Molecular Structure of 3,4,6-Tri-*O*-acetyl-1,2-*O*-[(1*S*)-1-(2-*p*-bromophenyl)-9*H*-imidazo[1,2-*a*]benzimidazol-3-yl]ethylidene]-α-D-glucopyranose Acetone Solvate

Hiroaki TAKAYANAGI, Haruo OGURA,* Nobuyasu TSUZUNO, Isao KUBOTA, and Yoichi IITAKA†

School of Pharmaceutical Sciences, Kitasato University, Shirokane, Minato-ku, Tokyo 108

† *Faculty of Pharmaceutical Sciences, University of Tokyo, Hongo, Bunkyo-ku, Tokyo*

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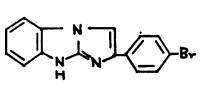
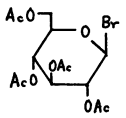
Synopsis. The structure of a product from a reaction mixture of 2-(*p*-bromophenyl)-9*H*-imidazo[1,2-*a*]benzimidazole and 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl bromide in the presence of NaI, hexamethyldisilazane, and $(NH_4)_2SO_4$ has been established as 3,4,6-tri-*O*-acetyl-1,2-*O*-[(1*S*)-1-[2-(*p*-bromophenyl)-9*H*-imidazo[1,2-*a*]benzimidazol-3-yl]ethylidene]-α-D-glucopyranose by means of X-ray crystal structure analysis.

In a series of synthesizing nucleoside analogs[1], we carried out the reaction of 2-(*p*-bromophenyl)-9*H*-imidazo[1,2-*a*]benzimidazole (**1**) and 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl bromide (**2**).[2] From the reaction mixture, three compounds were separated, two of them were identified by means of NMR, IR, and UV, but the rest was not. In this paper, we describe the molecular structure of the compound(**3**) determined by X-ray analysis.



(1)



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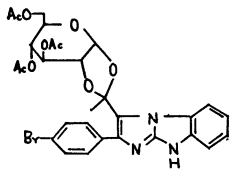

(3)

Experimental

A specimen of **3** with the approximate dimensions of 0.3×0.3×0.3 mm³ was used for the intensity measurements. The density was determined by the flotation methods in a mixture of petroleum ether and carbon tetrachloride. The cell constants were determined by the least-squares procedure from the 2θ values of 24 reflections measured on a diffractometer using monochromated Cu *Kα* radiation. Three dimensional intensity data were collected on a Fillips automatic four-circle diffractometer with graphite monochromated Cu *Kα* radiation. Background was counted for 5 s at both sides of each peak. Three standard reflections were measured every 100 reflections during the course of collection. A total of 4604 independent reflections were collected. Reflections having an intensity exceeding the corresponding standard deviations by a factor of three were treated as observed. 4201 reflections were retained and corrected for Lorentz and polarization factors but not for absorption factor. The crystal of compound **3** belongs to the triclinic, space group P1, and $Z=2$. $a=9.485(2)$, $b=20.080(2)$, $c=9.708(1)$ Å, $\alpha=100.31(2)$, $\beta=109.60(1)$, $\gamma=92.45(2)°$.

Determination and Refinement of the Structure. The structure was determined by the heavy atom method. All the non-hydrogen atoms in the asymmetric unit were obtained from the Fourier map phased by the two bromine atoms. The oxygen and nitrogen atoms were identified by the structural considetations. Refinement of atomic parameters was carried out by the full-matrix least-squares method, the quantity minimized being $\Sigma w(|F_o|-|F_c|)^2$, with $w=1.0$ for all the reflections used. The final ***R*** values was 0.069. The atomic scattering factors for C, O, N were given by Cromer and Mann,[3] and that for H by Stewart *et al.*,[4] and that for Br from International Tables for X-ray Crystallography.[5] The final atomic parameters and equivalent isotropic temperature factors are given in Table 1.†

TABLE 1. ATOMIC COORDINATES (×10⁴) AND THEIR STANDARD DEVIATIONS IN PARENTHESES AND EQIVALENT ISOTROPIC TEMPERATURE FACTORS

