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Crystal and Molecular Structure of *cis*- and *trans*-2,4-Dihydroxy-2,4-dimethylcyclohexane-trans-1-acetic Acid γ-Lactone

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ABSTRACT

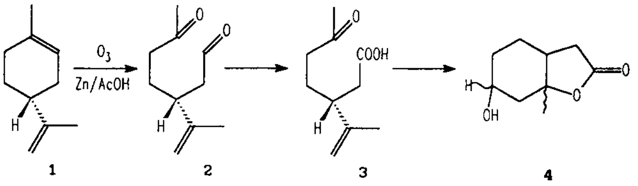
During the transformation process of limonene to tetrahydrofuran derivatives, the title compounds (±)-(4) have been obtained as crystalline products and subjected to X-ray analysis. The crystals of trans-(4) are orthorhombic, space group $P2_12_12_1$, with the lattice constants a = 7.0445(5) Å, b = 10.0908(4) Å, c = 14.0309(6) Å; the absolute configuration at atoms C1, C2, and C4 is R_{c1}, S_{c2}, and R_{c4}, respectively. The isomeric form cis-(4) crystallizes in the monoclinic system, space group $P2_1$, with the following unit-cell parameters: a = 10.8275(4) Å, b = 8.6994(5) Å, c = 16.4722(6) Å, β = 106.515(3)°. The asymmetric part of the unit cell of cis-(4) contains three independent molecules. Each of these three molecules has the identical absolute configuration at all centers of chirality: S_{c1}, S_{c2}, and R_{c4}.

INTRODUCTION

The results presented previously are the combination of synthetic and structural research work on the limonene transformation into tetrahydrofuran derivatives. According to the procedure published by Woliński and Chan [1], a 2,4-dihydroxy-2,4-dimethyl-1-acetic acid γ-lactone (**4**) has been obtained from (+) limonene (**1**). Keto aldehyde **2** was obtained by ozonolysis of limonene **1** [2]. Its oxidation by the Jones reagent caused formation of keto acid **3**, which spontaneously underwent a cyclization to two diastereoisomeric hydroxy lactones **4** [1] (Scheme 1). Although the structure of these lactones has already been explained in principle [1,3], their absolute configuration has never been defined, and this fact inspired our research work.

We obtained isomer **4**-*trans* according to the Woliński procedure [1], while **4**-*cis* isomer was obtained by cyclization of the keto acid in acetic acid in the presence of 50% H_2SO_4. Both products have been purified by multiple crystallization.

Reports on the structure of compound **4** [1,3] up until now have not explained anything about the optical activity and the absolute configuration at the asymmetric atoms. This article presents the full structural research for both isomers with designa-



SCHEME 1

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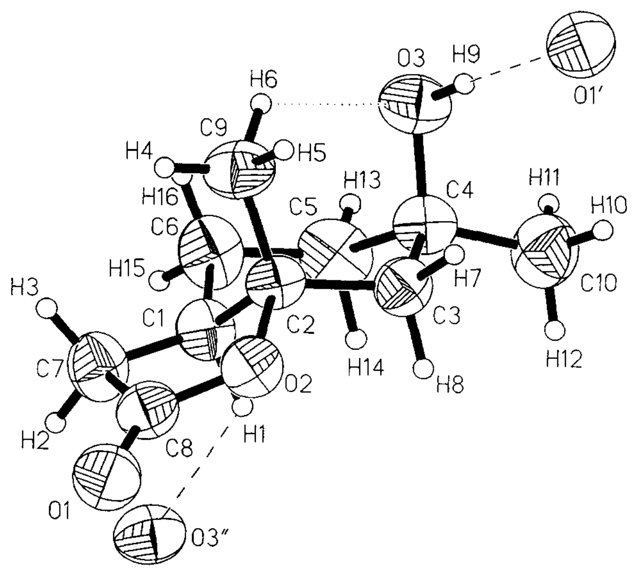


FIGURE 1 Thermal ellipsoidal plot of the molecule of *trans*-2,4-dihydroxy-2,4-dimethylcyclohexane-*trans*-1-acetic acid γ-lactone (**4**-*trans*) with atom-numbering scheme.

tion of bond lengths, valence angles, and geometry of the molecule as well as the absolute configuration at C1, C2, and C4 atoms. The optical rotation established for both diastereoisomers is different: $[\alpha]_D^{20}$ is equal to $-74.7(1)°$ and $-10.5(1)°$ for isomers *trans* and *cis*, respectively.

