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Reaction of Grayanotoxin-II with Lead Tetraacetate[1]

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The 3,6-diacetate (**3**) of grayanotoxin-II (**1**), a diterpene isolated from *Leucothoe grayana*, was treated with lead tetraacetate to afford 1,3,6-triacetyl-1(*R*),6(*R*)-grayanol (**4**.) The structure of **4** was established by spectroscopic means and X-ray analysis of the ethylidene derivative (**5**). Alkaline hydrolysis of **4** gave a ketal (**7**).

Keywords——grayanotoxin-II; diterpene; grayanol; lead tetraacetate; *Leucothoe grayana*; X-ray analysis; ^{13}C-NMR; skeletal rearrangement

Grayanotoxin-II (**1**), one of the toxic diterpenoids isolated from *Leucothoe grayana*, is known to undergo interesting reactions with metallic salts, *e.g.* mercuric acetate,[2] thallium (III) nitrate,[3] and palladium acetate.[4] As a part of our investigation on the reaction of **1** with metallic salts, we investigated the reaction of **1** with lead tetraacetate.

Iwasa and his co-workers reported that **1** reacted with lead tetraacetate to yield a β,γ-unsaturated keto-γ-lactol (**2**).[5] In order to avoid the glycol cleavage, we converted **1** into its 3,6-diacetate (**3**).[6] Treatment of **3** in benzene with lead tetraacetate at room temperature gave colorless crystals **4**, $C_{26}H_{38}O_9$, mp 218.5—220.5°, in 79% yield. The carbon-13 nuclear magnetic resonance spectrum (^{13}C-NMR) of **4** disclosed the presence of the following groups: six methyls, five methylenes, two methines, two quaternary carbons, four methines adjacent to oxygen, one tertiary carbinyl carbon, one triplet olefinic carbon, one singlet olefinic carbon, three acetyl carbonyl carbons, and one carbonyl carbon. On comparing the proton magnetic resonance spectrum (^{1}H-NMR) of **4** with that of the starting material **3** (see Table I), it is evident that **4** has one more acetoxyl group, originating from the reagent. Moreover, the *exo* methylene signals and the signals at the attachment positions of acetoxyl groups were shifted downfield. These data suggest that skeletal rearrangement had occurred in the course of the reaction. In order to determine the structure of **4**, the following reactions were carried out.

Table I. ^{1}H-NMR Data for 3 and 4 in $CDCl_3$ (100 MHz, δ_{ppm}, J shown in Hz)

	3	4
CH_3–	1.04 1.09 1.34	1.02 1.17 1.37
CH_3CO–	2.07 2.09 —	2.00 2.10 2.16
$\rangle$CHOH	4.40 (s, C_{14}–H)	4.40 (s, C_{14}–H)
$\rangle$CHOAc	4.73 (dd, $J=1$, 5) 4.86 (m)	5.31 (dd, $J=5$, 10) 5.60 (m) 5.80 (d, $J=8$)
$CH_2=C\langle$	4.90 (s) 5.08 (s)	5.54 (s) 5.60 (s)

