Structure of 4-(3,4-Dihydroxyphenyl)-5-(*O*-β-D-galactopyranosyl)-7-methoxycoumarin Trihydrate*

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Abstract. $C_{22}H_{22}O_{11}.3H_2O$, $M_r = 516.4$, orthorhombic, $P2_12_12_1$, $a = 10.977$ (2), $b = 12.894$ (2), $c = 31.135$ (6) Å, $V = 4407$ (1) Å^3, $Z = 8$, $D_x = 1.557$ Mg m^{-3}, λ(Cu $K\alpha$) = 1.54178 Å, $\mu = 1.084$ mm^{-1}, $F(000) = 2176$, $T = 293$ K, $R = 0.048$ for 2779 observed reflections. The X-ray study confirms that the structure of the title compound is as inferred from chemical evidence. There are two crystallographically independent molecules, A and B. There are no significant discrepancies in the bond lengths between these two molecules. Both cyclohexenone rings are almost planar. The methoxy groups are nearly coplanar with C—C—O—C torsion angles of 6.6 (8) and -2.5 (7)° for molecules A and B, respectively. The angles between the best planes through the cyclohexenone and the dihydroxyphenyl rings in molecules A and B are 104.1 (2) and 101.2 (2)°, respectively. The molecules in the crystal are held together by hydrogen bonds and van der Waals interactions.

Experimental. The title compound was crystallized in a mixture of acetone/ethanol and gave colourless crystals. Size of crystal $0.18 \times 0.26 \times 0.10$ mm. Nicolet *P3F* four-circle diffractometer, Ni-filtered Cu $K\alpha$ radiation. Lattice parameters from 25 machine-centred reflections with $11.0 < 2\theta < 23.8°$. 3175 reflections with $3 < 2\theta < 110°$ for one octant, 2779 independent with $I > 2.8\sigma(I)$, index range h 0 to 11, k 0 to 13, l 0 to 32, $2\theta/\theta$ scan mode, variable scan speed. Two standard reflections ($\overline{1}3\overline{2}$, $\overline{1}15$) monitored every 50 measurements; no significant variation. Intensities were corrected for Lp effects but not for absorption. Data adjusted to an approximately absolute scale and an overall U value of 0.034 Å^2. Structure solved using a combination of direct methods and partial structure expansion by an itera-

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å$^2 \times 10^3$)

$$U_{eq} = (U_{11} \times U_{22} \times U_{33})^{1/3}.$$

	x	y	z	U_{eq}
O(1)	676 (4)	489 (4)	901 (1)	70 (2)
O(2)	3834 (5)	5528 (5)	164 (2)	123 (3)
O(3)	6270 (6)	4716 (6)	483 (3)	156 (4)
O(1a)	8706 (3)	1189 (3)	2133 (1)	38 (1)
O(2a)	10325 (5)	1205 (5)	1725 (1)	66 (2)
C(2a)	9911 (6)	1399 (6)	2076 (2)	45 (2)
C(3a)	10534 (6)	1823 (6)	2435 (2)	42 (2)
C(4a)	10025 (5)	1989 (5)	2824 (2)	33 (2)
C(5a)	8026 (4)	1927 (4)	3241 (2)	35 (2)
O(5a)	8644 (4)	2258 (4)	3599 (1)	43 (2)
C(6a)	6778 (4)	1751 (4)	3246 (2)	38 (2)
C(7a)	6228 (5)	1347 (4)	2874 (2)	38 (2)
O(7a)	5016 (3)	1123 (3)	2847 (1)	49 (1)
C(8a)	6884 (5)	1157 (4)	2511 (2)	39 (2)
C(9a)	8107 (5)	1375 (4)	2516 (1)	31 (2)
C(10a)	8737 (4)	1770 (4)	2871 (1)	32 (2)
C(1'a)	10801 (4)	2473 (4)	3158 (2)	35 (2)
C(2'a)	11245 (5)	1905 (4)	3504 (2)	43 (2)
C(3'a)	11985 (5)	2362 (5)	3807 (2)	44 (2)
O(3'a)	12395 (5)	1812 (4)	4149 (1)	81 (2)
C(4'a)	12264 (5)	3404 (4)	3770 (2)	37 (2)
O(4'a)	12987 (4)	3814 (3)	4089 (1)	56 (1)
C(5'a)	11825 (5)	3966 (4)	3434 (2)	48 (2)
C(6'a)	11104 (5)	3506 (4)	3127 (2)	44 (2)
C(11a)	8022 (5)	2309 (4)	3992 (2)	40 (2)
O(11a)	7335 (3)	3234 (3)	3987 (1)	37 (1)
C(12a)	8962 (5)	2333 (4)	4351 (2)	36 (2)
O(12a)	9630 (4)	1384 (3)	4366 (1)	51 (1)
C(13a)	8261 (5)	2471 (4)	4775 (2)	34 (2)
O(13a)	9074 (4)	2580 (3)	5134 (1)	48 (1)
C(14a)	7458 (5)	3427 (4)	4758 (2)	38 (2)
O(14a)	8195 (4)	4340 (3)	4714 (1)	51 (1)
C(15a)	6636 (4)	3352 (4)	4368 (1)	34 (2)
C(16a)	5844 (5)	4301 (4)	4309 (2)	39 (2)
O(16a)	5075 (3)	4350 (3)	4671 (1)	38 (1)
C(17a)	4240 (5)	1403 (5)	3192 (2)	57 (2)
O(1b)	3604 (3)	9395 (3)	2153 (1)	38 (1)
O(2b)	5291 (3)	9463 (4)	1779 (1)	57 (1)
C(2b)	4826 (5)	9179 (4)	2108 (2)	44 (2)
C(3b)	5396 (5)	8703 (4)	2466 (2)	38 (2)
C(4b)	4823 (4)	8450 (4)	2836 (2)	33 (2)
C(5b)	2744 (4)	8431 (4)	3215 (1)	33 (2)
O(5b)	3258 (3)	7907 (3)	3557 (1)	37 (1)
C(6b)	1514 (4)	8689 (4)	3212 (2)	39 (2)
C(7b)	1035 (4)	9180 (4)	2852 (2)	38 (2)
O(7b)	-170 (3)	9469 (3)	2825 (1)	45 (1)
C(8b)	1746 (5)	9398 (4)	2502 (1)	37 (2)
C(9b)	2964 (4)	9154 (4)	2518 (2)	33 (2)
C(10b)	3518 (4)	8675 (4)	2869 (1)	31 (2)
C(1'b)	5573 (4)	8055 (4)	3199 (2)	34 (2)
C(2'b)	5951 (4)	8710 (5)	3519 (2)	46 (2)
C(3'b)	6740 (5)	8386 (4)	3834 (2)	42 (2)
O(3'b)	7137 (4)	9088 (4)	4141 (2)	86 (2)
C(4'b)	7134 (5)	7367 (4)	3844 (2)	42 (2)

