(161)	1.967	0.798	0.740	10.9
H(162)	1.807	0.972	0.766	10.9
H(171)	1.860	0.708	0.818	13.1
H(172)	2.004	0.510	0.792	13.1
H(181)	2.152	1.108	0.811	16.0
H(182)	2.297	0.910	0.785	16.0
H(183)	2.238	0.824	0.831	16.0
H(21')	0.123	-0.251	0.328	2.7
H(22')	0.269	-0.400	0.361	2.7
H(31')	0.548	0.034	0.369	7.5
H(32')	0.398	0.204	0.340	7.5
H(41')	0.440	-0.124	0.291	4.5
H(42')	0.607	-0.268	0.320	4.5
H(51')	0.886	0.188	0.325	6.5
H(52')	0.719	0.332	0.295	6.5
H(61')	0.765	0.004	0.248	5.8
H(62')	0.935	-0.135	0.277	5.8
H(71')	1.211	0.326	0.281	7.0
H(72')	1.041	0.463	0.251	7.0
H(81')	1.085	0.133	0.205	6.0
H(82')	1.255	-0.004	0.235	6.0
H(91')	1.531	0.448	0.238	8.0
H(92')	1.361	0.586	0.208	8.0
H(101')	1.403	0.257	0.161	6.7
H(102')	1.571	0.116	0.191	6.7
H(111')	1.852	0.570	0.194	8.3
H(112')	1.684	0.709	0.164	8.3
H(121')	1.729	0.376	0.118	7.0
H(122')	1.904	0.246	0.148	7.0
H(131')	2.174	0.706	0.150	6.6
H(132')	2.000	0.831	0.119	6.6
H(141')	2.053	0.496	0.073	6.4
H(142')	2.223	0.366	0.104	6.4
H(151')	2.491	0.826	0.108	8.5
H(152')	2.320	0.958	0.078	8.5
H(161')	2.371	0.623	0.032	6.5
H(162')	2.546	0.499	0.062	6.5
H(171')	2.817	0.957	0.063	8.0
H(172')	2.642	1.083	0.033	8.0
H(181')	2.687	0.744	-0.013	8.5

Table 4 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
H(182')	2.864	0.619	0.017	8.5
H(191')	3.137	1.088	0.319	8.5
H(192')	2.961	1.211	-0.312	8.5
H(201')	2.988	0.849	-0.054	8.3
H(202')	3.175	0.744	-0.024	8.3
H(211')	3.440	1.215	-0.028	10.7
H(212')	3.254	1.312	-0.059	10.7
H(221')	3.307	0.960	-0.100	11.8
H(222')	3.500	0.876	-0.069	11.8
H(231')	3.732	1.362	-0.072	16.0
H(232')	3.546	1.417	-0.107	16.0
H(241')	3.645	1.081	-0.143	16.0
H(242')	3.831	1.026	-0.109	16.0
H(243')	3.880	1.361	-0.129	16.0

The average C-C bond distance is 1.496 Å [$\sigma = 0.037$ Å, where $\sigma = \{\sum_N(X_N - \bar{X})^2 / (N-1)\}^{1/2}$] and the average C-C-C angle is 115.7° ($\sigma = 2.1^\circ$). Relatively short bond lengths and large bond angles have previously been reported for long hydrocarbon chains, *e.g.* 1.51 Å and 114.6° for β -tricaprin (Jensen & Mabis, 1966), 1.511 Å and 114.2° for DL-2-methyl-7-oxododecanoic acid (O'Connell, 1968), 1.516 Å and 113.9° for triacetyl sphingosine (O'Connell & Pascher, 1969), 1.512 Å and 113.9° for 13-oxoisostearic acid (Dahlén, 1972). These values can most probably be explained as the result of thermal motion of the chains. The effect is even more pronounced in this structure because of the large anisotropic thermal vibrations in the ceramide. The thermal ellipsoids of the molecule are shown in Fig. 2, which illustrates that the thermal motion is, as expected, large perpendicular to the chain direction but small in the chain direction. The distances and angles have not been corrected for thermal motion. If, however, the riding-motion model is used for the atoms with the largest vibrations the C(17)-C(18) bond would increase from 1.372 to 1.436 Å and the C(23')-C(24') bond from 1.406 to 1.439 Å.

Such a model is however not applicable for the whole molecule. It is also difficult to say whether the apparently large thermal motion is real or due to disorder.

The average C-O bond is 1.452 (14) Å and none of the individual bonds is significantly different. The geometry around the amide group is similar to that found in other peptide linked compounds, *e.g.* *N*-acetyl glycine (Donohue & Marsh, 1962) and α -glycylglycine (Biswas, Hughes, Sharma & Wilson, 1968).

