Structures of Four *trans*-2-Hydroxy- and Methoxy-2-methyl-3,4-dihydro-4-alkyl-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-ones

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Abstract. Derivatives of 2-methyl-3,4-dihydro-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-one. (1) Racemic *trans*-2-methoxy-4-(2-propyl), $M_r = 288.3$, monoclinic, $P2_1/c$, $a = 13.737$ (3), $b = 13.228$ (6), $c = 17.229$ (4) Å, $\beta = 102.93$ (2)°, $V = 3051.4$ Å^3, $Z = 8$ (two molecules/asymmetric unit), $D_x = 1.255$ g cm^{-3}, λ(Mo Kα) = 0.71073 Å, $\mu = 0.908$ cm^{-1}, $F(000) = 1232$, $T = 298$ K, final $R = 0.050$ for 3988 unique intensities. Dihydropyran rings in $C_{17}H_{20}O_4$ are half-chairs, one being distorted toward the *d,e*-diplanar form. (2) Resolved *trans*-2-methoxy-4-cyclohexyl, $M_r = 328.4$, orthorhombic, $P2_12_12_1$, $a = 10.468$ (5), $b = 11.245$ (5), $c = 14.465$ (4) Å, $V = 1702.7$ Å^3, $Z = 4$, $D_x = 1.281$ g cm^{-3}, λ(Mo Kα) = 0.71073 Å, $\mu = 0.823$ cm^{-1}, $F(000) = 704$, $T = 298$ K, final $R = 0.051$ for 2481 unique intensities. Compound, $C_{20}H_{24}O_4$, spontaneously resolves on crystallization from methanol:acetone; data specimen determined to be 2*R*,4*R* by circular dichroism spectrum and comparison with structures of known configuration. Dihydropyran ring has a *d,e*-diplanar conformation. (3) Racemic *trans*-2-hydroxy-4-(2-propyl). Compound crystallizes as the hemihydrate $C_{16}H_{18}O_4.\frac{1}{2}H_2O$; $M_r = 283.3$, triclinic, $P\bar{1}$, $a = 9.015$ (4), $b = 10.216$ (4), $c = 16.208$ (5) Å, $\alpha = 103.08$ (3), $\beta = 95.42$ (3), $\gamma = 95.28$ (3)°, $V = 1437.6$ Å^3, $Z = 4$ (two molecules/asymmetric unit), $D_x = 1.309$ g cm^{-3}, λ(Mo Kα) = 0.71073 Å, $\mu = 0.890$ cm^{-1}, $F(000) = 604$, $T = 298$ K, final $R = 0.040$ for 4656 unique reflections. One dihydropyran ring is a half-chair, the other has an *e,f*-diplanar conformation. Intermolecular hydrogen bonding occurs between the water and the hydroxyls and lactone carbonyls of each coumarin with O$\cdots$O distances between 2.82 and 2.90 Å. (4) Racemic *trans*-2-hydroxyl-4-(2-propyl) derivative also cocrystallizes with 4-hydroxy-2*H*-benzo-pyran-2-one (1:1), $M_r = 436.4$, triclinic, $P\bar{1}$, $a = 8.669$ (2), $b = 10.506$ (4), $c = 12.559$ (2) Å, $\alpha =$ 102.98 (2), $\beta = 107.56$ (2), $\gamma = 93.63$ (2)°, $V = 1052.0$ Å^3, $Z = 2$, $D_x = 1.378$ g cm^{-3}, λ(Mo Kα) = 0.71073 Å, $\mu = 0.941$ cm^{-1}, $F(000) = 460$, $T = 298$ K, final $R = 0.041$ for 3322 unique reflections. Co-crystalline $C_{16}H_{18}O_4.C_9H_6O_3$ shows chains of H bonds linking the hydroxyls of the coumarins alternately with the lactone carbonyls, O$\cdots$O distances 2.68 and 2.75 Å. The dihydropyran ring has a half-chair conformation.

