Chemistry of Natural Compounds and Bioorganic Chemistry

Crystal and molecular structure of subchrysine (3-*O*-acetylridentine), a new germacranolide from *Artemisia subchrysolepis*

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A new sesquiterpenoid lactone was isolated from terrestrial parts of *Artemisia subchrysolepis* Filat. and studied by X-ray diffraction analysis and CD spectroscopy. This compound was called subchrysine and identified as (1*R*,3*S*,4*E*,6*R*,7*S*)-3-acetoxy-1-hydroxygermacra-4,10(14),11(13)-trien-12,6-olide. Pronounced temperature dependence of the ^1H and ^{13}C NMR spectra of subchrysine was observed. The results of conformational analysis of subchrysine by quantum-chemical (PM3) and molecular mechanics (MMX) methods are also presented.

Key words: sesquiterpenoids; germacranolides; X-ray diffraction analysis; NMR spectra; circular dichroism; conformational analysis.

Sesquiterpenoid lactones are typical components of extracts from the terrestrial parts of many plants of the Asteraceae family including various species of *Artemisia*.[1,2] These compounds often possess high biological activities of various types.[2] Among the plants of Central Kazakhstan, whose chemical compositions have not been studied, *Artemisia subchrysolepis* Filat. has been described relatively recently as a separate species[3] included in the Seriphidium (Bess.) Peterm. subgenus, Sclerophyllum Filat. section, and Kazakhstaniceae Filat. subsection.[4]

Using a general procedure,[5] we isolated a new sesquiterpenoid lactone (yield 0.03%) from the aerial part of *Artemisia subchrysolepis* Filat. and called it subchrysine. The composition of this compound corresponds to the molecular formula $C_{17}H_{22}O_5$ but the peak with the largest mass in the high-resolution mass spectrum corresponds to $C_{15}H_{20}O_4$ ions, whose formation can be accounted for by the abstraction of $CH_2{=}C{=}O$ from the molecular ion. The signals in the ^{13}C and ^1H NMR spectra of subchrysine are broadened owing to the conformation exchange, which occurs in both $CDCl_3$ and pyridine-d_5 solutions and hampers interpretation of the signals. This set of tentative results has stimulated an X-ray diffraction study of this compound.

The structure and the relative configuration of the subchrysine molecule, which correspond to formula **1**,

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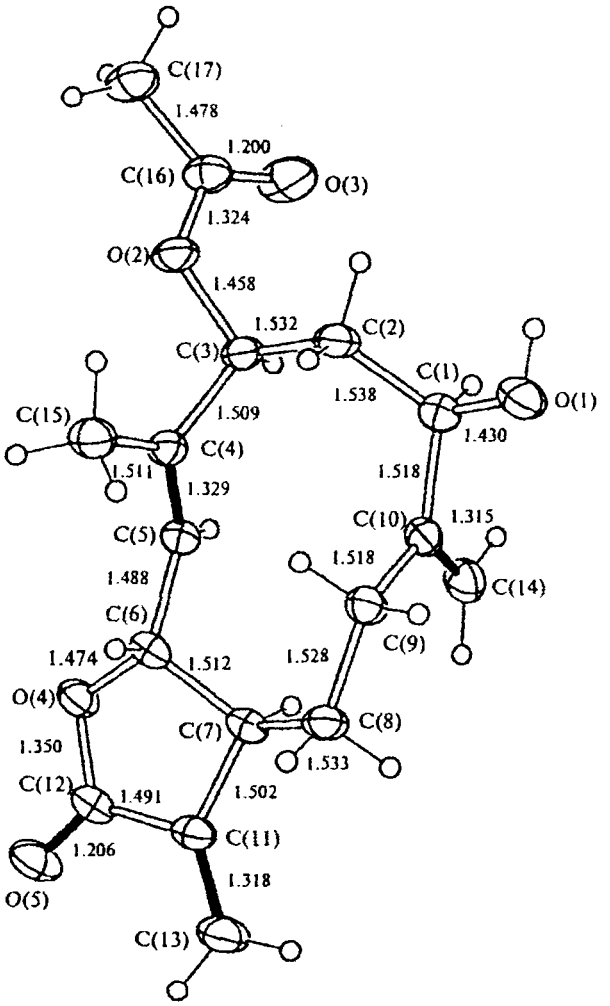


