The Crystal and Molecular Structure of Grayanotoxin XIX. A New Minor Diterpene from *Leucothoe Grayana Max.*

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The molecular structure of grayanotoxin XIX, $C_{20}H_{30}O_3$, has been determined by means of X-ray crystal analysis. The crystals are triclinic, with two molecules in a unit cell with dimensions of $a=10.406$, $b=10.648$, $c=8.003$ Å, $\alpha=90.00$, $\beta=94.25$, and $\gamma=102.76°$; the space group is P1. 2671 unique intensity data were collected on a four-circle diffractometer with Ni-filtered Cu $K\alpha$ radiation. The structure was elucidated by the Monte Carlo direct method, using the 50 strongest reflections as the starting set. The block-diagonal least-squares refinement reduced the R value to 0.038. The structure obtained corresponds to 14-deoxygrayanotoxin VII. The two independent molecules exist in different conformations: one has a half-chair A-ring, and the other, an envelope A-ring. In both molecules, the B-ring takes a conformation intermediate between the chair and twist-chair forms, and the C-ring adopts a boat conformation. The crystal consists of infinite hydrogen-bonded molecular chains along the c axis.

A number of diterpenoids, such as grayanotoxins,[1,2] leucothols,[3] and grayathols,[4] have thus far been isolated from *Leucothoe grayana Max.* In this paper, we wish to report on the X-ray structure determination and molecular geometry of grayanotoxin (hereafter G) XIX, a new minor constituent from the same plant.

Experimental

Isolation of G XIX. Grayathol A was crystallized from a diethyl ether solution of the unknown-compound-containing fraction (81 mg)[5] obtained from the crude extract of *Leucothoe grayana Max.* The chromatography of the filtrate on silica gel (1 g) afforded G XIX (21 mg) in a 5×10^{-7} % yield from dried leaves; mp 132—133 °C (recrystallized from diethyl ether), $[\alpha]_D$ −12° (*c* 1, MeOH); IR (Nujol) 3496, 3370^{sh}, 1658, 1637 cm^{-1}; ^{1}H-NMR ($CDCl_3$) 1.05, 1.29 (each 3H, s), 1.69 (3H, d, $J=2$ Hz), 3.00 (1H, q, $J_{AX+BX}=8+11$ Hz), 3.60 (1H, q, $J_{AX+BX}=2+7$ Hz), 3.73 (1H, q, $J_{AX+BX}=4+11$ Hz), 4.91, 5.04 (each 1H, s), 5.18 (1H, bs); MS *m/e* 318 (M^+). Found: C, 74.91; H, 9.37%. Calcd for $C_{20}H_{30}O_3$: C, 75.43; H, 9.50%. The ^{1}H-NMR spectrum was recorded on a Hitachi R-20B spectrometer, using TMS as the internal reference. The chemical shifts are given on the δ scale (s=singlet, d=doublet, q=quartet, bs=broad singlet). The IR spectrum was obtained on a JASCO Model IR-S spectrophotometer.

X-Ray Measurement. A colorless single crystal cut into a cube with an edge of about 0.3 mm was used. The crystal data are summarized in Table 1. The cell dimensions and reflection intensities were measured on a Rigaku four-circle diffractometer with Ni-filtered Cu $K\alpha$ radiation (40 kV, 60 mA, $\lambda=1.5418$ Å). The θ-2θ continuous-scan technique was applied at a θ scan rate of 8° min^{-1}; the background was measured for 5 s at each end of the scan range. Three standard reflections, measured at intervals of every 60 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 125°, 2671 unique structure factor amplitudes above the $\sigma(F)$ level were selected for the structure determination.