RESULTS AND DISCUSSION

Synthesized product **4**-*trans* was subjected to crystallization from a mixture of hexane/ethyl acetate (3 : 2), which gave crystals in the form of needles, with mp = 145(1)° and $[\alpha]_D^{20} = -74.7(1)°$ (MeOH, $c = 1.0$). The melting point of the compound *trans*-2,4-dihydroxy-2,4-dimethyl-cyclohexane-*trans*-1-acetic acid γ-lactone obtained by us is the same as that published by Burnett and Rossmann [3]. This fact suggests that this is the same isomer *trans*—unidentified up to now as there was no information about optical rotation in the previously mentioned report [3].

The general views of the molecules of **4**-*trans* and **4**-*cis* with the atom-numbering scheme are presented in Figures 1 and 2, respectively. In the structure **4**-*trans*, there is observed one strong intermolecular hydrogen bond 03–H9 . . 01, with distance H9 . . 01 equal to 2.06(5) Å, and two weaker contacts: intramolecular C9–H6 . . 03 [2.28(3) Å] and intermolecular C1–H1 . . 03 [2.54(2) Å]. In the structure **4**-*cis*, there is no contact C1–H1 . . 03, while two others are as follows: 03–H9 . . 01: 2.02(7) Å, 2.10(8) Å, 2.21(6) Å, and C9–H6 . . 03: 2.43(5) Å, 2.45(6) Å, 2.55(7) Å, respectively, for molecules **a**, **b**, and **c**.

The X-ray analysis of compound **4**-*trans* revealed that the absolute configuration at C1, C2, and C4 atoms is R_{c1}, S_{c2}, and R_{c4}. The absolute configuration at these atoms of isomer **4**-*cis*, obtained in a manner presented in the experimental synthetic part of this work, is, respectively, S_{c1}, S_{c2}, and R_{c4}. The absolute configuration for both compounds has been determined by means of two crystallographic methods: the statistical Hamilton test [4] and Rogers' method [5]. As seen from the preceding, a difference between the absolute configurations of compounds **4**-*trans* and **4**-*cis* occurs only in the configuration of substituents at the C1 atom.

In Tables 1 and 2, torsional angles and asymmetry parameters [6] of the five- and six-membered rings in compounds **4**-*trans* and **4**-*cis*, as well as for structure published by Burnett and Rossmann [3], are presented. The comparison of the values given in these tables shows that the structure of **4**-*trans* corresponds to the structure of the compound published by Burnett and Rossmann [3] from the point of view of the geometry of both rings.

By analysis of the geometry of the molecules of all three compounds, it has been concluded that the five-membered lactone ring adopts a deformed envelope conformation with atom C1 opening the envelope. The difference between the values of angles of opening of the envelope (dihedral angle between planes passing through atoms C2, 02, C8, C7 and C2, C1, C7) in compounds **4**-*cis* and **4**-*trans* (or [3]) is about 8.5°.

The six-membered ring in isomer **4**-*cis* adopts an almost ideal chair conformation, with atoms C2, C5 in the flap position, whereas in compounds **4**-*trans* and [3], it adopts a deformed chair conformation, with atoms C1, C4 in the flap position. One can see in Table 2 that the asymmetry parameters of the six-membered ring in compound **4**-*cis* have similar values, and absolute values of endocyclic torsion angles are in the narrow range from 44.7° to 56.3°. In the case of compounds **4**-*trans* and [3], the asymmetry parameters have differential values: ΔCs(C1) is smallest, and ΔC2(C2–C3) is greatest. In these compounds, the absolute values of the endocyclic torsion angles of the six-membered ring are in the wide range from 45.4° to 67.8°.

The molecules of **4**-*trans* and **4**-*cis* and their geometry are depicted in detail by bond lengths and valence angles (Tables 3 and 4).

Comparing the values obtained by us for compound **4**-*trans* with values given by Burnett and Rossman [3], one can see that all distances and angles are almost identical; small differences in the corresponding values may be influenced by the smaller accuracy and precision of the Burnett–Rossmann experiment.

