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ANTITUMOR AGENTS, 157.[1] ABSOLUTE STRUCTURES OF CUMINGIANOSIDES A–F, ANTILEUKEMIC TRITERPENE GLUCOSIDES, AND STRUCTURES OF THE HYDROLYSATES OF CUMINGIANOSIDE A[1]

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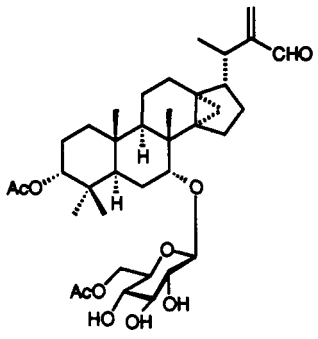
ABSTRACT.—The stereostructures of cumingianosides A–F, a series of triterpene glucosides with a 14,18-cycloapoeuphane skeleton, have been established by X-ray crystallographic analysis on an aglycone [**1c**] the acid hydrolysate of cumingianoside A [**1**], which is a potent cytotoxic triterpene against MOLT-4 human leukemia cells with an EC_{50} value of <0.00625 μM. The 14,18-cyclopropane ring in cumingianoside A [**1**] was opened under acidic conditions in two different directions to give compounds with an apoeuphane skeleton and a dammarane skeleton. Furthermore, it was found that subsequent hydrolysis yielded not only an aglycone with an apoeuphane skeleton [**1c**] but also an *apo*-rearrangement product [**1d**].

Our previous investigation of the MeOH extract of the leaves of *Dysoxylum cumingianum* C. D.C. (Meliaceae) led to the isolation and characterization of cumingianosides A–F [**1–6**], which are triterpene glucosides with a 14,18-cycloapoeuphane skeleton, along with cumindysosides A [**7**] and B [**8**], and trisnortriterpene and tetranortriterpene glucosides as antileukemic principles (2). Cumingianosides A [**1**] and C [**3**] demonstrated potent selective cytotoxicity against MOLT-4 human leukemia cells with EC_{50} values of <0.00625 and <0.0045 μM, respectively (2). However, the stereochemistry of C-20, C-23, and C-24 in these cumingianosides could not be assigned in the previous study. In order to determine the absolute stereochemistry, X-ray crystallographic analysis was carried out on the hydrolysate of cumingianoside A [**1**]. This paper describes the determination of the absolute stereostructures of **1–6**, as well as the structure of the hydrolysates of **1**.

RESULTS AND DISCUSSION

Treatment of deacetylcumingianoside A [**1a**] with *p*-toluenesulfonic acid in Me_2CO at room temperature yielded deacetylcumingianoside A 23,24-acetonide [**1b**]. Further reaction of **1b** with *p*-toluenesulfonic acid in Me_2CO at reflux furnished two hydrolysates [**1c** and **1d**], together with 1,2,5,6-diisopropylidine-D-glucose [**9**]. Hydrolysate **1d** was acetylated and purified, yielding compound **1e**.

[1]For Part 156, see Miyahara *et al.* (1).



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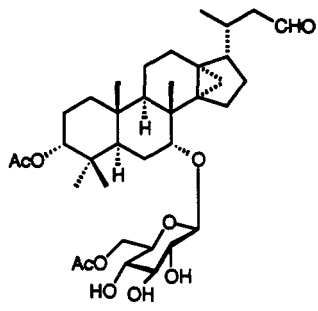

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The negative fabms of **1c** exhibited an $[M-H]^-$ ion peak at *m/z* 531, and the molecular formula was confirmed as $C_{33}H_{56}O_5$ by hrfabms. The ^{1}H-nmr spectrum of **1c** exhibited signals at relatively lowfield due to oxygen-bearing methine groups [δ 3.41 (1H, br s), 3.49 (1H, d, J=8 Hz), 3.89 (1H, br s), and 3.97 (1H, dt, J=2 and 8 Hz)], which were assignable to H-3, H-24, H-7, and H-23, respectively. It also showed, together with a secondary methyl [δ 1.06 (d, J=7 Hz)] and the two methyls of the isopropylidene group [δ 1.39 and 1.40 (each 3H, s)], the presence of seven tertiary methyl groups [δ 0.85, 0.89, 0.95, 1.03, 1.05, 1.17, 1.26 (each 3H, s)]; in contrast, **1** contains only six tertiary methyls. In addition, the absence of cyclopropyl methylene signals, characteristic of 14,18-cycloapoeuphane-type triterpenes, as well as the appearance of an olefinic proton signal at δ 5.42 (1H, d, J=2.5 Hz) in the ^{1}H-nmr spectrum of **1c**, indicated that the cyclopropane moiety in **1b** had opened under the acidic hydrolysis conditions, forming an additional tertiary methyl and a double bond. This conversion is similar to that of a 9,19-cyclolanostane triterpene to its isomeric lanost-9(11)-ene counterpart under acidic conditions (3).

