TWO NEW SESQUITERPENE LACTONES FROM *CALEA SUBCORDATA* AND THE MOLECULAR STRUCTURE AND ABSOLUTE CONFIGURATION OF SUBCORDATOLIDE D

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ABSTRACT.—Chemical analysis of *Calea subcordata* from Venezuela afforded two new sesquiterpene lactones, subcordatolide D [1], a *trans*-4, *cis*-9-cyclodecadien-12,8β-olide, and subcordatolide E [5], a eudesman-12,8α-olide. The structures of the two new lactones were established by chemical and spectroscopic methods. The molecular structure and absolute configuration of subcordatolide D was determined by single crystal X-ray diffraction analysis.

In continuation of our chemotaxonomic study of the genus *Calea* (Asteraceae, Heliantheae) we have further analyzed *C. subcordata* S.F. Blake from Venezuela for its sesquiterpene lactones. Previous chemical investigations of this species afforded guaianolides (1) and eudesmanolides (2,3). We report here the isolation and structure determination of two new sesquiterpene lactones, subcordatolide D [1] and the eudesmanolide subcordatolide E [5]. X-ray diffraction analysis of 1, an uncommon cyclodeca-*trans*-4, *cis*-9-dienolide (4), established its molecular structure including the absolute configuration.

RESULTS AND DISCUSSION

Subcordatolide D [1], $C_{19}H_{26}O_5$, was a crystalline solid (mp 246°) the ir spectrum of which indicated the presence of hydroxyl group(s) (3600 and 3555 cm^{-1}), a saturated ester (1730 cm^{-1}), and double bonds (1660 and 1605 cm^{-1}). The presence of an
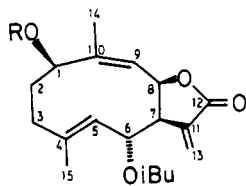
1   R=H

2   R= Cl_3C-C-NH-C-
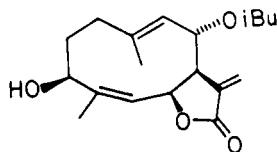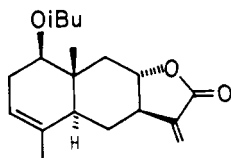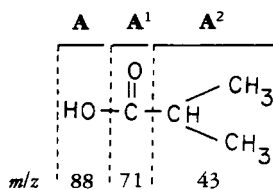
4   R= Br———C-O-

5

TABLE 1. ¹H-nmr Spectral Data of Compounds **1**, **2**, **4**, and **5**[a]

Protons	Compounds			
	1	2	4	5
H-1	4.42[4.48]brd(10.0)	5.50brd(10.0)	5.62brd	4.72brd(4.0)
H-2a	2.09[1.90-2.10]m	2.26m	2.20-2.40m	2.46-2.60
H-2b	1.70-1.85[1.66-1.75]m	1.89m	1.85-2.00m	2.25-2.36
H-3	2.25[2.10-2.40]m(2H)	2.30m	2.20-2.40m	5.29brm
H-5	4.92[4.87]brd(10.1)	5.05brd(10.3)	5.01brd(10.3)	—
H-6a	5.37[5.51]dd(10.1;9.2)	5.55dd(10.3;9.0)	5.80dd(10.3;9.0)	2.45-2.65
H-6b				1.95-2.20
H-7	3.53[3.64]dddd(10.0;9.2;3.5;3.2)	3.58m	3.61m	2.41m
H-8	5.27[5.29]t(10.0)	5.27t(10.0)	5.30t(10.0)	4.07ddd(11.0;11.0;4.5)
H-9a	4.98[5.18]brd(10.0)	5.10brd(10.0)	5.13brd(10.0)	1.88dd(11.0;4.5)
H-9b				1.76brd(11.0)
H-13a	6.26[6.10]d(3.5)	6.27d(3.5)	6.26d(3.5)	6.09d(3.0)
H-13b	5.58[5.56]d(3.2)	5.58d(3.2)	5.59d(3.2)	5.46d(3.0)
H-14	1.70[1.70]brs	1.74brs	1.77d(1.8)	0.94s
H-15	1.82[1.81]d(1.2)	1.86d(1.8)	1.86d(1.5)	1.75br
O iBu	2.55[2.53]h(7.0)	2.58h(7.0)	2.58h(7.0)	—
	1.18/1.16[1.16/1.13](7.0)	1.19/1.17d(7.0)	1.19/1.18d(7.0)	1.19/1.16d(7.0)
OR	—	—	7.86d(9.0)	—
	—	—	7.57d(9.0)	—

[a]Spectra were run in CDCl₃ [acetone-d_6] at ambient temperatures at 200 MHz and TMS was used as internal standard. Chemical shifts are in ppm (δ) and figures in parentheses are coupling constants or line separations in hertz.

