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IRIDOID GLYCOSIDES OF PLANTS OF THE GENUS *Incarvillea*

I. 7-0-BENZOYLTECOMOSIDE FROM *Incarvillea olgae*

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Aucubin and five substances of iridoid nature designated as A, B, C, D, and E have been isolated from two species of plants — Lagotis integrifolia *(Willd.) Schisk and* Incarvillea olgae *(Rgl.). The IR, UV, mass, PMR and ^{13}C NMR spectra of substance A have been studied, and an x-ray structural investigation has been made of its tetrahydro derivative. This has shown that substance A is 7-benzoyltecomoside.*

In continuation of our investigations of iridoid glycosides from representatives of the family Scrophulariaceae growing in Uzbekistan and Kyrgystan, we have subjected to analysis two species of plants of this family, *Lagotis integrifolia* (Willd.) Schisk and *Incarvillea olgae* (Rgl.) [1,2].

From a methanolic extract of the epigeal part of *Lagotis integrifolia* gathered in the vegetation period we isolated iridoid (**1**). On the basis of an analysis of IR, UV, PMR, and ^{13}C NMR spectra and by the formation of an acetyl derivative (**2**), glycoside (**1**) was identified as aucubin [3, 4].

By qualitative chromatographic analysis of a methanolic extract of the epigeal part of *Incarvillea olgae* we revealed the presence in it of five substances of iridoid nature, which were designated in order of increasing polarity as A, B, C, D, and E.

In the present communication, we consider the structure of substance A (**3**), one of the main components of the total iridoids. The UV spectrum of (**3**) had an absorption maximum at 235 nm (log ε 4.10), which is typical for iridoids with a conjugated aldehyde group at C-4 [5, 6]. The acid hydrolysis of iridoid (**3**) led to glucose and the black product that is characteristic for iridoids. The acetylation of (**3**) with acetic anhydride in pyridine gave a tetraacetate (**5**). The mass spectrum of the latter showed intense peaks with *m/z* 331, 271, 229, and 169, which are characteristic for tetraacetylglucose [7].

The ^{13}C NMR spectrum of (**3**) showed at 98.98 ppm the signal of one anomeric carbon atom, and in the PMR spectrum the same proton appeared in the form of a doublet at 4.70 ppm with $^{3}J = 7.9$ Hz. The value of the spin–spin coupling constant (SSCC) of this proton showed the β-configuration of the anomeric center. Consequently, the compound under consideration was an iridoid monoside.

In the PMR spectrum in D_2O with the addition of trace amounts of CH_3OD as standard at 30°C the resonance signals were appreciably broadened and not all the SSCCs appeared. Table 1 therefore also gives the characteristics of the PMR spectra recorded at 50°C. At 7.35 ppm a doublet with J = 3.7 Hz, characteristic for H-3, appeared, and at 9.12 ppm a singlet typical for the proton of an aldehyde group. On the other hand, two protons linked to one another by a geminal interaction of 14.7 Hz resonated at 2.16 and 2.52 ppm. Each of them appeared in the form of a doublet with broadened components resulting from vicinal interaction with $^{3}J = 3.0$ and 4.5 Hz, respectively. The H-7 proton responsible for this interaction appeared at 4.91 ppm in the form of a broadened singlet with a half-width of 14 Hz. The chemical shift of this signal showed that the (**3**) molecule contained another oxygen function directly linked with a carbon atom of the iridoid moiety. Allowing for the two SSCCs with 2H-6 and the natural broadening of this signal, we find that H-7 interacts with another vicinal proton, which is

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TABLE 1. Chemical Shifts (δ, ppm) and Spin–spin Coupling Constants (Hz) of the Protons and Groups of 7-Benzoyltecomoside (**3**) (in D_2O with CH_3OD as Standard, H_0 — 500 MHz), Tecomoside (**4**) (in CD_3OD [10]), and the Tetraacetate (**5**) (in $CDCl_3$, H_0 — 100 MHz)

