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Structures of Three 2,2-Dimethyl-3a,4,5,7a-tetrahydro-1,3-benzodioxolan-4-ols

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Abstract. $T = 295$ (1) K, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å. (3aα,4α,5β,7aα)-5-Methoxy-2,2-dimethyl-3a,4,5,7a-tetrahydro-1,3-benzodioxolan-4-ol (2), $C_{10}H_{16}O_4$, $M_r = 200.2$, monoclinic, $P2_1/n$, $a = 8.264$ (1), $b = 6.988$ (1), $c = 18.288$ (1) Å, $\beta = 96.27$ (1)°, $V = 1049.8$ (3) Å^3, $Z = 4$, D_m (flotation) = 1.271 (5), $D_x = 1.267$ Mg m^{-3}, $\mu = 0.72$ mm^{-1}, $F(000) = 432$, final $R = 0.043$ for 1601 observed data. (3aα,4α,5β,7aα)-4-Hydroxy-2,2-dimethyl-3a,4,5,7a-tetrahydro-1,3-benzodioxolan-5-yl benzoate (3), $C_{16}H_{18}O_5$, $M_r = 290.3$, monoclinic, $P2_1/n$, $a = 12.792$ (1), $b = 8.937$ (1), $c = 13.089$ (1) Å, $\beta = 91.37$ (1)°, $V = 1495.9$ (2) Å^3, $Z = 4$, D_m (flotation) = 1.292 (5), $D_x = 1.289$ Mg m^{-3}, $\mu = 0.71$ mm^{-1}, $F(000) = 616$, final $R = 0.048$ for 1994 observed data. (3aα,4α,5α,7aα)-4-Hydroxy-2,2-dimethyl-3a,4,5,7a-tetrahydro-1,3-benzodioxolan-5-yl benzoate (4), $C_{16}H_{18}O_5$, $M_r = 290.3$, orthorhombic, $Pbca$, $a = 10.773$ (1), $b = 25.953$ (1), $c = 10.818$ (1) Å, $V = 3024.6$ (3) Å^3, $Z = 8$, D_m (flotation) = 1.276 (5), $D_x = 1.275$ Mg m^{-3}, $\mu = 0.70$ mm^{-1}, $F(000) = 1232$, final $R = 0.048$ for 2055 observed data. In each molecule the cyclohexene ring adopts a sofa conformation with C(4) lying out of the plane formed by the other five atoms. The *cis*-fused dioxolane ring adopts a conformation between a half chair and an envelope in (2) and (3), but has an envelope form in (4).

Introduction. The cyclitols and aminocyclitols (Ferrier, 1990) constitute a large class of polyfunctionalized cyclohexanes or cyclohexenes and many of these compounds display useful antibacterial (Knapp, Ornaf & Rodriques, 1983), antiviral (Datema, Romero, Legler & Schwarz, 1982; Legler, 1977), plant growth regulating (Soloway, Vogel, Le Drian & Powell, 1986, 1987) and/or insect antifeedant (Ley, Sternfeld & Taylor, 1987) properties. We are attempting to use microbially derived and commercially available dihydrocatechols [*e.g.* (1)] as starting materials for the efficient chemical synthesis of these molecules. In connection with this work we have now prepared the three cyclitols shown as (2), (3) and (4). These compounds have each been prepared (M. G. Banwell, J. N. Lambert, M. E. Reum, S. L. Richards & S. Stasi, unpublished results) in two steps from the acetonide derivative (Banwell, 1989) of (1). Very recently, an alternate synthesis of compound (2) has been reported (Hudlicky, Price, Rulin & Tsunoda, 1990). The crystal structure determinations of the three 2,2-dimethyl-3a,4,5,7a-tetrahydro-

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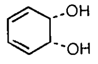
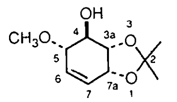
1,3-benzodioxol-4-ols were undertaken to confirm the structural assignments based on mechanistic and steric considerations.