The locations of the additional tertiary methyl group and the double bond were assigned at C-13 and C-14(15), respectively, based on ^{1}H-^{1}H, ^{1}H-^{13}C, and ^{1}H-^{13}C long-range COSY nmr examination; the ^{1}H-^{13}C long-range correlations in **1c** are summarized in Figure 1. Furthermore, the absolute stereostructure of **1c** was confirmed unequivocally by X-ray crystallographic analysis (Tables 1 and 2). The data collection information is listed in Table 1. The crystal of **1c** possessed two crystallographically independent molecules, A and B, as shown in Figure 2. Based on the X-ray crystal structure of **1c**, the absolute structure of **1** was determined. Furthermore, the

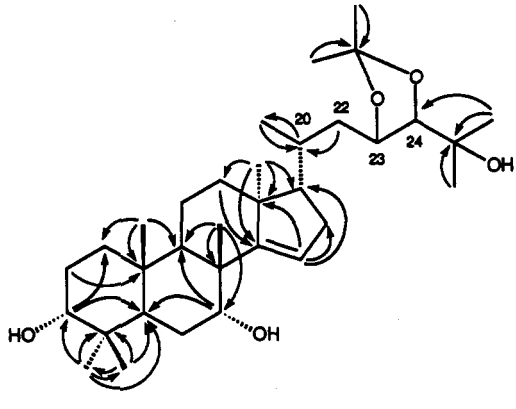


FIGURE 1. ^{1}H-^{13}C nmr long-range correlations in **1c**.

TABLE 1. Crystallographic Data for Compound **1c**.

Chemical formula	$C_{33}H_{56}O_5$
Formula weight	532.80
Crystal system	monoclinic
Space group	$P2_1$
Z	4
Cell dimensions	
a (Å)	18.463 (4)
b (Å)	11.737 (2)
c (Å)	15.232 (1)
α (°)	90.00 (1)
β (°)	108.88 (1)
γ (°)	90.00 (1)
V (Å^3)	3123.2 (8)
Crystal size	0.3×0.3×0.3
d(calcd)(gcm^{-1})	1.13045
F(000)	1172
μ(CuK$_\alpha$)(mm^{-1})	0.548
Max θ (°)	60
Total reflections	5517
Unique reflections	4791
Observed ($I>2.3\sigma$)	4498
No. of variables	978
Final R	0.057
Rw	0.084

stereostructures of cumingianosides B–F were also established to be as represented by formulas **2–6**, respectively, from the chemical correlations of these cumingianosides as shown in Scheme 1 (2).

Compound **1e**, the acetate of hydrolysate **1d**, gave a $[M]^+$ ion peak at m/z 556 in the fdms, while the negative fabms gave an $[M-CH_3]^-$ ion peak at m/z 541 as the base peak. The elemental composition of this latter peak was analyzed as $C_{34}H_{53}O_5$ by hrfabms, and thus, the molecular formula of **1e** was concluded to be $C_{35}H_{56}O_5$. Because **1e** possesses an acetyl group as revealed by its ^{1}H-nmr spectrum [δ 2.07 (3H, s)], the molecular mass of **1d** is presumed to be 514 daltons, which is 18 mass units fewer than that of **1c**.

The ^{1}H-nmr spectrum of **1e** exhibited the presence of six tertiary methyl groups [δ 0.76, 0.86, 0.97, 1.11, 1.13, 1.20 (3H each, s)], a secondary methyl group [δ 1.02 (3H, d, J=7 Hz)], two methyls of an isopropyridine group [δ 1.33 and 1.40 (3H each, s)], and an acetyl group [δ 2.07 (3H, s)]. The absence of the cyclopropyl methylene signals suggested that, as in **1c**, the cyclopropane moiety was opened. However, no olefinic proton signal was present in the ^{1}H-nmr spectrum, suggesting that the cyclopropane moiety had opened in a different manner from that determined for **1c**.

The methine proton signal at δ 2.84 (1H, m) could be assigned to H-20, since this signal was shown to be coupled with the secondary methyl signal at δ 1.02 (d, J=7 Hz), ascribable to Me-20. The chemical shift of H-20 suggested the presence of a double bond at C-17. Therefore, the double bond formed from the opening of the cyclopropane ring moiety was concluded to be at C-13(17).