Atom	*x*		*y*		*z*		B_{eq}[a]/Å	
	3A	3B	3A	3B	3A	3B	3A	3B
Br(1)	8302(2)	1769(2)	9572(1)	449(1)	-1879(2)	11896(2)	12.9	13.3
C(1)	4459(12)	5692(15)	8977(4)	1025(5)	1843(10)	8273(12)	4.5	5.7
C(2)	3165(11)	6933(16)	8553(4)	1453(6)	1497(9)	8583(13)	5.2	6.5
C(3)	3760(13)	6427(16)	9240(5)	777(6)	3696(10)	6282(15)	5.8	4.5
C(4)	2046(13)	8173(17)	9094(6)	945(6)	4704(11)	5385(13)	7.0	6.9
C(5)	1575(12)	8588(16)	8614(5)	1441(7)	3341(11)	6780(13)	4.2	8.4
C(6)	255(14)	9794(15)	8196(6)	1912(7)	2786(13)	7237(13)	7.0	6.6
C(7)	-618(14)	10727(18)	8200(7)	1872(8)	3680(13)	6330(20)	8.2	6.6
C(8)	-136(17)	10390(17)	8670(8)	1396(7)	5101(14)	5021(15)	9.4	6.4
C(9)	1108(13)	9054(20)	9135(7)	957(7)	5593(12)	4506(16)	6.6	11.3
C(10)	5379(14)	4716(13)	9087(5)	934(5)	887(12)	9071(11)	7.4	4.5
C(11)	6970(14)	3158(15)	9220(6)	810(6)	1549(12)	8363(15)	6.7	8.0
C(12)	7777(12)	2116(19)	9355(7)	660(7)	737(13)	9192(15)	6.1	11.7
C(13)	7054(19)	2921(15)	9352(6)	650(7)	-771(15)	10689(15)	10.6	8.9
C(14)	5532(16)	4506(16)	9208(7)	757(5)	-1481(13)	11414(13)	8.4	5.5
C(15)	4709(13)	5454(17)	9088(5)	911(6)	-624(12)	10642(13)	4.8	8.4
C(16)	732(14)	9117(15)	8188(7)	1767(7)	-690(12)	11062(13)	8.6	8.6
C(17)	2223(13)	7789(14)	8019(6)	2027(5)	211(12)	9872(12)	5.6	6.1
C(18)	3152(12)	6012(16)	6990(5)	2786(6)	822(11)	9860(13)	3.8	9.0
C(19)	4030(12)	6976(16)	7317(5)	2955(6)	-16(11)	8919(15)	5.1	6.1
C(20)	4348(11)	7721(17)	6858(5)	3709(7)	-1222(11)	9332(16)	4.7	7.4
C(21)	3006(13)	8165(17)	6309(6)	4050(7)	-2221(12)	10973(17)	6.9	6.0
C(22)	1789(13)	7518(18)	6264(6)	3687(6)	-1540(13)	11887(14)	4.0	6.3
C(23)	6955(18)	6632(45)	6741(9)	4346(16)	-283(16)	7423(31)	8.2	49.8
C(24)	8130(18)	6063(23)	6282(10)	5031(10)	520(19)	7040(21)	14.1	13.9
C(25)	2797(19)	10685(44)	6385(9)	4662(11)	-4719(16)	11840(51)	9.4	11.6
C(26)	1779(19)	12386(28)	6613(9)	4565(17)	-6139(16)	12575(52)	13.7	7.4
C(27)	770(17)	7435(28)	5579(7)	4178(8)	-2118(16)	13265(19)	4.4	15.7
C(28)	1682(46)	6514(45)	4463(23)	5256(17)	-2656(95)	13463(61)	10.1	12.9
C(29)	2498(36)	5419(27)	3924(12)	5682(12)	-1779(37)	12454(30)	16.4	22.2
C(S1)	7900(27)	3097(36)	7092(14)	2676(19)	5975(22)	2999(31)	18.5	15.4
C(S2)	6597(27)	4320(32)	7417(12)	2654(21)	5038(24)	4406(43)	6.2	48.6
C(S3)	5606(51)	5745(63)	7830(16)	2321(22)	5697(40)	4458(36)	30.7	51.2
O(1)	3090(8)	8262(9)	7785(3)	2581(4)	-718(7)	9448(8)	5.8	4.9
O(2)	1979(9)	6768(10)	7426(4)	2286(4)	820(8)	10581(8)	6.1	6.0
O(3)	2491(9)	6079(11)	6322(3)	3361(4)	77(9)	11017(10)	5.7	7.7
O(4)	5540(8)	6522(12)	6450(4)	4076(5)	-540(8)	8531(12)	5.5	12.2
O(5)	7216(12)	7274(30)	7291(7)	3954(14)	-510(14)	6736(21)	7.1	47.0
O(6)	2207(8)	9797(13)	6525(4)	4052(5)	-3588(8)	11606(13)	6.4	7.9
O(7)	3964(12)	9888(31)	6137(6)	5104(12)	-4519(6)	11256(54)	14.7	10.8
O(8)	1673(17)	6355(18)	5036(5)	4654(6)	-1746(15)	12697(13)	9.8	15.1
O(9)	1122(55)	7363(39)	4366(32)	5463(11)	-4015(90)	14747(29)	27.3	21.8
O(S1)	6263(17)	4182(46)	7360(9)	2914(25)	3648(17)	5583(62)	14.3	14.1
N(1)	4821(11)	5267(11)	9411(4)	612(5)	3246(9)	6780(10)	4.9	5.8
N(2)	2739(10)	7450(11)	8734(4)	1303(4)	2767(9)	7333(9)	5.5	4.7
N(3)	3391(12)	6786(12)	9483(5)	553(5)	4995(9)	5141(10)	5.6	7.2

