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

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Structures of Five *trans*-2-Hydroxy and *trans*-2-Methoxy-2-methyl-3,4-dihydro-4-aryl-2*H*,5*H*-pyrano[3,2-*c*]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-phenyl, $M_r = 322.4$, monoclinic, $P2_1/n$,

$a = 5.858$ (1), $b = 16.732$ (9), $c = 16.383$ (9) Å, $\beta = 94.82$ (3)°, $V = 1600.1$ Å³, $Z = 4$, $D_x = 1.338$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.866$ cm⁻¹, $F(000) =$

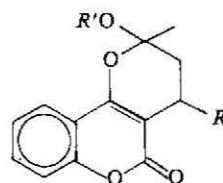
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680, $T = 298$ K, final $R = 0.047$ for 1513 intensities. The *trans* methyl ketal of warfarin ($C_{20}H_{18}O_4$) contains a half-chair dihydropyran ring distorted toward the *d,e*-diplanar conformation. (2) Resolved (2*R*,4*R*)-*trans*-2-methoxy-4-phenyl, $M_r = 322.4$, orthorhombic, $P2_12_12_1$, $a = 11.521$ (1), $b = 14.061$ (2), $c = 10.055$ (2) Å, $V = 1628.9$ Å³, $Z = 4$, $D_x = 1.314$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 0.851$ cm⁻¹, $F(000) = 680$, $T = 298$ K, final $R = 0.056$ for 1660 intensities. The *trans* methyl ketal ($C_{20}H_{18}O_4$) from *R*(+)-warfarin; its dihydropyran ring is a half-chair distorted toward the *d,e*-diplanar conformation. (3) Resolved *trans*-2-hydroxy-4-(4-methoxyphenyl), $M_r = 338.4$, orthorhombic, $P2_12_12_1$, $a = 10.584$ (1), $b = 10.621$ (5), $c = 14.778$ (2) Å, $V = 1661.2$ Å³, $Z = 4$, $D_x = 1.353$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 0.908$ cm⁻¹, $F(000) = 712$, $T = 298$ K, final $R = 0.044$ for 1165 unique intensities. Compound $C_{20}H_{18}O_5$ spontaneously resolves on crystallization from acetone and water, and absolute configuration of data specimen was not determined. It has a dihydropyran ring with a half-chair conformation; hydroxyl and lactone carbonyl are intermolecularly H-bonded at $O \cdots O = 2.79$ Å. (4) Racemic *trans*-2-hydroxy-4-(2-methyl-6-methoxyphenyl), $M_r = 372.4$, monoclinic, $P2_1/n$, $a = 9.637$ (2), $b = 14.345$ (4), $c = 13.224$ (2) Å, $\beta = 91.09$ (1)°, $V = 1827.8$ Å³, $Z = 4$, $D_x = 1.353$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 0.961$ cm⁻¹, $F(000) = 784$, $T = 298$ K, final $R = 0.048$ for 2339 unique intensities. A synthetic derivative of warfarin, it crystallizes as the hydrate $C_{20}H_{18}O_6 \cdot H_2O$ and has a dihydropyran ring with a half-chair conformation and intermolecular H bonds with $O \cdots O$ distances between 2.67 and 2.77 Å. (5) Racemic *trans*-2-hydroxy-4-(4-dimethylaminophenyl), $M_r = 369.4$, triclinic, $P\bar{1}$, $a = 9.066$ (3), $b = 9.509$ (2), $c = 12.681$ (3) Å, $\alpha = 98.50$ (2), $\beta = 91.25$ (3), $\gamma = 116.96$ (2)°, $V = 958.8$ Å³, $Z = 2$, $D_x = 1.279$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 0.854$ cm⁻¹, $F(000) = 392$, $T = 298$ K, final $R = 0.045$ on 2773 unique intensities. A synthetic derivative of warfarin, it also crystallizes as a hydrate, $C_{21}H_{21}NO_4 \cdot H_2O$, and has a dihydropyran ring with a half-chair conformation and intermolecular H bonds with $O \cdots O$ distances between 2.70 and 3.07 Å.

