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STRUCTURAL INVESTIGATION OF PARVIFOLINONE TRANSFORMATION PRODUCTS

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The structures of the transformation products of parvifolinone, trans-2,3-dihydro-3,6-dimethyl-7-acetoxy-2-carboxymethylenebenzopyran-4-one and 5-methyl-6-(2',4'-diacetoxy-5-methylphenyl)pyran-2-one, are proved by X-ray methods. The conformation of the dihydropyran-4-one moiety in the former is a distorted half-chair. The pyran-2-one ring in the latter is planar.

Parvifoline (2-hydroxy-3,6,10-trimethylbenzocycloocta-4a→10a,6-diene), which is isolated from *Corcopsis* [1] and *Pereziae* [2] plant species, was transformed into the known terpenoids cucurquinone, hantonizal, perezon, hydroperezon, and others.

Parvifolinone (**1**) is prepared *via* oxidation of parvifoline by selenium dioxide [2]. Treatment of parvifolinone by peracetic acid gives a product that is assigned as 5-(2'-acetoxy-4'-hydroxy-5'-methylphenyl)-3-hydroxy-5-oxovaleric acid (**2**) on the basis of ^{1}H and ^{13}C NMR spectroscopy data.* The ^{13}C NMR spectrum with proton decoupling contains 15 signals, 6 of which appear in the region corresponding to sp^3-hybridized carbon and 9, to sp^2-hybridized carbon. The spectrum without proton decoupling has only two signals in the sp^2 region that correspond to carbon atoms bound to hydrogen atoms (aromatic $C_{(3')}$ and $C_{(5')}$). The remaining 7 signals are singlets belonging to three carbonyl groups and to carbon atoms of a benzene ring that are not bounded to hydrogen atoms ($C_{(1')}$, $C_{(2)}$, $C_{(4)}$, $C_{(5)}$). The sp^3 region has two doublets from the β-C and γ-C, one triplet from an α-CH_2, and three quartets corresponding to methyl groups.

We treated the acid **2** with Ac_2O/AcONa and obtained a mixture of *trans*-7-acetoxy-2-carboxymethylene-2,3-dihydro-3,6-dimethylbenzopyran-4-one (from hereon parvibenzopyran-4-one) (**3**) and 6-[2',4'-diacetoxy-5'-methylphenyl]-5-methylpyran-2-one (from hereon parvipyran-2-one) (**4**). The mixture of **3** and **4** was separated by chromatography on silica-gel. The isolated compounds are white crystalline solids with melting points 173 and 105°C.

In order to prove the structures of the parvifolinone transformation products, we performed X-ray structural studies. Figure 1 shows a general view of parvibenzopyran-4-one **3**. Table 1 contains the bond lengths and angles (the atomic numbering differs from that recommended by IUPAC).

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* The results have been previously reported [3].

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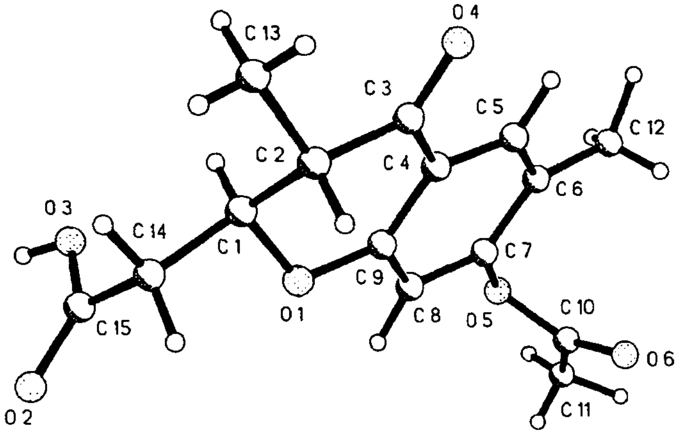
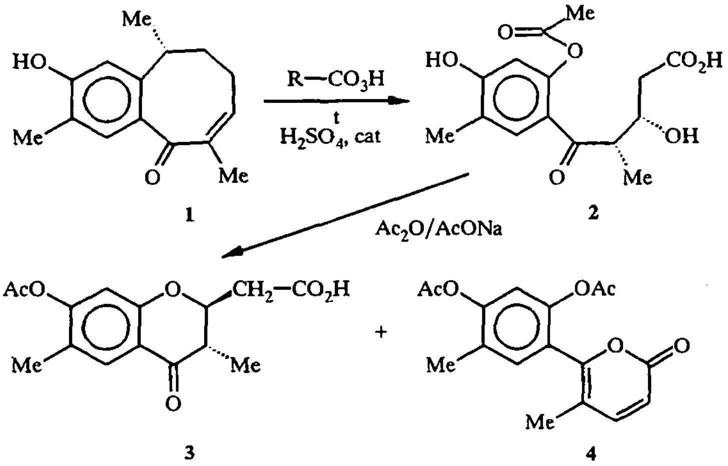