Table 1. The crystal data

$C_{20}H_{30}O_3$	M.W.=318.46
Crystal system	Triclinic
Space group	P1
Cell dimensions	$a=10.406(2)$ Å
	$b=10.648(2)$ Å
	$c=8.003(2)$ Å
	$\alpha=90.00(7)°$
	$\beta=94.25(3)°$
	$\gamma=102.76(2)°$
V	862.4 Å^3
Z	2
D_x	1.226 g cm^{-3}
μ(Cu $K\alpha$)	5.99 cm^{-1}

Structure Determination

The structure was elucidated by the Monte Carlo direct method,[6] using the 50 strongest reflections as the starting set. In order to extend the tentative phase set derived from successively-generated random numbers, 10 cycles of the tangent procedure were performed by the use of 556 $|E|$ values above 1.30. Since the 208th phase set gave a low R_K value of 0.296 ($R_K=\sum||E_o|-k|E_c||/\sum|E_o|$) and a moderate q value of 0.424 ($q=\sum_h|E_h|(|\sum_k|E_kE_{h-k}|\exp\{2\pi i(\phi_k+\phi_{h-k})\}|/\sum_k|E_kE_{h-k}|)/\sum_h|E_h|$), 6 additional cycles of the tangent procedure were carried out using 604 $|E|$ values above 1.25; the R_k and q values were 0.299 and 0.356 respectively. An E-map based on 560 phases afforded all the 46 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 57 of the 60 independent hydrogen atoms had been located in a difference Fourier map, further least-squares refinement including these hydrogen atoms with isotropic temperature factors was carried out. The weighting scheme used was as follows: $w=1/\{\sigma(F)^2\exp(AX^2+BY^2+CXY+DX+EY)\}$, where $X=|F_o|$ and $Y=\sin\theta/\lambda$. The A, B, C, D, and E coefficients are constants which were determined from the $(\Delta F)^2$ values. In this manner, the R value reached 0.038. The final atomic parameters are listed in Table 2. The table of

TABLE 2. THE FINAL ATOMIC PARAMETERS AND ESTIMATED STANDARD DEVIATIONS

The coordinates of the non-hydrogen and hydrogen atoms are multiplied by 10^4 and 10^3 respectively.

(1) The non-hydrogen atoms.

Atom	x	y	z	B_{eq}[a)]/Å^2	Atom	x	y	z	B_{eq}/Å^2
O(A1)	6513(3)	8506(3)	4043(3)	5.38	O(B1)	312(2)	−1847(2)	−1978(3)	3.64
O(A2)	7452(2)	7991(2)	7370(3)	3.44	O(B2)	−969(2)	−1332(2)	1468(3)	3.24
O(A3)	6259(3)	8460(2)	10241(3)	3.61	O(B3)	222(3)	−1821(2)	4400(3)	4.19
C(A1)	5728(3)	6037(3)	6592(3)	2.41	C(B1)	518(3)	675(3)	1025(3)	2.47
C(A2)	5412(4)	6322(3)	4732(4)	3.59	C(B2)	563(4)	326(3)	− 825(4)	3.56
C(A3)	5323(3)	7732(3)	4631(4)	3.24	C(B3)	1121(3)	− 894(3)	− 887(4)	3.02
C(A4)	5177(4)	8142(3)	6454(4)	3.59	C(B4)	1321(3)	−1307(3)	973(4)	3.14
C(A5)	6092(3)	7378(3)	7489(4)	2.64	C(B5)	360(3)	− 648(3)	1895(4)	2.63
C(A6)	5905(3)	7235(3)	9367(4)	2.79	C(B6)	590(3)	− 526(3)	3808(4)	2.81
C(A7)	6672(3)	6310(3)	10232(4)	2.91	C(B7)	−187(3)	329(3)	4618(4)	2.80
C(A8)	6083(3)	4854(3)	10021(4)	2.56	C(B8)	335(3)	1793(3)	4529(3)	2.40
C(A9)	6442(3)	4263(3)	8378(4)	2.75	C(B9)	−180(3)	2370(3)	2876(4)	2.52
C(A10)	6708(3)	5194(3)	6949(4)	2.73	C(B10)	−498(3)	1452(3)	1381(3)	2.41
C(A11)	5362(4)	3074(3)	7769(4)	3.55	C(B11)	828(4)	3606(3)	2369(4)	3.33
C(A12)	4627(4)	2228(3)	9106(4)	3.78	C(B12)	1598(4)	4469(3)	3800(4)	3.69
C(A13)	4465(3)	3025(3)	10674(4)	3.18	C(B13)	1932(3)	3686(3)	5342(4)	3.03
C(A14)	4587(3)	4434(3)	10200(4)	2.80	C(B14)	1847(3)	2281(3)	4834(4)	2.84
C(A15)	6583(3)	4129(3)	11475(4)	3.00	C(B15)	− 104(3)	2491(3)	5980(4)	2.83
C(A16)	5672(3)	3108(3)	11874(4)	3.19	C(B16)	812(3)	3530(3)	6483(4)	3.01
C(A17)	5777(4)	2110(4)	13161(5)	4.36	C(B17)	785(4)	4493(4)	7821(5)	4.28
C(A18)	5610(6)	9613(4)	6719(5)	6.51	C(B18)	1026(5)	−2776(4)	1121(4)	4.87
C(A19)	3724(4)	7670(5)	6797(5)	5.42	C(B19)	2770(4)	− 749(4)	1584(5)	4.31
C(A20)	7734(4)	5243(4)	6060(5)	4.31	C(B20)	−1595(3)	1400(3)	406(4)	3.44