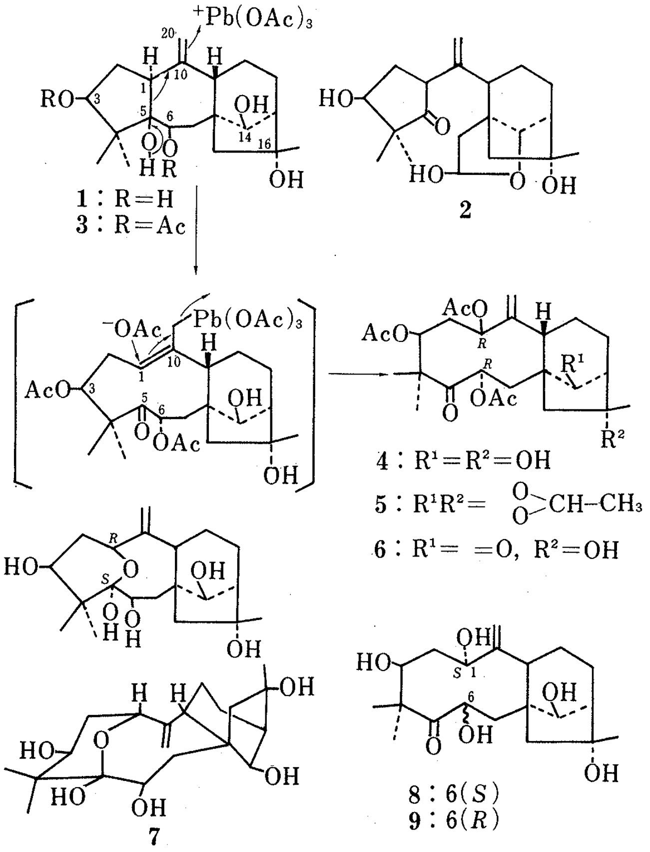

Fig. 1

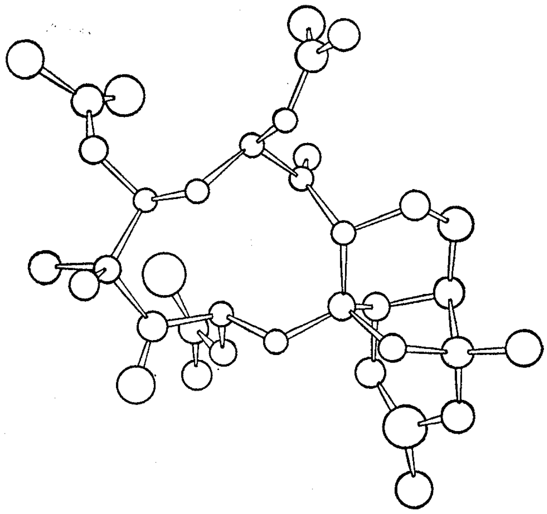

Fig. 2. A Perspective Drawing of the Molecular Structure of **5**

TABLE II. The Atomic Parameters for the Crystal of **5**

x, y and z are the fractional coordinates multiplied by 10^4 and β_{ij}'s are included in the temperature factor T, expressed as follows: $T=\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$ The values of β_{ij} are also multiplied by 10^4. Estimated standard deviations are given in the parentheses and refer to the least significant digits.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C 1	2432(5)	9633(2)	7936(5)	76(4)	16(1)	76(5)	6(2)	−13(4)	−1(2)
C 2	2349(5)	9108(2)	8886(6)	63(4)	17(1)	89(5)	3(2)	4(4)	3(2)
C 3	2430(4)	8466(2)	8272(6)	56(4)	19(1)	96(6)	1(2)	4(4)	−1(2)
C 4	2920(5)	7947(3)	9095(6)	64(4)	21(1)	102(6)	2(2)	12(4)	8(2)
C 5	4179(6)	8039(3)	9272(8)	69(4)	29(2)	127(8)	10(2)	14(5)	19(3)
C 6	4828(5)	8536(2)	8529(6)	55(3)	19(1)	93(5)	3(2)	16(4)	4(2)
C 7	5291(5)	9027(3)	9399(5)	73(4)	21(1)	73(5)	4(2)	5(4)	2(2)
C 8	5495(5)	9685(3)	8883(5)	74(4)	23(1)	62(5)	3(2)	8(4)	−7(2)
C 9	4386(5)	10043(2)	8548(5)	73(4)	19(1)	65(4)	0(2)	8(4)	−4(2)
C 10	3612(5)	9778(2)	7555(5)	83(5)	18(1)	67(5)	3(2)	5(4)	4(2)
C 11	4607(7)	10763(3)	8255(7)	137(8)	19(1)	112(7)	−8(3)	13(7)	1(3)
C 12	5608(7)	10843(4)	7475(9)	123(7)	30(2)	136(8)	−9(4)	6(8)	6(4)
C 13	6614(8)	10452(4)	7810(8)	122(7)	33(2)	112(7)	−20(3)	7(7)	−9(3)
C 14	6326(5)	9735(3)	7785(6)	64(5)	31(2)	89(6)	−7(2)	12(5)	−12(3)
C 15	6096(6)	10097(4)	9889(7)	79(5)	35(2)	92(6)	1(3)	−7(5)	−17(3)
C 16	7005(7)	10477(4)	9199(8)	95(6)	39(2)	134(9)	−13(3)	14(7)	−24(4)
C 17	7213(10)	11146(4)	9715(10)	179(11)	32(2)	184(12)	−30(4)	−3(11)	−30(4)
C 18	2706(8)	7282(3)	8502(10)	152(9)	18(1)	174(10)	6(3)	−25(9)	−9(3)
C 19	2360(7)	7933(4)	10367(7)	90(6)	33(2)	112(7)	3(3)	30(6)	22(3)
C 20	3857(7)	9702(3)	6393(6)	120(7)	27(1)	70(5)	9(3)	8(5)	1(3)
C 21	1424(7)	10616(3)	7822(7)	107(6)	30(2)	88(6)	15(3)	1(6)	10(3)
C 22	964(9)	11159(3)	8505(10)	181(10)	26(2)	167(11)	39(4)	30(10)	12(4)