Fig. 1. General view of **3** and numbering of atoms.



The six-membered heterocycle in **3** has a distorted half-chair conformation. Atoms $C_{(1)}$ and $C_{(2)}$ deviate by 0.576 and 0.065 Å, respectively, to different sides of the plane drawn through $O_{(1)}$, $C_{(9)}$, $C_{(4)}$, and $C_{(3)}$ (the deviation of these atoms from the average plane is 0.008 Å). The dihedral angle between this plane of the heterocycle and the benzene ring is 2.0°. Figure 2 shows a projection of the molecule along the $C_{(1)}–C_{(2)}$ bond, which illustrates the *trans*-orientation of $H_{(1)}$ and $H_{(2)}$ (the $H_{(1)}–C_{(1)}–C_{(2)}–H_{(2)}$ torsion angle is -179.3°). The remaining geometric features of **3** have their usual values [4].

An analysis of the crystal packing of **3** demonstrated that the intermolecular hydrogen bonds $O_{(3)}–H_{(30)}\cdots O_{(2)}$ $(-0.5 - x, -0.5 + y, z)$ [$O_{(3)}\cdots O_{(2)}$ 2.636(6), $O_{(3)}–H_{(30)}$ 0.88(4), $H_{(30)}\cdots O_{(2)}$ 1.79(4) Å, angle $O_{(3)}–H_{(30)}\cdots O_{(2)}$ 162(2)°] join the molecules into infinite chains that extend along the *b* axis (Fig. 3).

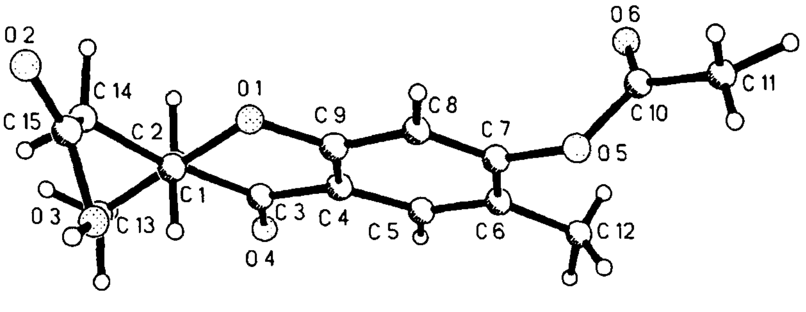


Fig. 2. Projection of **3** along the $C_{(1)}–C_{(2)}$ bond.