a) $B_{eq}=8\pi^2\ (u_1^2+u_2^2+u_3^2)/3$, where u_i is the root-mean-square deviation in the i-th principal axis of the thermal ellipsoid.

(2) The hydrogen atoms.

Atom[a)]	x	y	z	B/Å^2	Atom	x	y	z	B/Å^2
H(OA1)	635(5)	847(5)	303(7)	8.8(14)	H(OB3)	33(4)	−185(4)	549(5)	5.5(9)
H(OA2)	753(4)	812(4)	641(5)	4.9(9)	H(B1)	138(4)	115(3)	146(4)	4.2(8)
H(OA3)	717(5)	863(5)	1047(6)	8.1(13)	H(B2a)	104(4)	99(4)	− 124(5)	5.0(9)
H(A1)	492(3)	562(3)	705(3)	2.2(6)	H(B2b)	− 42(4)	6(3)	− 131(4)	4.1(8)
H(A2a)	440(5)	563(4)	439(6)	6.7(11)	H(B3)	198(3)	− 76(3)	− 142(4)	3.3(7)
H(A2b)	613(5)	622(4)	412(6)	6.1(10)	H(B6)	154(3)	− 18(3)	408(4)	3.0(7)
H(A3)	451(3)	782(3)	392(4)	4.0(8)	H(B7a)	− 14(4)	17(3)	581(5)	4.0(8)
H(A6)	484(3)	694(3)	951(4)	3.7(7)	H(B7b)	−114(3)	13(3)	436(4)	3.8(8)
H(A7a)	672(3)	651(3)	1143(4)	3.2(7)	H(B9)	−101(3)	259(3)	310(4)	2.5(6)
H(A7b)	762(3)	649(3)	986(4)	2.8(6)	H(B11a)	148(3)	324(3)	165(4)	3.2(7)
H(A9)	727(3)	403(3)	864(4)	2.8(6)	H(B11b)	29(4)	415(4)	159(5)	4.3(8)
H(A11a)	470(4)	340(3)	710(5)	4.2(8)	H(B12a)	252(5)	491(5)	345(6)	7.5(12)
H(A11b)	578(3)	260(3)	712(4)	4.1(8)	H(B12b)	107(4)	512(4)	420(5)	4.5(9)
H(A12a)	371(4)	181(4)	866(5)	5.4(10)	H(B13)	271(3)	399(3)	582(4)	3.6(7)
H(A12b)	507(4)	153(4)	945(5)	5.1(9)	H(B14a)	230(3)	217(3)	390(4)	3.6(7)
H(A13)	361(4)	261(4)	1126(5)	5.5(9)	H(B14b)	217(3)	177(3)	579(4)	2.6(6)
H(A14a)	403(3)	453(3)	920(4)	3.5(7)	H(B15)	−100(4)	213(4)	644(5)	4.5(8)
H(A14b)	435(3)	497(3)	1111(4)	3.2(7)	H(B17a)	3(4)	420(4)	852(5)	4.7(9)
H(A15)	759(4)	430(4)	1194(5)	4.7(9)	H(B17b)	89(5)	542(5)	733(7)	9.5(15)
H(A17a)	667(4)	227(4)	1376(5)	5.6(10)	H(B17c)	156(4)	455(4)	861(5)	6.1(10)
H(A17b)	577(4)	128(4)	1261(6)	6.7(11)	H(B18a)	116(4)	−302(4)	225(5)	5.4(9)
H(A17c)	519(5)	212(5)	1402(6)	8.2(13)	H(B18b)	164(5)	−313(5)	39(6)	7.0(12)
H(A19a)	311(5)	808(4)	603(6)	6.8(11)	H(B18c)	7(4)	−320(4)	73(5)	5.3(9)
H(A19b)	338(4)	782(4)	787(6)	6.6(11)	H(B19a)	339(5)	−115(4)	92(6)	7.0(12)
H(A19c)	344(5)	679(5)	653(6)	8.4(13)	H(B19b)	298(4)	−105(4)	280(5)	6.3(11)
H(A20a)	832(4)	475(4)	630(5)	5.9(10)	H(B19c)	311(5)	24(5)	153(7)	8.1(13)
H(A20b)	796(4)	585(4)	509(5)	5.0(9)	H(B20a)	−226(4)	197(4)	65(5)	4.7(8)
H(OB1)	− 48(5)	−200(5)	−165(6)	7.1(12)	H(B20b)	−179(3)	93(3)	−73(4)	3.7(7)
H(OB2)	−109(3)	−192(4)	221(4)	4.2(8)					