The ^{1}H-nmr spectrum of **1e** showed, at relatively lowfield, the existence of three oxygen-bearing methine groups at δ 3.41 (1H, d, J=8.5 Hz), 3.67 (1H, dt, J=2.5 and 8.5 Hz), and 4.67 (1H, br s); the first two of these signals were easily assignable to H-24 and H-23, respectively. From the coupling pattern, the lowest oxygen-bearing methine signal can be assigned to either H-3 or H-7; thus, a methine proton was absent from either C-3 or C-7. The ^{13}C-nmr spectrum of **1e** revealed the presence of two tetrasubstituted double bonds [δ 124.8, 131.1, 138.4, and 144.1 (each s)]; one pair must

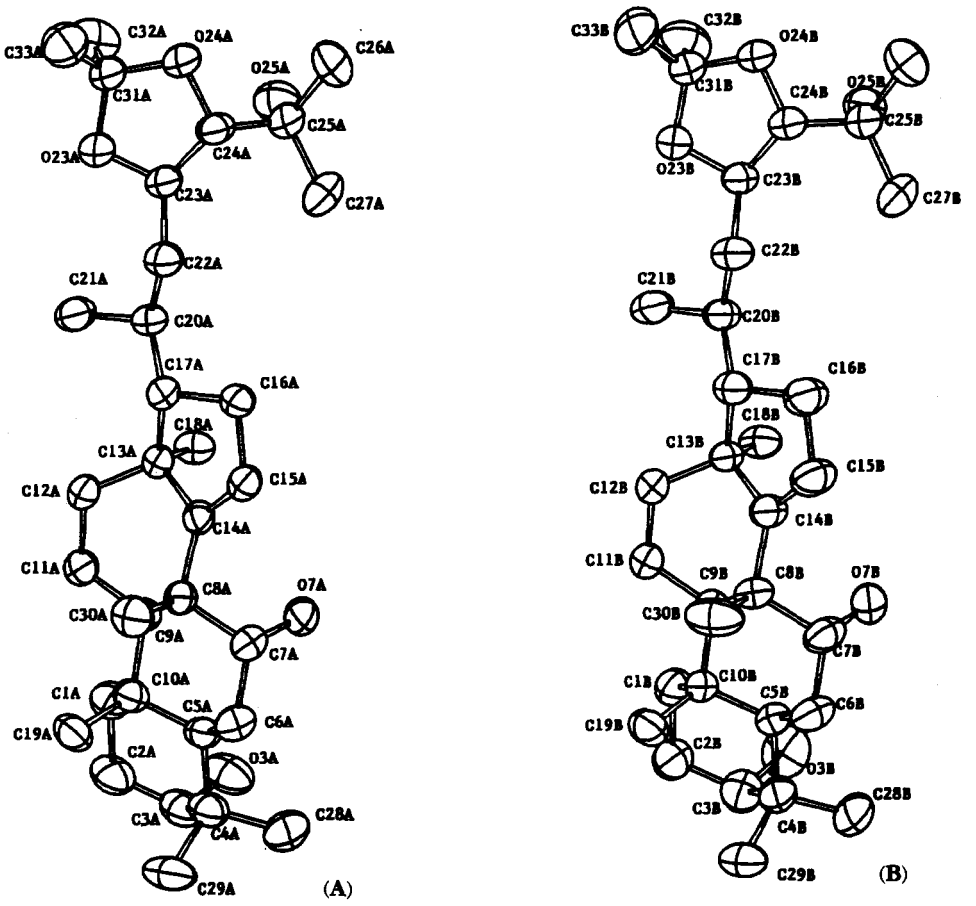
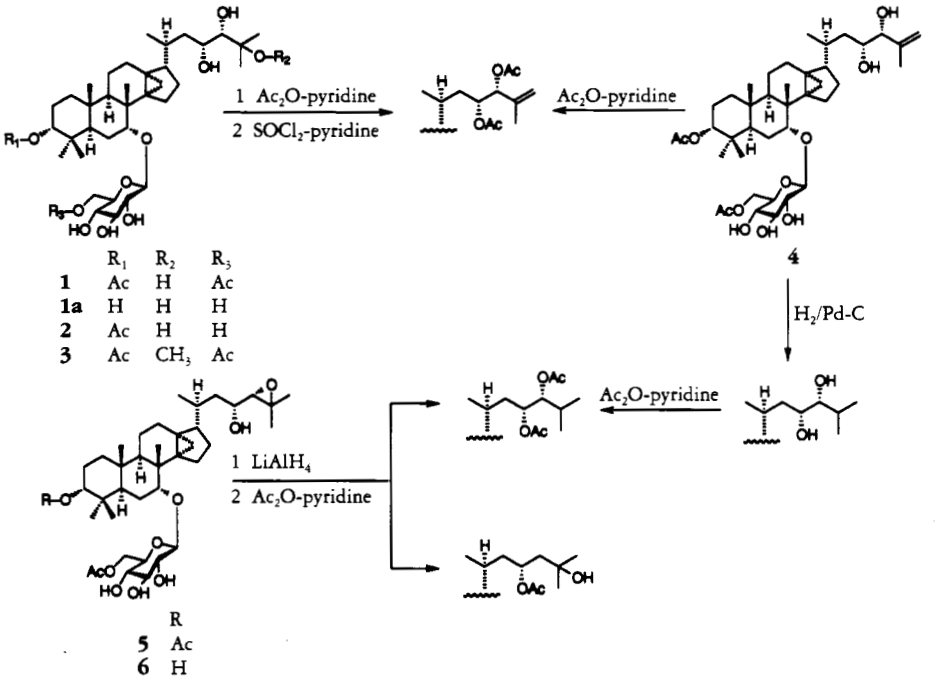