α-methylene-γ-lactone moiety was suggested by two one-proton doublets at δ 6.26 (H-13a) and 5.58 (H-13b) and a one-proton multiplet at δ 3.53 (H-7) in the ^{1}H-nmr spectrum of **1**. The ester substituent was assigned to an isobutyrate group on the basis of the typical ^{1}H-nmr signals (a one-proton heptet at δ 2.55, and two three-proton doublets at δ 1.18 and 1.16) together with mass spectral peaks at m/z 71 (**A**^{1}) and 43 (**A**^{2}). Detailed spin decoupling experiments in CDCl$_3$ and acetone-d_6 allowed the assignment of all protons of the basic terpene skeleton (Table 1).

   ^{13}C-nmr studies involving proton noise-decoupling, single frequency off-resonance decoupling, and heteronuclear multipulse experiments (DEPT and INEPT), corroborated the ^{1}H-nmr assignments (Table 2). The ^{13}C-nmr spectrum showed 5 quaternary, 7 tertiary, 3 secondary, and 4 primary carbon atoms accounting for 19 carbon atoms in the molecule, which is in agreement with the empirical formula of **1**.

   In situ acylation of subcordatolide D [**1**] with trichloroacetyl isocyanate (5) yielded the trichloroacetyl carbamate derivative **2**. Spin decoupling experiments allowed the assignment of all ^{1}H-nmr signals of **2** (Table 1). The presence of a secondary hydroxyl group at C-1 was in agreement with the paramagnetic acylation shift of H-1 from δ 4.42 in **1** to δ 5.50 in **2** (Δδ=1.08 ppm).

   Further configurational assignments of subcordatolide D involved single crystal X-ray diffraction providing its molecular structure, which could be represented by formula **1** or **3**. In order to distinguish between the two possible absolute configurations **1** or **3**, the *p*-bromobenzoate derivative [**4**] was prepared to be submitted to X-ray analysis. Although **4** was a crystalline compound (mp 172°; ^{1}H-nmr data in Table 1) crystals were of insufficient quality for X-ray analysis. Therefore, determination of the absolute configuration of subcordatolide D was attempted by anomalous scattering by oxygen and carbon with CuK$_α$ radiation. The results of this study are discussed below.

   CRYSTAL STRUCTURE ANALYSIS OF SUBCORDATOLIDE D [1].—The molecular structure of subcordatolide D is illustrated in Figure 1, and the conformations of the cyclodecadiene and lactone rings are specified by the torsion angles in Table 2, in which endocyclic torsion angles for tulirinol acetate,^{2} the only other known *trans*-4, *cis*-9-cy-
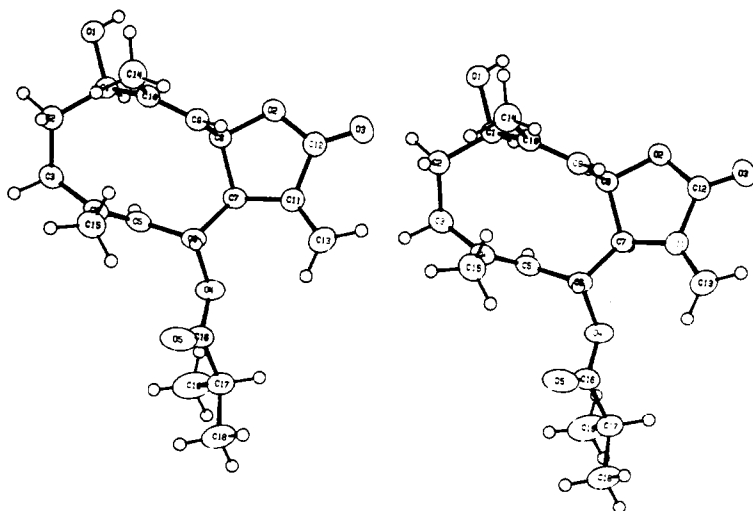

FIGURE 1.   Stereoview of subcordatolide D.