TABLE 1. Bond Lengths and Angles in the Structure of 3

Bond	*d*, Å	Angle	*φ*, deg
$O_{(1)}–C_{(1)}$	1,450(5)	$C_{(9)}–O_{(1)}–C_{(1)}$	115,4(3)
$O_{(2)}–C_{(15)}$	1,218(5)	$C_{(10)}–O_{(5)}–C_{(7)}$	119,5(4)
$O_{(3)}–C_{(15)}$	1,302(5)	$O_{(1)}–C_{(1)}–C_{(2)}$	111,8(3)
$O_{(4)}–C_{(3)}$	1,230(5)	$O_{(1)}–C_{(1)}–C_{(14)}$	104,4(3)
$O_{(5)}–C_{(10)}$	1,343(6)	$C_{(2)}–C_{(1)}–C_{(14)}$	113,5(4)
$O_{(5)}–C_{(7)}$	1,406(5)	$C_{(3)}–C_{(2)}–C_{(1)}$	109,8(3)
$O_{(6)}–C_{(10)}$	1,201(6)	$C_{(3)}–C_{(2)}–C_{(13)}$	111,1(4)
$C_{(1)}–C_{(2)}$	1,520(6)	$C_{(1)}–C_{(2)}–C_{(13)}$	112,4(4)
$C_{(1)}–C_{(14)}$	1,526(6)	$O_{(4)}–C_{(3)}–C_{(4)}$	121,9(4)
$C_{(2)}–C_{(3)}$	1,516(6)	$O_{(4)}–C_{(3)}–C_{(2)}$	120,8(4)
$C_{(3)}–C_{(4)}$	1,466(5)	$C_{(4)}–C_{(3)}–C_{(2)}$	117,3(3)
$C_{(2)}–C_{(13)}$	1,523(6)	$C_{(5)}–C_{(4)}–C_{(9)}$	118,8(4)
$C_{(4)}–C_{(5)}$	1,387(6)	$C_{(5)}–C_{(4)}–C_{(3)}$	121,7(4)
$C_{(4)}–C_{(9)}$	1,396(5)	$C_{(9)}–C_{(4)}–C_{(3)}$	119,5(4)
$C_{(5)}–C_{(6)}$	1,378(6)	$C_{(6)}–C_{(5)}–C_{(4)}$	123,2(4)
$C_{(6)}–C_{(7)}$	1,380(6)	$C_{(5)}–C_{(6)}–C_{(7)}$	115,4(4)
$C_{(6)}–C_{(12)}$	1,496(7)	$C_{(5)}–C_{(6)}–C_{(12)}$	121,6(4)
$C_{(7)}–C_{(8)}$	1,372(6)	$C_{(7)}–C_{(6)}–C_{(12)}$	122,9(4)
$C_{(8)}–C_{(9)}$	1,387(6)	$C_{(8)}–C_{(7)}–C_{(6)}$	124,4(4)
$C_{(10)}–C_{(11)}$	1,478(8)	$C_{(8)}–C_{(7)}–O_{(5)}$	114,9(4)
$C_{(14)}–C_{(15)}$	1,490(6)	$C_{(6)}–C_{(7)}–O_{(5)}$	120,4(4)
		$C_{(7)}–C_{(8)}–C_{(9)}$	118,4(4)
		$O_{(1)}–C_{(9)}–C_{(8)}$	117,6(4)
		$O_{(1)}–C_{(9)}–C_{(4)}$	122,6(4)
		$C_{(8)}–C_{(9)}–C_{(4)}$	119,7(4)
		$O_{(6)}–C_{(10)}–O_{(5)}$	123,0(5)
		$O_{(6)}–C_{(10)}–C_{(11)}$	126,3(6)
		$O_{(5)}–C_{(10)}–C_{(11)}$	110,7(6)
		$C_{(15)}–C_{(14)}–C_{(1)}$	113,9(4)
		$O_{(2)}–C_{(15)}–O_{(3)}$	121,6(4)
		$O_{(2)}–C_{(15)}–C_{(14)}$	123,5(4)
		$O_{(3)}–C_{(15)}–C_{(14)}$	114,8(4)

Figure 4 shows a general view of **4**. Table 2 lists the bond lengths and selected bond angles. Table 2 shows that there are no strongly distorted bonds in **4** that differ from the standard ones for this class of compounds [4]. The benzene ring and the pyran-2-one heterocycle bonded to it are planar (average deviations of the atoms are 0.008 and 0.009 Å). The dihedral angle between these two planes is 49.0°. The angles between the planes defined by the AcO groups and the benzene ring are 107° and 98° for $O_{(3)}C_{(13)}O_{(4)}C_{(14)}$ and $O_{(5)}C_{(15)}O_{(6)}C_{(16)}$, respectively.