The obtained values of bond lengths and angles for compound **4**-*cis* should be given consideration. Comparison of bond lengths in molecules of **4**-*cis* and **4**-*trans* shows that differences larger than 3σ appear at two bonds of the six-membered ring: C3–C4

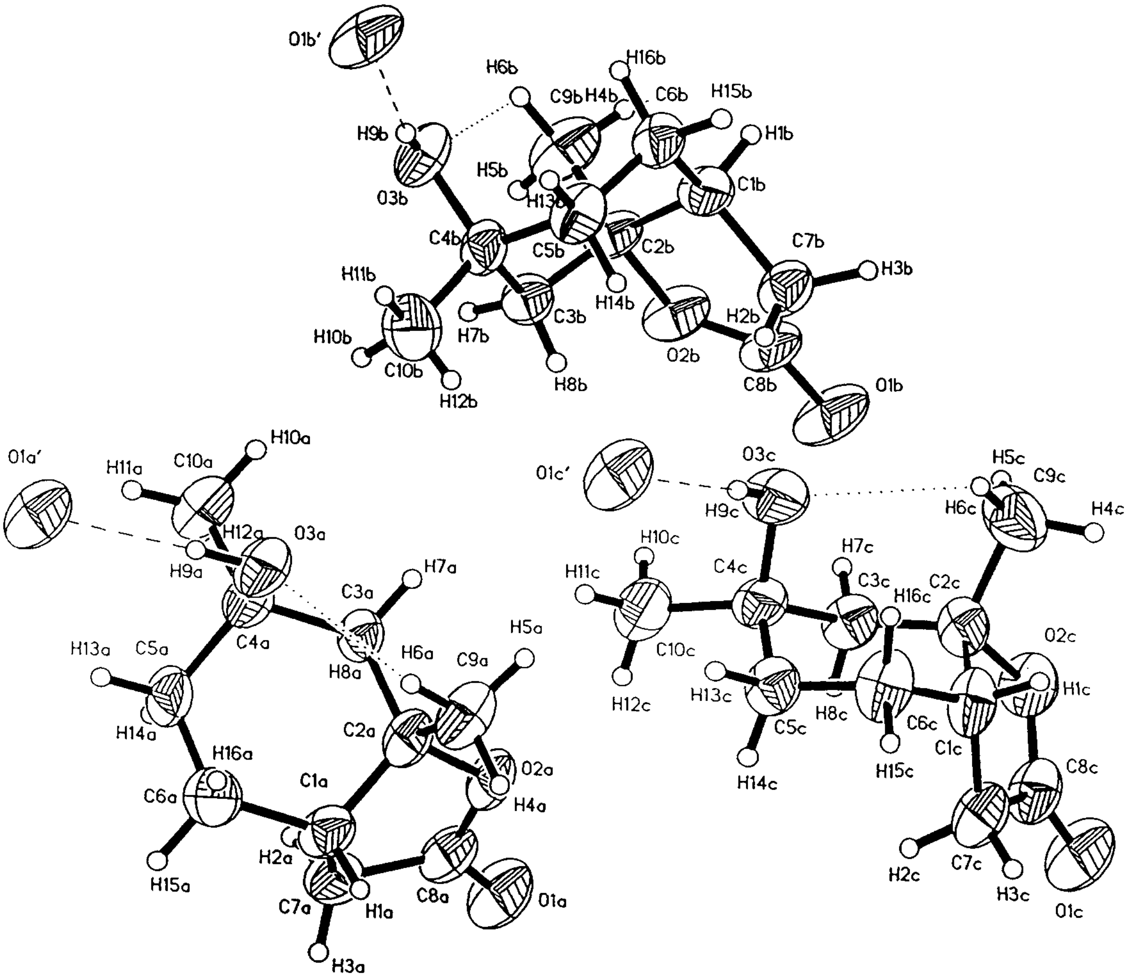


FIGURE 2 Thermal ellipsoidal plot of the molecule of *cis*-2,4-dihydroxy-2,4-dimethylcyclohexane-*trans*-1-acetic acid γ-lactone (**4**-*cis*) with atom-numbering scheme.

TABLE 1 Torsion Angles (°) and Asymmetry Parameters of Five-Membered Ring O2, C2, C1, C7, C8 for Compounds **4**-*cis* and **4**-*trans*. Comparison with Literature Data [3]