TABLE 2.   Comparison of Endocyclic Torsion Angles

Atoms	subcordatolide	tulirinol acetate
C1-C2-C3-C4	54.7	42.3
C2-C3-C4-C5	−105.8	−110.7
C3-C4-C5-C6	159.6	161.3
C4-C5-C6-C7	−121.3	−114.4
C5-C6-C7-C8	47.1	49.0
C6-C7-C8-C9	42.1	−91.2
C7-C8-C9-C10	−120.1	122.4
C8-C9-C10-C1	4.0	0.3
C9-C10-C1-C2	118.3	−123.1
C10-C1-C2-C3	−85.1	59.8
C7-C11-C12-O2	12.9	8.7
C11-C12-O2-C8	7.5	8.5
C12-O2-C8-C7	−23.9	−21.6
O2-C8-C7-C11	29.6	25.2
C8-C7-C11-C12	26.2	−20.8
C13-C11-C12-O3	15.2	8.2

clodecadienolide, are also given for comparison. The two molecules are quite similar in structure, differing only in substitution pattern and lactone fusion (tulirinol acetate has a *trans*-γ-lactone) but exhibit markedly different conformations. While the cyclodecadiene ring of tulirinol acetate is melampolide-like, with C14 below and C15 above the plane of the medium ring, that of subcordatolide D is much more germacrolide-like, with approximately parallel, β-oriented methyl groups.[3] The torsion angles of the two molecules agree quite well in the region of the ring C1 through C8 but differ in a "flip" of the *cis*-double bond to the opposite face of the molecule, causing torsion angles about bonds C1-C10 and C8-C9 to be similar in magnitude but opposite in sign. The cyclodecadiene flip effects little change in the center-to-center distance between the double bonds, 3.222Å in tulirinol acetate vs. 3.158Å in subcordatolide D. Curiously, this flip of the main ring preserves the conformation of the lactone ring, even though the lactones of the two molecules differ in configuration of fusion. Both lactones are in the half-chair conformation with C12 on the pseudo-twofold axis, and individual torsion angles agree well with an average difference of only 3.5°.

Bond distances (esd's 0.002-0.003Å) and angles (esd's 0.08-0.17°) of the main skeleton are normal with average values of 1.539Å C(sp^3)-C(sp^3), 1.503Å C(sp^3)-C(sp^2), 1.330Å C=C, 1.204Å C=O, and 0.99Å C-H for refined H. Distances involving the two methyl groups of the isobutyrate substituent are shortened somewhat by high thermal motion, averaging 1.491Å. The only intermolecular interaction of note is a hydrogen bond involving hydroxyl group O1 and lactone carbonyl O3, having O····O distance 2.812(2)Å, H····O distance 2.14(2)Å, and O-H····O angle 150(2)°.

The structure was initially solved by direct methods (MULTAN) (7) with data collected on an Enraf-Nonius CAD4 diffractometer using MoK$_\alpha$ radiation and refined to R=0.037 using 1440 observed data within the limits 1°<θ<25°. The precision of the determination was high (rms uncertainty in atomic positions 0.002Å), but the enantiomorphous ambiguity of 12,8β vs. 12,6β-lactonization (structure **1** vs. **3**) remained and could not be resolved by the Mo data. After failure to obtain suitable crystals of the

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[3]Conventions for the presentation of germacranolide conformations are discussed on pages 88 and 288 of Fischer, *et al.* (4).

[4]Atomic coordinates for structure **4** have been deposited with the Cambridge Crystallographic Data Centre and can be obtained on request from Dr. Olga Kennard, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, UK.

p-bromobenzoate derivative [4], we decided to attempt an absolute configuration determination based upon the anomalous scattering by oxygen and carbon of CuK_α radiation.

The results of the Mo determination were used as a beginning model for refinement. Nonhydrogen atoms were treated anisotropically, while all hydrogen atoms except those on the methyl and isobutyrate groups were refined isotropically. Those hydrogen atoms not refined were located from difference maps and assigned isotropic thermal parameters based on the observed thermal motion of the atoms to which they are bonded. Refinement was carried out by full-matrix least squares based upon F, with weights $w = \sigma^{-2}(Fo)$, using the Enraf-Nonius SDP (8) and anomalous coefficients of Cromer and Libermann (9,10) ($\Delta f'' = 0.032e$ for O and 0.009e for C). A secondary extinction coefficient refined to a value of $9.9(6) \times 10^{-6}$. Convergence was achieved with $R = 0.0362(0.0395$ for all data), $Rw = 0.0533$, error of fit $= 1.811$ for 269 variables. Maximum residual electron density was $0.22 \, e\text{Å}^{-3}$ in the isobutyrate region. The alternate enantiomorph **3** (12,6β-lactone) was refined under identical conditions, yielding $R = 0.0363$ (0.0396 for all data), $Rw = 0.0537$, error of fit $= 1.827$. The difference is significant at better than $\alpha = 0.005$ by the Hamilton R factor ratio test (11), and, thus, we consider the former structure **1** (12,8β-lactone) to be correct. Coordinates for this model are given in Table 3.