Protons	Compound			
	3 (30°C)	3 (50°C)	4 [5]	5
H-1	5.7 br.s	5.7 br.s	5.77 d ^3J=1.7	5.62 br.s
H-3	7.35 br.s	7.35 d ^3J 3.7	7.35 s	7.05 s
H-6	2.51 br.d $^2J\cong14$	2.52 br.d ^2J 14.7 ^4J=4.5	2.50 dd ^2J=5.8	2.3–2.7 m
H-6	2.13 br.d $^2J\cong14$	2.16 br.d ^2J=14.7 ^3J=3.0	2.18 dd ^2J=2.7	2.3–2.7 m
H-7	4.86 br.m $W_{1/2}$=14	4.91 br.m $W_{1/2}$=14	3.91 m ^3J=5.8 and 5.8; 2.7	5.20 m
H-8	1.58 m	1.64 m ^3J=5.9	1.63 m ^3J 12.0 and 5.8	1.76 m
H-9	2.4 br.m $^3J\cong12$	2.41 dd ^3J=12.2 and 2.5	2.32 dd ^3J=12.0 and 1.7	2.3–2.7 m
H-10	0.82 d ^3J=6.0	0.87 d ^3J=6.0	1.11 d	1.12 d ^3J=7.5
H-11	9.12 s	9.14 d ^4J=1.5	9.25 s	9.22 s
H-1′	4.7*	4.70 d ^3J=7.9	4.63 d ^3J=7.8	5.25 d ^3J=7.8
H-2′,6′	3.28–3.82	3.25–3.84		3.6–5.20
H-2″,6″	7.80 d ^3J=7.8	7.82 br.m		8.02 d ^3J=7.8
H-3″,5″	7.25 dd ^3J=7.8; 7.3	7.27 br.m		7.30 m
H-4″	7.38 dd ^3J=7.3	7.35 br.m		7.30 m
OAc				1.96; 2.00; 2.02 2.08

*Masked by the water signal.

TABLE 2. Chemical Shifts (ppm) of the ^{13}C Carbon Nuclei of 7-O-Benzoyltecomoside (**3**) (in CD_3OD), Tecomoside (**4**) (in D_2O with CH_3OD [5]), and the Tetraacetate (**5**) (in $CDCl_3$)

Carbon atom	Compound		
	3	4[5]	5
1	95.56	97.09	95.80
3	162.78	163.33	156.66
4	124.11	125.41	126.74
5	70.17	69.93	71.50
6	45.03	47.85	45.98
7	75.36	73.06	76.19
8	38.28	39.95	39.56
9	53.20	53.72	54.37
10	12.22	12.06	13.43
11	193.41	193.47	190.41
1′	98.98	99.72	96.91
2′	72.39	73.25	71.56
3′	76.24	76.18	72.50
4′	69.47	70.42	68.82
5′	76.40	77.25	73.02
6′	60.64	61.53	62.25
1″	129.56		130.45
2″, 6″	129.48		129.12
3″, 5″	128.67		130.34
4″	133.57		133.79
O<u>C</u>OAr	166.88		166.71
O<u>C</u>OCH$_3$			169.99;170.74 170.74;171.23
OCO<u>C</u>H$_3$			21.23; 21.23 21.32; 21.40

H-8, having $^3J \cong 5.9$ Hz. A multiplet from H-8 appeared at 1.64 ppm, with the half-width $\cong$ 25 Hz. The signal of the sole methyl group, CH_3-10 was represented by a doublet with ^3J = 6.0 Hz at 0.87 ppm.

It also followed from an analysis of the PMR spectrum of (**3**) that H-8 interacted vicinally with H-9 (2.11 ppm), ^3J = 12.2 Hz, and the latter with H-1 (2.41 ppm), ^3J = 2.5 Hz. A comparative analysis of the spectral characteristics of iridoid (**3**) with those of tecomoside (**4**) (Table 1) showed that the greatest differences existed in the chemical shifts of H-7 and CH_3-

TABLE 3. Bond Lengths (r, Å) and Valence Angles (ω, degrees) in the (**5**) Molecule