	4-*cis*				
	a	**b**	**c**	**4**-*trans*	*[3]*
		Torsion angles			
C8–O2–C2–C1	24.8(3)	23.2(3)	22.7(3)	−29.4(2)	−29.5(4)
O2–C2–C1–C7	−32.8(3)	−32.1(3)	−31.8(3)	40.6(2)	41.1(3)
C2–C1–C7–C8	29.7(3)	29.8(3)	29.8(3)	36.8(2)	37.2(4)
C1–C7–C8–O2	−16.0(4)	−16.9(4)	−17.1(4)	20.2(2)	20.4(4)
C7–C8–O2–C2	−5.7(4)	−4.1(4)	−3.6(4)	5.9(2)	5.7(4)
		Asymmetry parameters			
ΔC_s(O2)	37.1(6)	37.2(6)	37.1(6)	46.1(4)	46.6(7)
ΔC_s(C2)	17.9(6)	19.2(6)	19.6(6)	23.2(4)	23.7(7)
ΔC_s(C1)	6.6(6)	4.7(6)	4.2(6)	7.0(4)	7.0(7)
ΔC_s(C7)	28.9(6)	27.2(6)	26.6(6)	34.9(4)	35.2(7)
ΔC_s(C8)	41.5(6)	40.3(6)	39.9(6)	50.3(4)	50.6(7)
ΔC_2(O2-C2)	37.6(7)	38.5(7)	38.7(7)	47.2(4)	47.8(7)
ΔC_2(C2-C1)	8.1(7)	10.2(7)	10.8(7)	11.4(4)	11.7(7)
ΔC_2(C1-C7)	24.6(7)	22.1(7)	21.3(7)	28.8(4)	28.9(7)
ΔC_2(C7-C8)	47.8(7)	45.9(7)	45.2(7)	58.0(4)	58.4(7)
ΔC_2(C8-O2)	52.8(7)	52.2(7)	51.9(7)	65.0(4)	65.7(7)

TABLE 2 Torsion Angles (°) and Asymmetry Parameters of Six-Membered Ring C1, C2, C3, C4, C5, C6 for Compounds **4**-*cis* and **4**-*trans*. Comparison with Literature Data [3]

	4-*cis*				
	a	**b**	**c**	**4**-*trans*	*[3]*
		Torsion angles			
C6–C1–C2–C3	−44.7(4)	−45.4(4)	−46.3(4)	−67.2(2)	−67.8(4)
C1–C2–C3–C4	47.3(4)	47.0(4)	48.6(4)	55.0(2)	55.3(4)
C2–C3–C4–C5	−51.2(4)	−51.2(4)	−52.8(4)	−45.4(2)	−45.8(5)
C3–C4–C5–C6	54.0(4)	54.6(4)	55.3(4)	46.0(2)	46.6(5)
C4–C5–C6–C1	−54.4(4)	−56.3(4)	−56.1(4)	−53.9(2)	−54.4(5)
C5–C6–C1–C2	48.7(4)	51.1(4)	51.2(4)	64.5(2)	65.1(4)
		Asymmetry parameters			
$\Delta C_s(C1) = \Delta C_s(C4)$	5.0(7)	6.6(7)	5.4(7)	1.7(3)	1.7(7)
$\Delta C_s(C2) = \Delta C_s(C5)$	2.1(7)	1.3(7)	1.7(7)	13.9(4)	14.0(8)
$\Delta C_s(C3) = \Delta C_s(C6)$	6.7(8)	6.6(8)	6.4(8)	14.8(4)	14.8(8)
$\Delta C_2(C1-C2) = \Delta C_2(C4-C5)$	2.5(7)	4.6(8)	3.0(8)	9.0(4)	9.2(9)
$\Delta C_2(C2-C3) = \Delta C_2(C5-C6)$	5.9(8)	4.8(8)	5.4(8)	20.2(4)	20.3(9)
$\Delta C_2(C3-C4) = \Delta C_2(C6-C1)$	8.3(8)	9.4(8)	98.4(8)	11.4(4)	11.3(9)

TABLE 3 Bond Lengths (Å) for Nonhydrogen Atoms in Compounds **4**-*cis* and **4**-*trans*. Comparison with Literature Data [3]

	4-*cis*				
	a	**b**	**c**	**4**-*trans*	*[3]*
O1–C8	1.216(4)	1.218(4)	1.213(4)	1.206(2)	1.214(5)
O2–C2	1.484(4)	1.496(4)	1.500(4)	1.482(2)	1.482(5)
O2–C8	1.330(5)	1.336(5)	1.337(4)	1.345(2)	1.352(5)
O3–C4	1.435(5)	1.437(5)	1.425(4)	1.437(2)	1.443(5)
C1–C2	1.534(4)	1.533(5)	1.528(4)	1.524(2)	1.525(5)
C1–C6	1.524(5)	1.521(5)	1.523(5)	1.515(3)	1.523(6)
C1–C7	1.523(5)	1.522(5)	1.523(5)	1.515(2)	1.524(6)
C2–C3	1.529(5)	1.522(4)	1.528(5)	1.519(2)	1.514(5)
C2–C9	1.511(6)	1.518(5)	1.511(6)	1.512(3)	1.519(5)
C3–C4	1.531(5)	1.520(5)	1.537(5)	1.552(2)	1.549(5)
C4–C5	1.522(4)	1.528(5)	1.527(4)	1.539(3)	1.532(6)
C4–C10	1.524(5)	1.530(5)	1.528(6)	1.527(3)	1.535(6)
C5–C6	1.519(6)	1.515(4)	1.508(6)	1.529(4)	1.541(6)
C7–C8	1.503(5)	1.498(5)	1.496(5)	1.514(3)	1.515(6)