The cd spectrum of **1** showed a negative Cotton effect for the $n \mapsto \pi^*$ transition of the methylene lactone chromophore. Application of Beecham's rule (12) correlates the right-handed chirality of the torsion angle C13=C11-C12=O3 ($+15.2°$) of the lactone group in **1** with a positive Cotton effect which is contrary to the above findings. As we had pointed out before (4), the sign of the Cotton effect is sensitive to deviations from the normal lactone geometry in conformationally flexible 7,8-lactonized germacranolides. Therefore, the use of cd correlations for determinations of the absolute configuration of conformationally flexible 6,8-lactonized ten-membered rings appears to be unreliable and should be treated with caution.

Subcordatolide E [5], $C_{19}H_{26}O_4$, displayed in the ^{1}H-nmr spectrum two one-proton doublets at δ 6.09 (H-13a) and 5.46 (H-13b) and a one-proton multiplet at δ 2.41 (H-7) that are characteristic of α,β-unsaturated-γ-lactones. Its ir spectrum with an absorption band at 1765 cm^{-1} corroborated the presence of a γ-lactone moiety and also showed a second carbonyl band at 1725 cm^{-1} indicating an ester side chain. The nature of the ester side chain was evident from the ^{1}H-nmr and mass spectral data, which indicated an isobutyrate ester as in **1**. Assignments of the ^{1}H-nmr signals of **5** were deduced from detailed spin decoupling experiments (Table 1). On the basis of the spectral evidence, subcordatolide E [5] must be formulated as a eudesman-12,8-olide with an isobutyrate group at C-1.

Stereochemical assignments were based on considerations outlined below. The large coupling constant $J_{7,8} = 11.0$ Hz suggested an antiperiplanar arrangement of H-7 and H-8, and on the basis of the biogenetic assumption that H-7 is α-oriented as in all sesquiterpene lactones from higher plants (4), the presence of a *trans*-12,8α-lactone in **5** was derived. The configuration of the isobutyrate side chain at C-1 was assigned β on the basis of the small coupling constant $J_{1,2} \sim 4$ Hz, which suggested an equatorial disposition of H-1. A broad three-proton singlet at δ 1.75 (H-15) corresponded to an olefinic methyl group, which sharpened upon irradiation of a one-proton broadened peak at δ 5.29 (H-3) clearly indicating an endocyclic 3,4-double bond. From the above spectroscopic evidence, and from the comparison of the ^{1}H-nmr spectrum of **5** with the one of subcordatolide B, the structure of which was established by X-ray diffraction analysis (2), we propose for subcordatolide E a stereostructure as shown in **5**.

TABLE 3.   Coordinates and Isotropic Thermal Parameters for Subcordatolide D [1]