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

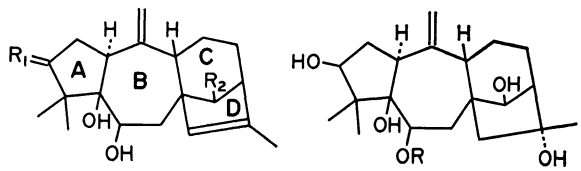
the anisotropic thermal parameters and that of the observed and calculated structure factors are kept at the Chemical Society of Japan (Document No. 8128).

The calculations were performed on an ACOS 700 computer at the Institute for Protein Research, Osaka University, and on a FACOM 230-75 computer at the Hokkaido University Computing Center. The atomic scattering factors were taken from the International Tables.[7]

Results and Discussion

Molecular Structure. The skeletons of the two independent G XIX molecules, **A** and **B**, are illustrated in Fig. 1. The bond distances and angles and the torsion angles are given in Table 3 and Fig. 2 respectively. From these results, it is concluded that G XIX has the **1** structure.

The five-membered A-ring in the **A** molecule takes a half-chair form with an approximate two-fold rotation axis through the C(A2) atom, while that in the **B**



1 (GXIX): $R_1 = <^{OH}_{H}$ $R_2 = H$ 3 (GII): R = H

2 (GXVIII): $R_1 = O$ $R_2 = OH$ 4 (GXVI): R = Ac

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.

(1) The bond distances.

	Mol. A	Mol. B		Mol. A	Mol. B
C(1)–C(2)	1.545(4)	1.533(4)	C(7)–C(8)	1.540(4)	1.537(4)
C(1)–C(5)	1.555(4)	1.552(4)	C(8)–C(9)	1.562(4)	1.567(4)
C(1)–C(10)	1.512(5)	1.521(5)	C(8)–C(14)	1.539(4)	1.545(4)
C(2)–C(3)	1.527(5)	1.538(5)	C(8)–C(15)	1.519(4)	1.529(4)
C(3)–C(4)	1.551(5)	1.565(4)	C(9)–C(10)	1.515(4)	1.515(4)
C(3)–O(1)	1.439(4)	1.419(4)	C(9)–C(11)	1.547(4)	1.564(4)
C(4)–C(5)	1.575(5)	1.567(5)	C(10)–C(20)	1.318(5)	1.324(4)
C(4)–C(18)	1.541(5)	1.532(5)	C(11)–C(12)	1.535(5)	1.528(4)
C(4)–C(19)	1.529(6)	1.536(5)	C(12)–C(13)	1.555(5)	1.550(5)
C(5)–C(6)	1.534(4)	1.533(4)	C(13)–C(14)	1.528(5)	1.532(5)
C(5)–O(2)	1.432(4)	1.430(4)	C(13)–C(16)	1.510(5)	1.514(5)
C(6)–C(7)	1.533(5)	1.519(5)	C(15)–C(16)	1.331(4)	1.331(4)
C(6)–O(3)	1.440(4)	1.437(4)	C(16)–C(17)	1.496(5)	1.489(5)

(2) The bond angles.