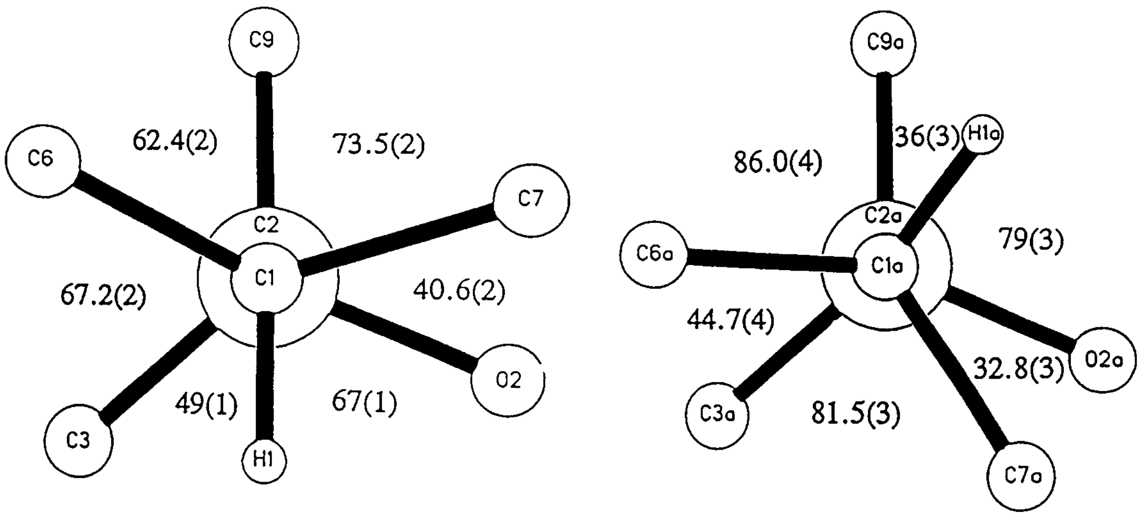
TABLE 4 Valence Angles (°) of Nonhydrogen Atoms in Compounds **4**-*cis* and **4**-*trans*. Comparison with Literature Data [3]

	4-*cis*				
	a	**b**	**c**	**4**-*trans*	*[3]*
C2–O2–C8	110.3(3)	109.8(3)	109.8(3)	109.0(1)	108.9(3)
C2–C1–C6	113.4(3)	112.6(3)	113.3(3)	110.9(1)	110.6(3)
C2–C1–C7	101.8(3)	102.5(3)	102.9(3)	101.8(1)	102.1(3)
C6–C1–C7	116.7(3)	117.8(3)	117.4(3)	125.7(2)	125.0(3)
O2–C2–C1	102.8(3)	102.8(2)	102.6(3)	100.9(1)	100.8(3)
O2–C2–C3	106.5(3)	106.5(2)	106.2(3)	110.6(1)	110.5(3)
O2–C2–C9	106.3(3)	107.0(3)	106.2(3)	106.0(1)	105.8(3)
C1–C2–C3	112.9(3)	112.7(3)	111.7(3)	108.6(1)	108.6(3)
C1–C2–C9	114.7(3)	113.4(3)	115.2(3)	116.5(2)	116.2(3)
C3–C2–C9	112.6(3)	113.5(3)	113.9(3)	113.4(2)	114.1(3)
C2–C3–C4	115.6(3)	115.9(3)	115.4(3)	111.7(1)	111.6(3)
O3–C4–C3	106.9(3)	106.6(3)	106.6(3)	110.1(1)	110.3(3)
O3–C4–C5	110.0(3)	110.3(3)	110.9(3)	105.3(1)	105.1(3)
O3–C4–C10	108.9(3)	109.6(3)	109.0(3)	108.7(2)	108.5(3)
C3–C4–C5	109.6(3)	109.9(3)	109.2(3)	113.0(1)	113.3(3)
C3–C4–C10	110.6(3)	109.9(3)	110.0(3)	109.2(2)	109.2(3)
C5–C4–C10	110.7(3)	110.4(3)	111.1(3)	110.4(2)	110.4(4)
C4–C5–C6	113.2(3)	111.8(3)	112.0(3)	115.0(2)	114.7(4)
C1–C6–C5	113.1(3)	113.1(3)	113.0(3)	106.1(2)	105.4(3)
C1–C7–C8	103.3(3)	103.0(3)	102.8(3)	100.5(1)	99.8(3)
O1–C8–O2	121.7(3)	121.5(3)	120.1(3)	121.0(2)	120.5(4)
O1–C8–C7	127.9(3)	127.5(3)	128.8(4)	128.7(2)	128.8(4)
O2–C8–C7	110.4(3)	111.0(3)	111.1(3)	110.3(2)	110.7(3)