Table 1 (cont.)

	x	y	z	U_{eq}
O(4'b)	7930 (4)	7109 (3)	4168 (1)	58 (1)
C(5'b)	6760 (5)	6698 (4)	3529 (2)	44 (2)
C(6'b)	5990 (4)	7033 (4)	3207 (2)	42 (2)
C(11b)	2455 (4)	7454 (4)	3860 (2)	34 (2)
O(11b)	1949 (3)	8244 (2)	4107 (1)	33 (1)
C(12b)	3190 (4)	6717 (4)	4140 (2)	33 (2)
O(12b)	3618 (3)	5853 (3)	3894 (1)	45 (1)
C(13b)	2364 (4)	6287 (4)	4478 (1)	33 (2)
O(13b)	3048 (3)	5631 (3)	4760 (1)	43 (1)
C(14b)	1742 (5)	7167 (4)	4727 (2)	41 (2)
O(14b)	2642 (4)	7790 (3)	4941 (1)	59 (2)
C(15b)	1062 (5)	7845 (4)	4410 (2)	39 (2)
C(16b)	415 (5)	8749 (4)	4613 (2)	47 (2)
O(16b)	−383 (4)	9202 (3)	4306 (2)	61 (2)
C(17b)	−951 (5)	9220 (5)	3169 (2)	52 (2)

Table 2. Selected bond lengths (Å), angles (°) and geometry of hydrogen bonds (Å, °)

	Molecule A	Molecule B
O(1)—C(2)	1.361 (7)	1.377 (6)
C(4)—C(10)	1.450 (7)	1.466 (7)
O(5)—C(11)	1.402 (6)	1.418 (6)
C(1')—C(2')	1.392 (7)	1.371 (7)
C(1')—C(6')	1.376 (8)	1.396 (8)
C(3')—O(3')	1.357 (7)	1.386 (7)
O(11)—C(15)	1.419 (5)	1.449 (6)
C(12)—C(13)	1.537 (7)	1.495 (7)
C(13)—C(14)	1.517 (7)	1.536 (7)
C(5)—O(5)—C(11)	118.9 (4)	117.4 (4)
C(4)—C(1')—C(6')	119.8 (5)	121.2 (4)
O(5)—C(11)—O(11)	106.9 (4)	108.3 (4)
C(11)—C(12)—C(13)	107.1 (4)	108.3 (4)
O(12)—C(12)—C(13)	109.2 (4)	106.6 (4)
C(12)—C(13)—O(13)	111.7 (4)	109.5 (4)
O(13)—C(13)—C(14)	107.9 (4)	111.1 (4)
O(11)—C(15)—C(14)	110.7 (4)	107.4 (4)
C(15)—C(16)—O(16)	106.5 (4)	109.0 (4)

