The Crystal and Molecular Structure of Grayanotoxin II

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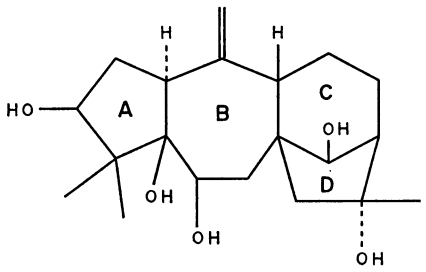
The detailed molecular geometry of grayanotoxin II has been examined by means of X-ray crystallographic analysis. The crystals are orthorhombic, with four molecules in a unit cell with dimensions of $a=10.040$, $b=26.517$, and $c=6.672$ Å; the space group is $P2_12_12_1$. 1908 unique intensity data were collected on a four-circle diffractometer with LiF-monochromated Cu $K\alpha$ radiation. The structure was solved by the Monte Carlo direct method, using the 20 strongest reflections as the starting set; the 3rd random phase set led to the correct solution. The R value reached 3.8% by repeated block-diagonal least-squares refinements. The A, B, C, and D rings take envelope, twist-chair, chair, and half-chair conformations respectively. The conformation of the B ring closely resembles the preferred one of cycloheptane itself. The crystal consists of hydrogen-bonded double molecular layers piled parallel to the (010) plane.

A number of grayanane diterpenoids have been isolated from *Leucothoe grayana Max.*, *Pieris japonica* D. Don, *Rhododendron japonicum* Suringer, *etc.*, and their structures have been extensively investigated.[1-3] Since these diterpenoids contain four rings, especially a flexible seven-membered ring, their chemical reactivities are closely related to the ring conformations. Although one of the grayanoids, grayanotoxin (hereafter G) I, was subjected to X-ray crystallographic analysis, details of the molecular geometry have not yet been published.[4] In the present paper, we wish to report on the X-ray structure determination and molecular geometry of another grayanoid, G II (**1**).



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Experimental

A colorless, single crystal with dimensions of about $0.3\times 0.4\times 0.6$ mm^3 was used for the X-ray measurement. The crystal data are summarized in Table 1. The cell dimensions and reflection intensities were measured on a Rigaku four-circle diffractometer using Cu $K\alpha$ radiation ($\lambda=1.5418$ Å) monochromatized with an LiF crystal. The intensity measurement was made by the θ-2θ continuous-scan technique at a 2θ scan rate of 2° min^{-1}; the background was measured for 30—60 s at each end of the scan range. Three standard reflections, measured at intervals of every 62 reflections, showed no significant decrease in intensity during the course of data collection. The intensities were corrected for the Lorentz and polarization factors, but not for the absorption or the extinction effect. In the range of 2θ values up to 140°, 1908 unique structure factor magnitudes above the $2\sigma(F)$ level were selected for the structure determination.

Table 1. The crystal data

Mol. formula	$C_{20}H_{32}O_5$
Mol. weight	352.5
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Cell dimensions	$a=10.040(3)$ Å
	$b=26.517(5)$
	$c=6.672(2)$
V	1776.3 Å^3
Z	4
D_x	1.318 g cm^{-3}
μ(Cu $K\alpha$)	7.14 cm^{-1}

Structure Determination

In the early stage of the structure determination, attempts were made to solve the structure by the symbolic-addition method,[5] but all such attempts were unsuccessful. The structure was finally elucidated by the Monte Carlo direct method.[6] The 20 strongest reflections were chosen as members of the starting set. Tentative phase values for the starting reflections were derived from successively-generated random numbers. In order to extend this tentative phase set, 10 cycles of the tangent procedure were performed using 421 $|E|$ values above 1.30; during the first 5 cycles, the phases of the starting reflections were kept constant. The 3rd phase set, which showed a low R_K value of 24.6% ($R_K=\Sigma||E_o|-k|E_c||/\Sigma|E_o|$), led to the correct solution. An E-map calculated with 407 phases clearly revealed the locations of all 25 non-hydrogen atoms.