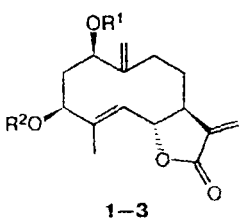
Fig. 1. Structure of molecule **1**. The error in the determination of the bond lengths is 0.004—0.006 Å.

are shown in Fig. 1. The bond lengths in the molecule are close to the average statistical values; only the C(6)—C(7) bond is somewhat shortened (1.512(5) Å compared to 1.542(11) Å in a typical $(C)_2CH—CH(C)_2$ fragment).[6] The conformation of the lactone ring is close to the twist-form (Table 1). The ten-membered ring occurs in a conformation referred to as "C_2-twist".[7,8] The approximate twofold axis passes through the centers of the C(4)—C(5) and C(9)—C(10) bonds. According to the data presented in the publications cited, the C_2-twist conformation is the optimum one for *trans*-cyclodecene. The hydroxy and acetoxy groups are pseudoequatorial. The latter is oriented in such a way that its carbonyl group occupies an eclipsed position in relation to the C(3)—O(2) bond (the C(3)—O(2)—C(16)—O(3) torsion angle is equal to 1.9(7)°). Note that the planes of the exo- and endocyclic double bonds in the 10-membered ring are virtually parallel to each other; the corresponding dihedral angle is 9.1(3)°. In the crystal, the molecules of subchrysine **1** are joined into infinite chains, arranged along the *a* axis, through O(1)—H...O(5) hydrogen bonds (O—H 0.82, O(1)...O(5) 2.857(4), H...O(5) 2.12 Å, O(1)—H...O(5) 150°).

Table 1. Main torsion angles (φ) in the molecule of subchrysine **1**

Angle	φ/deg
O(1)—C(1)—C(2)—C(3)	175.7(3)
C(1)—C(2)—C(3)—O(2)	156.8(3)
C(2)—C(3)—C(4)—C(5)	102.2(4)
C(15)—C(4)—C(5)—C(6)	17.0(6)
C(4)—C(5)—C(6)—C(7)	118.4(4)
C(5)—C(6)—C(7)—C(8)	−80.8(4)
C(7)—C(8)—C(9)—C(10)	57.7(5)
C(8)—C(9)—C(10)—C(1)	−165.3(3)
C(2)—C(1)—C(10)—C(9)	53.6(5)
C(6)—C(7)—C(11)—C(12)	−24.8(4)
C(7)—C(11)—C(12)—O(4)	8.5(4)
C(17)—C(16)—O(2)—C(3)	−178.1(4)
C(2)—C(3)—O(2)—C(16)	−86.2(4)
C(7)—C(6)—O(4)—C(12)	−28.6(3)
C(10)—C(1)—C(2)—C(3)	55.6(5)
C(1)—C(2)—C(3)—C(4)	−85.1(4)
C(3)—C(4)—C(5)—C(6)	−153.1(3)
C(4)—C(5)—C(6)—O(4)	−124.6(4)
O(4)—C(6)—C(7)—C(11)	32.0(3)
C(6)—C(7)—C(8)—C(9)	49.9(5)
C(8)—C(9)—C(10)—C(14)	19.6(5)
C(2)—C(1)—C(10)—C(14)	−131.1(4)
C(8)—C(7)—C(11)—C(13)	27.0(6)
C(13)—C(11)—C(12)—O(5)	11.5(6)
O(3)—C(16)—O(2)—C(3)	1.9(7)
C(4)—C(3)—O(2)—C(16)	153.1(4)
C(11)—C(12)—O(4)—C(6)	12.6(4)

According to its structure, subchrysine is formally the 3-*O*-acetate of the known germacranolide ridentine **2** isolated from *Artemisia tripartita* Rudb. ssp. *rupicola* Beetle.[9,10] The structure and stereochemistry of lactone **2** were established based on spectral data.[9,10] Acetylation of ridentine has given liquid diacetate,[9] whereas subchrysine yields crystalline 1-*O*-acetate **3**. The CD curve recorded for this acetate at 258 nm, like that of ridentine,[10] exhibits a negative Cotton effect corresponding to the $n\rightarrow\pi^*$ transition in the methylene-lactone chromophore.[11] Therefore, the absolute configuration of the subchrysine molecule is similar to that proposed for ridentine.