	Mol. A	Mol. B		Mol. A	Mol. B
C(2)–C(1)–C(5)	105.0(2)	103.0(2)	C(7)–C(8)–C(9)	113.4(2)	112.5(2)
C(2)–C(1)–C(10)	116.6(3)	115.1(3)	C(7)–C(8)–C(14)	115.4(3)	116.0(3)
C(5)–C(1)–C(10)	115.2(2)	116.0(2)	C(7)–C(8)–C(15)	110.4(2)	111.1(2)
C(1)–C(2)–C(3)	107.5(3)	107.5(3)	C(9)–C(8)–C(14)	110.0(2)	110.2(2)
C(2)–C(3)–C(4)	105.2(3)	106.2(3)	C(9)–C(8)–C(15)	107.0(3)	106.6(3)
C(2)–C(3)–O(1)	110.6(3)	111.4(3)	C(14)–C(8)–C(15)	99.4(2)	99.3(2)
C(4)–C(3)–O(1)	109.5(3)	115.5(2)	C(8)–C(9)–C(10)	115.0(3)	115.1(3)
C(3)–C(4)–C(5)	101.7(3)	103.0(3)	C(8)–C(9)–C(11)	111.1(3)	111.1(2)
C(3)–C(4)–C(18)	111.8(3)	111.4(3)	C(10)–C(9)–C(11)	109.2(2)	108.3(2)
C(3)–C(4)–C(19)	107.3(3)	107.6(3)	C(1)–C(10)–C(9)	116.5(3)	117.2(2)
C(5)–C(4)–C(18)	113.4(3)	114.0(3)	C(1)–C(10)–C(20)	122.5(3)	123.0(3)
C(5)–C(4)–C(19)	111.8(3)	111.4(3)	C(9)–C(10)–C(20)	121.0(3)	119.7(3)
C(18)–C(4)–C(19)	110.4(4)	109.3(3)	C(9)–C(11)–C(12)	117.6(3)	116.7(3)
C(1)–C(5)–C(4)	102.1(2)	102.8(2)	C(11)–C(12)–C(13)	112.2(3)	112.3(3)
C(1)–C(5)–C(6)	110.4(2)	113.0(2)	C(12)–C(13)–C(14)	109.4(3)	110.5(3)
C(1)–C(5)–O(2)	111.8(3)	106.4(2)	C(12)–C(13)–C(16)	108.2(3)	108.4(3)
C(4)–C(5)–C(6)	116.8(3)	116.5(3)	C(14)–C(13)–C(16)	101.6(2)	100.9(2)
C(4)–C(5)–O(2)	110.1(2)	108.8(2)	C(8)–C(14)–C(13)	100.8(3)	100.6(3)
C(6)–C(5)–O(2)	105.9(2)	108.8(2)	C(8)–C(15)–C(16)	111.8(3)	111.4(3)
C(5)–C(6)–C(7)	113.6(3)	114.7(3)	C(13)–C(16)–C(15)	108.1(3)	108.4(3)
C(5)–C(6)–O(3)	111.7(2)	105.1(2)	C(13)–C(16)–C(17)	122.7(3)	122.1(3)
C(7)–C(6)–O(3)	108.9(2)	110.4(3)	C(15)–C(16)–C(17)	129.0(3)	129.3(3)
C(6)–C(7)–C(8)	117.8(2)	117.4(3)			