a) B_{eq} refined according to Hamilton (1959).

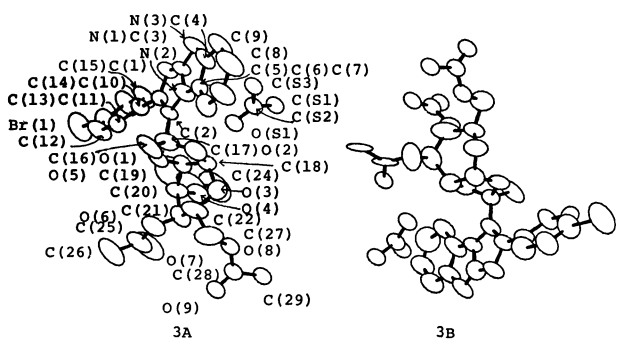

Fig. 1. A view of 3A, 3B, and acetone molecules defining the atom numbering.

† The F_o-F_c data are deposited as Document No. 8350 at the Office of the Editor of the Bull. Chem. Soc. Jpn.

Table 2. Bond lengths and their standard deviations in parentheses

Bond length	l/Å 3A	l/Å 3B	Bond length	l/Å 3A	l/Å 3B
Br(1)-C(13)	1.93(2)	1.93(2)	C(17)-O(2)	1.46(2)	1.43(2)
C(1)-C(2)	1.37(2)	1.34(2)	C(18)-C(19)	1.54(2)	1.56(2)
C(1)-C(10)	1.51(2)	1.42(2)	C(18)-O(2)	1.44(2)	1.41(2)
C(1)-N(1)	1.40(2)	1.45(2)	C(18)-O(3)	1.41(2)	1.44(2)
C(2)-C(17)	1.48(3)	1.51(3)	C(19)-C(20)	1.48(2)	1.57(2)
C(2)-N(2)	1.41(2)	1.44(2)	C(19)-O(1)	1.43(2)	1.45(2)
C(3)-N(1)	1.28(2)	1.39(2)	C(20)-C(21)	1.56(3)	1.52(3)
C(3)-N(2)	1.34(2)	1.40(3)	C(20)-O(4)	1.47(2)	1.46(2)
C(3)-N(3)	1.43(2)	1.28(2)	C(21)-C(22)	1.52(2)	1.50(3)
C(4)-C(5)	1.41(2)	1.45(3)	C(21)-O(6)	1.44(2)	1.46(2)
C(4)-C(9)	1.43(2)	1.38(3)	C(22)-C(27)	1.55(3)	1.54(3)
C(4)-N(3)	1.38(2)	1.43(2)	C(22)-O(3)	1.47(2)	1.40(2)
C(5)-C(6)	1.36(2)	1.35(3)	C(23)-C(24)	1.57(3)	1.56(4)
C(5)-N(2)	1.42(2)	1.40(2)	C(23)-O(4)	1.36(2)	1.32(4)
C(6)-C(7)	1.39(2)	1.44(3)	C(23)-O(5)	1.20(2)	1.25(5)
C(7)-C(8)	1.44(3)	1.38(3)	C(25)-C(26)	1.55(3)	1.57(5)
C(8)-C(9)	1.36(3)	1.40(3)	C(25)-O(6)	1.38(2)	1.39(4)
C(10)-C(11)	1.42(2)	1.39(2)	C(25)-O(7)	1.20(2)	1.28(5)
C(10)-C(15)	1.39(2)	1.46(2)	C(27)-O(8)	1.44(2)	1.47(3)
C(11)-C(12)	1.32(2)	1.52(3)	C(28)-C(29)	1.57(7)	1.57(5)
C(12)-C(13)	1.39(2)	1.40(2)	C(28)-O(8)	1.32(6)	1.27(4)
C(13)-C(14)	1.37(2)	1.42(2)	C(28)-O(9)	1.22(12)	1.22(5)
C(14)-C(15)	1.36(2)	1.41(2)	C(S1)-C(S2)	1.52(4)	1.48(4)
C(16)-C(17)	1.48(2)	1.58(2)	C(S2)-C(S3)	1.50(6)	1.52(7)
C(17)-O(1)	1.45(2)	1.36(2)	C(S2)-O(S1)	1.26(3)	1.22(7)