In Fig. 3 the molecular packing projected on the (010) plane is shown. The molecules are connected by a system of hydrogen bonds in the polar part of the molecule. The hydrocarbon chains are thus pointing out in opposite directions from the polar group to allow space for the hydroxyl groups in the apices of the V-shaped molecules.

The molecules are linked together by three inter- and one intramolecular hydrogen bond.

The distances between the hydrogen bonded atoms are

N(1)···O(1')	(0, -1, 0)*	2.977 (12) Å
O(1)···O(2)	(-1, 0, 0)	2.687 (10)
O(2)···O(3)	(0, -1, 0)	2.755 (9)
O(1)···O(3)	(0, 0, 0)	2.724 (11)

Each of the three hydroxyl oxygens participates in two hydrogen bonds, acting both as an acceptor and as a donor. As mentioned above, none of these hydrogens could, however, be located from the Fourier difference map.

The hydrogen bonding forces are, as shown in Fig.

* Unit-cell translation of the second atom.

Table 5. Bond distances with standard deviations ($\times 10^3$)

O(1)—C(1)	1.414 (16) Å	C(1')—C(2')	1.476 (18) Å
O(2)—C(3)	1.448 (11)	C(2')—C(3')	1.474 (13)
O(3)—C(4)	1.495 (14)	C(3')—C(4')	1.532 (19)
O(1')—C(1')	1.281 (16)	C(4')—C(5')	1.516 (14)
N(1)—C(2)	1.443 (16)	C(5')—C(6')	1.531 (19)
N(1)—C(1')	1.320 (15)	C(6')—C(7')	1.525 (14)
C(1)—C(2)	1.552 (13)	C(7')—C(8')	1.493 (17)
C(2)—C(3)	1.513 (17)	C(8')—C(9')	1.498 (14)
C(3)—C(4)	1.455 (20)	C(9')—C(10')	1.512 (20)
C(4)—C(5)	1.476 (21)	C(10')—C(11')	1.515 (17)
C(5)—C(6)	1.516 (13)	C(11')—C(12')	1.519 (21)
C(6)—C(7)	1.507 (22)	C(12')—C(13')	1.506 (16)
C(7)—C(8)	1.523 (16)	C(13')—C(14')	1.513 (20)
C(8)—C(9)	1.497 (22)	C(14')—C(15')	1.492 (17)
C(9)—C(10)	1.474 (18)	C(15')—C(16')	1.500 (21)
C(10)—C(11)	1.511 (24)	C(16')—C(17')	1.511 (17)
C(11)—C(12)	1.461 (18)	C(17')—C(18')	1.525 (22)
C(12)—C(13)	1.512 (22)	C(18')—C(19')	1.527 (19)
C(13)—C(14)	1.478 (19)	C(19')—C(20')	1.451 (22)
C(14)—C(15)	1.484 (24)	C(20')—C(21')	1.544 (20)
C(15)—C(16)	1.442 (21)	C(21')—C(22')	1.452 (27)
C(16)—C(17)	1.538 (29)	C(22')—C(23')	1.496 (27)
C(17)—C(18)	1.372 (30)	C(23')—C(24')	1.406 (37)

Table 6. Bond angles (with standard deviations)