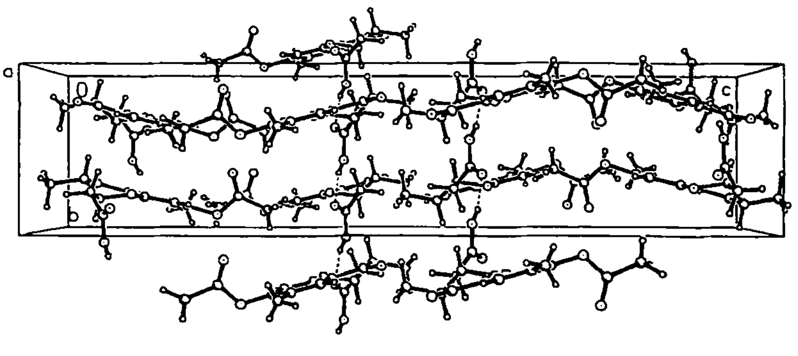


Fig. 3. Projection of the crystal packing on the OYZ plane in **3**.

TABLE 2. Bond Lengths and Angles in the Structure of **4**

Bond	*d*, Å	Angle	*φ*, deg
$O_{(1)}–C_{(5)}$	1,379(3)	$C_{(5)}–O_{(1)}–C_{(1)}$	122,8(2)
$O_{(1)}–C_{(1)}$	1,384(4)	$C_{(13)}–O_{(3)}–C_{(8)}$	116,6(2)
$O_{(2)}–C_{(1)}$	1,207(4)	$C_{(15)}–O_{(5)}–C_{(10)}$	119,0(2)
$O_{(3)}–C_{(13)}$	1,372(3)	$O_{(2)}–C_{(1)}–O_{(1)}$	116,2(3)
$O_{(3)}–C_{(8)}$	1,399(3)	$O_{(2)}–C_{(1)}–C_{(2)}$	128,1(3)
$O_{(4)}–C_{(13)}$	1,191(4)	$O_{(1)}–C_{(1)}–C_{(2)}$	115,7(3)
$O_{(5)}–C_{(15)}$	1,346(4)	$C_{(3)}–C_{(2)}–C_{(1)}$	120,5(3)
$O_{(5)}–C_{(10)}$	1,394(4)	$C_{(2)}–C_{(3)}–C_{(4)}$	122,7(3)
$O_{(6)}–C_{(15)}$	1,177(4)	$C_{(5)}–C_{(4)}–C_{(3)}$	117,5(3)
$C_{(1)}–C_{(2)}$	1,428(5)	$C_{(5)}–C_{(4)}–C_{(6)}$	123,9(3)
$C_{(2)}–C_{(3)}$	1,325(5)	$C_{(3)}–C_{(4)}–C_{(6)}$	118,6(3)
$C_{(3)}–C_{(4)}$	1,418(4)	$C_{(4)}–C_{(5)}–O_{(1)}$	120,7(2)
$C_{(4)}–C_{(5)}$	1,345(4)	$C_{(4)}–C_{(5)}–C_{(7)}$	127,7(2)
$C_{(4)}–C_{(6)}$	1,508(4)	$O_{(1)}–C_{(5)}–C_{(7)}$	111,6(2)
$C_{(5)}–C_{(7)}$	1,471(4)	$C_{(12)}–C_{(7)}–C_{(8)}$	116,9(3)
$C_{(7)}–C_{(8)}$	1,403(4)	$C_{(12)}–C_{(7)}–C_{(5)}$	121,3(2)
$C_{(7)}–C_{(12)}$	1,391(4)	$C_{(8)}–C_{(7)}–C_{(5)}$	121,7(2)
$C_{(8)}–C_{(9)}$	1,365(4)	$C_{(9)}–C_{(8)}–O_{(3)}$	120,1(2)
$C_{(9)}–C_{(10)}$	1,377(4)	$C_{(9)}–C_{(8)}–C_{(7)}$	121,5(3)
$C_{(10)}–C_{(11)}$	1,396(4)	$O_{(3)}–C_{(8)}–C_{(7)}$	118,3(2)
$C_{(11)}–C_{(12)}$	1,384(5)	$C_{(8)}–C_{(9)}–C_{(10)}$	119,4(3)
$C_{(11)}–C_{(17)}$	1,501(5)	$C_{(9)}–C_{(10)}–O_{(5)}$	119,1(3)
$C_{(13)}–C_{(14)}$	1,460(5)	$C_{(9)}–C_{(10)}–C_{(11)}$	122,1(3)
$C_{(15)}–C_{(16)}$	1,484(5)	$O_{(5)}–C_{(10)}–C_{(11)}$	118,6(3)
		$C_{(12)}–C_{(11)}–C_{(10)}$	116,5(3)
		$C_{(12)}–C_{(11)}–C_{(17)}$	121,1(4)
		$C_{(10)}–C_{(11)}–C_{(17)}$	122,4(4)
		$C_{(11)}–C_{(12)}–C_{(7)}$	123,5(3)
		$O_{(4)}–C_{(13)}–O_{(3)}$	121,9(3)
		$O_{(4)}–C_{(13)}–C_{(14)}$	126,9(3)
		$O_{(3)}–C_{(13)}–C_{(14)}$	111,2(3)
		$O_{(6)}–C_{(15)}–O_{(5)}$	122,8(3)
		$O_{(6)}–C_{(15)}–C_{(16)}$	126,6(4)
		$O_{(5)}–C_{(15)}–C_{(16)}$	110,6(4)