Introduction. Analogs of the clinically useful oral anticoagulant drug warfarin, with alkyl substituents in place of the side-chain phenyl group, can be prepared by Michael-type addition of α,β-unsaturated methyl ketones with 4-hydroxycoumarin. Products invariably crystallize as one of the cyclic diastereomeric hemiketals but in solution the open-chain keto form generally predominates. Methyl ketals can be made by treatment of the hemiketal/keto mixture with acidic methanol. Structures of 4-alkyl-2-hydroxy- and methoxy-2-methyl-3,4-dihydro-2*H*,5*H*-pyrano[3,2-*c*]-[1]benzopyran-5-ones are presented as part of a study of the shape of the dihydropyran ring near the ground-state conformation.
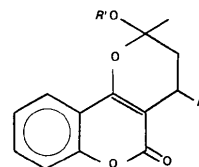
	R	R'	
(1)	CH(CH₃)₂	CH₃	
(2)	C₆H₁₁	CH₃	resolved (2*R*,4*R*)
(3)	CH(CH₃)₂	H	½H₂O
(4)	CH(CH₃)₂	H	4-hydroxycoumarin

Table 1. *Experimental details*

	(1)	(2)	(3)	(4)
Crystal size (mm)	$0.85 \times 0.45 \times 0.2$	$0.75 \times 0.45 \times 0.5$	$0.6 \times 0.6 \times 0.35$	$0.6 \times 0.2 \times 0.2$
$\theta_{max}(°)$	30	30	28	27.5
No. of unique intensities measured	8874	2765	6929	4849
No. used	3988	2481	4656	3322
Scale factor	0.300 (1)	0.219 (2)	0.152 (1)	0.244 (1)
R	0.050	0.051	0.040	0.041
wR	0.060	0.040	0.053	0.051
S	1.4	1.9	1.4	1.36
No. of variables refined	468	305	522	386

Experimental. Synthesis of hemiketals and methyl ketals follows reported procedures for aliphatic warfarin analogs (Valente, Santarsiero & Schomaker, 1979). Using 5-methylhex-3-en-2-one, (4) is obtained by crystallization of the product gum from ethyl acetate:hexane (1:1), m.p. 393.3–394.9 K; column chromatography (silica gel, $CHCl_3$:benzene, 1:1) gives pure (3) as the faster eluting material, m.p. 347.1–348.1 K; colorless prisms from ethyl acetate:hexane, 1:1. *trans*-Methyl ketal (1) is purified (silica gel, $CHCl_3$:ethyl acetate, 9:1) from the diastereomeric mixture and recrystallized from cold ether:pentane, 1:1, m.p. 375.2–356.2 K. D_m's were not measured. The 4-cyclohexyl methyl ketal analog (Wheeler, 1980), m.p. 481.1 K, crystallizes as a conglomerate on evaporation from methanol:acetone (1:5) solutions at room temperature.

After structure determination showed the specimen to be chiral, the data crystal was subsequently dissolved in CH_3CN and the circular dichroism spectrum recorded over the 200–360 nm range (Jobin–Yvon Dichrograph III, 0.1 mm path, highest amplifier sensitivity). Cotton effects of decreasing intensity at 208, 219 and 308 nm for positive features and a lone negative feature at 270 nm are seen, consistent with known configurations, and these allow the assignment of the absolute configuration (2R, 4R).

Information pertinent to the crystallography of (1)–(4) is given in Table 1. For each, cell constants were determined from 25 carefully centered reflections for which $30° \le 2\theta \le 35°$. Intensities were collected on a CAD-4 diffractometer; intensities less than three times their estimated standard deviations were marked weak and not used in the refinements, except for (2) in which only data with $I < 0$ were marked weak. Data were corrected for polarization and coincidence losses, no deterioration was noted. No correction for absorption. Secondary extinction ($g \times 10^7$) was included: (2), 1.58 (30); (3), 0.39 (1); (4), 0.253 (1). For (1), 001 was seriously affected and was omitted in refinement. Structures were discovered with *MULTAN* (Germain, Main & Woolfson, 1971), and refined on F by full-matrix least squares. First, non-hydrogen-atom positions and their U_{iso}'s were refined, then with their U_{ij}'s. H atoms were refined from calculated positions with their U_{iso}'s. Least-squares weights were taken as