Bond	r	Bond	r	Angle	ω	Angle	ω
O1–C1	1.35(2)	O1–C12	1.34(2)	C1–O1–C12	122.2(9)	C1–O2–C3	125.2(10)
O2–C1	1.41(2)	O2–C3	1.28(2)	C12–O3–C22	106.0(9)	C13–O4–C14	119.8(11)
O3–C12	1.45(2)	O3–C22	1.33(2)	C16–06–C17	121.3(11)	C19–O8–C20	126.5(10)
O4–C13	1.39(2)	O4–C14	1.21(2)	C23–O10–C24	128.7(12)	C7–O14–C26	111.4(11)
O5–C14	1.14(2)	O6–C16	1.38(2)	O1–C1–O2	104.8(10)	O1–C1–C9	116.6(10)
O6–C17	1.30(2)	O7–C17	1.12(2)	O2–C1–C9	109.6(11)	O2–C3–C4	119.2(15)
O8–C19	1.36(2)	O8–C20	1.30(2)	C3–C4–C5	120.3(14)	C3–C4–C11	108.4(14)
O9–C20	1.10(2)	O10–C23	1.34(2)	C5–C4–C11	131.1(13)	O13–C5–C4	106.3(12)
O10–C24	1.27(2)	O11–C24	1.14(2)	O13–C5–C6	113.5(10)	C4–C5–C6	109.9(12)
O12–C11	1.12(2)	O13–C5	1.27(2)	O13–C5–C9	106.0(12)	C4–C5–C9	119.7(11)
O14–C7	1.41(2)	O14–C26	1.28(2)	C6–C5–C9	101.5(11)	C5–C6–C7	111.8(11)
O15–C26	1.18(2)	C1–C9	1.42(2)	O14–C7–C6	117.8(11)	O14–C7–C8	100.9(11)
C3–C4	1.21(2)	C4–C5	1.43(2)	C6–C7–C8	98.8(12)	C7–C8–C9	112.9(11)
C4–C11	1.40(2)	C5–C6	1.55(2)	C7–C8–C10	111.7(13)	C9–C8–C10	111.4(12)
C5–C9	1.47(2)	C6–C7	1.44(2)	C1–C9–C5	106.7(11)	C1–C9–C8	123.4(11)
C7–C8	1.38(2)	C8–C9	1.48(2)	C5–C9–C8	99.5(11)	O12–C11–C4	122.2(15)
C8–C10	1.45(2)	C12–C13	1.48(2)	O1–C12–O3	103.7(10)	O1–C12–C13	116.2(11)
C13–C16	1.42(2)	C14–C15	1.45(2)	O3–C12–C13	107.9(10)	O4–C13–C12	106.7(11)
C16–C19	1.50(2)	C17–C18	1.44(2)	O4–C13–C16	106.8(11)	C12–C13–C16	115.3(11)
C19–C22	1.46(2)	C20–C21	1.37(2)	O4–C14–O5	111.9(14)	O4–C14–C15	111.1(13)
C22–C23	1.44(2)	C24–C25	1.31(3)	O5–C14–C15	136.9(15)	O6–C16–C13	117.0(10)
C26–C27	1.47(2)	C27–C28	1.32(3)	O6–C16–C19	105.3(11)	C13–C16–C19	109.3(11)
C27–C32	1.29(3)	C28–C29	1.38(3)	O6–C17–O7	126.4(15)	O6–C17–C18	115.8(13)
C29–C30	1.35(4)	C30–C31	1.29(4)	O7–C17–C18	117.6(14)	O8–C19–C16	105.7(10)
C31–C32	1.38(3)			O8–C19–C22	119.3(10)	C16–C19–C22	108.0(11)
				O8–C20–O9	124.2(14)	O8–C20–C21	120.0(13)
				O9–C20–C21	115.8(14)	O3–C22–C19	117.2(10)
				O3–C22–C23	103.7(11)	C19–C22–C23	111.4(13)
				O10–C23–C22	115.8(11)	O10–C24–011	121.0(17)
				O10–C24–C25	124.8(16)	O11–C24–C25	114.0(18)
				O14–C26–O15	123.9(14)	O14–C26–C27	107.9(14)
				O15–C26–C27	128.1(15)	C26–C27–C28	113.5(17)
				C26–C27–C32	129.5(16)	C28–C27–C32	116.9(17)
				C27–C28–C29	115.0(20)	C28–C29–C30	124.4(23)
				C29–C30–C31	121.1(23)	C30–C31–C32	111.5(23)
				C27–C32–C31	130.9(18)		

TABLE 4. Coordinates of the Atoms ($\times 10^4$) and Temperature Parameters U_{eq} ($Å^2 \times 10^3$) of the (**5**) Molecule