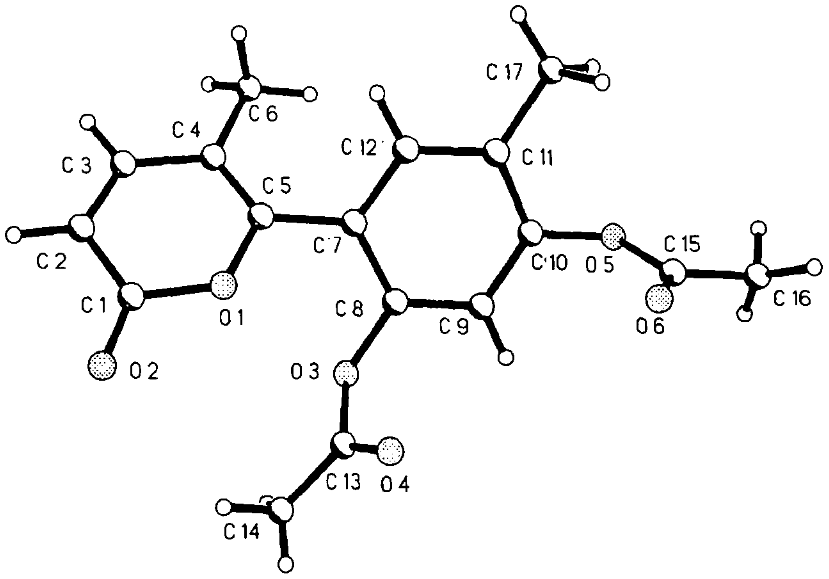


Fig. 4. General view of **4** and numbering of atoms.