The structure thus obtained was refined by the block-diagonal-matrix least-squares method, first with isotropic and then with anisotropic temperature factors. After all the 32 hydrogen atoms had been located in a difference Fourier map, further least-squares refinement was repeated including these hydrogen atoms with isotropic temperature factors. For this refinement, the following weighting scheme was used:

$$W = 1/\{\sigma(F)^2\exp(AX^2+BY^2+CXY+DX+EY)\},$$

where $X=|F_o|$ and $Y=\sin\theta/\lambda$. The coefficients, A, B, C, D, and E, are constants which were determined from the $(\Delta F)^2$ values. The final value of $R=\Sigma||F_o|-k|F_c||/\Sigma|F_o|$ was 3.8%. The atomic parameters thus obtained are listed in Table 2. The tables of the observed and calculated structure factors are kept at the Chemical Society of Japan (Document No. 8025).

TABLE 2. THE FINAL ATOMIC PARAMETERS AND ESTIMATED STANDARD DEVIATIONS

(1) The non-hydrogen atoms.

The temperature factors are defined as $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$.

Atom	$x(\times 10^4)$	$y(\times 10^5)$	$z(\times 10^4)$	$\beta_{11}(\times 10^4)$	$\beta_{22}(\times 10^5)$	$\beta_{33}(\times 10^4)$	$\beta_{12}(\times 10^5)$	$\beta_{13}(\times 10^4)$	$\beta_{23}(\times 10^4)$
O (1)	3228 (2)	14147 (8)	8918 (4)	84 (2)	170 (3)	303 (6)	−61 (11)	148 (6)	−47 (2)
O (2)	5990 (1)	12968 (5)	8326 (2)	56 (1)	96 (2)	111 (2)	−44 (7)	10 (3)	−20 (1)
O (3)	7065 (2)	2594 (5)	7829 (2)	69 (1)	66 (1)	139 (3)	−24 (7)	−30 (3)	12 (1)
O (4)	8604 (2)	7031 (5)	1494 (2)	82 (1)	60 (1)	141 (3)	14 (7)	57 (3)	−6 (1)
O (5)	11011 (2)	12035 (6)	1501 (3)	58 (1)	97 (2)	216 (4)	68 (8)	81 (4)	3 (1)
C (1)	5032 (2)	12248 (6)	4938 (3)	39 (1)	75 (2)	115 (3)	31 (9)	−5 (4)	−5 (1)
C (2)	3530 (2)	13215 (9)	5385 (4)	43 (2)	125 (3)	244 (5)	92 (11)	18 (5)	21 (2)
C (3)	3202 (2)	10507 (8)	7342 (4)	46 (2)	108 (2)	233 (5)	−6 (10)	57 (5)	1 (2)
C (4)	4306 (2)	6487 (7)	7580 (3)	44 (2)	99 (2)	173 (4)	−84 (9)	10 (4)	8 (2)
C (5)	5560 (2)	9491 (6)	6820 (3)	40 (1)	68 (2)	103 (3)	−40 (8)	10 (3)	−5 (1)
C (6)	6757 (2)	6181 (6)	6276 (3)	47 (1)	62 (2)	104 (3)	14 (8)	−12 (4)	1 (1)
C (7)	8047 (2)	9031 (6)	5848 (3)	41 (1)	72 (2)	101 (3)	51 (8)	3 (3)	4 (1)
C (8)	8186 (2)	13220 (5)	4275 (2)	37 (1)	58 (2)	99 (3)	14 (8)	4 (3)	−1 (1)
C (9)	7239 (2)	17876 (6)	4618 (3)	50 (2)	56 (2)	117 (3)	15 (8)	8 (4)	−3 (1)
C (10)	5762 (2)	16910 (6)	4163 (3)	47 (1)	74 (2)	131 (3)	79 (9)	14 (4)	1 (2)
C (11)	7781 (2)	22354 (6)	3398 (3)	62 (2)	56 (2)	177 (4)	13 (9)	18 (5)	0 (2)
C (12)	8058 (2)	20983 (6)	1209 (3)	61 (2)	69 (2)	153 (4)	10 (9)	−8 (4)	18 (2)
C (13)	8833 (2)	16005 (6)	1019 (3)	58 (2)	71 (2)	100 (3)	−17 (9)	6 (4)	5 (1)
C (14)	8024 (2)	11809 (6)	2040 (3)	50 (1)	58 (2)	105 (3)	5 (8)	2 (3)	−1 (1)
C (15)	9680 (2)	14919 (7)	4381 (3)	42 (1)	93 (2)	115 (3)	−30 (9)	−11 (4)	5 (2)
C (16)	10147 (2)	16061 (6)	2213 (3)	48 (1)	72 (2)	138 (4)	3 (9)	25 (4)	4 (2)
C (17)	10987 (2)	20809 (8)	1986 (4)	57 (2)	97 (2)	210 (5)	−91 (10)	23 (5)	15 (2)
C (18)	4410 (3)	4625 (13)	9743 (5)	80 (2)	203 (4)	215 (6)	−163 (17)	53 (6)	51 (3)
C (19)	3961 (2)	2071 (8)	6195 (5)	65 (2)	87 (2)	309 (7)	−158 (11)	−21 (6)	−9 (2)
C (20)	5059 (2)	20031 (9)	2999 (4)	55 (2)	132 (3)	267 (6)	117 (12)	20 (6)	51 (2)