Atom	x	y	z	U_{eq}	Atom	x	y	z	U_{eq}
O1	3068(7)	5675(7)	-100(4)	41(3)	C10	2183(11)	8213(13)	1211(7)	52(6)
O2	2050(7)	7002(7)	-518(4)	47(3)	C11	4173(14)	8357(13)	-1332(8)	65(7)
O3	2110(7)	4314(7)	318(4)	41(3)	C12	2401(12)	4831(10)	-279(7)	38(5)
O4	3251(7)	4560(8)	-1275(4)	52(4)	C13	3042(11)	4061(10)	-693(6)	38(5)
O5	4930(9)	4818(9)	-978(6)	85(5)	C14	4262(14)	4920(12)	-1393(8)	61(6)
O6	2991(7)	2322(7)	-1127(4)	44(3)	C15	4316(14)	5319(14)	-2042(9)	85(9)
O7	2155(9)	2521(11)	-2058(5)	96(5)	C16	2361(11)	3126(12)	-828(7)	45(5)
O8	1164(8)	1837(7)	-386(4)	51(4)	C17	2780(14)	2088(13)	-1724(7)	55(6)
O9	2357(8)	547(8)	-192(7)	98(5)	C18	3511(15)	1237(15)	-1983(8)	91(9)
O10	1693(9)	2448(8)	1078(4)	56(4)	C19	1893(11)	2661(11)	-214(6)	33(5)
O11	759(12)	2248(10)	1950(6)	112(6)	C20	1469(13)	851(11)	-380(8)	54(6)
O12	5055(9)	8816(9)	-1311(5)	83(5)	C21	669(15)	112(12)	-614(8)	67(7)
O13	5021(7)	7137(7)	-190(4)	50(3)	C22	1364(10)	3513(11)	169(6)	39(5)
O14	4250(7)	8872(7)	1281(4)	41(3)	C23	940(12)	3134(14)	781(7)	62(6)
O15	5158(8)	10398(8)	1215(5)	67(4)	C24	1578(15)	2040(16)	1631(9)	93(9)
C1	2530(10)	6600(11)	61(6)	36(5)	C25	2299(20)	1302(16)	1865(8)	96(9)
C3	2677(13)	7496(12)	-940(8)	53(6)	C26	4965(13)	9601(14)	1490(8)	61(7)
C4	3652(13)	7893(12)	-790(7)	40(6)	C27	5398(12)	9290(15)	2127(8)	49(6)
C5	4121(11)	7773(12)	-153(7)	41(5)	C28	6159(16)	9978(16)	2390(10)	81(9)
C6	4486(11)	8861(11)	121(7)	45(5)	C29	6555(17)	9725(23)	2998(12)	91(11)
C7	3760(12)	9128(12)	674(6)	39(5)	C30	6259(18)	8829(25)	3305(12)	97(12)
C8	2842(12)	8374(12)	615(7)	44(5)	C31	5506(18)	8159(22)	3058(10)	99(10)
C9	3308(10)	7365(10)	351(6)	29(5)	C32	5109(14)	8477(14)	2464(9)	58(7)

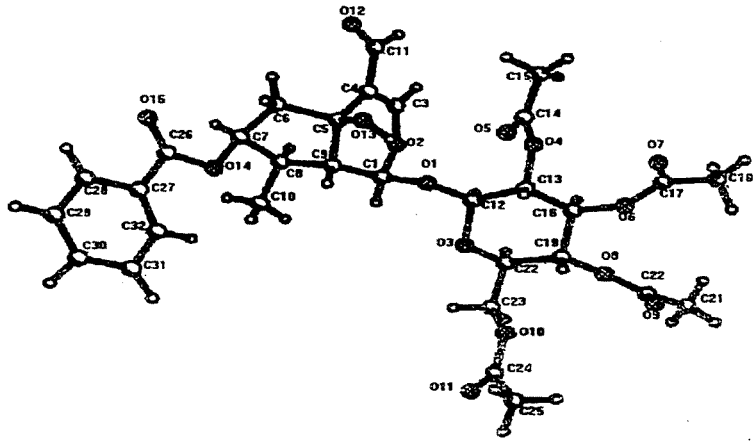


Fig. 1

10. In (**3**), the former underwent a paramagnetic shift by +0.95 ppm, and the signal of the methyl group a diamagnetic shift by −0.29 ppm. Such changes are possible under the influence of an acyl group at C-7.