(1)



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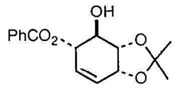

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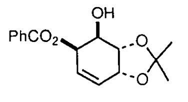


(4)

Experimental. The syntheses of (2), (3) and (4) will be described elsewhere. Prismatic crystals from benzene (2), mother liquors (3) and from dichloromethane/petroleum spirit (b.p. 313–333 K) (4); crystals *ca* 0.42 × 0.58 × 0.63 mm (2), triangular fragment of side 0.49 mm and thickness 0.27 mm (3), and 0.21 × 0.21 × 0.39 mm (4) aligned on a Rigaku-AFC diffractometer; cell parameters determined by least squares from 2θ values for 25 strong reflections ($41 < 2\theta < 78°$) (2), ($43 < 2\theta < 67°$) (3), ($44 < 2\theta < 77°$) (4); Cu $K\alpha$ radiation (graphite-crystal monochromator, $\lambda = 1.5418$ Å); ω–2θ scan, 2θ rate 4° min^{-1} for (2), 2° min^{-1} for (3) and (4), scan range $(1.20 + 0.5\tan\theta)°$, $2\theta_{\max} = 130°$, 10 s stationary background counts; three standard reflections monitored every 50 reflections, no significant intensity variation; 1819 unique data (h −9 to 9, k 0 to 8, l 0 to 21), 1601 observed (2); 2523 unique data (h −14 to 14, k 0 to 10, l 0 to 15), 1994 observed (3); 2564 unique data (h 0 to 12, k 0 to 30, l 0 to 12), 2055 observed (4); intensities corrected for Lorentz and polarization effects and for absorption, transmission factors 0.628 to 0.789 for (2), 0.654 to 0.841 for (3) and 0.814 to 0.873 for (4). Structures solved by direct methods with *SHELX76* (Sheldrick, 1976). All H-atom sites located on difference maps, and atoms refined with individual isotropic temperature factors. Full-matrix refinements with data $[I \geq 2\sigma(I)]$ and with anisotropic temperature factors given to C and O atoms, converged at $R = 0.043$, $wR = 0.051$, $S = 2.17$ (192 parameters varied, 1601 data) for (2), $R = 0.048$, $wR = 0.064$, $S = 1.83$ (262 parameters varied, 1994 data) for (3), $R = 0.048$, $wR = 0.054$, $S = 1.27$ (262 parameters varied, 2055 data) for (4); function minimized $\sum w(|\Delta F|)^2$ with $w = [\sigma^2(|F|) + m|F|^2]^{-1}$ for which $m = 0.0003$ for (2), 0.0007 for (3) and 0.001 for (4); at convergence $(\Delta/\sigma)_{\max} = 0.003$ for (2), 0.005 for (3) and 0.02 for (4); $(\Delta\rho)_{\max}$, $(\Delta\rho)_{\min} = 0.19$, -0.17 for (2), 0.17, -0.20 for (3) and 0.19, -0.31 e Å^{-3} for (4); an isotropic extinction parameter of the form $F_c = F[1 - 2.7\,(2) \times 10^{-6}|F|^2/\sin\theta]$ was applied to the calculated structure amplitudes of (2); three intense low-order terms [020, 211, 021 for (3)] and [200, 020, 122 for (4)] seriously affected by extinction were excluded from refinements of (3) and (4). Atom-scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99, 149). Figures prepared from output of *ORTEP*II (Johnson, 1976). Major calculations made with *SHELX76* (Sheldrick, 1976) on a VAX 8800 computer.

Table 1. *Fractional coordinates* (× 10^4) *and equivalent isotropic temperature factors* (Å^2) *for the non-*H *atoms of* (2), (3) *and* (4) *with e.s.d.'s in parentheses*