O(1)—C(1)—C(2)	112.4 (0.8)°	N(1)—C(1')—O(1')	121.5 (1.2)°
N(1)—C(2)—C(1)	108.6 (0.8)	N(1)—C(1')—C(2')	116.6 (1.1)
N(1)—C(2)—C(3)	115.0 (0.9)	O(1')—C(1')—C(2')	121.6 (1.0)
C(1)—C(2)—C(3)	116.0 (0.9)	C(1')—C(2')—C(3')	115.2 (0.9)
O(2)—C(3)—C(2)	107.0 (0.8)	C(2')—C(3')—C(4')	112.7 (0.9)
O(2)—C(3)—C(4)	108.3 (0.9)	C(3')—C(4')—C(5')	115.4 (0.8)
C(2)—C(3)—C(4)	116.7 (1.0)	C(4')—C(5')—C(6')	114.4 (0.9)
O(3)—C(4)—C(3)	109.7 (1.1)	C(5')—C(6')—C(7')	114.6 (0.8)
O(3)—C(4)—C(5)	111.6 (1.0)	C(6')—C(7')—C(8')	113.9 (0.9)
C(3)—C(4)—C(5)	114.8 (1.0)	C(7')—C(8')—C(9')	115.3 (0.9)
C(4)—C(5)—C(6)	118.6 (1.1)	C(8')—C(9')—C(10')	115.1 (0.9)
C(5)—C(6)—C(7)	112.0 (1.0)	C(9')—C(10')—C(11')	115.2 (0.9)
C(6)—C(7)—C(8)	118.7 (1.1)	C(10')—C(11')—C(12')	115.9 (1.0)
C(7)—C(8)—C(9)	115.5 (1.1)	C(11')—C(12')—C(13')	115.9 (1.0)
C(8)—C(9)—C(10)	116.6 (1.2)	C(12')—C(13')—C(14')	115.2 (0.9)
C(9)—C(10)—C(11)	115.6 (1.2)	C(13')—C(14')—C(15')	112.8 (0.9)
C(10)—C(11)—C(12)	114.9 (1.2)	C(14')—C(15')—C(16')	113.7 (1.0)
C(11)—C(12)—C(13)	116.2 (1.1)	C(15')—C(16')—C(17')	116.3 (1.0)
C(12)—C(13)—C(14)	119.1 (1.2)	C(16')—C(17')—C(18')	115.1 (1.0)
C(13)—C(14)—C(15)	117.4 (1.2)	C(17')—C(18')—C(19')	113.9 (1.0)
C(14)—C(15)—C(16)	116.8 (1.3)	C(18')—C(19')—C(20')	110.9 (1.0)
C(15)—C(16)—C(17)	118.5 (1.4)	C(19')—C(20')—C(21')	114.7 (1.1)
C(16)—C(17)—C(18)	120.2 (1.9)	C(20')—C(21')—C(22')	117.9 (1.3)
C(2)—N(1)—C(1')	123.4 (0.9)	C(21')—C(22')—C(23')	116.8 (1.6)
		C(22')—C(23')—C(24')	119.3 (1.8)

4(a), strongest in the **b** direction which is compatible with the crystals growing fastest along this axis.

A detail of the packing in the methyl group layers is given in Fig. 4(b) with the shortest intermolecular hydrogen-hydrogen contacts indicated.

The closest non-bonded carbon-carbon distances are

C(24)'···C(17)	(2, 0, -1)*	4.30 (3) Å
C(24)'···C(17)	(2, 1, -1)	4.15 (3)
C(24)'···C(18)	(1, 0, -1)	4.34 (3)
C(24)'···C(18)	(2, 0, -1)	4.29 (4)
C(22)'···C(18)	(1, 0, -1)	4.50 (3)

These contacts are fairly long but a correction for thermal motion as mentioned above would tend to decrease them.

However, the packing in the methyl end group planes is in general less effective when the carbon chains are tilted so much to the end group planes that there are direct packing contacts between CH₃ and CH₂ groups (Abrahamsson, Ställberg-Stenhagen & Stenhagen, 1963). The two chains of the V-shaped molecule intersect at an angle of 101°. The fatty acid chain has an angle of tilt of 51° to the end group planes and the sphingosine chain, 50°. The corresponding angle found for the V-shaped 1,3-diglyceride of 3-thiadodecanoic acid is 55° (Larsson, 1963). As expected from the complicated packing the density of the ceramide is relatively low ($D_m = 1.015 \text{ g.cm}^{-3}$).

The least-squares plane through the sphingosine chain and the fatty acid chain are given in Table 7 with the out of plane deviations. The sphingosine chain is planar within 0.041 Å from C(7) to C(18) and the fatty acid chain from C(3') to C(20') within 0.035 Å. The end carbon atoms C(21') to C(24') are significantly out of the latter plane. The plane containing N(1), O(1'),

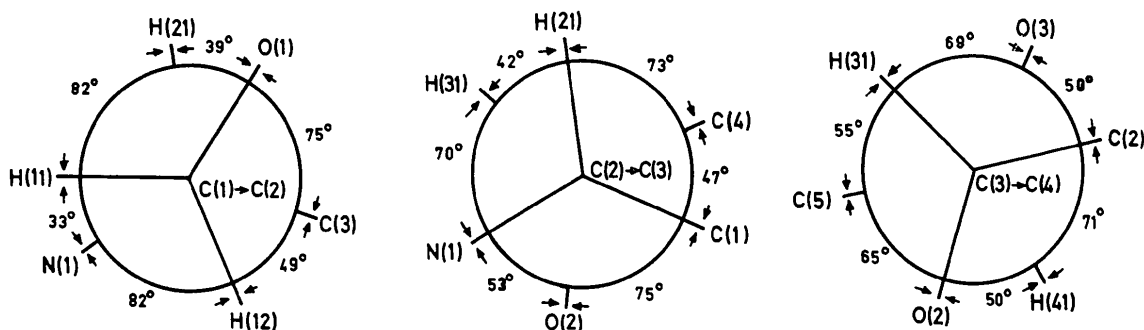


Fig. 5. The molecular conformation around the bonds (a) C(1)–C(2), (b) C(2)–C(3) and (c) C(3)–C(4). The figures are drawn to show their orientation with respect to the *b* axis which is vertical.