A consideration of the characteristics of the ^{13}C NMR spectra of compounds (**3**) and (**4**) [5], which are given in Table 2, led to the same conclusion. Thus, for glycoside (**3**) the C-7 signal was shifted downfield by +2.30 ppm and, conversely, the signals of C-6 and C-8 upfield by −2.82 and −1.67, respectively.

Characteristics of protons and carbon atoms in Tables 1 and 2 showed that the acyl group consisted of a benzoyl residue.

The chemical shifts of the C-4 and C-5 carbon atoms (124.11 and 70.17 ppm, respectively) unambiguously witnessed the location of the aldehyde and hydroxy groups at these atoms, respectively.

The physicochemical properties and structure of compound (**3**) proved to be identical with those of the known [9, 10] iridoid 7-O-benzoyltecomoside.

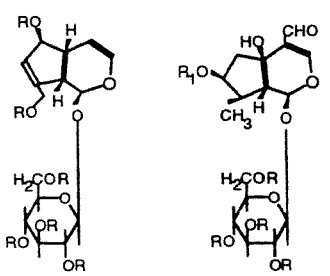
However, there is no spectral description of this substance in [10]. We therefore give detailed information on the ^{1}H and ^{13}C NMR spectra of (**3**) and its acetyl derivative (**5**) and the results of an x-ray structural investigation (XSI) of the latter.

The XSI results, which are of independent value, enabled all the geometric parameters of compound (**5**), including stereochemical questions, to be determined unambiguously. The spatial structure of the molecule of (**5**) is shown in Fig. 1. The iridoid part of (**5**) contains *cis*-linked cyclopentane and pyran rings. The sugar residue is present in the 1β-position and is that of tetraacetylglucose. The double bond is located at carbon atoms C-3—C-4 and the aldehyde group at C-4. The benzoate group at C-7 has the β-orientation. The hydroxy group at C-5, the methyl group at C-8, and H-9 are also β-oriented.

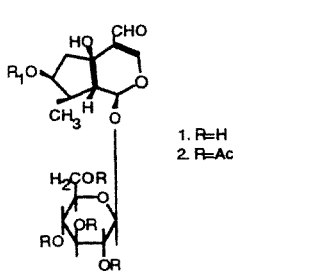
The XSI results showed that in the molecule of (**5**) the cyclopentane ring has the form of a 8α,9β half-chair. The aromatic ring of the acyl group assumes a planar form, while the six-membered heterocycle of the sugar residue has a chair conformation. The aldehyde carbonyl group and the C-3=C-4 double bond are *trans*-oriented with respect to one another about the ordinary C-4—C-11 bond (torsional angle 165°).

The bond lengths and valence angles in the molecule of (**5**) are given in Table 3. The mean values for the C=O, C—O, and C—C bonds in Table 3 agree with their standard values [8]. The mean square deviations for the bond lengths and valence angles amount to 0.03 Å and 1.5°, respectively. The reason for such a high error is the difficulty of obtaining high-quality single crystals. The level of statistics and the high value of the discrepancy factor are explained in the same way (see the Experimental section).

Thus, the structure proposed on the basis of spectral characteristics has found complete confirmation in the XSI results, and the iridoid glycoside (**3**) is 7-O-benzoyltecomoside.



1. R=H
2. R=Ac



3. R=H $R_1=C_6H_5CO$
4. R=H $R_1=H$
5. R=Ac $R_1=C_6H_5CO$

EXPERIMENTAL

Thin-layer chromatography (TLC) was conducted on Silufol plates. For column chromatography we used silica gel of types KSK and L 100/160 μm (Czechoslovakia). In TLC, the iridoid glycosides were detected by spraying with vanillin/sulfuric acid and then heating at 110-120°C for 2-5 min [11].

UV spectra were taken on a Hitachi instrument, IR spectra on a UR-20 spectrophotometer in KBr, mass spectra on MKh-1310 and MKh-1303 instruments, each fitted with a system for direct injection into the ion source (ionizing voltage 50 V, temperature 210-140°C), PMR spectra on a BS-567 A instrument (100 MHz, Tesla, in D_2O or $CDCl_3$, δ, 0 — HMDS), and ^{13}C NMR spectra on CFT (Varian) and BS 567 A (Tesla) instruments. Tetramethylsilane (TMS) was used as the standard in the measurement of the ^{13}C chemical shifts.