$4F_o^2/\sigma^2(I)$ where $\sigma^2(I) = \sigma^2(I)_c + p(I)_c^2$, $p = 0.05$. Scattering factors were from *International Tables for X-ray Crystallography* (1974) except for H (Stewart, Davidson & Simpson, 1965). In all cases final $\Delta/\sigma_{ave,max}$ were less than 0.08, 0.35 respectively and positive $\Delta\rho$ excursions were less than 0.35 e Å^{-3}, no troughs were less than -0.237 e Å^{-3}.

Discussion. Final atomic coordinates and associated B_{eq}'s are given in Tables 2–5.*

The structures of methyl ketals (1) and (2) have no unusual intermolecular contacts. Structure (1) has two molecules in the asymmetric unit. Structure (2) is pseudoisomorphous with the (2R,4R) *trans*-4-phenyl analog (Valente, Eggleston & Schomaker, 1986) from a comparison of cell constants and molecular arrangements. Of the top 25 normalized structure factors for (2), 11 coincide with equivalent stronger diffraction planes for the phenyl compound, most notably that for (035) which is the strongest in each. Excluding the cyclohexyl ring, non-hydrogen positions in the cell differ by only 0.17 Å from corresponding atoms in the phenyl structure. Packing is generally similar. Structure (3) has two molecules in the asymmetric unit. Hydrogen bonding in (3) extensively involves the water of crystallization which donates and accepts twice. Hemiketal hydroxyls of each coumarin molecule are H-bonded to the water, O···O 2.900 (2), 2.818 (2) Å, and the water is H-bonded to both lactone carbonyl oxygens, O···O 2.873 (2), 2.880 (2) Å. In (4), the 2-hydroxyl of the 4-(2-propyl) derivative H· bonds to the lactone carbonyl oxygen of the 4-hydroxycoumarin molecule, O···O 2.749 (2) Å, and its 4-hydroxyl H bonds to the lactone carbonyl oxygen of another neighboring 4-(2-propyl) derivative, O···O 2.683 (2) Å.

All six molecules in the four structures have the 2-oxygen *trans* to the 4-alkyl substituent, and the hydroxyl or methoxyl is axial (anomeric effect). Hemiketal hydroxyl H's and ketal methyls are *gauche* synclinal to the dihydropyran ring oxygen and *exo* to

the ring (exoanomeric effect). Enol ether C—O bonds in the dihydropyran rings are generally observed to be longer (1·45–1·47 Å) than found in tetrahydropyrans like sugars (1·42–1·43 Å) because of the influence of the ring unsaturation which locally widens intraring

Table 2. Positions [×10⁴, some z ×10⁵(*)] and B_{eq}'s for (1) with e.s.d.'s in parentheses