Introduction. Michael-type addition of 4-arylbut-3-en-2-ones to 4-hydroxycoumarin leads to 3-substituted

4-hydroxycoumarins which exist in a solution equilibrium with the two diastereomeric cyclic hemiketal forms. Crystals invariably contain the cyclic structure which incorporates a substituted dihydropyran ring. Hemiketals can be converted to the cyclic methyl ketal in acidic methanol. Diastereomeric *cis* and *trans* (2-oxygen substituent relative to 4-substituent) methyl ketal methoxyls are found in axial orientations owing to an operative anomeric effect. The structures of five 4-aryl analogs of warfarin (2-hydroxy-2-methyl-4-phenyl-3,4-dihydro-2*H*,5*H*-pyrano[3,2-*c*] [1]benzopyran-5-one) are presented here as part of a study of the conformational flexibility of dihydropyran ring near their ground state. A companion study of 4-aliphatic warfarin analogs is in preparation.



| R | R' |
|---|---|
| (1) C ₆ H ₅ | CH ₃ , racemic (2 <i>R</i> ,4 <i>R</i> :2 <i>S</i> ,4 <i>S</i>) |
| (2) C ₆ H ₅ | CH ₃ , resolved (2 <i>R</i> ,4 <i>R</i>) |
| (3) <i>p</i> -C ₆ H ₄ OCH ₃ | H resolved, spontaneous |
| (4) <i>o,o</i> -C ₆ H ₃ (OCH ₃) ₂ (CH ₃) | H racemic |
| (5) <i>p</i> -C ₆ H ₄ N(CH ₃) ₂ | H racemic |

Experimental. Syntheses of hemiketals generally follow reported procedures (Ikawa, Stahmann & Link, 1944) except for (5) (Bush & Trager, 1983). The *trans*-warfarin methyl ketal racemic compound (1) was separated from the mixture of diastereomers produced on methylation (Valente, Lingafelter, Porter & Trager, 1977). Warfarin, $R = C_6H_5$, $R' = H$, was resolved with quinidine and quinine (West, Preis, Schroeder & Link, 1961) and the *trans*-2*R*,4*R*-methyl ketal (2) was prepared by refluxing *R*(+) warfarin in acidic methanol, and fractionally crystallizing the product from ethanol. Hemiketal (3) crystallized as a conglomerate as determined by the crystal structure, and spontaneously resolves on crystallization from 1:1 water:acetone. Melting points: (1) 440.3–441.5; (2) 451–453; (3) 431–432; (4) 436–438; (5) 376–378 K. D_m 's were not measured. Data on the crystallographic specimens and for intensity measurements are given in Table 1. Cell constants were

Table 1. Crystal data, intensity measurements, refinements

| Structure | Crystal size (mm) | θ_{max} (°) | No. unique intensities | No. used | Scale factor | S | wR | No. variables |
|-----------------------------|-------------------|--------------------|------------------------|----------|--------------|------|-------|---------------|
| 1 (racemic) | 0.7 × 0.2 × 0.2 | 27.5 | 3674 | 1513 | 0.395 (1) | 1.42 | 0.057 | 289 |
| 2 (2 <i>R</i> ,4 <i>R</i>) | 0.4 × 0.3 × 0.2 | 27.5 | 2171 | 1660 | 0.638 (2) | 1.93 | 0.028 | 280 |
| 3 | 0.75 × 0.2 × 0.2 | 28 | 2268 | 1165 | 0.404 (2) | 1.16 | 0.049 | 298 |
| 4 | 0.45 × 0.45 × 0.2 | 30 | 5331 | 2339 | 0.306 (1) | 1.32 | 0.057 | 333 |
| 5 | 0.6 × 0.4 × 0.25 | 28 | 4626 | 2773 | 0.155 (1) | 1.69 | 0.062 | 336 |

determined by careful centering of 25 [(1),(3)-(5)] or 30 (2) reflections having higher θ 's. Crystal symmetry and space groups were initially assigned from systematic absences; for (1) and (4): $h0l$, $h + l$ odd; $0k0$, k odd; for (2) and (3): $h00$, h odd; $0k0$, k odd; $00l$, l odd; and they were later confirmed by structure determination. Standard reflections were monitored for orientation and crystal stability, and no unusual trends were seen. Intensities were collected on a CAD-4 diffractometer except for (2) for which data were taken on a Picker FACS-1 instrument. Intensities were corrected for coincidence, polarization and specimen deterioration but not for absorption, and converted to F 's. Associated $\sigma(F_o)$'s are based on counting statistics