FIGURE 2. ORTEP view of **1c**. (A) molecule A; (B) molecule B.

be due to the double bond at C-13(17). It also exhibited the presence of three oxygen-bearing methine carbons [δ 78.3, 76.6, and 75.0] and an oxygen-bearing quaternary carbon (δ 69.6); one less than found in **1c**. These data, together with the difference in the mol wts of **1c** and **1e**, suggested that the oxygen function at either C-3 or C-7 had been eliminated. Moreover, a three-proton singlet at δ 1.74 in the ^{1}H-nmr spectrum of **1d** indicated the presence of a vinyl methyl group, suggesting that, together with the elimination of the oxygen function, one methyl group had migrated. The locations of the second double bond and the vinyl methyl group were assigned by ^{1}H-^{13}C long-range COSY examination; the ^{1}H-^{13}C long-range correlations in **1e** are shown in Figure 3. The vinyl methyl signal showed ^{1}H-^{13}C long-range correlations with the carbon resonances at δ 124.8 and 138.4. The carbon resonance at δ 138.4 also showed long-range coupling with the methyl signal at δ 1.11, which further exhibited long-range correlations with C-13, C-14, and C-15. Thus, this methyl signal could be assigned as Me-14, with the carbon resonance at δ 138.4 assigned to C-8. Because the vinyl methyl signal also exhibited long-range coupling with the methylene carbon resonance at δ 32.5, assignable to C-6, the location of the double bond is at C-7(8). Therefore, the vinyl methyl was concluded to be at C-7. On the basis of the spectral evidence described above, the structure of **1e** was concluded to be as shown in Scheme 2.

Under acidic conditions, the 14,18-cyclopropane ring was opened in two different directions to give compounds with an apoeuphane skeleton (**A**) and a dammarane



	R_1	R_2	R_3
1	Ac	H	Ac
1a	H	H	H
2	Ac	H	H
3	Ac	CH_3	Ac

	R
5	Ac
6	H

SCHEME 1

skeleton (**B**). Furthermore, subsequent hydrolysis yielded not only an aglycone with an apoeuphane skeleton (**1c**) but also an *apo*-rearrangement product [**1d**] via the intermediate shown in Scheme 2.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—All mps were determined on a Fisher-Johns micro melting-point apparatus and are uncorrected. Optical rotations were determined with a Rudolph Research Autopol III polarimeter. ^{1}H- and ^{13}C-nmr spectra were obtained on a Bruker AC-300 spectrometer with TMS as internal standard. Fabms measurements were carried out on JEOL JMS-HX110 mass spectrometers.