$$B_{eq} = 8\pi^2 U_{eq} = (8\pi^2/3)\textstyle\sum_i\sum_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
(2)				
O(1)	4455 (1)	4560 (2)	3657 (1)	4.46 (3)
C(2)	4412 (2)	6596 (2)	3633 (1)	3.93 (4)
O(3)	5996 (1)	7185 (1)	3467 (1)	4.38 (3)
C(3a)	6932 (2)	5541 (2)	3326 (1)	3.28 (4)
C(4)	8222 (2)	5123 (2)	3957 (1)	3.11 (4)
C(5)	9019 (2)	3204 (2)	3833 (1)	3.59 (4)
C(6)	7774 (2)	1659 (2)	3686 (1)	3.98 (4)
C(7)	6265 (2)	2008 (2)	3416 (1)	4.21 (4)
C(7a)	5671 (2)	3964 (2)	3199 (1)	3.80 (4)
C(1′)	3143 (3)	7298 (3)	3035 (1)	5.33 (5)
C(2′)	4114 (3)	7325 (4)	4380 (1)	5.63 (5)
O(4)	9386 (1)	6635 (2)	4001 (1)	4.21 (3)
O(5)	10098 (1)	2788 (2)	4481 (1)	4.50 (3)
C(5′)	11386 (3)	1513 (3)	4358 (2)	5.56 (5)
(3)				
O(1)	3265 (1)	6801 (2)	2486 (1)	5.15 (4)
C(2)	4314 (2)	6308 (2)	2353 (2)	4.48 (5)
O(3)	4502 (1)	5271 (2)	3180 (1)	4.49 (4)
C(3a)	3525 (1)	4665 (2)	3485 (1)	3.86 (5)
C(4)	3419 (1)	4820 (2)	4629 (1)	3.74 (5)
C(5)	2299 (2)	4498 (3)	4903 (2)	4.21 (5)
C(6)	1571 (2)	5542 (3)	4354 (2)	5.36 (7)
C(7)	1776 (2)	6036 (3)	3440 (2)	5.58 (7)
C(7a)	2697 (2)	5531 (3)	2855 (2)	4.69 (5)
C(1′)	4446 (3)	5523 (4)	1345 (2)	6.29 (8)
C(2′)	5037 (2)	7630 (4)	2502 (3)	6.51 (8)
O(4)	4120 (1)	3794 (2)	5108 (1)	4.80 (4)
O(5)	2251 (1)	4689 (2)	6002 (1)	4.72 (4)
C(1‴)	1530 (1)	3895 (2)	6492 (2)	4.21 (5)
O(1‴)	900 (1)	3095 (2)	6051 (1)	5.69 (4)
C(1″)	1593 (1)	4112 (2)	7613 (2)	3.93 (5)
C(2″)	862 (2)	3407 (3)	8215 (2)	4.81 (5)
C(3″)	867 (2)	3624 (3)	9254 (2)	5.73 (7)
C(4″)	1615 (2)	4532 (3)	9702 (2)	6.44 (8)
C(5″)	2360 (2)	5211 (3)	9119 (2)	6.36 (8)
C(6″)	2350 (2)	5005 (3)	8070 (2)	4.95 (5)
(4)				
O(1)	2059 (1)	−4487 (1)	5230 (1)	3.58 (5)
C(2)	2212 (2)	−4299 (1)	6472 (2)	2.74 (5)
O(3)	2890 (1)	−4687 (1)	7117 (1)	2.91 (3)
C(3a)	3547 (2)	−4979 (1)	6214 (2)	2.66 (5)
C(4)	3847 (2)	−5508 (1)	6732 (2)	2.75 (5)
C(5)	2660 (2)	−5794 (1)	7055 (2)	2.55 (5)
C(6)	1722 (2)	−5780 (1)	6036 (2)	3.15 (6)
C(7)	1714 (2)	−5407 (1)	5201 (2)	3.48 (6)
C(7a)	2646 (2)	−4984 (1)	5136 (2)	2.96 (6)
C(1′)	2936 (3)	−3801 (1)	6433 (3)	4.12 (8)
C(2′)	964 (2)	−4247 (1)	7094 (3)	4.39 (8)
O(4)	4523 (2)	−5761 (1)	5778 (2)	3.97 (3)
O(5)	3050 (1)	−6320 (1)	7348 (1)	3.00 (3)
C(1‴)	2274 (2)	−6605 (1)	8021 (2)	2.91 (5)
O(1‴)	1240 (1)	−6466 (1)	8303 (2)	4.10 (5)
C(1″)	2809 (2)	−7108 (1)	8390 (2)	3.22 (6)
C(2″)	2108 (3)	−7422 (1)	9148 (2)	4.76 (8)
C(3″)	2592 (4)	−7889 (1)	9546 (3)	6.13 (9)
C(4″)	3764 (4)	−8041 (1)	9205 (3)	6.18 (9)
C(5″)	4449 (3)	−7731 (1)	8446 (3)	6.03 (8)
C(6″)	3989 (2)	−7263 (1)	8031 (3)	4.50 (8)

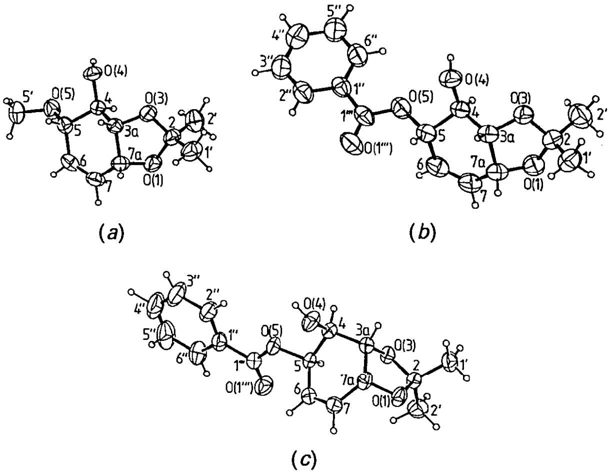
Table 2. *Bond lengths* (Å), *interbond angles* (°) *and torsion angles* (°) *for* (2), (3) *and* (4)

E.s.d.'s are in parentheses for the lengths, for the interbond angles they range between 0.1 and 0.2° and for the torsion angles they range between 0.2 and 0.3°.