TABLE 3. Coordinates of Non-hydrogen Atoms* (Å × 10^4) and Their Equivalent Isotropic Temperature Factors ($Å^2$ × 10^3) in the Structures of **3** and **4**

Atom	*x*	*y*	*z*	*U*
Structure 3				
$O_{(1)}$	637(2)	2246(4)	6171(1)	36(1)
$O_{(2)}$	-2491(3)	1483(4)	6044(1)	50(1)
$O_{(3)}$	-1230(3)	-631(4)	5895(1)	46(1)
$O_{(4)}$	3159(3)	3127(5)	5331(1)	52(1)
$O_{(5)}$	3187(3)	879(5)	7238(1)	51(1)
$O_{(6)}$	3977(4)	3537(6)	7430(1)	73(1)
$C_{(1)}$	423(3)	1976(6)	5731(1)	30(1)
$C_{(2)}$	1177(3)	3179(6)	5464(1)	33(1)
$C_{(3)}$	2398(4)	2893(6)	5585(1)	32(1)
$C_{(4)}$	2627(3)	2340(5)	6015(1)	29(1)
$C_{(5)}$	3717(4)	2125(6)	6161(1)	33(1)
$C_{(6)}$	3962(4)	1644(6)	6565(1)	34(1)
$C_{(7)}$	3044(4)	1464(6)	6825(1)	38(1)
$C_{(8)}$	1945(4)	1659(6)	6702(1)	37(1)
$C_{(9)}$	1730(3)	2078(6)	6289(1)	30(1)
$C_{(10)}$	3635(4)	2035(8)	7519(2)	50(1)
$C_{(11)}$	3621(8)	1210(16)	7938(2)	80(2)
$C_{(12)}$	5144(5)	1293(12)	6704(2)	53(2)
$C_{(13)}$	1003(5)	2842(10)	5001(2)	52(2)
$C_{(14)}$	-829(4)	2390(7)	5680(2)	35(1)
$C_{(15)}$	-1581(3)	1064(6)	5897(1)	32(1)
Structure 4				
$O_{(1)}$	7428(2)	4433(2)	3625(1)	58(1)
$O_{(2)}$	7213(3)	5273(4)	4605(1)	95(1)
$O_{(3)}$	9574(2)	2266(2)	3379(1)	54(1)
$O_{(4)}$	11104(2)	4360(3)	3548(1)	86(1)
$O_{(5)}$	11001(3)	2739(3)	1245(1)	85(1)
$O_{(6)}$	12301(3)	4958(3)	1485(1)	94(1)
$C_{(1)}$	6619(3)	4659(4)	4150(2)	65(1)
$C_{(2)}$	5171(3)	4184(4)	4078(2)	72(1)
$C_{(3)}$	4682(3)	3517(4)	3544(2)	68(1)
$C_{(4)}$	5545(3)	3245(3)	3020(1)	55(1)
$C_{(5)}$	6905(3)	3715(3)	3076(1)	49(1)
$C_{(6)}$	4902(4)	2417(5)	2441(2)	73(1)
$C_{(7)}$	8005(3)	3541(3)	2607(1)	51(1)
$C_{(8)}$	9321(3)	2824(3)	2761(1)	50(1)
$C_{(9)}$	10311(3)	2584(4)	2316(1)	58(1)
$C_{(10)}$	10032(3)	3100(4)	1706(2)	65(1)
$C_{(11)}$	8758(4)	3859(4)	1523(1)	66(1)
$C_{(12)}$	7770(3)	4038(4)	1985(1)	60(1)
$C_{(13)}$	10453(3)	3226(4)	3754(2)	59(1)
$C_{(14)}$	10468(5)	2651(7)	4407(2)	84(1)
$C_{(15)}$	12132(3)	3734(4)	1187(2)	66(1)
$C_{(16)}$	13082(6)	3069(7)	705(3)	96(1)
$C_{(17)}$	8449(7)	4432(6)	860(2)	95(1)