(2) The hydrogen atoms.

The positional and thermal parameters are multiplied by 10^3 and 10 respectively.

Atom[a)]	x	y	z	B/Å^2	Atom	x	y	z	B/Å^2
H (1)	510 (3)	100 (1)	386 (5)	24 (5)	H (17a)	1181 (4)	204 (1)	268 (6)	34 (6)
H (2a)	304 (5)	120 (2)	422 (7)	48 (8)	H (17b)	1053 (4)	237 (1)	242 (6)	36 (6)
H (2b)	333 (5)	170 (2)	566 (7)	49 (8)	H (17c)	1123 (4)	213 (2)	67 (7)	45 (8)
H (3)	231 (3)	87 (1)	732 (5)	27 (5)	H (18a)	486 (6)	17 (2)	1003 (9)	66 (11)
H (6)	650 (3)	42 (1)	510 (4)	17 (4)	H (18b)	355 (6)	35 (2)	1015 (9)	70 (12)
H (7a)	868 (3)	65 (1)	557 (4)	19 (4)	H (18c)	481 (6)	71 (2)	1083 (9)	61 (11)
H (7b)	829 (3)	104 (1)	715 (5)	23 (5)	H (19a)	321 (5)	4 (2)	683 (7)	46 (8)
H (9)	728 (3)	187 (1)	599 (5)	25 (5)	H (19b)	466 (4)	−5 (2)	622 (7)	43 (7)
H (11a)	714 (3)	250 (1)	342 (5)	29 (5)	H (19c)	379 (5)	30 (2)	485 (7)	46 (8)
H (11b)	859 (3)	234 (1)	394 (5)	30 (5)	H (20a)	542 (4)	230 (1)	245 (7)	40 (7)
H (12a)	723 (4)	206 (1)	62 (5)	33 (6)	H (20b)	413 (3)	193 (1)	265 (5)	31 (6)
H (12b)	855 (3)	238 (1)	64 (4)	21 (4)	H (O1)	266 (4)	133 (2)	977 (7)	46 (8)
H (13)	900 (3)	152 (1)	−35 (5)	31 (6)	H (O2)	538 (4)	143 (1)	877 (6)	35 (6)
H (14)	713 (2)	119 (1)	164 (4)	15 (4)	H (O3)	741 (4)	39 (1)	863 (5)	33 (6)
H (15a)	1014 (4)	123 (1)	494 (5)	34 (6)	H (O4)	825 (3)	47 (1)	216 (5)	26 (5)
H (15b)	979 (4)	177 (2)	527 (7)	44 (8)	H (O5)	1055 (5)	96 (2)	151 (8)	52 (9)

a) The hydrogen atoms are denoted by the number of the carbon atom to which they are attached, suffixed by a, b, or c where necessary.

All the calculations were performed on a FACOM 230-75 computer at the Hokkaido University Computing Center, using our own programs. Random numbers were generated by calling a function RANDOM which existed in the program library of the Computing Center. The atomic scattering factors were taken from the International Tables.[7)]

Results and Discussion

Molecular Structure. The molecular structure of G II is illustrated in Fig. 1, where each atom is represented as a thermal ellipsoid enclosing a 50%

Table 3. The bond distances (l/Å) and angles (ϕ/°), with their standard deviations

The standard deviations given in parentheses refer to the last decimal position.