	(2)	(3)	(4)
O(1)—C(2)	1.424 (2)	1.426 (3)	1.438 (3)
O(1)—C(7a)	1.438 (2)	1.438 (3)	1.440 (3)
C(2)—O(3)	1.436 (2)	1.441 (3)	1.426 (3)
C(2)—C(1′)	1.512 (3)	1.507 (4)	1.510 (4)
C(2)—C(2′)	1.503 (3)	1.510 (4)	1.509 (3)
O(3)—C(3a)	1.425 (2)	1.428 (2)	1.425 (2)
C(3a)—C(4)	1.512 (2)	1.513 (2)	1.518 (4)
C(3a)—C(7a)	1.517 (2)	1.536 (3)	1.517 (3)
C(4)—O(4)	1.425 (2)	1.418 (2)	1.424 (3)
C(4)—C(5)	1.521 (2)	1.513 (3)	1.519 (3)
C(5)—C(6)	1.495 (2)	1.491 (4)	1.496 (3)
C(5)—O(5)	1.433 (2)	1.451 (3)	1.463 (3)
C(6)—C(7)	1.313 (2)	1.308 (4)	1.324 (3)
C(7a)—C(7)	1.492 (2)	1.490 (4)	1.489 (3)
O(5)—C(5′)	1.425 (3)		
O(5)—C(1‴)		1.339 (2)	1.333 (2)
C(1‴)—O(1‴)		1.213 (2)	1.210 (3)
C(1‴)—C(1″)		1.480 (4)	1.482 (4)
C(1″)—C(2″)		1.388 (3)	1.381 (4)
C(1″)—C(6″)		1.380 (3)	1.389 (3)
C(2″)—C(3″)		1.374 (4)	1.388 (4)
C(3″)—C(4″)		1.376 (4)	1.373 (6)
C(4″)—C(5″)		1.375 (4)	1.366 (5)
C(5″)—C(6″)		1.385 (4)	1.387 (4)
C(2)—O(1)—C(7a)	106.7	106.4	108.7
O(1)—C(2)—O(3)	105.9	104.3	106.0
O(1)—C(2)—C(1′)	111.1	112.1	108.9
O(1)—C(2)—C(2′)	108.5	108.5	110.1
O(3)—C(2)—C(1′)	109.3	109.8	110.7
O(3)—C(2)—C(2′)	109.8	108.4	107.5
C(1′)—C(2)—C(2′)	112.2	113.3	113.3
C(2)—O(3)—C(3a)	109.4	108.8	107.1
O(3)—C(3a)—C(4)	111.7	110.0	109.5
O(3)—C(3a)—C(7a)	103.7	104.8	102.3
C(4)—C(3a)—C(7a)	113.1	114.1	114.3
C(3a)—C(4)—C(5)	109.7	109.0	110.3
C(3a)—C(4)—O(4)	108.4	107.9	105.0
C(5)—C(4)—O(4)	111.2	111.4	111.8
C(4)—C(5)—C(6)	111.3	110.5	112.8
C(4)—C(5)—O(5)	107.2	106.0	105.3
C(6)—C(5)—O(5)	110.8	111.3	112.1
C(5)—C(6)—C(7)	122.7	121.0	121.7
C(6)—C(7)—C(7a)	122.8	123.1	124.5
O(1)—C(7a)—C(3a)	102.3	103.3	102.6
O(1)—C(7a)—C(7)	109.9	110.3	111.1
C(3a)—C(7a)—C(7)	115.1	114.8	113.7
C(5)—O(5)—C(5′)	113.9		
C(5)—O(5)—C(1‴)		117.3	117.1
O(5)—C(1‴)—O(1‴)		122.8	123.4
O(5)—C(1‴)—C(1″)		112.5	113.1
O(1‴)—C(1‴)—C(1″)		124.7	123.6
C(1‴)—C(1″)—C2″)		118.8	117.9
C(1‴)—C(1″)—C(6″)		121.8	122.4
C(2″)—C(1″)—C(6″)		119.4	119.7
C(1″)—C(2″)—C(3″)		120.7	119.6
C(2″)—C(3″)—C(4″)		119.5	120.9
C(3″)—C(4″)—C(5″)		120.5	119.3
C(4″)—C(5″)—C(6″)		120.1	121.2
C(1″)—C(6″)—C(5″)		119.8	119.4
C(7a)—O(1)—C(2)—O(3)	−25.8	−35.9	−0.2
C(2)—O(1)—C(7a)—C(3a)	34.8	31.8	−20.9
O(1)—C(2)—O(3)—C(3a)	5.2	25.4	23.1
C(2)—O(3)—C(3a)—C(4)	−106.1	−128.8	−157.1
C(2)—O(3)—C(3a)—C(7a)	15.9	−5.7	−35.5
O(3)—C(3a)—C(4)—C(5)	171.7	167.5	60.7
C(7a)—C(3a)—C(4)—C(5)	55.3	50.1	−53.4
O(3)—C(3a)—C(7a)—O(1)	−30.6	−15.7	34.0
C(4)—C(3a)—C(7a)—C(7)	−28.6	−15.5	32.2
C(3a)—C(4)—C(5)—C(6)	−52.5	−58.4	48.5
C(3a)—C(4)—C(5)—O(5)	−173.9	−179.1	171.1
O(4)—C(4)—C(5)—C(6)	−172.4	−177.3	−67.9
O(4)—C(4)—C(5)—O(5)	66.3	61.9	54.6
C(4)—C(5)—C(6)—C(7)	24.7	32.9	−24.9
C(4)—C(5)—O(5)—C(5′)	−156.0		
C(4)—C(5)—O(5)—C(1‴)		−152.1	159.6
C(5)—C(6)—C(7)—C(7a)	3.1	4.1	3.2
C(6)—C(7)—C(7a)—C(3a)	−1.3	−13.2	−6.6