and C4–C5, and at one bond of the five-membered ring: C7–C8 (the average bond lengths of three independent molecules **a**, **b**, and **c** of compound **4**-*cis* were taken for comparison). Greater differences, up to 23σ (C1–C6–C5: 105.4–to 113.1°) and 28σ (C6–C1–C7: 116.7–125.7°) are observed for valence angles. This may be connected with the conformational differences in molecules of compounds **4**-*trans* and **4**-*cis*.

The conformational differences between compounds **4**-*trans* and **4**-*cis* are better evident when shown as Newman projections perpendicular to the C1–C2 bond (Figure 3). Hydrogen atom H1, in compound **4**-*trans*, is situated synclinally with respect to atom 02, with the corresponding torsion angle −67(1)°, whereas its position in compound **4**-*cis* is also synclinal, but the corresponding torsion angle is positive: 79(3)°.

By analysis of the results of our X-ray studies, one can conclude that compound **4**-*trans* has an analogous crystal structure and molecular geometry with that examined by Burnett and Rossmann [3]. Because there is no information in the literature [3] about optical rotation and absolute configuration,



Compound 4-*trans*

Compound 4-*cis*
Molecule a

FIGURE 3 The Newman projections perpendicular to the C1–C2 bond for compounds **4**-*trans* and **4**-*cis*. The asymmetric part of the unit cell of **4**-*cis* contains three independent molecules **a**, **b**, **c**, which are, within the experimental error, identical.

TABLE 5 Crystal Data and Experimental Details for Compounds **4**-*trans* and **4**-*cis*

	4-*trans*	**4**-*cis*
Molecular formula	$C_{10}H_{16}O_3$	$C_{10}H_{16}O_3$
$[\alpha]_D^{20}$ (°)	−74.7(1)	−10.5(1)
Space group	$P2_12_12_1$	$P2_1$
a (Å)	7.0445(5)	10.8275(4)
b (Å)	10.0908(4)	8.6994(5)
c (Å,)	14.0309(6)	16.4722(6)
β (°)	90	106.515(3)
V (Å^3)	997.4(1)	1487.4(14)
Z	4	6
D_c (g/cm^3)	1.227(2)	1.177(2)
μ (cm^{-1})	69.4	67.0
Crystal dimensions (mm)	0.35, 0.3, 0.4	0.3, 0.4, 0.4
Maximum 2*θ* (°)	150	130
Radiation, *λ* (Å)	CuK_α, 1.54178	CuK_α, 1.54178
Scan mode	*ω*/2*θ*	*ω*/2*θ*
Scan width (°)	0.78 + 0.14 • tan *θ*	0.65 + 0.14 • tan *θ*
hkl ranges		
h =	−8 0	−12 12
k =	0 12	0 10
l =	0 17	0 19
No. of reflections:		
unique	1230	2819
with $I \geqslant 3\sigma(I)$	1185	2463
No. of parameters refined	184	545
Largest diffraction peak (eÅ^{-3})	0.221	0.222
Largest diffraction hole (eÅ^{-3})	−0.127	−0.181
Absolute configuration at		
C1 atom	*R*	*S*
C2 atom	*S*	*S*
C4 atom	*R*	*R*
R	0.0352	0.0359
R_w	0.0393	0.0414