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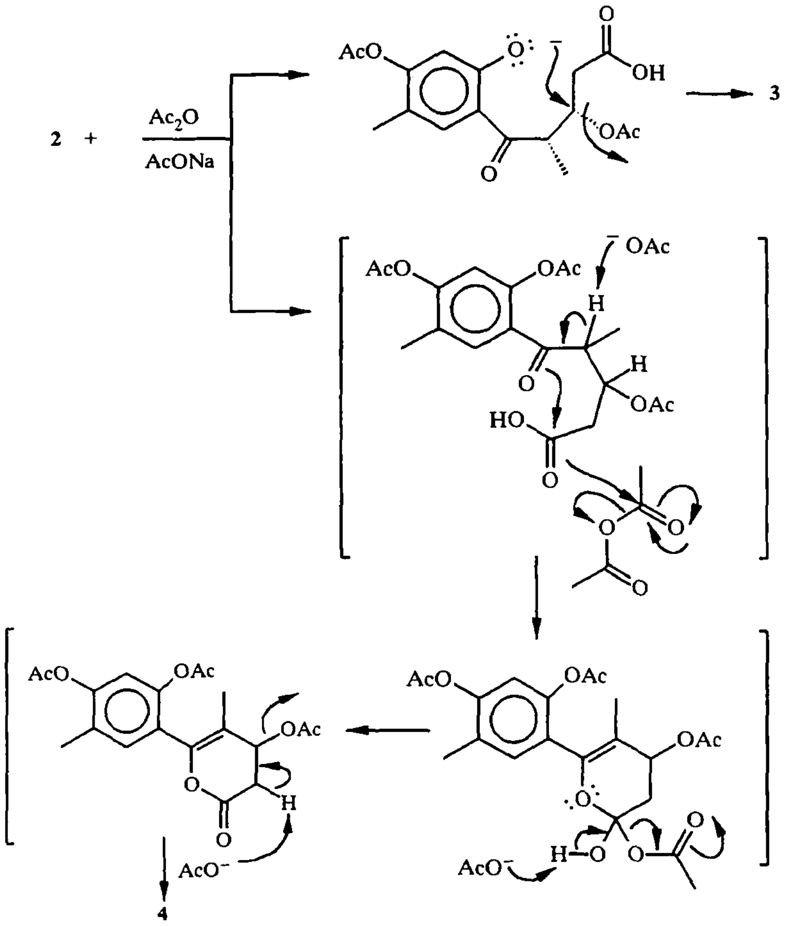
* Coordinates of hydrogen atoms can be obtained from the authors.

The crystal packing shows that the intermolecular and intramolecular contacts in the structure of **4** are typical of van-der-Waals distances [5].

Based on the structural results, the mechanism of formation of **3** and **4** from **2** can be proposed as follows.



EXPERIMENTAL

IR spectra were recorded on a Perkin–Elmer 399B instrument. NMR spectra were obtained on a Varian Gemini (200 MHz for ^{1}H and 50 MHz for ^{13}C) instrument in $CDCl_3$ solutions. Parvifolinone **1** was prepared by the literature method [2].

5-(2'-Acetoxy-4'-hydroxy-5'-methylphenyl)-3-hydroxy-5-oxovaleric Acid (2). Cooled 40% peracetic acid (1.6 ml) is added to a mixture of **1** (0.42 g, 1.83 mmol), AcOH (2.5 ml), and H_2SO_4 (0.025 ml). Chloroform (10 ml) is added for better dissolution. The reaction mixture is left at room temperature for 72 h. Then water (30 ml) is added and the mixture is extracted with $CHCl_3$. The organic layer is washed with water until the pH ~ 7 and dried over anhydrous Na_2SO_4. An amber oil corresponding to **2** is obtained by chromatography of the residue after evaporation. Yield 0.2 g (26%). IR spectrum: 3300 (br., COOH), 1720, 1630 (C=O), 1600, 1500 cm^{-1} (arom.). PMR spectrum: 12.61 (1H, s, COOH), 7.75 and 6.34 (2H, s, H_{arom}), 5.53 (1H, ddd, J = 7, 8 and 4 Hz, β-H), 4.6 (br. s, OH), 3.98 (1H, m, γ-H), 2.73 and 2.21 (2H, dd, J = 16.4 and 16.8 Hz, respectively, two α-H), 2.19 (3H, s, CH_3CO), 2.03 (3H, s, 5'-Me), 1.22 ppm (3H, d, γ-Me). ^{13}C NMR spectrum: 204.13 (CO), 175.31 (Me$\underline{C}$OO), 171.30 (COOH), 164.05 and 162.92 ($C_{(2')}$ and $C_{(4')}$), 132.46 ($C_{(3')}$), 117.44 and 112.51 ($C_{(1')}$ and $C_{(5')}$), 102.36 ($C_{(5')}$), 71.54 (β-C), 42.23 (γ-C), 34.86 (α-CH_2), 20.84 (5'-Me), 15.24 ($\underline{Me}$COO), 11.67 (γ-Me).