	x	y	z	$B_{eq}(\text{Å}^2)$
O(1A)	4293 (1)	−5120 (1)	69580 (9)*	4·32 (4)
O(2A)	3760 (1)	−4034 (1)	59897 (9)*	4·77 (4)
O(3A)	3423 (1)	−1947 (1)	82748 (9)*	3·97 (4)
O(4A)	2916 (1)	−3584 (1)	84797 (8)*	3·89 (3)
C(2A)	3720 (2)	−4281 (2)	6655 (1)	3·62 (5)
C(3A)	3159 (2)	−3776 (2)	7160 (1)	3·17 (4)
C(4A)	3299 (2)	−4070 (2)	7926 (1)	3·21 (4)
C(5A)	4009 (2)	−5298 (2)	9010 (1)	4·29 (6)
C(6A)	4594 (2)	−6134 (2)	9254 (2)	5·18 (7)
C(7A)	5066 (2)	−6623 (2)	8732 (2)	5·26 (7)
C(8A)	4959 (2)	−6292 (2)	7968 (2)	4·63 (6)
C(9A)	4364 (2)	−5451 (2)	7722 (1)	3·73 (5)
C(10A)	3891 (2)	−4944 (2)	8234 (1)	3·37 (5)
C(11A)	2471 (2)	−2914 (2)	6822 (1)	3·38 (5)
C(12A)	1945 (2)	−2526 (2)	7456 (1)	4·12 (5)
C(13A)	2587 (2)	−2547 (2)	8282 (1)	3·64 (5)
C(14A)	2035 (2)	−2265 (2)	8918 (2)	5·16 (6)
C(15A)	1715 (2)	−3193 (2)	6046 (1)	4·34 (6)
C(16A)	1054 (2)	−2292 (3)	5721 (2)	7·34 (9)
C(17A)	1099 (2)	−4121 (3)	6136 (2)	7·52 (9)
C(18A)	4159 (2)	−1877 (2)	9006 (2)	5·56 (7)
O(1B)	516 (1)	3629 (1)	70664 (9)*	4·43 (4)
O(2B)	661 (1)	2495 (1)	6177 (1)	5·33 (4)
O(3B)	2056 (1)	524 (1)	87020 (9)*	4·38 (4)
O(4B)	2548 (1)	2201 (1)	88305 (8)*	3·82 (3)
C(2B)	964 (2)	2767 (2)	6855 (1)	3·79 (5)
C(3B)	1733 (2)	2273 (2)	7451 (1)	3·13 (4)
C(4B)	1907 (2)	2622 (2)	8207 (1)	3·20 (4)
C(5B)	1550 (2)	3876 (2)	9197 (1)	4·33 (6)
C(6B)	1030 (2)	4715 (2)	9354 (2)	5·18 (6)
C(7B)	360 (2)	5187 (2)	8746 (2)	5·18 (6)
C(8B)	199 (2)	4832 (2)	7988 (2)	4·76 (6)
C(9B)	720 (2)	3984 (2)	7831 (2)	3·66 (5)
C(10B)	1400 (2)	3504 (2)	8428 (1)	3·38 (5)
C(11B)	2262 (2)	1348 (2)	7231 (1)	3·34 (5)
C(12B)	3129 (2)	1091 (2)	7923 (1)	3·77 (5)
C(13B)	2870 (2)	1169 (2)	8719 (1)	3·65 (5)
C(14B)	3746 (2)	996 (2)	9414 (2)	4·93 (6)
C(15B)	2589 (2)	1423 (2)	6433 (1)	4·40 (6)
C(16B)	3246 (2)	2324 (3)	6386 (2)	7·99 (9)
C(17B)	3089 (2)	448 (3)	6259 (2)	7·28 (8)
C(18B)	1689 (2)	473 (2)	9410 (2)	6·03 (7)

Table 3. Positions (×10⁴) and B_{eq}'s for (2) with e.s.d.'s in parentheses

	x	y	z	$B_{eq}(\text{Å}^2)$
O(1)	3969 (1)	2567 (1)	946 (1)	3·70 (6)
O(2)	2622 (1)	1360 (1)	1644 (1)	4·55 (8)
O(3)	4046 (1)	3708 (1)	4201 (1)	3·70 (7)
O(4)	3632 (1)	5049 (1)	3012 (1)	3·12 (6)
C(2)	3104 (2)	2335 (2)	1647 (1)	3·39 (6)
C(3)	2885 (1)	3256 (1)	2335 (1)	2·95 (6)
C(4)	3622 (1)	4235 (1)	2323 (1)	2·81 (6)
C(5)	5150 (2)	5560 (1)	1459 (1)	3·48 (7)
C(6)	5926 (2)	5733 (2)	707 (1)	3·88 (8)
C(7)	6076 (2)	4837 (2)	54 (1)	3·79 (8)
C(8)	5424 (2)	3788 (1)	142 (1)	3·50 (8)
C(9)	4611 (2)	3626 (1)	889 (1)	3·12 (6)
C(10)	4475 (1)	4497 (1)	1566 (1)	2·85 (6)
C(11)	1889 (2)	3026 (1)	3068 (1)	3·18 (6)
C(12)	1910 (2)	4024 (2)	3795 (1)	3·76 (7)
C(13)	3211 (2)	4597 (2)	3912 (1)	3·12 (7)
C(14)	3194 (2)	5677 (2)	4531 (1)	4·05 (8)
C(15)	5362 (2)	4030 (2)	4307 (1)	5·16 (8)
C(16)	535 (2)	2851 (2)	2651 (1)	3·28 (6)
C(17)	30 (2)	3922 (2)	2123 (1)	4·54 (8)
C(18)	−1276 (2)	3669 (2)	1693 (1)	5·5 (1)
C(19)	−2223 (2)	3266 (2)	2415 (1)	5·6 (1)
C(20)	−1734 (2)	2215 (2)	2956 (1)	5·3 (1)
C(21)	−419 (2)	2458 (2)	3378 (1)	4·1 (1)