TABLE 6 Nonhydrogen Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å^2 $\times$ 10^4) for Compounds **4**-*trans* and **4**-*cis*

	x	*y*	*z*	*U(eq)*[a]	*x*	*y*	*z*	*U(eq)*
		4-*trans*				**4**-*cis*, Molecule **b**		
O1	9954(2)	5519(1)	4536(1)	657(4)	1682(3)	6174(3)	6269(2)	735(8)
O2	9638(2)	6780(1)	3248(1)	510(4)	658(2)	8222(3)	6572(2)	520(6)
O3	6572(2)	9838(1)	1525(1)	580(4)	960(3)	13,272(3)	6845(2)	546(6)
C1	6408(2)	7213(2)	3299(1)	487(4)	962(3)	10,000(4)	5559(2)	435(6)
C2	8248(2)	7761(2)	2886(1)	420(4)	594(3)	9909(3)	6390(2)	417(7)
C3	8131(2)	7702(2)	1806(1)	483(4)	1584(3)	10,669(4)	7126(2)	442(7)
C4	6345(2)	8430(2)	1425(1)	500(4)	2040(3)	12,254(4)	6951(2)	445(6)
C5	4533(3)	8088(2)	1986(2)	607(4)	2471(3)	12,215(4)	6145(2)	467(7)
C6	4750(3)	8115(2)	3070(2)	617(4)	1426(3)	11,591(4)	5399(2)	458(7)
C7	7026(3)	6794(2)	4288(1)	583(4)	1897(3)	8664(4)	5642(2)	500(7)
C8	9004(3)	6284(2)	4079(1)	500(4)	1433(3)	7540(4)	6179(2)	485(7)
C9	8894(3)	9092(2)	3260(2)	597(4)	−779(3)	10,415(5)	6303(3)	627(10)
C10	6086(4)	8106(3)	370(2)	723(4)	3147(5)	12,783(6)	7704(3)	681(10)
		4-*cis*, Molecule **a**				**4**-*cis*, Molecule **c**		
O1	7673(3)	7588(0)	10,253(2)	699(8)	6515(3)	1552(3)	7037(2)	751(8)
O2	7987(2)	9612(3)	9511(2)	518(5)	5467(2)	3577(3)	6371(2)	572(6)
O3	7667(2)	14,677(3)	9415(2)	513(5)	5222(3)	8626(3)	6557(2)	615(6)
C1	8991(3)	11,349(4)	10,598(2)	486(7)	7160(3)	5369(4)	6535(2)	528(8)
C2	8262(3)	11,277(4)	9653(2)	445(7)	5693(3)	5270(4)	6314(2)	498(7)
C3	6957(3)	12,089(4)	9441(2)	411(6)	5182(3)	6027(4)	6991(2)	465(7)
C4	6963(3)	13,693(4)	9824(2)	424(6)	5710(3)	7643(4)	7268(2)	444(6)
C5	7628(4)	13,632(4)	10,771(2)	529(8)	7180(3)	7597(4)	7524(2)	492(7)
C6	8969(4)	12,936(4)	10,985(3)	588(8)	7685(4)	6962(4)	6828(3)	581(9)
C7	8363(4)	10,047(4)	10,956(2)	568(8)	7601(3)	4042(4)	7153(3)	556(9)
C8	7969(3)	8932(4)	10,231(2)	514(7)	6526(4)	2908(4)	6867(2)	537(8)
C9	9047(4)	11,735(5)	9066(3)	625(10)	4980(7)	5738(6)	5420(3)	791(14)
C10	5594(4)	14,305(5)	9653(3)	611(9)	5218(4)	8203(6)	7999(3)	641(9)

[a] Equivalent isotropic thermal parameter *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

we can suspect, only with a 50% probability, that the literature analog of **4**-*trans* possesses the same (or opposite) absolute configuration. The absolute configuration of diastereoisomer **4**-*cis* is different as also its molecular geometry and physicochemical constants (mp and $[\alpha]_D^{20}$) are different.

EXPERIMENTAL

Synthesis of cis-2,4-dihydroxy-2,4-dimethylcyclohexane-trans-1-acetic Acid γ-lactone (4-cis)

As a substrate for the synthesis, (+)-limonene from caraway, with optical rotation $[\alpha]_D^{20} = +123.8°$ (neat), was used. A mixture of keto acid **3** (1.5 g), acetic acid (5 mL), and 50% sulfuric acid (0.05 mL) was maintained during 12 hours at room temperature, then hydrated sodium carbonate (0.03 g) was added, and acetic acid was distilled off in a vacuum process. To the residue, 10 mL of H_2O was added, and the product was extracted with chloroform (2 × 10 mL). After having been washed and concentrated, the product was subjected to crystallization from a mixture of hexane/ethyl acetate (2 : 1) and amounted to 1.1 g. The repeated crystallization from the same set of solvents gave the crystals of *cis*-lactone **4** (0.5 g) in the form of needles. Its melting point was 117–118°C and optical rotation $[\alpha]_D^{20} = -10.49°$ (MeOH, $c = 1$).