C (1) - C (2)	1.559 (3)	C (16) - C (17)	1.523 (3)	C (7) - C (8) - C (14)	118.4 (1)
C (1) - C (5)	1.547 (2)	C (16) - O (5)	1.455 (2)	C (7) - C (8) - C (15)	105.3 (1)
C (1) - C (10)	1.527 (2)	C (2) - C (1) - C (5)	104.7 (2)	C (9) - C (8) - C (14)	105.5 (1)
C (2) - C (3)	1.526 (4)	C (2) - C (1) - C (10)	113.3 (2)	C (9) - C (8) - C (15)	110.2 (1)
C (3) - C (4)	1.546 (3)	C (5) - C (1) - C (10)	119.5 (1)	C (14) - C (8) - C (15)	102.3 (1)
C (3) - O (1)	1.428 (3)	C (1) - C (2) - C (3)	107.1 (2)	C (8) - C (9) - C (10)	115.1 (1)
C (4) - C (5)	1.574 (3)	C (2) - C (3) - C (4)	105.0 (2)	C (8) - C (9) - C (11)	108.3 (1)
C (4) - C (18)	1.528 (4)	C (2) - C (3) - O (1)	108.0 (2)	C (10) - C (9) - C (11)	111.5 (1)
C (4) - C (19)	1.532 (3)	C (4) - C (3) - O (1)	112.2 (2)	C (1) - C (10) - C (9)	122.1 (1)
C (5) - C (6)	1.531 (2)	C (3) - C (4) - C (5)	101.0 (2)	C (1) - C (10) - C (20)	116.4 (2)
C (5) - O (2)	1.430 (2)	C (3) - C (4) - C (18)	111.6 (2)	C (9) - C (10) - C (20)	121.4 (2)
C (6) - C (7)	1.527 (2)	C (3) - C (4) - C (19)	107.7 (2)	C (9) - C (11) - C (12)	112.7 (1)
C (6) - O (3)	1.440 (2)	C (5) - C (4) - C (18)	114.4 (2)	C (11) - C (12) - C (13)	112.0 (2)
C (7) - C (8)	1.535 (2)	C (5) - C (4) - C (19)	111.9 (2)	C (12) - C (13) - C (14)	108.6 (1)
C (8) - C (9)	1.575 (2)	C (18) - C (4) - C (19)	109.8 (2)	C (12) - C (13) - C (16)	112.5 (1)
C (8) - C (14)	1.545 (2)	C (1) - C (5) - C (4)	103.1 (1)	C (14) - C (13) - C (16)	103.3 (1)
C (8) - C (15)	1.568 (2)	C (1) - C (5) - C (6)	110.3 (1)	C (8) - C (14) - C (13)	101.4 (1)
C (9) - C (10)	1.535 (3)	C (1) - C (5) - O (2)	111.7 (1)	C (8) - C (14) - O (4)	114.5 (1)
C (9) - C (11)	1.539 (2)	C (4) - C (5) - C (6)	114.5 (1)	C (13) - C (14) - O (4)	108.1 (1)
C (10) - C (20)	1.336 (3)	C (4) - C (5) - O (2)	109.9 (1)	C (8) - C (15) - C (16)	107.1 (1)
C (11) - C (12)	1.531 (3)	C (6) - C (5) - O (2)	107.4 (1)	C (13) - C (16) - C (15)	102.8 (1)
C (12) - C (13)	1.537 (2)	C (5) - C (6) - C (7)	115.2 (1)	C (13) - C (16) - C (17)	115.5 (2)
C (13) - C (14)	1.536 (2)	C (5) - C (6) - O (3)	112.1 (1)	C (13) - C (16) - O (5)	109.6 (1)
C (13) - C (16)	1.542 (3)	C (7) - C (6) - O (3)	106.2 (1)	C (15) - C (16) - C (17)	114.9 (2)
C (14) - O (4)	1.441 (2)	C (6) - C (7) - C (8)	124.3 (1)	C (15) - C (16) - O (5)	110.0 (1)
C (15) - C (16)	1.551 (3)	C (7) - C (8) - C (9)	114.4 (1)	C (17) - C (16) - O (5)	104.1 (2)

Table 4. The dihedral angles (ϕ/°)

The A-B-C-D angle is positive if, when looking along B to C, A has to be rotated clockwise to eclipse D.