Discussion. Final atomic coordinates of the non-H atoms for (2), (3) and (4) are given in Table 1.* The molecular conformations for the three structures are illustrated in Fig. 1, which also includes the atom numbering. Bond lengths, bond angles and selected torsion angles are listed in Table 2.

The cyclohexene ring in each of the three molecules adopts a sofa conformation in which C(4), which has the hydroxyl substituent, is out of the plane formed by the other five atoms [coplanar to within 0.02 Å in (2), 0.09 Å in (3) and 0.03 Å in (4)] by 0.66, 0.68 and 0.60 Å in (2), (3) and (4) respectively. In both (2) and (3) the hydroxyl substituent is equatorial whereas in (4) it occupies the axial position. This has resulted in the cyclohexene ring adopting a 4β-sofa† conformation in the latter case in contrast to a 4α-sofa conformation observed in the former cases. The conformation of the *cis*-fused dioxolane ring in (2) and (3) is between a half chair and an envelope as is indicated by the pseudorotation parameters (Altona, Geise & Romers, 1968) $\Delta = 16.50°$, $\varphi_m = 35.2°$ for (2), and $\Delta = -16.9°$, $\varphi_m = -36.3°$ for (3). Its conformation in (4), on the other hand, is 3aβ-envelope, atoms O(1), C(2), O(3), C(7a) being coplanar to within experimental error, C(3a) lying 0.53 Å out of plane, and $\Delta = 32.4°$, $\varphi_m = 37.0°$. The substituents at C(5) on the cyclohexene



(*a*) (*b*)

(*c*)

Fig. 1. Perspective views of the molecules with thermal ellipsoids scaled to 50% probability. The C symbol is omitted and H atoms are denoted by spheres of arbitrary radius. (*a*) (2), (*b*) (3) and (*c*) (4).