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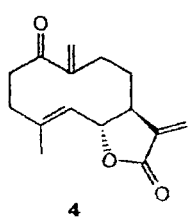

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1: R^1 = H, R^2 = Ac; **2**: R^1 = R^2 = H; **3**: R^1 = R^2 = Ac

Table 2. Parameters of the ^{1}H NMR spectra of lactone **1** (δ, J/Hz)

Atom	Pyridine-d_5 (+90 °C)	CD_2Cl_2 (−30 °C)	
		Major (55%)[a]	Minor (45%)[a]
H(1)	4.28 (dd, J = 10.0, 4.0)	4.37 (dd, J = 10, 5)	3.75 (dd, J = 10, 5)
H(2)	2.40 (m, H(2a))[b]	[c]	[c]
	2.43 (m, H(2b))[b]	[c]	[c]
H(3)	5.43 (dd, J = 10.0, 4.5)	5.00 (d, J = 11.0)	5.18 (dd, J = 11.5, 5.0)
H(5)	5.56 (br.d, J = 10)	5.38 (br.d, J = 10)	5.39 (br.d, J = 10)
H(6)	4.54 (td, J = 10, 1.2)	4.57 (t, J = 10)	4.33 (t, J = 9.8)
H(7)	2.87 (tq, J = 10, 3)	[c]	[c]
H(8)	2.23 (tt, H(8a), J = 10.0, 3.0)	[c]	[c]
	1.57 (m, H(8b))	[c]	[c]
H(9)	2.53 (br.dd, H(9a), J = 16, 10)	[c]	[c]
	2.15 (br.ddd, H(9b), J = 16, 7.5, 2.5)	[c]	[c]
H(13)	6.22 (dd, H(13a), J = 3.5, 1.0)	6.09 (d, J = 3.5)	6.13 (d, J = 3.5)
	5.42 (dd, H(13b), J = 3.5, 1.0)	5.47 (d, J = 3.5)	5.51 (d, J = 3.5)
H(14)	5.31 (br.s, H(14a))	5.29 (d, J = 2.0)	5.13 (br.s)
	4.96 (br.s, H(14b))	4.88 (br.s)	4.91 (d, J = 2.0)
H(15)	1.77 (dd, 3 H, J = 1.4, 0.6)	1.83 (br.s)	1.52 (br.s)
H(17)	2.03 (s, 3 H)	2.05 (s)	2.05 (s)

[a] Conformers. [b] Strongly coupled AB part of the ABMX system. [c] The signal is masked by other signals.

The closest structural analog of lactone **1** contained in the Cambridge database[12] is 1-dehydropygallicin[13] (**4**). The ten-membered ring in the molecule of **4** occurs in a crown-like conformation. According to calculations carried out previously,[13] this conformation is the most stable in the gas phase. Thus, the conformations of lactones **1** and **4** in the crystal are different.

As noted above, most of the signals in the ^{1}H and ^{13}C NMR spectra of lactone **1** are broadened. When the temperature of the solution is increased to 90 °C, signal broadening in these spectra disappears almost completely. Both NMR spectra were interpreted using the ^{1}H—^{1}H (COSY) and ^{13}C—^{1}H (COSY) 2D NMR techniques (Tables 2 and 3).

Gradual decrease in the temperature of a CD_2Cl_2 solution of lactone **1** has an effect on the ^{1}H NMR spectral pattern: from +20 to −20 °C, it markedly changes, whereas al lower temperatures (−20 to −60 °C), it remains virtually unchanged and exhibits signals for two conformers of the lactone, present in a ratio of approximately 55 : 45 (see Table 2). The same type of behavior was found for the ^{13}C NMR spectrum: at low temperatures, it contains signals for two conformers present in different amounts (see Table 3).

In order to identify the most stable conformation of molecule **1**, we carried out conformational analysis in the gas phase using molecular mechanics (MMX program,[14] version of 1988) and quantum chem-