Table 3. Bond angles and their standard deviations in parentheses

Bond angle	ϕ/° 3A	ϕ/° 3B	Bond angle	ϕ/° 3A	ϕ/° 3B
C(2)-C(1)-C(10)	129.6(8)	132.8(1)	O(2)-C(18)-O(3)	109.3(8)	106.8(9)
C(2)-C(1)-N(1)	111.5(10)	110.7(12)	C(18)-C(19)-C(20)	117.0(8)	115.2(11)
C(10)-C(1)-N(1)	118.5(8)	116.4(10)	C(18)-C(19)-O(1)	105.4(9)	101.9(10)
C(1)-C(2)-C(17)	136.4(11)	134.0(14)	C(20)-C(19)-O(1)	106.0(8)	102.6(10)
C(1)-C(2)-N(2)	103.4(7)	107.5(9)	C(19)-C(20)-C(21)	114.0(10)	115.1(13)
C(17)-C(2)-N(2)	120.2(10)	118.5(12)	C(19)-C(20)-O(4)	118.5(8)	103.9(10)
N(1)-C(3)-N(2)	115.4(9)	110.2(11)	C(21)-C(20)-O(4)	103.3(8)	105.4(12)
N(1)-C(3)-N(3)	133.9(9)	135.5(10)	C(20)-C(21)-C(22)	112.0(9)	115.6(11)
N(2)-C(3)-N(3)	110.8(11)	114.3(13)	C(20)-C(21)-O(6)	109.7(9)	105.6(13)
C(5)-C(4)-C(9)	118.3(10)	118.6(13)	C(22)-C(21)-O(6)	101.6(9)	106.3(12)
C(5)-C(4)-N(3)	113.8(11)	109.5(13)	C(21)-C(22)-C(27)	113.9(11)	111.7(12)
C(9)-C(4)-N(3)	127.9(9)	131.8(10)	C(21)-C(22)-O(3)	109.4(9)	110.4(10)
C(4)-C(5)-C(6)	124.4(12)	122.2(15)	C(27)-C(22)-O(3)	105.6(11)	109.4(15)
C(4)-C(5)-N(2)	102.4(8)	103.4(11)	C(24)-C(23)-O(4)	108.9(14)	126.2(33)
C(6)-C(5)-N(2)	133.1(10)	134.4(12)	C(24)-C(23)-O(5)	127.0(14)	126.2(25)
C(5)-C(6)-C(7)	117.7(10)	116.9(12)	O(4)-C(23)-O(5)	123.7(15)	107.7(27)
C(6)-C(7)-C(8)	118.8(12)	122.4(14)	C(26)-C(25)-O(6)	110.3(14)	109.6(23)
C(7)-C(8)-C(9)	123.4(15)	119.2(17)	C(26)-C(25)-O(7)	128.8(16)	139.0(33)
C(4)-C(9)-C(8)	116.8(11)	120.3(12)	O(6)-C(25)-O(7)	120.9(13)	110.9(29)
C(1)-C(10)-C(11)	119.6(9)	121.8(11)	C(22)-C(27)-O(8)	109.3(11)	106.6(12)
C(1)-C(10)-C(15)	121.8(11)	115.6(11)	C(29)-C(28)-O(8)	111.8(57)	107.6(32)
C(11)-C(10)-C(15)	118.6(12)	122.3(13)	C(29)-C(28)-O(9)	124.1(51)	126.3(30)
C(10)-C(11)-C(12)	119.9(10)	122.0(12)	O(8)-C(28)-O(9)	124.0(54)	126.2(36)
C(11)-C(12)-C(13)	119.3(11)	111.7(13)	C(S1)-C(S2)-C(S3)	122.6(23)	123.1(33)
Br(1)-C(13)-C(12)	117.0(11)	117.1(11)	C(S1)-C(S2)-O(S1)	122.5(23)	118.4(36)
Br(1)-C(13)-C(14)	119.5(11)	115.9(10)	C(S3)-C(S2)-O(S1)	114.9(23)	118.5(33)
C(12)-C(13)-C(14)	123.4(16)	127.0(15)	C(17)-O(1)-C(19)	106.9(8)	107.9(10)
C(13)-C(14)-C(15)	116.7(12)	120.7(11)	C(17)-O(2)-C(18)	109.5(9)	109.5(10)
C(10)-C(15)-C(14)	122.0(11)	116.3(12)	C(18)-O(3)-C(22)	112.3(8)	116.0(11)
C(2)-C(17)-C(16)	116.9(10)	111.1(9)	C(20)-O(4)-C(23)	113.4(10)	120.4(21)
C(2)-C(17)-O(1)	109.4(9)	113.8(10)	C(21)-O(6)-C(25)	116.2(10)	117.5(17)
C(2)-C(17)-O(2)	106.5(9)	108.0(10)	C(27)-O(8)-C(28)	126.9(30)	119.2(21)
C(16)-C(17)-O(1)	111.3(9)	112.1(10)	C(1)-N(1)-C(3)	103.4(8)	104.7(9)
C(16)-C(17)-O(2)	108.1(10)	108.2(9)	C(2)-N(2)-C(3)	106.3(9)	106.6(11)
O(1)-C(17)-O(2)	103.7(8)	103.0(9)	C(2)-N(2)-C(5)	143.0(7)	145.7(9)
C(19)-C(18)-O(2)	103.6(8)	103.1(11)	C(3)-N(2)-C(5)	110.4(9)	107.5(10)
C(19)-C(18)-O(3)	112.3(9)	111.6(10)	C(3)-N(3)-C(4)	102.6(8)	105.3(10)