C (5) - C (1) - C (2) - C (3)	−6.6	C (7) - C (8) - C (9) - C (10)	−72.5
C (10) - C (1) - C (2) - C (3)	−138.5	C (7 (- C (8) - C (9) - C (11)	162.0
C (2) - C (1) - C (5) - C (4)	30.7	C (14) - C (8) - C (9) - C (11)	−66.1
C (2) - C (1) - C (5) - C (6)	153.3	C (15) - C (8) - C (9) - C (11)	43.6
C (2) - C (1) - C (5) - O (2)	−87.3	C (7) - C (8) - C (14) - C (13)	−155.0
C (10) - C (1) - C (5) - C (6)	−78.4	C (9) - C (8) - C (14) - C (13)	75.5
C (2) - C (1) - C (10) - C (20)	−34.5	C (15) - C (8) - C (14) - C (13)	−39.9
C (5) - C (1) - C (10) - C (9)	23.7	C (15) - C (8) - C (14) - O (4)	76.3
C (5) - C (1) - C (10) - C (20)	−158.7	C (7) - C (8) - C (15) - C (16)	142.3
C (1) - C (2) - C (3) - C (4)	−20.7	C (9) - C (8) - C (15) - C (16)	−93.9
C (1) - C (2) - C (3) - O (1)	99.1	C (14) - C (8) - C (15) - C (16)	18.0
C (2) - C (3) - C (4) - C (5)	39.1	C (8) - C (9) - C (10) - C (1)	47.3
C (2) - C (3) - C (4) - C (18)	161.1	C (11) - C (9) - C (10) - C (1)	171.1
C (2) - C (3) - C (4) - C (19)	−78.3	C (11) - C (9) - C (10) - C (20)	−6.4
O (1) - C (3) - C (4) - C (5)	−77.8	C (8) - C (9) - C (11) - C (12)	50.6
C (3) - C (4) - C (5) - C (1)	−43.1	C (10) - C (9) - C (11) - C (12)	−76.9
C (18) - C (4) - C (5) - C (1)	−163.1	C (9) - C (11) - C (12) - C (13)	−46.9
C (19) - C (4) - C (5) - C (1)	71.2	C (11) - C (12) - C (13) - C (14)	58.0
C (18) - C (4) - C (5) - C (6)	77.0	C (11) - C (12) - C (13) - C (16)	−55.7
C (18) - C (4) - C (5) - O (2)	−44.0	C (12) - C (13) - C (14) - C (8)	−71.4
C (1) - C (5) - C (6) - C (7)	73.4	C (16) - C (13) - C (14) - C (8)	48.2
C (1) - C (5) - C (6) - O (3)	−165.0	C (16) - C (13) - C (14) - O (4)	−72.5
C (4) - C (5) - C (6) - O (3)	−49.3	C (12) - C (13) - C (16) - C (15)	80.6
O (2) - C (5) - C (6) - O (3)	73.1	C (12) - C (13) - C (16) - C (17)	−45.3
C (5) - C (6) - C (7) - C (8)	−55.7	C (12) - C (13) - C (16) - O (5)	−162.5
O (3) - C (6) - C (7) - C (8)	179.6	C (14) - C (13) - C (16) - C (15)	−36.2
C (6) - C (7) - C (8) - C (9)	59.3	C (8) - C (15) - C (16) - C (13)	11.0
C (6) - C (7) - C (8) - C (14)	−66.0	C (8) - C (15) - C (16) - C (17)	137.3
C (6) - C (7) - C (8) - C (15)	−179.5	C (8) - C (15) - C (16) - O (5)	−105.6