Table 4. Positions [×10⁴, some z ×10⁵(*)] and B_{eq}'s for (3) with e.s.d.'s in parentheses

	x	y	z	$B_{eq}(\text{Å}^2)$
O(W)	2514 (1)	2343 (1)	80561 (7)*	3·59 (2)
O(1A)	5153 (1)	672 (1)	15921 (7)*	3·17 (2)
O(2A)	7404 (1)	321 (1)	1650 (1)	5·14 (3)
O(3A)	4395 (1)	3082 (1)	−3182 (6)*	3·39 (2)
O(4A)	3132 (1)	2173 (1)	6403 (7)	3·27 (2)
C(2A)	6082 (2)	392 (1)	1470 (1)	3·16 (3)
C(3A)	5426 (2)	1466 (1)	11691 (9)*	2·55 (3)
C(4A)	3917 (2)	1291 (1)	9453 (9)*	2·52 (3)
C(5A)	1417 (2)	−109 (2)	786 (1)	3·34 (3)
C(6A)	608 (2)	−1273 (2)	866 (1)	3·69 (3)
C(7A)	1333 (2)	2236 (2)	1179 (1)	3·35 (3)
C(8A)	2848 (2)	−2031 (1)	14285 (9)*	2·97 (3)
C(9A)	3649 (2)	−854 (1)	13410 (9)*	2·54 (3)
C(10A)	2968 (2)	111 (1)	10161 (9)*	2·54 (3)
C(11A)	6366 (2)	2721 (1)	10666 (9)*	2·63 (3)
C(12A)	5327 (2)	3831 (1)	11175 (9)*	2·71 (3)
C(13A)	3934 (2)	3391 (1)	4858 (9)*	2·65 (3)
C(14A)	2787 (2)	4380 (2)	563 (1)	3·48 (3)
C(15A)	7837 (2)	3197 (2)	1673 (1)	3·10 (3)
C(16A)	8780 (2)	4298 (2)	1386 (1)	4·28 (4)
C(17A)	7601 (2)	3659 (2)	2600 (1)	4·66 (4)
O(1B)	473 (1)	−711 (1)	30571 (7)*	3·64 (2)
O(2B)	−49 (1)	−2847 (1)	30507 (8)*	4·18 (3)
O(3B)	5307 (1)	−2921 (1)	29886 (7)*	3·92 (3)
O(4B)	4942 (1)	−796 (1)	37686 (7)*	3·53 (2)
C(2B)	913 (2)	−1885 (2)	3231 (1)	3·26 (3)
C(3B)	2434 (2)	−1879 (2)	35984 (9)*	3·02 (3)
C(4B)	3456 (2)	−825 (2)	35728 (9)*	2·94 (3)
C(5B)	3994 (2)	1504 (2)	3315 (1)	3·59 (4)
C(6B)	3452 (2)	2604 (2)	3088 (1)	4·26 (4)
C(7B)	1931 (2)	2597 (2)	2867 (1)	4·54 (4)
C(8B)	937 (2)	1489 (2)	2862 (1)	4·18 (4)
C(9B)	1490 (2)	392 (2)	3096 (1)	3·29 (3)
C(10B)	3002 (2)	367 (2)	33269 (9)*	3·04 (3)
C(11B)	2851 (2)	−3076 (2)	3928 (1)	3·32 (3)
C(12B)	4485 (2)	−2769 (2)	4331 (1)	3·91 (4)
C(13B)	5477 (2)	−2102 (2)	3806 (1)	3·49 (3)
C(14B)	7092 (2)	−1728 (2)	4198 (1)	4·62 (4)
C(15B)	1791 (2)	−3467 (2)	4552 (1)	3·96 (4)
C(16B)	2344 (3)	−4583 (2)	4946 (1)	5·47 (5)
C(17B)	1516 (2)	−2267 (2)	5245 (1)	5·13 (5)