Crystal structure of trans- and cis-2,4-dihydroxy-2,4-dimethylcyclohexane-trans-1-acetic acid γ-lactone (4-trans and 4-cis)

Crystal and molecular structures of *trans*- and *cis*-2,4-dihydroxy-2,4-dimethylcyclohexane-*trans*-1-acetic acid γ-lactone (**4**-*trans* and **4**-*cis*) were determined using data collected on a CAD4 diffractometer. Compound **4**-*trans* crystallizes in the orthorhombic system, in space group $P2_12_12_1$, with a unit cell consisting of four molecules (one molecule constitutes an asymmetric part of the unit cell). Compound **4**-*cis* crystallizes in the monoclinic system, space group $P2_1$, with six molecules in the unit cell (three independent molecules build an asymmetric part of the unit cell). Crystal data and experimental details, nonhydrogen atomic coordinates, and equivalent isotropic displacement coefficients for both compounds **4**-*trans* and **4**-*cis* are shown in Tables 5 and 6. Intensity data were collected at room temperature using a diffractometer with graphite monochromatized CuK_α

radiation. Lattice constants were refined by least-squares fit of 25 reflections in θ range 20.0–27.9° for 4-*trans* and 20.3–32.8° for 4-*cis*. Declines in intensities of three standard reflections ($-2,1,7$; $-1,-5,1$; $-1,-4,-2$ for 4-*trans*, and $2,3,6$; $-5,2,-1$; $-2,2,7$ for 4-*cis*) were 0.1% during 11.5 hours of exposure for 4-*trans* and 3.1% during 45.8 hours for 4-*cis*. A total of 1185 observed reflections for 4-*trans* and 2463 for 4-*cis* [with $I \geqslant 3\sigma(I)$] were used to solve the structures by direct methods and to refine them by full matrix least squares using F's. Hydrogen atoms were found on a difference Fourier map and refined with isotropic thermal parameters. Anisotropic thermal parameters were refined for all nonhydrogen atoms. The final refinement of structure 4-*trans* converged to $R = 0.035$ with weight $1/(\sigma^2(F) + 0.000162 * F^2)$ for 184 refined parameters, with inclusion of the extinction parameter into the refinement [the obtained value of extinction parameter was 0.084(6)]. The final refinement of structure 4-*cis* converged to $R = 0.036$ with weight $1/(\sigma^2(F) + 0.0039 * F^2)$ for 545 refined parameters, also with inclusion of the extinction parameter into the refinement [the obtained value of the extinction parameter for 4-*cis* was 0.012(2)].

Structure solutions of both compounds 4-*trans* and 4-*cis* were carried out with the Enraf-Nonius SDP crystallographic computing package [7] and SHELXS-86 program [8]; structure refinement with SHELXTL package [9]. Scattering factors were taken from *International Tables for X-ray Crystallography* [10]. Full crystallographic data, with values of F_{obs} and F_{calc}, are deposited at the Cambridge Crystallographic Data Centre [11].

REFERENCES

[1] J. Woliński, D. Chan, *J. Org. Chem.*, *31*, 1966, 2471.
[2] J. Kula, J. Podlejski, *Liebigs Am. Chem.*, 1985, 2098.
[3] R. M. Burnett, M. G. Rossmann, *Acta Crystallogr.*, *B24*, 1971, 1378.
[4] W. C. Hamilton, *Acta Crystallogr.*, *18*, 1965, 502.
[5] D. Rogers, *Acta Crystallogr.*, *A37*, 1981, 734.
[6] C. Altona, H. J. Geise, C. Romers, *Tetrahedron*, *24*, 1968, 13.
[7] B. A. Frenz: *SDP—Structure Determination Package*, Enraf-Nonius, Delft, Holland, 1984.
[8] G. M. Sheldrick, G. M. Krüger, R. Goddard: *SHELXS-86. Crystallographic Computing 3*, Oxford University Press, England, 1985, 175.
[9] *SHELXTL PC, Release 4.1 (May 1990)*, Siemens Analytical X-Ray Instruments, Inc., Madison, WI.
[10] *International Tables for X-ray Crystallography*, The Kynoch Press, Birmingham, England (1974).
[11] Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, United Kingdom.