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Structure of 4-Cyclohexyl-3,4-dihydro-2-hydroxy-2-methyl-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-one

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Structure of 4-Cyclohexyl-3,4-dihydro-2-hydroxy-2-methyl-2*H*,5*H*-pyrano-[3,2-*c*][1]benzopyran-5-one

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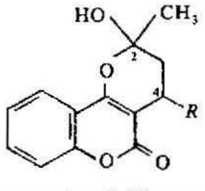
bstract. $C_{19}H_{22}O_4$, monoclinic, $P2_1/c$, a = 2·515 (2), b = 17·472 (3), c = 7·489 (1) Å, β = 00·40 (1)°. The structure was solved by direct ethods. The cyclohexyl group is pseudo-equatorial nd *trans* to the axial hydroxyl; the dihydropyran ring a half-chair distorted towards the *d,e*-diplanar conrmation. Hydrogen bonding between the coumarin arbonyl and the hydroxyl groups at an O···O istance of 2·834 (4) Å is found. In $CDCl_3$ solution, is compound exists predominantly in the open-chain eto form.

troduction. Michael-type addition of 4-alkyl- or 4-ylbut-3-en-2-ones to 4-hydroxycoumarin produces 3-ubstituted 4-hydroxycoumarins that may exist as yclic hemiketals (Ikawa, Stahmann & Link, 1944). oth isomers are diastereomeric, and the configuration the molecule in the crystal will depend on the steric teractions between the substituents on the dihydroyran (hemiketal) ring. Substituents at the 2 and 4 ositions have the largest interactions. The 2-hydroxyl r alkoxyl group normally prefers the axial conormation, related to the anomeric effect. The 4-eudo-axial substituent will therefore have a short axial contact while a 4-pseudo-equatorial substituent close to the coumarin carbonyl oxygen. Previously, 1) was found to induce distortions in the dihydroyran ring relative to (2) in both 4 placements (Valente, antarsiero & Schomaker, 1979). The present contriution extends this series to R = cyclohexyl, (3), a subtituent envisioned to be larger than methyl, and scribes the conformation of the distorted dihydroyran ring obtained in the crystal, and the structure in lution revealed by nuclear magnetic resonance.



(1) $R = CH_3$

(2) $R = C_6H_5$

(3) $R = C_6H_{11}$

Colorless rods of (3) crystallize from ethyl acetate or tone solutions. After a preliminary photographic study of several crystals which established the space group as $P2_1/c$ ($h0l$ absent for l odd, $0k0$ absent for k odd), an individual 0·156 × 0·063 × 0·469 mm was mounted along the long crystal axis. Cell constants were measured from 12 reflections (2θ > 30°) and 2385 reflections were observed on a Picker FACS-I automated diffractometer with quartz-monochromatized Mo $K\alpha$ radiation (λ = 0·70926 Å). Of these, 1621 exceeded $1\cdot5\sigma(I)$ and were used in the final refinement stages. The structure was discovered with *MULTAN* (Main, 1978), and refined by full-matrix least-squares calculations until the model, represented by anisotropic and isotropic U's associated with the non-hydrogen and hydrogen-atom positions respectively, converged at R = 0·055; goodness-of-fit = 1·8. No absorption or extinction corrections were applied to the data. The atom positions appear in Table 1.[*]

In $CDCl_3$, the ^1H and ^{13}C magnetic resonance spectra of (3) (HA-100 spectrometer) and its methyl ketal, (3*a*), formed by treatment of (3) with methanol and acid, were recorded and show that for (3) a mixture of one cyclic diastereomeric hemiketal and the open form is present. By integration, the open form represents 75% of the mixture. The spectra of (3*a*) indicate that it is the *trans* diastereomer.

Discussion. An ellipsoid plot (Johnson, 1965) of the structure is given in Fig. 1 together with the numbering scheme which is based on the coumarin heterocycle. The cyclohexyl group is pseudo-equatorial on the dihydropyran ring and *trans* to the axial hydroxyl group. The dihydropyran ring has a half-chair conformation distorted towards the *d,e*-diplanar form (Valente, Santarsiero & Schomaker, 1979). Relevant torsion angles are shown in Fig. 2. Both methylenes C(16) and C(20), bound to C(15), are plainly disposed