Isolation of Iridoids from the Epigeal Part of *Lagotis integrifolia*. The dry comminuted epigeal part of the plant (140 g) was extracted with methanol (5 × 700 ml). The combined methanolic extract was concentrated and was mixed with water, and the aqueous solution was extracted first with chloroform and then with butanol. The residue obtained after the butanol had been distilled off was chromatographed on SiO_2. Elution with chloroform—methanol (4:1) yielded aucubin (**1**) — 3.64 g (yield calculated on the air-dry raw material — 2.6%), $C_{15}H_{22}O_9$, mp 170-172°C (chloroform—methanol), $[\alpha]_D^{22} -159 \pm 2°$ (c 0.64; methanol).

Substance (**1**) (533 mg) was acetylated with acetic anhydride at room temperature for two days. The reaction product was chromatographed on a column of Al_2O_3. The column was eluted with the chloroform—benzene (1:1) system. This gave 350 mg of aucubin hexaacetate (**2**), $C_{27}H_{22}O_{15}$, mp 127-128°C (methanol—water), $[\alpha]_D^{22} -154 \pm 2°$ (c 0.3; methanol).

Isolation of Iridoids from the Epigeal Part of *Incarvillea olgae*. The air-dry comminuted leaves were extracted with methanol (4 × 5 liters). The extract was concentrated, the residue was diluted with water (1 liter), the precipitate that deposited was removed, and the aqueous solution was extracted first with chloroform (7 × 3 liters), then with ethyl acetate (6 × 2 liters), and finally with chloroform—isopropanol (1:1). The residue obtained after the ethyl acetate had been distilled off (50 g) was chromatographed on SiO_2. Elution of the column with the chloroform—methanol—water (4:1:0.1) system yielded an amorphous substance (**4**), $C_{23}H_{28}O_{11}$, $[\alpha]_D^{22} -25 \pm 2°$ (c 0.47; methanol), λ_{max} (C_2H_5OH, nm) 235 (log ε 4.10), ν_{max}, (KBr, cm^{-1}): 3300-3500 (OH), 1730, 1290 (ester), 1685 (C=O), 1630 (C=C).

Acid Hydrolysis. A solution of 15 mg of glycoside (**3**) in 5 ml of 5% sulfuric acid was heated in the water bath for 1 h. The resulting precipitate was filtered off. After the usual working up, glucose was detected in the filtrate with the aid of PC.

The Tetraacetate (5). A solution of 1 g of glycoside (**3**) in 8 ml of pyridine was treated with 8 ml of acetic anhydride at room temperature for 24 h. Then the reaction mixture was diluted with water, and the precipitate that deposited (1.031 g) was filtered off and chromatographed on a column of silica gel. Elution with chloroform gave 872 mg of the tetraacetate (**5**), $C_{31}H_{36}O_{15}$, mp 202-204°C (methanol), $[\alpha]_D^{22} -60 \pm 2°$ (c 0.56; chloroform).

X-Ray Structural Analysis. Crystals of (**5**) grown from solution in dimethyl sulfoxide were first investigated by the photo method. The parameters of the unit cell and the space group were determined from precession x-ray diagrams and were refined on a Syntex $P2_1$ diffractometer: a = 10.782(3), b = 12.701(4), c = 20.942(6) Å, d_{calc} = 1.502 g/cm^3, space group $P2_12_12_1$, Z = 4. A three-dimensional set of intensities was obtained on the same diffractometer: $\theta/2\theta$ method of scanning with CuK_α radiation (graphite monochromator), $\sin\theta/\lambda < 0.55$, rate of scanning 10 deg/min, number of independent nonzero reflections with $I > 2\sigma$ (I) 1677. The search for the structure was conducted by the SHELXS-86 program [12] (PC DOS version) and here in the automatic regime it was possible to find a model of the (**5**) molecule.

Subsequent Fourier syntheses enabled all the nonhydrogen atoms to be localized. The structure was refined by the method of least squares (MLS) successively in the isotropic-anisotropic approximation by the SHELX-76 program [13]. The coordinates of the H-atoms bound to carbon atoms were calculated and refined isotropically. The final divergence factors were R = 0.120, R_w = 0.099. The coordinates of the nonhydrogen atoms from the last stage of the MLS are given in Table 4.

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