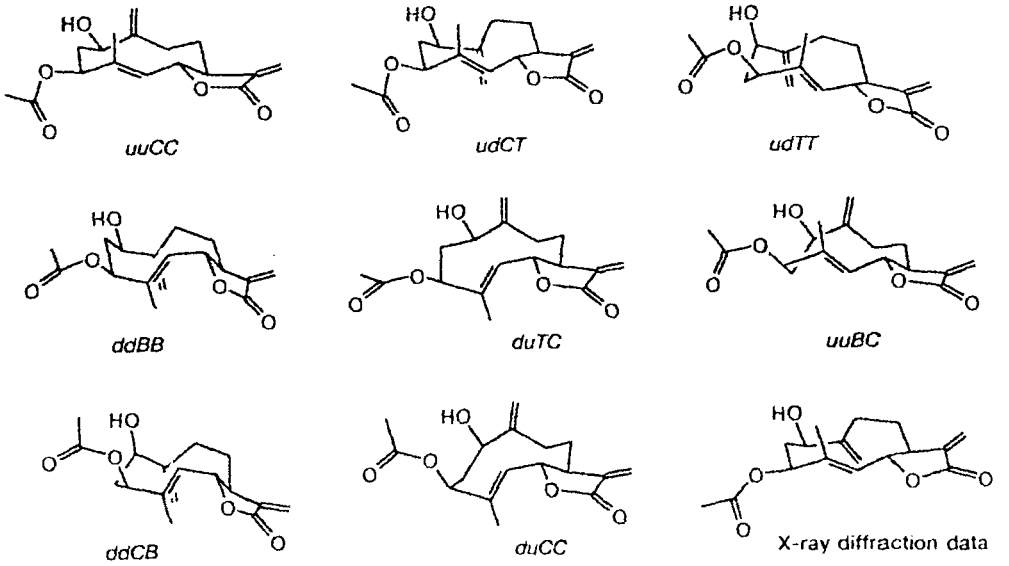

Fig. 2. Main calculated and experimental conformations of the molecule of lactone **1** (*cf.* Note to Table 4).

Table 3. Parameters of the ^{13}C NMR spectra of lactone **1** (δ)

Atom	Pyridine-d_5	CD_2Cl_2 (−60 °C)	
	(+90 °C)	Major*	Minor*
C(1)	74.87 (d)	73.57	73.18
C(2)	38.81 (t)	33.66	36.92
C(3)	76.53 (d)	75.14	75.33
C(4)	142.50 (s)	139.32	144.63
C(5)	124.47 (d)	124.15	120.54
C(6)	79.52 (d)	77.76	79.07
C(7)	47.74 (d)	41.08	49.40
C(8)	26.24 (t)	21.35	21.90
C(9)	30.39 (t)	33.74	26.50
C(10)	150.66 (s)	145.89	148.72
C(11)	140.80 (s)	138.66	137.89
C(12)	169.15 (s)	169.63	169.69
C(13)	117.44 (t)	118.31	118.89
C(14)	111.06 (t)	115.52	108.58
C(15)	11.94 (q)	10.62	11.86
C(16)	169.51 (s)	169.81	169.81
C(17)	20.34 (q)	20.45	20.45

* Conformers.

Table 4. Calculated conformational characteristics of the molecule of subchrysine **1**

Conformer	$\Delta H°_f$/kcal mol^{-1}		Transition	ΔH^* (MMX) /kcal mol^{-1}
	PM3	MMX		
uuCC	−170.2	−172.9	*uuCC*→*udCT*	15.9
udCT	−167.1	−171.3	*uuCC*→*duTC*	15.5
udTT	−166.4	−173.2	*udTT*→*ddCB*	15.8
ddBB	−165.9	−173.3	*uuCC*→*uuBC*	9.7
duTC	−166.0	−170.8	*ddCB*→*ddBB*	9.3
uuBC	−164.9	−170.2	*duCC*→*duTC*	5.7
ddCB	−162.2	−173.9	*udTT*→*udCT*	5.1
duCC	−160.7	−169.3		

Note. The symbols *u* (up) and *d* (down) denote the orientation of the Δ^4 and $\Delta^{10(14)}$ double bonds, respectively, in relation to the carbon ring plane; *C* stands for chair, *T* stands for twist, and *B* stands for boat.

istry (semiempirical PM3 method, MNDO program,[15] version of 1992). The calculations demonstrated the flexibility of the ten-membered ring: the MMX results show that eight of the sixteen most stable conformations considered differ by no more than 5 kcal mol^{-1} (the H atoms are not shown in the gas phase) (Table 4).

According to the MMX calculations, the highest ΔH^* barrier encountered in conformational transitions between the major conformations (identified by MMX), *ddCB*, *udBB*, *udTT*, and *uuCC*, amounts to 16.9 kcal mol^{-1}. It can be seen from Table 4 that the MMX and PM3 methods predict different conformations as the most stable ones.