***trans*-7-Acetoxy-2-carboxymethylene-2,3-dihydro-3,6-dimethyl-benzopyran-4-one (3) and 6-(2',4'-diacetoxy-5'-methylphenyl)-5-methylpyran-2-one (4).** A mixture of **2** (0.5 g, 1.6 mmol), Ac_2O (3 ml), and AcONa (0.2 g, 2.44 mmol) is refluxed with stirring for 15 min. The reaction mixture is cooled to room temperature, poured into cold water and extracted with ethylacetate. The organic layer is washed with water, dried over anhydrous Na_2SO_4, and concentrated. The products **3** and **4** are isolated from the residue by column chromatography on silica gel (hexane–ethylacetate, 9:1). Yield of **3**, 61 mg (13%); mp 172-173°C. Found, %: C 61.64; H 5.52. $C_{15}H_{16}O_6$. Calculated, %: C 61.51; H 5.39. Yield of **4**, 102 mg (20%); mp 105°C. Found, %: C 64.55, H 5.10. $C_{17}H_{16}O_6$. Calculated, %: C 64.63; H 5.02.

X-ray Structural Studies. Colorless single crystals of **3** and **4** were grown by slow evaporation of ethanol solutions over 3 days.

The X-ray diffraction study of **3** ($C_{15}H_{16}O_6$) was carried out at 25°C on an automated 4-circle Siemens P3/PC diffractometer (Mo $K\alpha$-radiation, graphite monochromator, $\theta/2\theta$-scanning, $2\theta < 56°$). The crystals at 25°C are orthorhombic: $a = 11.877(3)$, $b = 7.280(3)$, $c = 32.184(6)$ Å, $V = 2783(1)$ Å^3, $d_{calc} = 1.395$ g/cm^3, $\mu = 0.109$ mm^{-1}, $F(000) = 1232$, M = 292.28, space group Pbca, $Z = 8$.

The X-ray diffraction study of **4** ($C_{17}H_{16}O_6$) was carried out at 28°C on an automated 4-circle Enraf–Nonius CAD4 diffractometer (Mo $K\alpha$-radiation, graphite monochromator, $\theta/5/2\theta$-scanning, $2\theta < 58°$). The crystals at 28°C are monoclinic: $a = 9.476(5)$, $b = 8.031(4)$, $c = 21.228(11)$ Å, $\beta = 91.83(4)°$, $V = 1614(1)$ Å^3, $d_{calc} = 1.301$ g/cm^3, $\mu = 0.099$ mm^{-1}, $F(000) = 664$, M = 316.30, space group $P2_1/n$, $Z = 4$. Of a total of 3038 and 3081 (for **3** and **4**, respectively) measured reflections, 2983 and 2868 were used in the structure refinements.

The structures were refined using anisotropic and isotropic full-matrix least-squares methods for F^2. The hydrogen atoms were located in difference electron-density syntheses and were refined isotropically in the final stage.

The final agreement factors for **3** are: $wR_2 = 0.215$, GOF = 1.062 over all 2983 measured reflections [$R_1 = 0.081$ for 1394 reflections with $I > 2\sigma(I)$ calculated for F]. For **4**: $wR_2 = 0.2616$, GOF = 1.028 over all 2868 measured reflections [$R_1 = 0.584$ for 1728 reflections with $I > 2\sigma(I)$ calculated for F]. All calculations were performed on an IBM PC/AT using the SHELXTL PLUS (version 5) programs. Table 3 lists the coordinates of nonhydrogen atoms and their thermal parameters.

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