TREATMENT OF DEACETYLCUMINGIANOSIDE A WITH *P*-TOLUENESULFONIC ACID IN Me_2CO.—A mixture of deacetylcumingianoside A (575 mg), which was prepared in the same way as described in a previous paper (2), and *p*-toluenesulfonic acid (15 mg) in dry Me_2CO (20 ml) was stirred at room temperature for 2 h. The

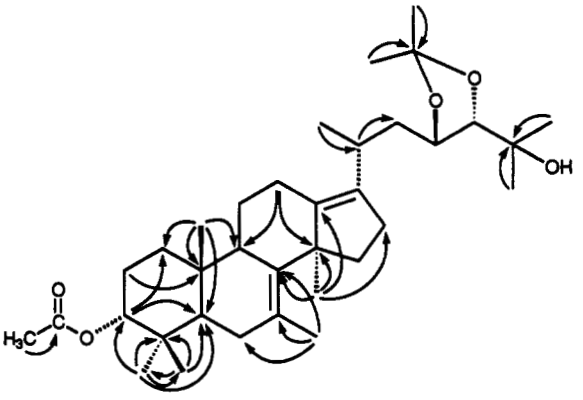
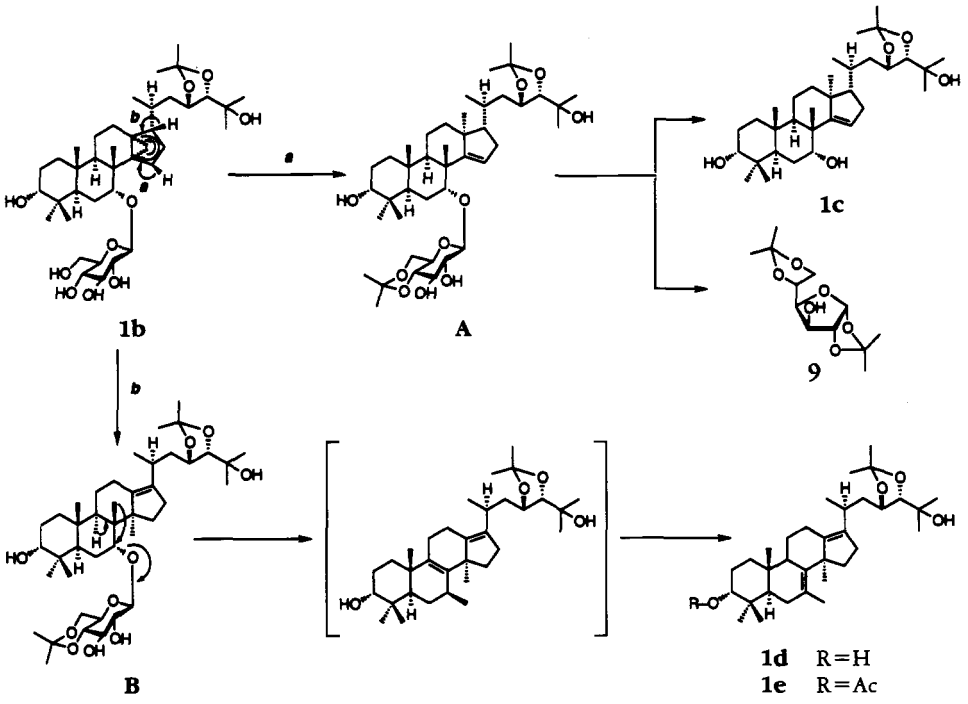


FIGURE 3. ^{1}H-^{13}C nmr long-range correlations in **1e**.



SCHEME 2

product [**1b**], which crystallized from the reaction mixture, was collected by filtration (colorless needles, 425 mg): mp 205–207°; $[\alpha]^{20}D$ −34.2° (*c*=0.68, MeOH); negative fabms *m/z* 693 $[M-H]^-$; positive-ion fabms *m/z* 717 $[M+Na]^+$; hrfabms *m/z* calcd for $C_{39}H_{66}O_{10}Na$ 717.4554, found 717.4543; ^1H nmr (pyridine-d_5) δ 0.62, 0.73 (1H each, d, *J*=5.5 Hz, H-18), 0.93 (3H, s, Me-4β), 0.95 (3H, s, Me-10), 1.06 (3H, s, Me-8), 1.20 (3H, d, *J*=6.5 Hz, Me-10), 1.36 (3H, s, Me-4α), 1.43, 1.52 (3H each, s, Me_2-25), 1.54 (6H, s, isopropylidine-Me_2), 2.59 (1H, d, *J*=11.5 Hz, H-5), 3.64 (1H, br s, H-3), 3.82 (1H, t, *J*=7.5 Hz, H-24), 3.99 (1H, m, glucosyl H-5), 4.02 (1H, t, *J*=8.5 Hz, glucosyl H-2), 4.15 (1H, br s, H-7), 4.18 (1H, t, *J*=8.5 Hz, glucosyl H-3), 4.26 (1H, t, *J*=8.5 Hz, glucosyl H-4), 4.35–4.43 (2H, m, H-23 and glucosyl H-6), 4.59 (1H, dd, *J*=2.5 and 11.5 Hz, glucosyl H-6), 4.91 (1H, d, *J*=7.5 Hz, glucosyl H-1); ^{13}C-nmr data, see Table 3.