Atom	x	y	z	B_{eq} or B	Atom	x	y	z	B_{iso}
O1	0.4592(1)	0	0.53626(6)	4.33(2)	H1	0.450(2)	−0.185(2)	0.447(1)	3.0(3)
O2	0.0228(1)	−0.4276(1)	0.39354(6)	3.73(2)	H21	0.672(3)	0.066(3)	0.456(1)	5.6(5)
O3	−0.2368(1)	−0.5495(2)	0.34128(8)	5.03(2)	H22	0.509(2)	0.165(3)	0.383(1)	4.5(4)
O4	0.2285(2)	−0.4256(2)	0.12491(6)	4.48(2)	H31	0.677(3)	−0.143(3)	0.337(2)	6.3(5)
O5	0.197(2)	−0.2062(2)	0.02871(8)	6.00(3)	H32	0.707(3)	0.026(3)	0.300(1)	5.9(5)
C1	0.4285(2)	−0.0559(2)	0.44595(8)	3.38(2)	H5	0.485(3)	−0.335(3)	0.277(1)	4.6(4)
C2	0.5620(2)	0.0464(2)	0.40361(10)	4.21(3)	H6	0.148(2)	−0.209(2)	0.174(1)	2.9(3)
C3	0.6131(2)	−0.0409(3)	0.32223(10)	4.50(3)	H7	0.207(2)	−0.520(2)	0.274(1)	3.6(3)
C4	0.4547(2)	−0.0826(2)	0.25709(9)	3.89(3)	H8	0.280(2)	−0.376(2)	0.398(1)	3.0(3)
C5	0.4021(2)	−0.2470(2)	0.24154(8)	3.70(3)	H9	0.019(3)	−0.120(3)	0.338(1)	5.0(4)
C6	0.2225(2)	−0.3069(2)	0.19816(8)	3.48(2)	H131	−0.123(2)	−0.439(3)	0.111(1)	4.5(4)
C7	0.1454(2)	−0.4144(2)	0.26385(8)	3.26(2)	H132	−0.283(3)	−0.497(3)	0.169(2)	6.0(5)
C8	0.1627(2)	−0.3360(2)	0.35807(8)	3.11(2)	H141	0.171	0.190	0.474	6.0
C9	0.1282(2)	−0.1473(2)	0.36454(8)	3.22(2)	H142	0.049	0.162	0.376	6.0
C10	0.2372(2)	−0.0242(2)	0.40380(8)	3.26(2)	H143	0.249	0.236	0.385	6.0
C11	−0.0474(2)	−0.4574(2)	0.24199(10)	3.75(3)	H151	0.291	0.041	0.145	6.0
C12	−0.1032(2)	−0.4850(2)	0.32779(10)	3.70(3)	H152	0.442	0.164	0.203	6.0
C13	−0.1592(2)	−0.4681(3)	0.16595(12)	5.74(4)	H153	0.269	0.108	0.243	6.0
C14	0.1710(2)	0.1574(2)	0.41110(12)	4.56(3)	H17	0.129	−0.590	−0.017	6.0
C15	0.3564(3)	0.0685(3)	0.20678(11)	4.96(3)	H181	0.179	−0.529	−0.159	8.0
C16	0.2110(2)	−0.3590(2)	0.04363(9)	4.18(3)	H182	0.050	−0.386	−0.126	8.0
C17	0.2194(3)	−0.5013(3)	−0.02323(11)	5.33(4)	H183	0.256	−0.339	−0.125	8.0
C18	0.1726(4)	−0.4334(4)	−0.11579(12)	7.06(6)	H191	0.391	−0.685	−0.050	9.0
C19	0.3914(4)	−0.5920(3)	−0.00498(15)	7.62(6)	H192	0.487	−0.509	−0.007	9.0
H10H	0.37(3)	−0.023(3)	0.552(1)	6.4(5)	H193	0.407	−0.647	0.055	9.0

The y coordinate of O1 was fixed to define the origin.

EXPERIMENTAL

C. subcordata was collected on September 12, 1979, in the State of Tachira, Venezuela, 13.3 km from Delicias along the road toward Villa Paez (L. Urbatsch, No. 3427, voucher deposited at LSU). The air-dried plant material (456 g) was extracted and worked up as previously described (2), yielding 16.4 g of the crude syrup. Column chromatography on Si gel of the crude terpenoid syrup with petroleum ether/Me_2CO mixtures of increasing polarity provided 64 fractions of 200 ml each. Fraction 20 (47 mg) was further purified by preparative tlc on Si gel with hexane-Me_2CO (9:1), giving 11 mg of subcordatolide E [**5**].

Fraction 29 (203 mg) yielded 160 mg of impure crystals, which upon recrystallization by vapor diffusion (hexane/$CHCl_3$) provided 147 mg of pure subcordatolide D [**1**].