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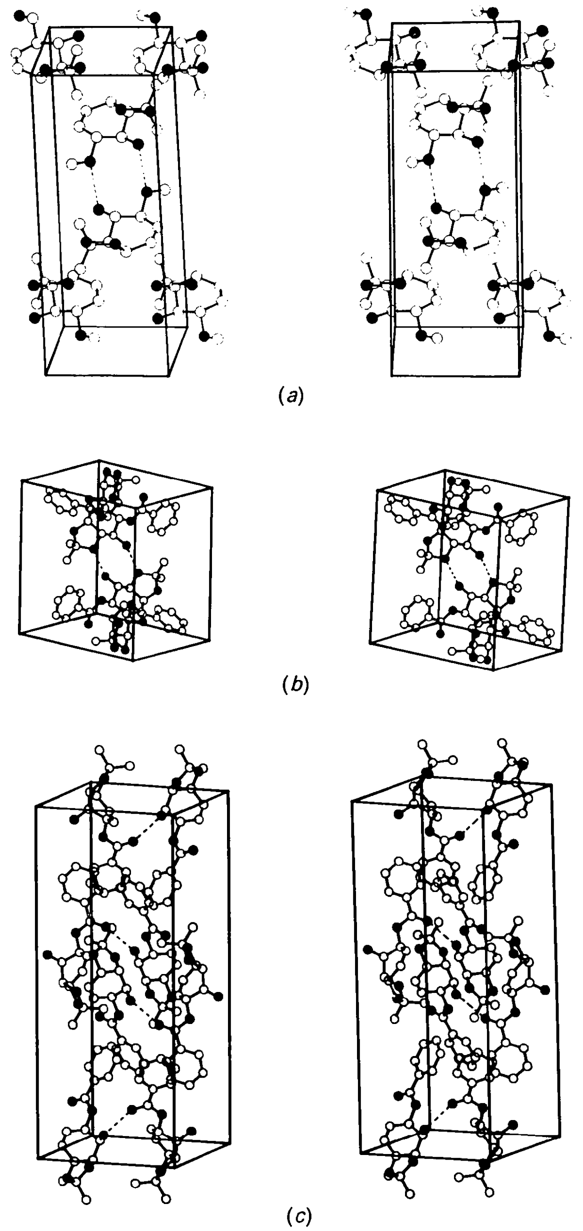
* Lists of anisotropic thermal parameters, H-atom parameters, short intermolecular contact distances and structure amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54161 (67 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AN0328]

† The α and β assignments refer to the enantiomers in Fig. 1.

ring, methoxyl in (2) and benzoate in (3) and (4), occupy equatorial positions. The orientation of the benzene rings in (3) and (4) relative to their associated cyclohexene rings is defined by the angles between their perpendiculars of 70.8 and 117.6° respectively. All interbond lengths and angles are in good agreement with values reported for comparable structures.


(a)

(b)

(c)

Fig. 2. Stereoviews of the crystal packing: (*a*) (2), direction of projection **a**, the *c* axis is vertical; (*b*) (3), direction of projection **b**, the *a* axis is vertical; (*c*) (4), direction of projection **c**, the *b* axis is vertical.

The crystal packings are stabilized by O—H···O intermolecular hydrogen bonding. In the structure of (2), two equivalent hydrogen bonds link the molecules into dimers across inversion centres (Fig. 2*a*). For these interactions the hydroxyl O is the donor atom to the methoxyl O atom at C(5), the O(4)···O(5), O(4)—H(O4), H(O4)···O(5)($2-x$, $1-y$, $1-z$) distances are 2.792 (3), 0.88 (3) and 1.95 (3) Å respectively with the O(4)—H(O4)···O(5) angle 160 (2)°. In the crystals of (3) the hydroxyl O atom at C(4) donates its proton to O(3) in the dioxolane ring of an adjacent molecule. As in (2), two such equivalent interactions link the molecules into dimers across inversion centres (Fig. 2*b*). For these hydrogen bonds the O(4)···O(3), O(4)—H(O4), H(O4)···O(3)($1-x$, $1-y$, $1-z$) distances have the respective values 2.939 (2), 0.92 (4), 2.08 (3) Å with the O(4)—H(O4)···O(3) angle 155 (3)°. In the structure of (4) the packing mode is different from that observed in the former two. In this case the hydroxyl at C(4) donates its proton to the carbonyl oxygen, O(1‴), of the benzoate moiety of a glide-related molecule. These interactions link the molecules into ribbons along the [100] direction (Fig. 2*c*) with the distances O(4)···O(1), O(4)—H(O4), H(O4)···O(1) ($0.5+x$, y, $1.5-z$) 2.785 (3), 0.83 (3), 1.96 (3) Å respectively and the angle O(4)—H(O4)···O(1) 172 (4)°. Apart from one close intermolecular approach between O(4)···(O4)($1-x$, $1-y$, $1-z$) of 3.135 (2) Å in (2) there are no other contacts less than 3.3 Å in the crystal structures.

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