For the two conformations of the molecule of lactone **1**, detected in the low-temperature ^1H NMR spectra, some spin-spin coupling constants $^3J_{H,H}$ were determined. Comparison of the experimental and calculated spin-spin coupling constants (Table 5) makes it possible to identify the observed conformers. Thus the major

Table 5. Calculated[17,18] from the MMX geometry and experimental spin-spin coupling constants $^3J_{H,H}$ (Hz) of the main conformers of the subchrysine (**1**) molecule

Conformer	$^3J_{1,2\alpha}$	$^3J_{1,2\beta}$	$^3J_{2\alpha,3}$	$^3J_{2\beta,3}$	$^3J_{5,6}$	$^3J_{6,7}$
			Calculation			
uuCC	2.9	11.6	4.5	11.0	9.9	10.5
*udCT**	5.0	10.6	1.9	11.5	11.3	10.5
udTT	0.9	7.6	4.7	2.2	11.6	10.4
ddBB	4.0	11.2	4.1	11.1	6.6	10.6
duTC	2.0	11.6	5.1	10.6	6.6	10.6
uuBC	2.0	5.0	4.2	2.7	10.0	10.5
ddCB	1.3	5.9	3.4	3.3	6.5	10.5
duCC	3.0	3.8	1.3	6.2	6.6	10.6
			Experiment			
Major (55%)	5	10.0	0	11.0	10.0	10.0
Minor (45%)	5	10.0	5	11.5	10.0	9.8

* The conformer corresponds to that found in the crystal.

conformer corresponds to the *udCT* conformation, which was found in the crystal, while the minor component is the *uuCC* conformation. It should be noted that the data obtained by PM3 prove to be closer to the experimental results than the MMX data. The quantum-chemical PM3 calculations and the molecular-mechanics calculations by the MMX program also led to different results.[16]

Experimental

Melting points were determined using the Kofler hot-stage apparatus. IR spectra were recorded on a UR-20 instrument. NMR spectra were measured on a Bruker DRX-500 instrument (operating at 500.13 MHz for ^1H and 125.76 MHz for ^{13}C) using standard Bruker software to record 2D COSY spectra. Mass spectra (EI, 70 eV) were run on a Finnigan MAT 8200 instrument. Optical rotation was measured for solutions in $CHCl_3$ using a Polamat A polarimeter (at 580 nm). The CD spectrum of lactone **3** was recorded on a Jacso J-600 dichrograph in MeOH.

The aerial part of *Artemisia subchrysolepis* gathered in 1994 in the blooming phase (July) in the neighborhood of settlement Urdzhar of the Semipalatinsk region was dried in air and crushed.

Isolation of lactone 1. Raw material (0.5 kg) was refluxed with 3.5 L of $CHCl_3$. After cooling, the extract was separated, and the raw material was again extracted with an additional 3 L of $CHCl_3$. Extraction was repeated with a new portion (0.5 kg) of the raw material. The combined extracts were concentrated to give 133 g of a dry extract as a dark green resin. This was stirred at 70 °C with a mixture of EtOH (0.2 L) and H_2O (0.1 L). The precipitate that formed was filtered off and treated twice with a mixture of EtOH (0.3 L) and H_2O (0.15 L) at 70 °C with subsequent filtration. The combined water—ethanol solutions were cooled to room temperature and extracted with $CHCl_3$ (3×0.2 L). The chloroform extracts were combined and concentrated to dryness (63 g), and the residue was chromatographed on SiO_2. Successive elution with benzene and its mixtures with EtOAc gave fractions containing β-sitosterol (0.05 g) and α-santonin (0.51 g), and a fraction (3.44 g)

Table 6. Coordinates ($\times 10^4$) and equivalent thermal parameters ($\times 10^3/Å^2$) of nonhydrogen atoms in the subchrysine (**1**) molecule