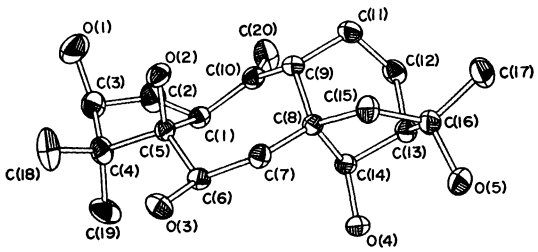

Fig. 1. A perspective view of the G II molecule. For the sake of clarity, hydrogen atoms are omitted.

probability. As can be seen in Fig. 1, the molecular framework obtained corresponds precisely to Structure **1** based on the chemical evidence.[1] The bond distances and angles and the dihedral angles are listed in Tables 3 and 4 respectively.

The five-membered A ring takes a deformed envelope conformation, with the C(4) atom deviating remarkably from the mean plane for the other four atoms in this ring. The O(1)H and O(2)H hydroxyl groups occupy the 1,3-diaxial positions in the A ring and form an intramolecular hydrogen bond, O(2)–H···O(1), with each other (see Table 5). The equatorial methyl carbon, C(18), is only 3.004(3) Å distant from the O(3) atom. Because of this close contact, the C(5)–C(4)–C(18) and C(5)–C(6)–O(3) angles, 114.4 and 112.1°, may become somewhat greater than the standard tetrahedral angle.

The seven-membered B ring has a somewhat complicated conformation an approximate two-fold rotation axis running through the C(10) atom and the middle point of the C(6)–C(7) bond. This conformation corresponds almost exactly to the most stable twist-chair form of cycloheptane itself.[8] It is an interesting fact that, notwithstanding its incorporation in the complicated ring-system, the B ring keeps such a flexible conformation. All the sp^3-valency angles in the B ring are greater than 109.5°. Especially the C(6)–C(7)–C(8) and C(5)–C(1)–C(10) angles, 124.3 and 119.5°, are quite within the range of the normal sp^2-valency angle. The exocyclic methylene group, $C(20)H_2$, nearly eclipses the $C(11)H_2$ group around the C(9)–C(10) bond. As a result, the distance between the H(20a) and H(11a) atoms is only 1.92(5) Å. The difference of 5° between the C(1)–C(10)–C(20) and C(9)–C(10)–C(20) angles is probably due to this steric repulsion.

Table 5. The hydrogen bonds, X-H···Y

X	Y	X···Y (l/Å)	H···Y (l/Å)	X-H···Y (ϕ/°)
(1) Intramolecular				
O(2)	O(1)	2.818(2)	2.17(4)	144(4)
O(5)	O(4)	2.757(2)	2.07(5)	144(5)
(2) Intermolecular				
O(1)	O(5)[a]	2.871(3)	2.04(4)	169(4)
O(3)	O(4)[b]	3.122(2)	2.41(4)	173(3)
O(4)	O(3)[c]	2.785(2)	2.02(3)	152(3)

Symmetry codes are: a) $-1+x$, y, $1+z$; b) x, y, $1+z$; c) $3/2-x$, $-y$, $-1/2+z$.

The six-membered C ring in G II adopts a chair conformation, although it has recently been found that, in some other grayanoids, the C ring takes a boat conformation.[9] Since the seven-membered ring composed of the C(8), C(9), C(11), C(12), C(13), C(15), and C(16) atoms takes a boat conformation, the axial hydrogen, H(11b), is close to the H(15b) and H(17b) atoms; the distances are 2.12(5) and 2.20(5) Å respectively.

The five-membered D ring has a half-chair conformation, with an approximate two-fold rotation axis running through the C(15) atom. Since this conformation gives the 1,3-diaxial positions to the O(4)H