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C 23	968(8)	8225(4)	6817(8)	116(7)	32(2)	139(9)	−3(3)	−29(7)	−11(4)
C 24	−138(8)	7901(5)	6670(10)	117(7)	46(3)	201(14)	−23(4)	−33(10)	−29(6)
C 25	5643(7)	7879(4)	6968(6)	92(6)	40(2)	88(6)	5(3)	−6(5)	−11(3)
C 26	6664(6)	7555(4)	6528(8)	90(5)	29(2)	129(8)	7(3)	22(6)	−11(4)
C 27	8051(9)	9505(7)	8901(17)	114(9)	74(5)	401(28)	36(6)	−95(15)	−125(10)
C 28	9147(8)	9239(6)	8870(12)	84(6)	72(4)	203(14)	12(4)	1(9)	−54(7)
O 1	1945(4)	10197(2)	8519(4)	93(4)	21(1)	79(4)	19(2)	−12(3)	−4(2)
O 2	1340(7)	10523(3)	6718(6)	222(10)	47(2)	112(6)	52(4)	−44(7)	7(3)
O 3	1281(4)	8258(2)	8003(4)	68(3)	28(1)	106(5)	−3(2)	−10(3)	−9(2)
O 4	1544(7)	8408(5)	6003(6)	194(8)	76(3)	126(7)	−49(5)	−42(7)	−17(4)
O 5	4658(4)	7698(3)	9970(7)	71(4)	60(2)	255(10)	4(2)	−5(6)	88(4)
O 6	5785(3)	8204(2)	7981(4)	59(3)	22(1)	102(4)	5(1)	4(3)	−10(2)
O 7	4726(6)	7833(5)	6521(7)	123(6)	99(4)	171(9)	34(4)	−36(7)	−74(6)
O 8	7305(4)	9363(3)	8003(5)	74(3)	38(1)	125(6)	2(2)	6(4)	−21(2)
O 9	8055(4)	10151(3)	9266(6)	78(4)	48(2)	167(7)	−15(2)	16(5)	−36(3)

Treatment of **4** in acetal with *p*-toluenesulfonic acid yielded a monoethylidene derivative **5**, $C_{28}H_{40}O_9$, mp 235—237°, whose infrared spectrum (IR) showed no hydroxyl group absorption. Jones oxidation of **4** gave a diketo compound **6**, $C_{26}H_{36}O_9$, mp 243—245°. These results reveal that no change in the C and D rings occurred in the course of the reaction of **3** with lead tetraacetate.

Alkaline hydrolysis of **4** yielded colorless crystals **7**, $C_{20}H_{32}O_6$, mp 228—231°, whose IR showed no carbonyl absorption. Its ^{13}C-NMR showed a ketal carbon at δ 102.6 ppm instead of the carbonyl carbon, and other signal patterns were the same as those of **4**, except for those related to acetyl groups.

From the above findings and consideration of the reaction mechanisms of **1** with other metallic salts,[2–4] the formation of **4** can be assumed to occur as follows: initially lead tetraacetate coordinates to the C-10 (20) double bond, followed by cleavage of the A–B ring junction to form a ten-membered ring, and then attack of an acetoxyl anion at C-1. At this stage, however, the configuration of the acetoxyl groups at C-1 and C-6 is obscure, because the former is newly formed and the latter is located adjacent to a carbonyl group.