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
C(1)	3036(4)	4725(8)	6838(3)	45(1)
C(2)	3001(4)	5069(8)	7987(3)	47(1)
C(3)	3220(3)	7177(8)	8358(2)	42(1)
C(4)	4864(3)	7680(7)	8500(2)	39(1)
C(5)	5486(3)	8752(7)	7793(2)	38(1)
C(6)	7109(3)	8677(7)	7581(3)	39(1)
C(7)	7370(3)	8009(8)	6513(2)	40(1)
C(8)	7310(4)	5798(8)	6322(3)	46(1)
C(9)	5941(3)	4722(7)	6699(3)	41(1)
C(10)	4407(3)	5408(7)	6297(3)	39(1)
C(11)	8847(4)	8962(8)	6323(3)	43(1)
C(12)	8948(3)	10686(8)	7014(3)	45(1)
C(13)	9928(4)	8500(9)	5719(3)	60(1)
C(14)	4193(4)	6447(8)	5465(3)	51(1)
C(15)	5721(4)	6658(9)	9361(3)	54(1)
C(16)	1116(4)	7825(8)	9354(3)	50(1)
C(17)	622(4)	8073(10)	10398(3)	65(1)
O(1)	2926(3)	2671(0)	6644(2)	64(1)
O(2)	2565(2)	7401(7)	9341(2)	51(1)
O(3)	333(3)	7978(9)	8594(2)	82(1)
O(4)	7811(3)	10627(6)	7652(2)	48(1)
O(5)	9843(3)	12009(7)	7033(3)	66(1)

containing lactone **1**. Repeated chromatography (with light petroleum containing 0 to 60% EtOAc as the eluent) gave 0.30 g of lactone **1**.

(1*R*,3*S*,4*E*,6*R*,7*S*)-3-Acetoxy-1-hydroxygermacra-4,10(14),11(13)-triene-12,6-olide (1). Crystals with m.p. 149–151 °C (EtOAc), $[\alpha]_{580}^{21}$ +145.4° (*c* 0.44). IR (KBr), ν/cm^{-1}: 3470 (OH), 1760 (γ-lactone), 1715 (C=O). MS, *m/z* (I_{rel} (%)): 264 (8), 246 (13), 203 (10), 191 (20), 175 (11), 149 (20), 121 (18), 119 (15), 105 (18), 43 (100). Found, *m/z*: 264.13794 $[M-ketene]^+$; calculated for $C_{15}H_{20}O_4$: 264.13615.

Found (%): C, 66.40; H, 7.20. $C_{17}H_{22}O_5$. Calculated (%): C, 66.65; H, 7.24. The data of the ^1H and ^{13}C NMR spectra are presented in Tables 2 and 3.

Diacetate 3. Lactone **1** (0.1 g) was dissolved in a mixture of Py (5 mL) and Ac_2O (2 mL) and kept for 5 h at ~20 °C. The usual workup gave 0.1 g of diacetate **3**, m.p. 65–68 °C (ethyl acetate), $[\alpha]_{580}^{20}$ +200° (*c* 1.67). IR, CCl_4), ν/cm^{-1}: 3080 (C=CH_2), 1780 (γ-lactone), 1740 (C=O). CD spectrum: $\Delta\varepsilon_{258} = -0.07$, $\Delta\varepsilon_{241} = 0$ ($C = 2.6 \cdot 10^{-4}$ mol L^{-1}, MeOH). The signals in the ^1H NMR spectra ($CDCl_3$) were broadened due to conformation exchange but correspond to those described previously.[9]

X-ray diffraction study of lactone 1 was carried out using a Syntex-$P2_1$ diffractometer. Crystal data: monoclinic system, $a = 8.915(2)$ Å, $b = 6.839(1)$ Å, $c = 13.212(3)$ Å, $\beta = 92.75(1)°$, $V = 804.6(3)$ $Å^3$, space group $P2_1$, $C_{17}H_{22}O_{25}$, M = 306.35, $Z = 2$, $d_{calc} = 1.264$ g cm^{-3}, $\lambda = 1.54178$ Å (Cu-Kα, graphite monochromator), $\mu = 0.76$ mm^{-1}, crystal size 1.2×0.45×0.25 mm. The intensities of 1235 independent reflections with $2\theta < 120°$ were measured using the $\theta/2\theta$-scan mode. The absorption corrections were applied by analytical method along the crystal faces (transmission 0.726–0.866). The structure was solved by the direct method using the SHELXS-86 program package and refined by the least-squares method in the full-matrix anisotropic or isotropic (for H atoms) approximation using the SHELXL-93 package to $wR_2 = 0.1306$, $S = 1.062$ for all reflections ($R = 0.0464$ for 1213 $F > 4\sigma$). The positions of hydrogen atoms were specified geometrically in each cycle of the refinement. The absolute configuration could not be determined from the X-ray diffraction data, because the Flack parameter is 0.29(43). The atomic coordinates thus found are listed in Table 6.

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