D—H···A	D···A	H···A	D—H···A
O(2)—H(2b)···O(3)	3.039 (9)	2.460 (12)	120.5 (7)
O(12a)—H(12b)···O(3'a)	3.158 (7)	2.431 (8)	135.3 (11)
O(16a)—H(16c)···O(13b)	2.785 (5)	2.343 (7)	157.2 (10)
O(1)—H(1a)···O(2a^i)	2.754 (5)	2.032 (7)	126.5 (7)
O(1)—H(1b)···O(14a^{ii})	2.720 (5)	1.924 (13)	159.9 (7)
O(3'a)—H(3'a)···O(13a^{iii})	2.999 (6)	2.124 (13)	159.8 (6)
O(13a)—H(13b)···O(16a^{iii})	2.787 (5)	1.895 (8)	168.2 (8)
O(4'a)—H(4'a)···O(12b^{iv})	2.786 (5)	1.810 (8)	166.2 (6)
O(3'b)—H(3'b)···O(16b^{iv})	2.774 (6)	2.016 (7)	152.0 (8)
O(14a)—H(14b)···O(3')	2.749 (10)	1.933 (16)	146.6 (6)
O(4'b)—H(4'b)···O(1^{vi})	2.598 (6)	1.633 (8)	167.7 (8)
O(13b)—H(13d)···O(2^{vii})	2.843 (7)	2.125 (11)	159.3 (10)
O(14b)—H(14d)···O(4'b^{viii})	2.795 (4)	1.912 (16)	159.3 (6)
O(16b)—H(16f)···O(12a^{ix})	2.820 (5)	1.990 (8)	161.3 (6)

Symmetry code: (i) $-1 + x$, y, z; (ii) $1 - x$, $-0.5 + y$, $0.5 - z$; (iii) $0.5 + x$, $0.5 - y$, $1 - z$; (iv) $1 + x$, y, z; (v) $1.5 - x$, $1 - y$, $0.5 + z$; (vi) $1 - x$, $0.5 + y$, $0.5 - z$; (vii) $0.5 - x$, $1 - y$, $0.5 + z$; (viii) $-0.5 + x$, $1.5 - y$, $1 - z$; (ix) $-1 + x$, $1 + y$, z.

tive E-Fourier procedure using *SHELXTL* (Sheldrick, 1985). Blocked-cascade least-squares refinement with all non-H atoms treated anisotropically; H atoms of CH, CH_2 and CH_3 were allowed to ride on bonded C with a fixed isotropic $U = 0.06 \text{ Å}^2$. The H atoms bonded to O atoms were located on a difference Fourier map at an advanced stage of anisotropic refinement and their coordinates refined. $\sum w(\Delta F)^2$ minimized, $w = [\sigma^2(F_o) + 0.002(F_o)^2]^{-1}$, where σ is the standard deviation of observed amplitudes, based on counting statistics, isotropic extinction parameter $X = 0.0014$. In the last
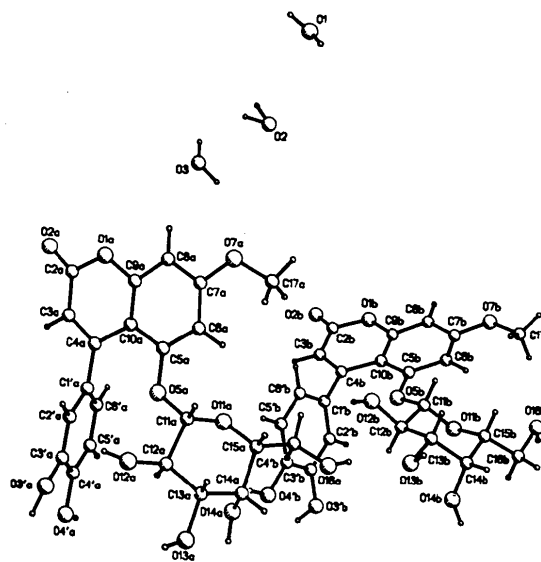

Fig. 1. Molecular structure of the title compound with atom-numbering scheme.

cycle, $(\Delta/\sigma)_{max} = 0.22$; $\Delta\rho$ from -0.23 to 0.24 e Å^{-3}, $S = 1.19$, final $R = 0.048$, $wR = 0.064$; scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). All computations were performed on a Nova 4S computer and plots drawn on a Tektronix plotter with the *SHELXTL* system of programs.

Atomic coordinates are in Table 1.* A perspective molecular drawing with atom labelling is displayed in Fig. 1. Selected bond distances, angles and geometry of hydrogen bonds are given in Table 2.

Related literature. The title compound has been isolated from the stem bark of *Exostema caribaeum* (Jacq.) Roem. et Schult. (syn. *Cinchona caribaea*, Rubiaceae) a tropical species found in the West Indies, Mexico and Costa Rica. Details of the source and chemical background of the title compound are given by Mata, Calzada, Garcia & Reguero (1987).

References

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