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[*] Lists of structure factors, thermal parameters and bond lengths and angles, and the tabulated spectra have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34561 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atom positions* ($\times 10^4$, *for* H $\times 10^3$) *with e.s.d.'s in parentheses*

	x	*y*	*z*		*x*	*y*	*z*
O(1)	−4736 (2)	2536 (2)	4987 (4)	H(31)	−340 (4)	110 (3)	46 (6)
O(2)	−3026 (2)	2818 (2)	5029 (4)	H(51)	−637 (4)	42 (3)	269 (6)
O(3)	−3520 (3)	612 (2)	368 (4)	H(61)	−812 (4)	92 (3)	290 (6)
O(4)	−4409 (2)	416 (2)	2793 (4)	H(71)	−822 (4)	214 (3)	420 (6)
C(2)	−3719 (3)	2323 (2)	4725 (5)	H(81)	−665 (5)	286 (3)	521 (8)
C(3)	−3547 (3)	1550 (2)	4140 (5)	H(111)	−221 (3)	162 (2)	299 (5)
C(4)	−4438 (3)	1106 (2)	3574 (5)	H(121)	−180 (4)	31 (3)	290 (5)
C(5)	−6460 (4)	923 (3)	3153 (6)	H(122)	−246 (3)	16 (2)	448 (6)
C(6)	−7458 (4)	1223 (3)	3314 (6)	H(141)	−420 (3)	−70 (2)	79 (5)
C(7)	−7534 (4)	1935 (3)	4072 (7)	H(142)	−357 (4)	−90 (3)	276 (6)
C(8)	−6624 (4)	2372 (3)	4671 (6)	H(143)	−290 (4)	−77 (2)	107 (6)
C(9)	−5624 (3)	2074 (2)	4469 (5)	H(151)	−154 (3)	201 (3)	584 (5)
C(10)	−5517 (3)	1356 (2)	3743 (5)	H(161)	−171 (4)	45 (3)	718 (7)
C(11)	−2411 (3)	1295 (2)	3964 (5)	H(162)	−247 (4)	118 (3)	755 (5)
C(12)	−2448 (4)	451 (3)	3382 (6)	H(171)	−97 (5)	185 (3)	926 (7)
C(13)	−3446 (3)	237 (2)	2028 (6)	H(172)	−107 (4)	104 (3)	1011 (7)
C(14)	−3542 (4)	−611 (3)	1637 (7)	H(181)	32 (4)	51 (3)	858 (7)
C(15)	−1537 (3)	1444 (3)	5671 (6)	H(182)	81 (5)	129 (3)	973 (8)
C(16)	−1749 (4)	1044 (3)	7378 (6)	H(191)	40 (4)	208 (3)	705 (7)
C(17)	−895 (5)	1270 (4)	9021 (7)	H(192)	118 (5)	134 (3)	681 (5)
C(18)	251 (5)	1104 (4)	8697 (8)	H(201)	−34 (4)	66 (3)	506 (6)
C(19)	456 (4)	1476 (4)	6972 (8)	H(202)	−26 (3)	147 (3)	417 (6)
C(20)	−401 (4)	1251 (3)	5337 (7)				

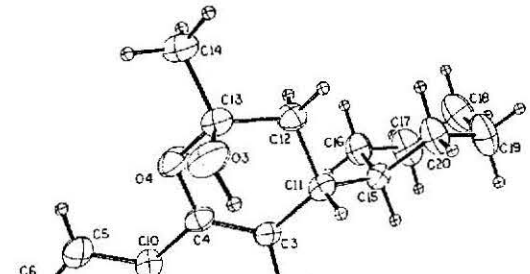

Fig. 1. An ellipsoid plot of (3) with the numbering scheme.

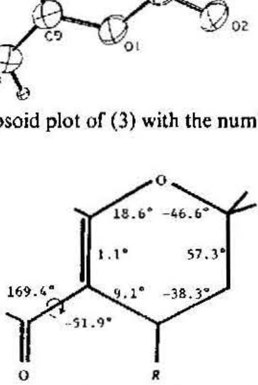

Fig. 2. Selected torsion angles for (3); e.s.d.'s are about 0·5°.

away from the carbonyl oxygen. The cyclohexyl group is accommodated as though it were an isopropyl group, and thus only small conformational differences between the dihydropyran rings of (3) and the *trans* (1) methyl ketal are seen.

Carbonyl and hydroxyl groups are intermolecularly hydrogen bonded along the **c** glide at an O···O distance of 2·834 (4) Å. The H on O(3) is antiperiplanar to the methyl C(14) and therefore disposed over the dihydropyran ring. This is in contrast to the more common conformation in which the substituent on O(3) is antiperiplanar to C(12) (Valente, Trager & Jensen, 1975; Valente, Lingafelter, Porter & Trager, 1977) and therefore directed away from the ring (McConnell, Schwartz & Stevens, 1979). The most obvious effect of this arrangement is the widening of O(3)–C(13)–C(12) to 113·4 (4)° and the closing of O(3)–C(13)–C(14) to 107·4 (4)° over the representative values of 109 and 112° respectively for the H antiperiplanar to C(12) (Valente, Santarsiero & Schomaker, 1979).

The solution spectra of (3) show that the open-chain keto form predominates, representing a continuation of the trend correlating decreased stability of the hemiketals with increasing bulk of the 4 substituent on the ring. The hemiketal diastereomer that constitutes the minor portion of (3) in solution is most likely the *trans* isomer, as in the crystal. This is suggested by the formation of the *trans* methyl ketal, (3*a*), as the product of methylation.

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