HYDROLYSIS OF DEACETYLCUMINGIANOSIDE A 23,24-ACETONIDE BY *P*-TOLUENE-SULFONIC ACID.—A mixture of **1b** (500 mg) and *p*-toluenesulfonic acid (45 mg) in dry Me_2CO (20 ml) was refluxed overnight with stirring. The reaction mixture was concentrated under reduced pressure to give a residue, which was subjected to Si gel cc. Elution with $CHCl_3$-MeOH (60:1→40:1) yielded compound **1c** (85 mg), compound **1d** (50 mg), and 1,2,5,6-diisopropylidine-D-glucose (45 mg). Compound **1d** was further treated with Ac_2O (1 ml) and pyridine (1 ml) at room temperature overnight, and purified by Si gel chromatography [hexane-EtOAc (4:1)] to furnish compound **1e** (32 mg) as colorless needles (from hexane). **1c**: colorless prisms (from hexane/EtOAc); mp 203–204°; $[\alpha]^{20}D$ −118.9° (*c*=0.31, $CHCl_3$); negative-ion fabms 531 $(M-H)^-$; positive-ion fabms *m/z* 555 $[M+Na]^+$; hrfabms *m/z* calcd for $C_{33}H_{56}O_5Na$ 555.4026, found 555.4030; ^1H nmr ($CDCl_3$) δ 0.85 (3H, s, Me-4β), 0.89 (3H, s, Me-10), 0.95 (3H, s, Me-4α), 1.03 (3H, s, Me-14), 1.05 (3H, s, Me-8), 1.06 (3H, d, *J*=7 Hz, Me-20), 1.17, 1.26 (3H each, s, Me_2-25), 1.39, 1.40 (3H each, s, isopropylidine-Me_2), 2.30 (1H, ddd, *J*=3.5, 7, and 15 Hz, H-16), 3.41 (1H, br s, H-3), 3.49 (1H, d, *J*=8 Hz, H-24), 3.89 (1H, br s, H-7), 3.97 (1H, dt, *J*=2 and 8 Hz, H-23), 5.42 (1H, d, *J*=2.5 Hz, H-15); ^{13}C-nmr data, see Table 3. **1e**: colorless needles (hexane); mp 180–182°; $[\alpha]^{20}D$ −76.9° (*c*=0.16, $CHCl_3$); fdms *m/z* 556 $[M]^+$; positive-ion fabms *m/z* 541 $[M-CH_3]^+$; hrfabms *m/z* calcd for $C_{34}H_{53}O_5$ 541.3893, found 541.3891; ^1H nmr ($CDCl_3$) δ 0.76 (3H, s, Me-10), 0.86 (3H, s, Me-4β), 0.97 (3H, s, Me-4α), 1.02 (3H, d, *J*=7 Hz, Me-20), 1.11 (3H, s, Me-14), 1.13, 1.20 (3H each, s, Me_2-25), 1.33, 1.40 (3H each, s, isopropylidine-Me_2), 1.74 (3H, s, Me-7), 2.06 (3H, s, OAc), 2.24 (1H, dd, *J*=6.5 and 11.5 Hz, H-16), 2.56 (1H, br d, *J*=10.5 Hz, H-12), 2.84 (1H, m, H-20), 3.67 (1H, d, *J*=8.5 Hz, H-24), 3.67 (1H, dt, *J*=2.5 and 8.5 Hz, H-23), 4.67 (1H, br s, H-3); ^{13}C-nmr data, see Table 3.

TABLE 2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors for Non-hydrogen Atoms of Compound **1c** (**A** and **B** forms) with Their Estimated Standard Deviations in Parentheses.