TABLE III. The Bond Lengths of the Crystal (**5**)

Atom 1	Atom 2	Length (STD)	Atom 1	Atom 2	Length (STD)
C 1	-C 2	1.532(8) Å	C 11	-C 12	1.488(12) Å
C 1	-C 10	1.511(9)	C 12	-C 13	1.512(13)
C 1	-O 1	1.479(7)	C 13	-C 14	1.562(11)
C 2	-C 3	1.524(8)	C 13	-C 16	1.600(13)
C 3	-C 4	1.543(8)	C 14	-O 8	1.437(8)
C 3	-O 3	1.480(7)	C 15	-C 16	1.556(12)
C 4	-C 5	1.538(9)	C 16	-C 17	1.550(13)
C 4	-C 18	1.576(10)	C 16	-O 9	1.441(10)
C 4	-C 19	1.554(10)	C 21	-C 22	1.481(12)
C 5	-C 6	1.547(9)	C 21	-O 1	1.332(9)
C 5	-O 5	1.202(10)	C 21	-O 2	1.235(10)
C 6	-C 7	1.521(8)	C 23	-C 24	1.506(13)
C 6	-O 6	1.478(7)	C 23	-O 3	1.360(10)
C 7	-C 8	1.526(8)	C 23	-O 4	1.196(12)
C 8	-C 9	1.578(8)	C 25	-C 26	1.488(11)
C 8	-C 14	1.571(9)	C 25	-O 6	1.322(9)
C 8	-C 15	1.586(9)	C 25	-O 7	1.211(10)
C 9	-C 10	1.543(8)	C 27	-C 28	1.434(16)
C 9	-C 11	1.584(8)	C 27	-O 8	1.369(17)
C 10	-C 20	1.322(9)	C 27	-O 9	1.428(16)

Grayanol A (**8**) and B (**9**), diterpenes also isolated from *Leucothoe grayana*,[7] have the same carbon skeleton and functional groups as **4**, but the spectral data obtained from **4** or **7** were not coincident with those reported for **8** and **9**. Thus, **4** must be an isomer of these compounds.

To ascertain the structure of **4**, we attempted to undertake an X-ray crystallographic analysis. However, a suitable crystal for the analysis could not be obtained from **4** and **7**, so the ethylidene derivative **5** was used for the experiment. Fig. 2 shows a perspective view of the molecule **5**, from which it is apparent that both C-1 and C-6 have *R* configurations. Consequently, the structure of **4** was determined as 1,3,6-triacetyl-1 (*R*), 6 (*R*)-grayanol, that is, 1,3,6-triacetyl-1-*epi*-grayanol B.

On alkaline hydrolysis of **4**, the C-1 hydroxyl group formed a ketal (**7**) with the C-5 carbonyl group, and the configuration of C-5 was assumed to be *S*, on the basis of a molecular model.[8]

TABLE IV. The Bond Angles of the Crystal (**5**)

Atom 1	Atom 2	Atom 3	Angle (STD)	Atom 1	Atom 2	Atom 3	Angle (STD)
C 2	-C 1	-C 10	113.5(5)°	C 12	-C 11	-C 9	111.2(6)
C 2	-C 1	-O 1	105.5(4)	C 13	-C 12	-C 11	116.4(7)
C 10	-C 1	-O 1	109.1(5)	C 14	-C 13	-C 12	110.6(7)
C 3	-C 2	-C 1	110.1(5)	C 14	-C 13	-C 16	96.5(6)
C 4	-C 3	-C 2	113.7(5)	C 12	-C 13	-C 16	116.8(7)
C 4	-C 3	-O 3	105.1(4)	O 8	-C 14	-C 8	110.8(5)
C 2	-C 3	-O 3	107.2(4)	O 8	-C 14	-C 13	110.6(6)
C 5	-C 4	-C 3	111.0(5)	C 8	-C 14	-C 13	101.2(5)
C 5	-C 4	-C 18	109.1(6)	C 16	-C 15	-C 8	105.3(6)
C 5	-C 4	-C 19	108.3(5)	C 17	-C 16	-C 13	115.3(8)
C 3	-C 4	-C 18	109.5(5)	C 17	-C 16	-C 15	114.2(7)
C 3	-C 4	-C 19	112.2(5)	C 17	-C 16	-O 9	106.2(7)
C 18	-C 4	-C 19	106.6(6)	C 13	-C 16	-C 15	104.1(7)
C 6	-C 5	-C 4	121.1(6)	C 13	-C 16	-O 9	106.9(7)
C 6	-C 5	-O 5	120.4(7)	C 15	-C 16	-O 9	109.9(7)
C 4	-C 5	-O 5	118.4(7)	C 22	-C 21	-O 1	113.7(7)
C 7	-C 6	-C 5	108.6(5)	C 22	-C 21	-O 2	126.4(8)
C 7	-C 6	-O 6	107.4(4)	O 1	-C 21	-O 2	119.9(7)
C 5	-C 6	-O 6	106.5(5)	C 24	-C 23	-O 3	111.8(7)
C 8	-C 7	-C 6	116.8(5)	C 24	-C 23	-O 4	125.3(9)
C 9	-C 8	-C 7	113.1(5)	O 3	-C 23	-O 4	122.8(8)
C 9	-C 8	-C 14	109.0(5)	C 26	-C 25	-O 6	114.2(7)
C 9	-C 8	-C 15	106.4(5)	C 26	-C 25	-O 7	125.5(8)
C 7	-C 8	-C 14	116.8(5)	O 6	-C 25	-O 7	120.1(8)
C 7	-C 8	-C 15	108.5(5)	C 28	-C 27	-O 8	119.8(12)
C 14	-C 8	-C 15	102.1(5)	C 28	-C 27	-O 9	112.5(11)
C 10	-C 9	-C 8	119.9(5)	O 8	-C 27	-O 9	114.7(11)
C 10	-C 9	-C 11	108.0(5)	C 1	-O 1	-C 21	118.5(5)
C 8	-C 9	-C 11	111.8(5)	C 3	-O 3	-C 23	117.8(5)
C 20	-C 10	-C 1	117.0(6)	C 6	-O 6	-C 25	119.5(5)
C 20	-C 10	-C 9	126.6(6)	C 14	-O 8	-C 27	122.4(8)
C 1	-C 10	-C 9	116.3(5)	C 16	-O 9	-C 27	116.3(8)