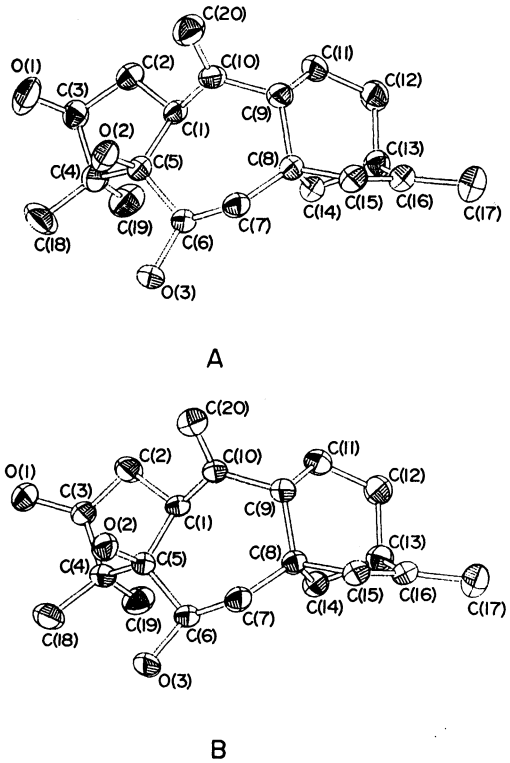


Fig. 1. Perspective views of the A and B molecules. Each non-hydrogen atom is represented as a thermal ellipsoid enclosing a 50% probability.

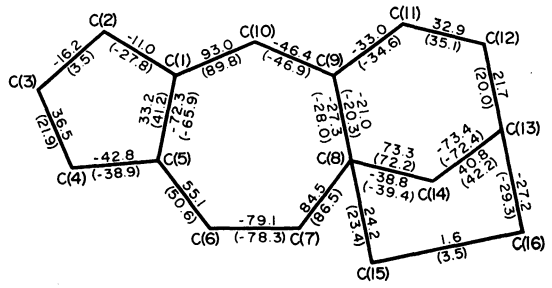


Fig. 2. The torsion angles (ϕ/°) of the A-, B-, C-, and D-rings. Only the torsion angles relevant to atoms which form the same ring are given in the ring. The values for the B molecule are given in parentheses.

molecule has an envelope form with an approximate mirror plane through the C(B5) atom. Although the former conformation permits the formation of the intramolecular hydrogen bond, O(2)–H···O(1) (see Table 4), the latter is unfavorable for this hydrogen bonding, the O(B1)···O(B2) distance being 3.248(3) Å. Consequently, the O(B2)H hydroxyl group forms a considerably bent hydrogen bond with the O(B3) atom of the same molecule; the O(B2)–H···O(B3) angle is 121°. Since, in the G XVIII (**2**) molecule[8] having almost the same ring conformation as the **B** molecule, the O(2)H hydroxyl group donates its proton to the exocyclic double bond, C(10)=C(20), the present O(B2)–H···O(B3) interaction will be nearly as weak as the O–H···π hydrogen bonding.[9] The O(1)–C(3)–C(4)–C(18) torsion angles in the **A** and **B** molecules are 38.9 and 20.4° respectively; the resulting difference in torsional strain results in a difference of 6.0° between the O(1)–C(3)–C(4) bond angles in the two molecules.

As is found also in other grayanotoxins, **2**—**4**,[8,10,11] the C(4)–C(5) bonds in the **A** and **B** molecules are somewhat lengthened. This bond lengthening is probably due to the steric repulsions between the C(18)H_3 and O(2)H groups and between the C(19)H_3 and C(6)H groups: C(A18)···O(A2), 2.871(7); C(A19)···C(A6), 3.061(6); C(B18)···O(B2), 2.872(6); C(B19)···C(B6), 3.034(5) Å. These steric repulsions further result in a distortion of the C(4)–C(18) and C(4)–C(19) bonds; the C(5)–C(4)–C(18) and C(5)–C(4)–C(19) bond angles are larger than the C(3)–C(4)–C(18) and C(3)–C(4)–C(19) bond angles by 1.6 and 4.5° respectively for the **A** molecule, and by 2.6 and 3.8° respectively for the **B** molecule.