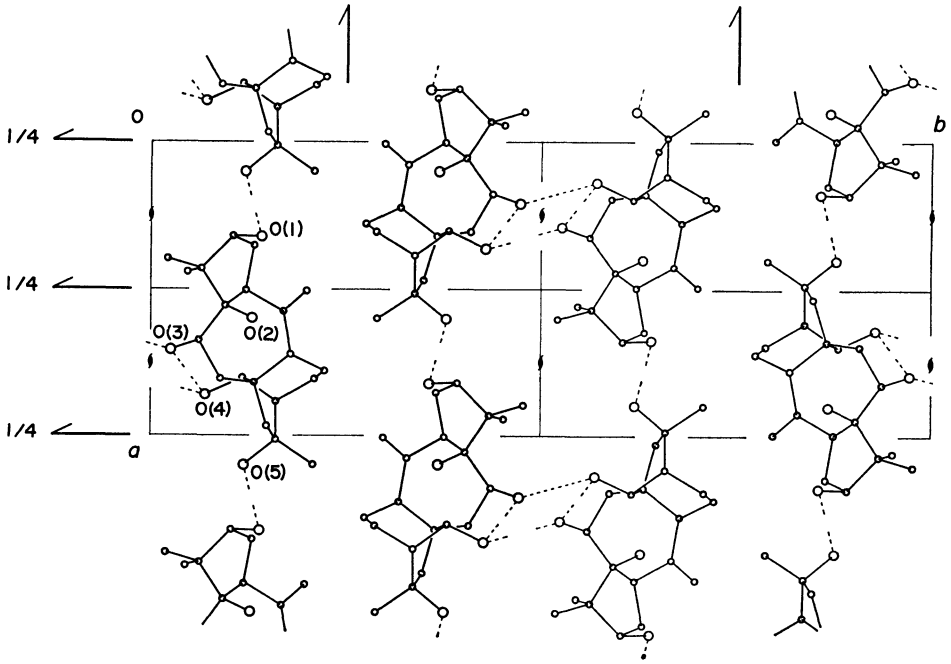

Fig. 2. The crystal structure viewed along the c axis.

and O(5)H hydroxyl groups, a stable intramolecular hydrogen bond, O(5)–H···O(4), is formed. The C(17)H_3 group, like the other two methyl groups, takes a stable staggered conformation.

Crystal Structure. The crystal structure viewed along the c axis is drawn in Fig. 2. The details of hydrogen bonding are given in Table 5. The molecules are connected by three kinds of intermolecular hydrogen bonds, forming a double molecular layer about the two-fold screw axes along the c axis. These molecular layers parallel to the (010) plane are further held together mainly by the van der Waals interactions.

References

1) S. Miyajima and S. Takei, *J. Agric. Chem. Jpn*, **10**, 1093 (1934); H. Kakisawa, M. Kurono, S. Takahashi, and H. Hirata, *ibid.*, **1961**, 59; J. Iwasa and Y. Nakamura, *Tetrahedron Lett.*, **1969**, 3937; H. Hikino, M. Ogura, T. Ohta, and T. Takemoto, *Chem. Pharm. Bull.*, **18**, 1072 (1970).

2) T. Okuno, N. Hamanaka, H. Miyakoshi, and T. Matsumoto, *Tetrahedron*, **26**, 4765 (1970); N. Hamanaka, H. Miyakoshi, A. Furusaki, and T. Matsumoto, *Chem. Lett.*, **1972**, 779; S. Gasa, R. Ikeda, N. Hamanaka, and T. Matsumoto, *Bull. Chem. Soc. Jpn.*, **49**, 835 (1976).

3) M. Yasue, Y. Kato, T. Kishida, and H. Ohta, *Chem. Pharm. Bull.*, **9**, 171 (1961); H. Hikino, K. Ito, and T. Takemoto, *ibid.*, **17**, 854 (1969); H. Hikino, M. Ogura, T. Ohta, and T. Takemoto, *ibid.*, **18**, 1071 (1970).

4) P. Narayanan, M. Rohl, K. Zechmeister, and W. Hoppe, *Tetrahedron Lett.*, **1970**, 3943.

5) J. Karle and I. L. Karle, *Acta Crystallogr.*, **21**, 849 (1966).

6) A. Furusaki, *Acta Crystallogr., Sect. A*, **35**, 220 (1979).

7) "International Tables for X-Ray Crystallography," The Kynoch Press, Birmingham (1974), Vol. IV.

8) J. B. Hendrickson, *J. Am. Chem. Soc.*, **83**, 4537 (1961).

9) A. Furusaki, S. Gasa, R. Ikeda, T. Matsumoto, N. Yasuoka, and Y. Matsuura, unpublished.