Experimental

All melting points were measured with a micro melting point apparatus (Yanaco) and are uncorrected. IR spectra were recorded on an EPI-G3 spectrometer (Hitachi). ^{1}H- and ^{13}C-NMR spectra were taken on a JNM-MH 100 (JEOL) and a JNM-FX 100 (JEOL) spectrometers at 100 and 25.1 MHz, respectively, with tetramethylsilane as an internal standard (δ value). The abbreviations used are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Mass spectra were measured with an M-52 spectrometer (Hitachi) at 20 eV. Column chromatography and preparative thin-layer chromatography (PTLC) were carried out with silica gel 60 (70—230 mesh, Merck) and silica gel 60 PF$_{254}$ (Merck), respectively.

1(*R*),6(*R*)-Triacetylgrayanol (4)——A solution of 3 (219 mg) in C_6H_6 (5 ml) was treated with 230 mg of $Pb(OAc)_4$ and the mixture was allowed to stand for 3 hr at room temperature. After filtration of the reaction mixture, the filtrate was concentrated *in vacuo*. The residue was purified by silica gel column chromatography (eluent: AcOEt) and recrystallized from AcOEt to give colorless plate crystals (196 mg), mp 218.5—220.5°. *Anal.* Calcd for $C_{26}H_{38}O_9$: C, 63.14: H, 7.75. Found: C, 63.20; H, 7.65. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3465, 3420 (OH), 1745, 1713 (CO), 1640 (C=C). ^{13}C-NMR (C_5D_5N) δ: 17.1, 20.7, 20.8, 21.1, 23.9, 24.0 (q, CH_3–), 24.6, 28.0, 36.9, 41.1, 56.9 (t, $-CH_2-$), 45.2, 54.1 (d, $-\overset{|}{\underset{|}{C}}H$), 53.2×2 (s, $-\overset{|}{\underset{|}{C}}-$), 68.4, 72.0, 78.2, 78.7 (d, $-\overset{|}{C}HOR$), 79.7 (s, $-\overset{|}{\underset{|}{C}}-OH$), 120.1 (t, $-C=CH_2$), 149.0 (s, $-C=CH_2$), 169.5, 169.9, 171.0 (s, acetyl C=O), 210.2 (s, $-\overset{|}{C}=O$).