In both molecules, the seven-membered B-rings adopt conformations intermediate between the chair form

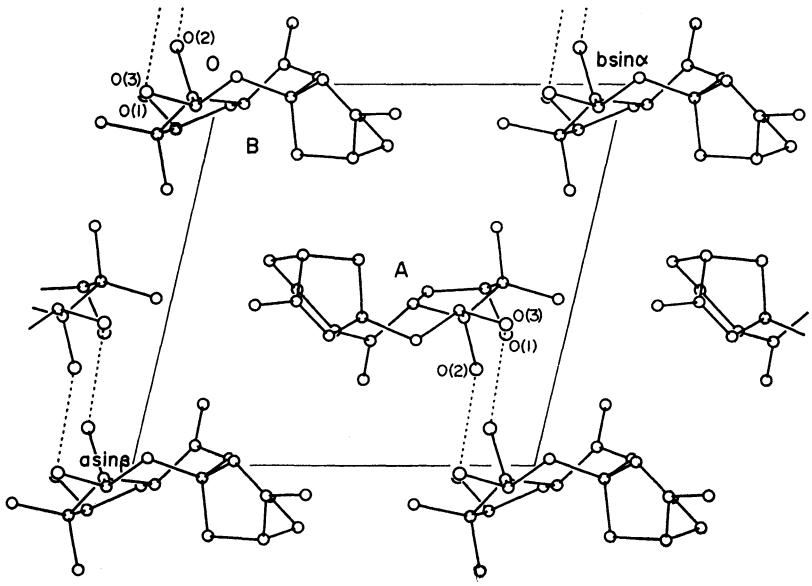


Fig. 3. The crystal structure viewed along the c axis.

characterized by the mirror plane through the C(5) atom and the twist-chair form characterized by the two-fold rotation axis through the C(9) atom. The corresponding torsion angles of these two B-rings are in good agreement with each other except for the three bonds associated with the A-ring atoms. If the present B-rings are considered to be of the chair form, the interaction between axial groups at the C(7) and C(10) atoms corresponds to the severe 3a-3'a repulsion in the chair cycloheptane.[12] However, since the C(10) atom forms a double bond with the C(20), the conformations of these B-rings are free from the 3a-3'a repulsion; hence, they are probably more stable than the B-ring conformations in G II[10] and XVI.[11]

The six-membered C-rings in both **A** and **B** molecules take boat conformations similar to that of the C-ring in G XVIII.[8] On the other hand, it has been found that, in all of the G I,[13] II, and XVI molecules where the C(15)–C(16) bond is a single bond, the C-rings possess the chair conformation. These facts suggest that the C-ring conformation depends largely on the nature of the C(15)–C(16) bond. Force-field calculations[14] for 6-methylbicyclo[3.2.1]octane and 6-methylbicyclo[3.2.1]oct-6-ene showed that, if the influence of the B-ring is neglected, the transformation of the C(15)–C(16) single bond into the double bond can reduce the chair-boat enthalpy difference of the C-ring by 1.8 kcal/mol, but that it cannot reverse the relative stabilities of the two C-ring conformations.[8] Accordingly, in order fully to understand the conformational behavior of the C-ring, the force-field calculations including the B-ring are now in progress.

Table 4. The hydrogen bonds, X–H···Y

	X	Y	X···Y l/Å	H···Y l/Å	X–H···Y ϕ/°
(1)	Intramolecular				
	O(A2)	O(A1)	2.863(4)	2.19(4)	145(4)
	O(B2)	O(B3)	2.676(3)	2.13(3)	121(3)
(2)	Intermolecular				
	O(A1)	O(A3)[a)]	3.034(3)	2.23(6)	171(5)
	O(A3)	O(B2)[b)]	2.938(4)	2.03(5)	165(5)
	O(B1)	O(A2)[c)]	2.950(3)	2.24(5)	140(4)
	O(B3)	O(B1)[d)]	2.894(3)	2.03(4)	171(4)

The symmetry codes are as follows: a) $x, y, -1+z$; b) $1+x, 1+y, 1+z$; c) $-1+x, -1+y, -1+z$; d) $x, y, 1+z$.

Crystal Structure. The crystal structure viewed along the c axis is shown in Fig. 3. The details of hydrogen bonding are given in Table 4. The **A** and **B** molecules are connected by the O(A3)–H···O(B2) and O(B1)–H···O(A2) hydrogen bonds, forming a dimer. These hydrogen-bonded dimers are further held together by the intermolecular hydrogen bonds, O(A1)–H···O(A3) and O(B3)–H···O(B1), to form a double molecular chain. The present crystal consists of such infinite hydrogen-bonded molecular chains along the c axis.

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