Table 5. Positions (×10⁴) and B_{eq}'s for (4) with e.s.d.'s in parentheses

	x	y	z	$B_{eq}(\text{Å}^2)$
O(1A)	124 (1)	1207 (1)	−3338 (1)	2·55 (2)
O(2A)	2507 (2)	1977 (1)	−2076 (1)	2·70 (3)
O(3A)	3675 (1)	3257 (1)	−5338 (1)	2·40 (2)
O(4A)	951 (1)	3400 (1)	−5514 (1)	2·21 (2)
C(2A)	1551 (2)	2061 (2)	−2990 (1)	2·17 (3)
C(3A)	1815 (2)	2959 (2)	−3653 (1)	1·91 (3)
C(4A)	745 (2)	2766 (2)	−4740 (1)	1·96 (3)
C(5A)	−1967 (2)	1708 (2)	−6229 (1)	2·43 (4)
C(6A)	−3400 (2)	870 (2)	−6528 (2)	2·89 (4)
C(7A)	−3626 (2)	135 (2)	−5779 (2)	3·15 (4)
C(8A)	−2452 (2)	243 (2)	−4736 (2)	2·85 (4)
C(9A)	−1032 (2)	1120 (2)	−4434 (1)	2·26 (3)
C(10A)	−758 (2)	1855 (2)	−5162 (1)	2·03 (3)
C(11A)	3292 (2)	4017 (2)	−3166 (1)	1·94 (3)
C(12A)	3104 (2)	4927 (2)	−3979 (1)	2·13 (3)
C(13A)	2583 (2)	4149 (2)	−5225 (1)	2·10 (3)
C(14A)	2341 (2)	4986 (2)	−6081 (1)	2·50 (4)
C(15A)	3588 (2)	4797 (2)	−1902 (1)	2·48 (4)
C(16A)	2100 (2)	5388 (2)	−1729 (2)	3·22 (4)
C(17A)	5080 (3)	5855 (2)	−1471 (2)	3·86 (5)
O(1B)	1183 (1)	2301 (1)	960 (1)	2·73 (3)
O(2B)	2784 (2)	1706 (1)	2437 (1)	3·22 (3)
O(4B)	−2749 (2)	−219 (1)	801 (1)	3·03 (3)
C(2B)	1414 (2)	1544 (2)	1740 (1)	2·46 (4)
C(3B)	62 (1)	659 (2)	1671 (1)	2·53 (4)
C(4B)	−1433 (2)	581 (2)	900 (1)	2·16 (3)
C(5B)	−3168 (2)	1403 (2)	−728 (2)	2·71 (4)
C(6B)	−3274 (3)	2190 (2)	−1478 (2)	3·40 (4)
C(7B)	−1896 (2)	2981 (2)	−1423 (2)	3·70 (4)
C(8B)	−413 (2)	3007 (2)	−613 (2)	3·19 (4)
C(9B)	−314 (2)	2224 (2)	152 (1)	2·31 (3)
C(10B)	−1673 (2)	1404 (2)	100 (1)	2·10 (3)

bond angles and influences the ring closure geometry. The first carbon of the 4-alkyl substituents in each structure bears a single (methine) H atom. The alkyl group is disposed pseudoequatorially with the methine H directed approximately toward the coumarin carbonyl to avoid crowding. Figs. 1–4 show plots of the molecular structures; atoms are drawn enclosing 50% of the non-hydrogen-atom electron density.