Atom	*x*	*y*	*z*	*Beq* (Å^2)
O-3A	8878 (2)	5960 (4)	7586 (3)	6.14 (13)
O-7A	6202 (2)	5530 (3)	5525 (3)	4.23 (9)
O-23A	1906 (2)	8862 (3)	6815 (4)	5.74 (13)
O-24A	912 (2)	7602 (3)	6533 (3)	5.22 (11)
O-25A	1706 (2)	5671 (4)	7450 (3)	5.33 (12)
C-1A	7898 (3)	8115 (5)	7386 (4)	4.90 (15)
C-2A	8748 (3)	8007 (6)	7464 (5)	5.53 (17)
C-3A	8919 (3)	6940 (5)	7022 (4)	4.94 (16)
C-4A	8416 (3)	6793 (5)	6011 (4)	4.40 (14)
C-5A	7572 (3)	6966 (4)	5948 (3)	3.64 (12)
C-6A	6997 (3)	6737 (5)	4977 (4)	4.22 (13)
C-7A	6198 (3)	6568 (4)	5015 (3)	3.59 (12)
C-8A	5909 (2)	7591 (4)	5450 (3)	3.10 (10)
C-7A	6522 (2)	7894 (4)	6398 (3)	3.27 (11)
C-10A	7360 (3)	8067 (4)	6389 (4)	3.82 (12)
C-11A	6249 (3)	8838 (5)	6916 (4)	4.53 (15)
C-12A	5384 (3)	8898 (4)	6741 (4)	3.94 (13)
C-13A	4970 (2)	7755 (4)	6459 (3)	3.17 (10)
C-14A	5170 (2)	7298 (4)	5618 (3)	2.96 (10)
C-15A	4575 (3)	6741 (4)	5049 (3)	3.61 (12)
C-16A	3879 (3)	6815 (4)	5358 (3)	3.67 (12)
C-17A	4080 (2)	7839 (4)	6037 (3)	3.22 (12)
C-18A	5209 (3)	6902 (5)	7265 (3)	3.95 (13)
C-19A	7454 (3)	9159 (5)	5879 (5)	5.01 (17)
C-20A	3593 (2)	7918 (4)	6675 (3)	3.38 (11)
C-21A	3764 (3)	8990 (5)	7274 (4)	4.88 (16)
C-22A	2740 (3)	7886 (4)	6122 (3)	3.83 (12)
C-23A	2198 (2)	7762 (4)	6690 (3)	3.81 (12)
C-24A	1484 (3)	7079 (4)	6228 (3)	3.84 (12)
C-25A	1514 (3)	5816 (4)	6465 (4)	4.27 (14)
C-26A	746 (4)	5270 (6)	5945 (6)	6.96 (23)
C-27A	2165 (4)	5241 (5)	6202 (5)	5.82 (19)
C-28A	8518 (3)	5557 (6)	5688 (6)	6.28 (21)
C-29A	8708 (3)	7596 (6)	5392 (5)	6.09 (20)
C-30A	5727 (3)	8586 (5)	4743 (4)	4.44 (14)
C-31A	1177 (3)	8709 (5)	6916 (4)	4.35 (14)
C-32A	1229 (4)	8711 (8)	7925 (5)	6.79 (22)
C-33A	657 (4)	9597 (6)	6348 (5)	6.13 (20)
O-3B	7223 (3)	5055 (4)	7464 (3)	6.64 (14)
O-7B	5769 (2)	4925 (4)	9649 (4)	6.01 (13)
O-23B	709 (2)	2038 (3)	7835 (3)	5.22 (11)
O-24B	−59 (2)	3092 (4)	8414 (3)	5.47 (11)
O-25B	473 (2)	5295 (3)	8233 (3)	5.14 (11)
C-1B	6378 (3)	2818 (5)	7444 (4)	4.50 (14)
C-2B	7159 (3)	2987 (6)	7305 (4)	5.07 (16)
C-3B	7591 (3)	3989 (5)	7846 (4)	4.90 (16)
C-4B	7672 (3)	3972 (4)	8882 (3)	3.91 (13)
C-5B	6869 (3)	3730 (4)	8982 (3)	3.44 (11)
C-6B	6871 (3)	3762 (5)	9985 (4)	4.62 (14)
C-7B	6062 (3)	3854 (6)	10030 (4)	4.72 (15)
C-8B	5546 (2)	2862 (4)	9519 (3)	3.60 (11)
C-9B	5597 (2)	2761 (4)	8527 (3)	3.39 (11)
C-10B	6425 (2)	2681 (4)	8465 (3)	3.47 (11)
C-11B	5033 (3)	1884 (5)	7922 (4)	4.79 (15)
C-12B	4270 (3)	1803 (5)	8092 (4)	4.46 (14)
C-13B	4053 (2)	2841 (4)	8562 (3)	3.33 (11)
C-14B	4706 (3)	3087 (4)	9438 (3)	3.74 (12)
C-15B	4442 (3)	3430 (6)	10102 (4)	5.27 (17)
C-16B	3590 (3)	3385 (6)	9826 (4)	5.28 (17)
C-17B	3380 (3)	2619 (4)	8960 (3)	3.88 (12)
C-18B	3884 (3)	3890 (5)	7922 (4)	4.36 (14)
C-19B	6812 (3)	1520 (4)	8820 (5)	4.96 (16)
C-20B	2551 (2)	2777 (4)	8308 (3)	3.86 (12)
C-21B	2344 (3)	2031 (6)	7452 (4)	5.53 (17)
C-22B	1983 (3)	2568 (5)	8836 (4)	4.30 (13)
C-23B	1168 (3)	2980 (4)	8311 (4)	3.92 (12)
C-24B	711 (3)	3406 (5)	8913 (4)	4.29 (14)
C-25B	740 (3)	4689 (5)	9096 (4)	4.63 (15)
C-26B	251 (4)	4996 (7)	9706 (5)	6.70 (23)
C-27B	1574 (4)	5069 (6)	9556 (5)	6.51 (21)
C-28B	7970 (3)	5134 (5)	9308 (5)	5.33 (17)
C-29B	8296 (3)	3079 (6)	9363 (4)	5.17 (16)
C-30B	5773 (3)	1762 (6)	10115 (5)	6.01 (19)
C-31B	−63 (3)	2275 (5)	7731 (4)	4.63 (15)
C-32B	−451 (4)	2796 (8)	6781 (5)	7.68 (25)
C-33B	−430 (5)	1187 (6)	7921 (7)	7.76 (29)