C(1') and C(2') forms an angle of 28° with the fatty acid zigzag plane. The torsion angles about three bonds in the polar region are given in Fig. 5.

Table 7. *Least-squares planes*

(a) The least-squares plane through the sphingosine chain using C(7)–C(18) in the plane calculation.

$$-0.2016x + 0.1599y + 0.9663z - 0.4848 = 0.$$

The equation refers to the crystal axes.

	Deviation		Deviation
C(7)	0.004 Å	C(16)	0.041 Å
C(8)	-0.030	C(17)	0.014
C(9)	0.031	C(18)	-0.020
C(10)	0.025	C(1)	-1.389
C(11)	-0.009	C(2)	-1.717
C(12)	-0.026	C(3)	-1.537
C(13)	-0.012	C(4)	-0.303
C(14)	0.010	C(5)	-0.115
C(15)	-0.028	C(6)	-0.144

(b) The least-squares plane through the fatty acid chain using C(3')–C(20') in the calculation.

$$0.1763x - 0.1119y + 0.9780z - 0.4144 = 0.$$

	Deviation		Deviation
C(3')	-0.004 Å	C(15')	0.012 Å
C(4')	-0.019	C(16')	0.034
C(5')	0.015	C(17')	0.005
C(6')	-0.006	C(18')	0.003
C(7')	-0.001	C(19')	-0.035
C(8')	-0.007	C(20')	-0.017
C(9')	0.003	C(1')	-0.271
C(10')	-0.006	C(2')	-0.142
C(11')	0.014	C(21')	-0.136
C(12')	0.007	C(22')	-0.078
C(13')	-0.011	C(23')	-0.245
C(14')	0.015	C(24')	-0.062

The chain packing is of the common triclinic type (*T*||) (Abrahamsson, 1959) and the dimensions of the methylene subcell are:

$$a_s = 4.68, \quad b_s = 5.35, \quad c_s = 2.54 \text{ \AA}$$

$$\alpha_s = 66, \quad \beta_s = 114, \quad \gamma_s = 122^\circ$$

The volume per CH₂ group is 23.9 Å³.

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References

- ABRAHAMSSON, S. (1959). *Ark. Kemi*, **14**, 65.
 ABRAHAMSSON, S., STÄLLBERG-STENHAGEN, S. & STENHAGEN, E. (1963). *Prog. Chem. Fats Other Lipids*, **7**, 66.
 ABRAHAMSSON, S., ALEBY, S., LARSSON, K., NILSSON, B., SELIN, K. & WESTERDAHL, A. (1965). *Acta Chem. Scand.* **19**, 758.
 BISWAS, A. B., HUGHES, E. W., SHARMA, B. D. & WILSON, J. N. (1968). *Acta Cryst.* **B24**, 40.
 DAHLÉN, B. (1972). *Acta Cryst.* In the press
 DAHLÉN, P. & PASCHER, I. (1972). To be published.
 DONOHUE, J. & MARSH, R. E. (1962). *Acta Cryst.* **15**, 941.
 HAKOMORI, S.-I. (1970). *Chem. Phys. Lipids*, **5**, 96.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
 JENSEN, L. H. & MABIS, A. J. (1966). *Acta Cryst.* **21**, 770.
 JOHNSON, C. K. (1965). *ORTEP*. Report 3794. Oak Ridge National Laboratory, Oak Ridge, Tennessee.
 KARLSSON, K.-A. (1964). *Acta Chem. Scand.* **18**, 2397.
 KARLSSON, K.-A. (1966). *Acta Chem. Scand.* **20**, 2884.
 KARLSSON, K.-A. (1970). *Chem. Phys. Lipids*, **5**, 6.
 KARLSSON, K.-A. & PASCHER, I. (1971). *J. Lipid Res.* **12**, 466.
 KARLSSON, K.-A., SAMUELSSON, B. E. & STEEN, G. O. (1971). *J. Membrane Biol.* **5**, 169.
 LARSSON, K. (1963). *Acta Cryst.* **16**, 741.
 MILLS, O. S. & ROLLETT, J. S. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, p. 107. London: Pergamon Press.
 O'CONNELL, A. M. (1968). *Acta Cryst.* **B24**, 1399.
 O'CONNELL, A. M. & PASCHER, I. (1969). *Acta Cryst.* **B25**, 2553.
 ROSEMAN, S. (1970). *Chem. Phys. Lipids*, **5**, 270.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.
 WIEGANDT, H. (1971). *Advanc. Lipid Res.* **9**, 249.
 YANG, H.-J. & HAKOMORI, S.-I. (1971). *J. Biol. Chem.* **246**, 1192.