Table 6 shows the intraring torsion angles for the embedded 3,4-dihydro-2H-pyran rings that are part of each structure. A wide variety of dihydropyran ring conformations are seen in the six derivatives contained in the four crystal structures studied. Dihydropyran ring structures in (1A), (3A) and (4) are slightly distorted half-chairs showing similar d and f torsions. In contrast, the dihydropyrans in (1B) and (2) are better described as having d,e-diplanar conformations, that is, these adjacent torsions are small. Structure (3B) has a dihydropyran ring strongly distorted in the alternate path toward the e,f-diplanar conformation.
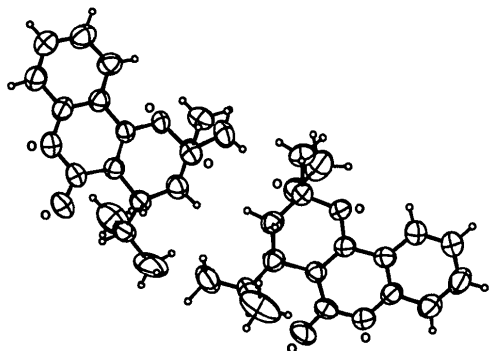
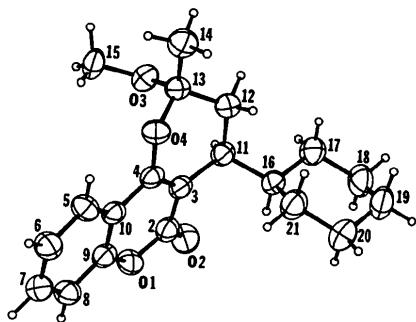Fig. 1. A plot of (1) showing each of the two molecules in the asymmetric unit.

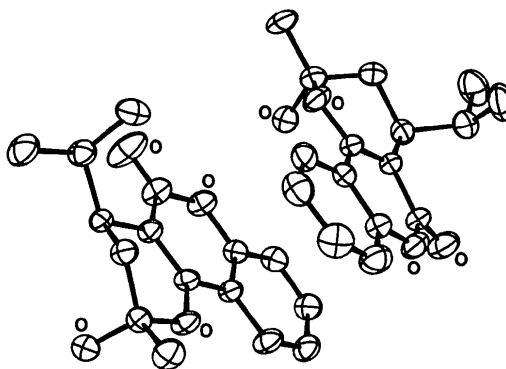Fig. 2. A plot of (2) and the numbering scheme.

Fig. 3. A plot of (3) showing each of the two molecules in the asymmetric unit. Hydrogens not drawn for clarity.
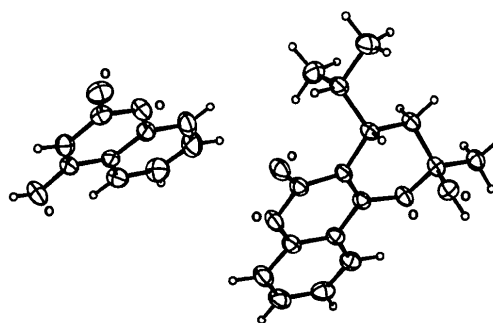

Fig. 4. A plot of (4) showing the subject molecule and the cocrystallized 4-hydroxycoumarin.

Table 6. Torsion angles (°) in the dihydropyran rings; e.s.d.'s are at most about 0.4°; common configuration

Compound	a	b	c	d	e	f
(1A)	−44·8	59·4	−42·8	13·2	0·1	16·5
(1B)	−48·7	58·7	−36·1	4·0	5·8	17·9
(2)	−53·7	56·7	−29·0	−2·9	6·7	23·4
(3A)	−47·6	62·4	−42·2	8·6	5·8	15·1
(3B)	−31·3	58·0	−54·2	26·2	−1·2	3·5
(4)	−45·6	63·6	−45·8	11·9	5·8	12·0

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