TABLE 3. ^{13}C-Nmr Data (δ) for Compounds **1**, **1b**, **1c**, and **1e** (75.5 MHz).

Carbon	Compound			
	1[a]	**1b**[b]	**1c**[a]	**1e**[a]
1	34.2	33.9	32.6	32.4
2	22.7	26.4	25.0	23.0
3	76.0	75.5	76.2	78.3
4	36.4	37.8	37.0	36.2
5	41.5	40.3	40.5	44.5
6	20.4	21.0	23.7	32.5
7	78.6	78.4	72.4	124.8
8	34.8	35.4	44.4	138.4
9	45.0	45.3	41.8	52.9
10	37.3	37.9	37.6	35.3
11	17.0	17.4	16.4	25.6
12	27.4	28.0	33.7	23.6
13	26.8	27.2	47.0	144.1
14	38.8	39.5	162.5	52.5
15	24.1	25.2	119.4	27.7
16	25.5	26.4	35.3	40.5
17	52.8	53.1	60.8	131.1
18	17.4	17.4	18.5	24.6
19	16.0	16.5	15.2	14.1
20	31.9	35.3	33.8	28.9
21	19.4	20.4	20.1	20.3
22	36.9	39.9	41.7	40.2
23	69.9	78.8	77.2	75.0
24	75.1	88.9	87.7	86.6
25	74.2	69.8	69.8	69.6
26	26.1	26.9	24.7	24.7
27	27.3	27.6	27.9	27.7
28	27.9	29.0	28.2	27.4
29	21.8	22.9	22.1	21.6
30	20.0	20.5	27.8	22.0
Isopropylidine				
CH_3		27.6, 28.0	27.6, 27.2	27.7, 26.8
C		108.5	108.5	107.6
Glucosyl				
1′	98.6	100.7		
2′	74.0	75.5		
3′	78.6	78.7		
4′	70.2	72.5		
5′	73.3	78.1		
6′	63.3	63.5		
Ac	20.8, 21.3 170.9, 171.7			21.3, 170.8

[a]Measured in $CDCl_3$.
[b]Measured in pyridine-d_5.

X-RAY CRYSTALLOGRAPHY.[2]—X-ray diffraction data were measured on an Enraf-Nonius CAD4 diffractometer. Intensity data collection was accomplished by the ω-2θ scan method with graphite-monochromated CuKα radiation up to θ=60°; 4498 unique reflections with $I>2.3\sigma$ were used for refinement. The structure was solved by the direct methods program SIR88.

[2]Hydrogen coordinates, thermal parameters, bond distances and angles, and observed and calculated structure factors have been deposited with the Cambridge Crystallographic Data Centre and can be obtained upon request from Dr. Olga Kennard, University Chemical Laboratory, 12 Union Road, Cambridge CB2 1EZ, UK.

All atomic parameters, with anisotropic temperature factors for non-hydrogen atoms and isotropic ones for hydrogen atoms, were refined by a block-diagonal least-squares method. The final R value was 0.057. Crystallographic data are given in Table 1, while final fractional atomic coordinates are shown in Table 2.

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