Results and Discussion

The molecular framework is shown in Fig. 1. It is concluded that the product from the reaction **1** and **2**, has the structure **3**.

The asymmetric carbon C(17) is specified as (S), and it is thought that the reaction proceeded stereospecific. In the crystal, **3** was found to be a (1:1) mixture of rotational isomers (**3A** and **3B**), and torsional angles

Table 4. Dihedral angles between the planes

Dihedral	θ/° 3A	θ/° 3B
Benzene plane[C(4)-C(5)-C(6)-C(7)-C(8)-C(9)] and imidazole plane[C(3)-N(3)-C(4)-C(5)-N(2)]	0.6	1.6
Benzene plane[C(4)-C(5)-C(6)-C(7)-C(8)-C(9)] and imidazole plane[C(1)-C(2)-N(2)-C(3)-N(1)]	3.3	5.3
Two imidazole planes[C(3)-N(3)-C(4)-C(5)-N(2)] and [C(1)-C(2)-N(2)-C(3)-N(1)]	3.3	4.7
Benzene plane[C(10)-C(11)-C(12)-C(13)-C(14)-C(15)] and imidazole plane[C(1)-C(2)-N(2)-C(3)-N(1)]	41.8	42.7

of C(1)–C(2)–C(17)–O(1) are 18.5° (for 3A) and −41.8° (for 3B) and N(2)–C(2)–C(17)–O(2) are −51.5° (for 3A) and 26.6° (for 3B), respectively.

In the heterocyclic moiety, one benzene ring and two imidazole rings are almost planar each other in the range of 0.6—5.3°, but the dihedral angles between the *p*-bromophenyl group and imidazole ring [C(1)–C(2)–N(2)–C(3)–N(1)] are 41.8° (for **3A**) and 42.7° (for **3B**) respectively.

The bond distances and angles are given in Table 2 and 3, respectively.

Two acetone molecules are found in an unit cell.

A view of **3A**, **3B** and acetone molecules defining the atom numbering is given in Fig. 1.

On the difference map, 8 peaks corresponding to two acetone molecules and the peaks corresponding to three acetyl groups showed broad peaks and some of their temperature factors are large. This is, in the case of acetyl group, presumably because of the rotation of acetyl groups around the axis C(20)–O(4)–, C(21)–O(6), and C(27)–O(8) respectively.

References

1) Previous paper (Part XXV): H. Ogura, H. Takahashi, and M. Kobayashi, *Nippon Kagaku Kaishi*, **1982**, 1673.

2) In contribution.

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4) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Phys. Chem.*, **42**, 3175 (1965).

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