SUBCORDATOLIDE D [**1**].—$C_{19}H_{26}O_5$, mp 246° (dec.); uv λ max (MeOH) 218 nm (ε 5.62×10^3), 224 nm (ε 5.46×10^3); cd (c 2.16×10^{-4}, MeOH); $[\theta]_{262} - 7.86 \times 10^3$, $[\theta]_{227} + 3.57 \times 10^4$, $[\theta]_{215} - 3.92 \times 10^4$, $[\theta]_{204} + 3.14 \times 10^4$; ir ν max ($CHCl_3$) 3600 (OH), 3555 (OH), 1765 (γ-lactone), 1730 (ester), 1660 (double bond), 1605 (double bond); eims (probe) m/z 246 (9, M-A), 228 (19, M-A-H_2O), 213 (10, M-A-H_2O-Me), 200 (13, M-A-H_2O-CO), 185 (33, M-A-H_2O-CO-Me), 71 (55, A^1), 43 (100, A^2). [*13]C nmr (50.32 MHz, $CDCl_3$, TMS), 69.4 (d, C-1), 38.2 (t, C-2), 29.4 (t, C-3), 144.4 (s, C-4), 121.8 (d, C-5), 70.9 (d, C-6), 47.0 (d, C-7), 74.5 (d, C-8), 120.0 (d, C-9), 144.1 (s, C-10), 136.3 (s, C-11), 169.7 (s, C-12), 121.6 (t, C-13), 17.5 (q, C-14), 16.5 (q, C-15), 176.0 (s, C-1'), 34.1 (d, C-2'), 18.9 (q, C-3', C-4').

SUBCORDATOLIDE D, *p*-BROMOBENZOATE [**4**].—Lactone **1** (90 mg) was dissolved in 5 ml of CH_2Cl_2 and reacted with 90 mg of *p*-bromobenzoyl chloride, 2 mg of 4-dimethylaminopyridine and 0.1 ml of NEt_3 at ambient temperature for 40 h. The reaction was stopped by addition of H_2O, and the mixture was extracted with $CHCl_3$. The organic layer was washed with 5% aqueous HCl, 5% aqueous Na_2CO_3, and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure gave 79 mg of an oily mixture, which after purification by preparative tlc on Si gel with $CHCl_3$-Me_2CO (9:1) yielded 42 mg of **4**. $C_{26}H_{29}O_6Br$, mp 172° (dec.); ir ν max ($CHCl_3$) 1770 (γ-lactone), 1725 (ester), 1710 (ester), 1600 (aromatic), 1270 (benzoate), 1110 (benzoate); eims (probe) m/z 317 (4, M-$C_7H_4O_2Br$), 229 (10, M-$C_7H_4O_2Br$-A), 228 (16, M-$C_7H_5O_2Br$-A), 200 (7, M-$C_7H_5O_2Br$-A-CO), 185 (90, BrC_6H_4CO), 183 (100, BrC_6H_4CO), 71 (31, A^1), 43 (14, A^2).

SUBCORDATOLIDE E [**5**].—$C_{19}H_{26}O_4$, gum; uv λ max (MeOH) 212 nm (ε 7.95×10^3); cd (c 2.40×10^{-3}, MeOH), $[\theta]_{280} - 3.76 \times 10^2$, $[\theta]_{228}$ 1.54×10^3, $[\theta]_{205} - 2.09 \times 10^3$; ir ν max ($CDCl_3$) 1765 (γ-lactone), 1725 (ester), 1650 (double bond); eims (probe) m/z 230 (91, M-A), 215 (78, M-A-Me), 202 (6, M-A-CO), 177 (5, M-A-Me-CO), 71 (43, A^1), 43 (54, A^2), cims (i-butane): 319.2 $[M+1]^+$.

CRYSTAL DATA[4].—$C_{19}H_{26}O_5$, MW=334.4, monoclinic space group $P2_1$, a=7.7493 (3), b=7.7146 (10), c=15.4084 (11)Å, β=100.916 (6)°, V=904.5 (3)Å³, Z=2, d_c=1.228 g cm^{-3}, μ(CuKα)=6.81 cm^{-1}, were determined by a least squares fit of the setting angles of 25 reflections having 67°<2θ<89°. Intensity data were collected using CuK$_\alpha$ radiation (λ=1.54184 Å) on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator by ω-2θ scans of variable rate from a prismatic crystal of dimensions 0.18×0.28×0.60 mm. Scan rates were designed to yield I=50σ(I) for all significant data with scan rates varying from 0.42 to 4.0 deg. min^{-1}. One quadrant of data was measured within the limits 2°<θ<75°, and, immediately after each measurement, its Friedel equivalent was measured, if accessible, under identical conditions. A total of 3660 unique (under symmetry C_2) data was thus measured, of which 3434 had I>3σ(I) and were used in the refinement. Data reduction included corrections for background, Lorentz, polarization, and absorption. The absorption corrections were based on ψ scans of reflections near χ=90° with minimum relative transmission coefficient 92.46%. Redundant data agreed to Rint=0.016, and the two Friedel-related quadrants agreed to Rint=0.022.

ACKNOWLEDGMENTS

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