Ethylidene Derivative of 4 (5)——Acetal (3 ml) and *p*-toluenesulfonic acid (60 mg) were added to 60 mg of 4 and the mixture was allowed to stand at room temperature for 15 min. The reaction mixture was then diluted with water, neutralized with 5% K_2CO_3 solution and extracted with AcOEt. The AcOEt layer was evaporated to dryness *in vacuo*, and the residue was purified by silica gel PTLC and recrystallized from EtOH to give colorless crystals (56 mg), mp 235—237°. *Anal.* Calcd for $C_{28}H_{40}O_9$: C, 64.59; H, 7.74. Found: C, 64.89; H, 7.89. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1735, 1715, (CO), 1640 (C=C). ^1H-NMR ($CDCl_3$) δ: 1.00, 1.15, 1.34 (each 3H, s), 1.26 (3H, d, $J=5$ Hz, $-\overset{|}{C}H-CH_3$), 2.00, 2.03, 2.16 (each 3H, s, $COCH_3$), 4.44 (1H, s, C_{14}–H), 5.27 (2H, m), 5.60 (1H, m), 5.67, 5.76 (each 1H, s, $-\overset{|}{C}=CH_2$), 6.13 (1H, m).

Jones Oxidation of 4 (Preparation of 6)——Jones reagent was added dropwise to a solution of 4 (62 mg) in acetone (2 ml) until its color persisted. The reaction mixture was diluted with water and extracted with ether. The ether layer was washed with water and evaporated to dryness *in vacuo*. The residue was purified by silica gel column chromatography [eluent: C_6H_6–AcOEt (1: 1)] and recrystallized from AcOEt to give colorless needles (59 mg), mp 243—245°. *Anal.* Calcd for $C_{26}H_{36}O_9$: C, 63.40; H, 7.37. Found: C, 63.61; H, 7.76. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3520 (OH), 1742, 1713 (CO), 1642 (C=C). ^1H-NMR ($CDCl_3$) δ: 1.08, 1.32, 1.50 (each 3H, s), 1.94 (3H, s, $COCH_3$), 2.08 (6H, s, $COCH_3$), 4.95 (1H, d, $J=6$ Hz), 5.22 (1H, m), 5.27, 5.47 (each 1H, s, $-\overset{|}{C}=CH_2$), 5.99 (1H, dd, $J=3$, 5 Hz).

Alkaline Hydrolysis of 4 (Preparation of 7)——One drop of 10% KOH solution was added to a solution of 4 (30 mg) in MeOH (2 ml), and the mixture was refluxed for 2 hr. The reaction mixture was concentrated *in vacuo* and the residue was purified by silica gel column chromatography [eluent: $CHCl_3$–MeOH (9: 1)] and recrystallized from AcOEt–MeOH mixture to give colorless crystals (18 mg), mp 228—231°. *Anal.* Calcd for $C_{20}H_{32}O_6$: C, 65.19; H, 8.75. Found: C, 65.17; H, 8.70. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3475, 3300 (OH), 1630 (C=C). ^{13}C-NMR (C_5D_5N): δ: 16.7, 23.9, 24.2 (q, $-CH_3$), 27.1, 27.8, 30.2, 43.7, 56.6 (t, $-CH_2-$), 49.3, 55.2 (d, $-\overset{|}{\underset{|}{C}}H$), 45.3, 53.0 (s, $-\overset{|}{\underset{|}{C}}-$), 68.5, 69.6, 74.7, 77.4 (d, $-\overset{|}{C}H-OR$), 79.9 (s, $-\overset{|}{\underset{|}{C}}-O-$), 111.3 (t, $-\underset{|}{C}=CH_2$), 156.7 (s, $-\underset{|}{C}=CH_2$), 102.6 (s, $>C\langle{}^{O-}_{O-}$).

X-Ray Analysis of 5——The crystals were grown in EtOH solutions as colorless prisms. The lattice parameters and intensities were measured on a Philips PW 1100 four circle diffractometer using CuKα radiation monochromated by means of a graphite plate.

Crystal data: $C_{28}H_{40}O_9$, MW=520.6, orthorhombic, space group $P2_12_12_1$, $Z=4$, $a=12.020(8)$, $b=21.224(12)$, $c=11.008(7)$ Å, U=2808.3 Å^3.

The intensities of 2536 reflections were measured as being above the $2\sigma(I_0)$ level out of 3236 theoretically possible reflections in a 2θ range of 6—156°.

The crystal structure was solved by the multisolution method[9] and refined by the block-diagonal least-squares method. The final R value calculated with 37 carbon and oxygen atoms was 0.09 for 2536 reflections. No hydrogen atom contributions were taken into account. The final atomic parameters are given in Table II. The bond lengths and angles are shown in Tables III and IV.

References and Notes

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9) P. Main, M.M. Woolfson, and G. Germain, *Acta Cryst.*, **A27**, 368 (1971).