alone. Data less than three times their estimated standard deviations were marked weak and not used in refinements. A secondary-extinction correction seemed necessary only for (4) and was later applied, $g = 2.53(1) \times 10^{-7}$. Structures were discovered with *MULTAN* (Germain, Main & Woolfson, 1971). Non-H-atom positions were refined with U_{iso} 's by full-matrix least squares, 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 $\sigma^2(I) = \sigma^2(I)_c + p(I)_c^2$ as defined by Corfield, Doedens & Ibers (1967); $p = 0.05$. Scattering factors from

Table 2. Positions ($\times 10^4$) and B_{eq} 's for (1)

For numbering scheme, see Fig. 1; e.s.d.'s in parentheses.
 $B_{eq} = \frac{1}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$

| | <i>x</i> | <i>y</i> | <i>z</i> | $B_{eq}(\text{\AA}^2)$ |
|-------|-----------|-----------|----------|------------------------|
| O(1) | 8673 (4) | 287 (1) | 1171 (1) | 3.54 (5) |
| O(2) | 10198 (4) | -149 (1) | 2359 (2) | 3.97 (6) |
| O(3) | 3555 (4) | 1462 (1) | 2244 (1) | 3.15 (5) |
| O(4) | 5871 (4) | 2166 (1) | 3219 (1) | 3.35 (5) |
| C(2) | 8621 (6) | 208 (2) | 2010 (2) | 3.17 (8) |
| C(3) | 6736 (6) | 564 (2) | 2396 (2) | 2.65 (7) |
| C(4) | 5188 (6) | 1015 (2) | 1936 (2) | 2.84 (7) |
| C(5) | 3576 (7) | 1468 (2) | 546 (2) | 3.66 (8) |
| C(6) | 3736 (7) | 1492 (2) | -283 (2) | 4.24 (9) |
| C(7) | 5551 (8) | 1113 (2) | -617 (2) | 4.24 (9) |
| C(8) | 7198 (7) | 721 (2) | -133 (2) | 3.76 (9) |
| C(9) | 6991 (6) | 694 (2) | 699 (2) | 3.04 (8) |
| C(10) | 5215 (6) | 1066 (2) | 1054 (2) | 2.77 (7) |
| C(11) | 6679 (6) | 487 (2) | 3315 (2) | 2.96 (7) |
| C(12) | 4558 (7) | 907 (2) | 3586 (2) | 3.66 (8) |
| C(13) | 3971 (6) | 1659 (2) | 3108 (2) | 2.95 (7) |
| C(14) | 1781 (7) | 2056 (2) | 3318 (2) | 4.14 (9) |
| C(15) | 5709 (7) | 2908 (2) | 2781 (2) | 4.46 (9) |
| C(16) | 6777 (6) | -373 (2) | 3623 (2) | 2.83 (7) |
| C(17) | 4992 (6) | -898 (2) | 3435 (2) | 3.57 (8) |
| C(18) | 5065 (7) | -1663 (2) | 3758 (3) | 4.30 (9) |
| C(19) | 6913 (7) | -1917 (2) | 4255 (2) | 4.38 (9) |
| C(20) | 8725 (7) | -1409 (2) | 4439 (2) | 4.25 (9) |
| C(21) | 8637 (6) | -640 (2) | 4120 (2) | 3.72 (8) |

Table 3. Positions ($\times 10^4$) and B_{eq} 's for (2)

E.s.d.'s in parentheses.

| | <i>x</i> | <i>y</i> | <i>z</i> | $B_{eq}(\text{\AA}^2)$ |
|-------|-----------|----------|----------|------------------------|
| O(1) | 7739 (1) | 4146 (1) | 1097 (2) | 3.56 (5) |
| O(2) | 6585 (2) | 3330 (1) | 2425 (2) | 4.50 (7) |
| O(3) | 8806 (2) | 784 (1) | 680 (2) | 3.82 (5) |
| O(4) | 10137 (1) | 1992 (1) | 1101 (1) | 2.69 (5) |
| C(2) | 7531 (2) | 3369 (2) | 1901 (2) | 3.32 (6) |
| C(3) | 8416 (2) | 2651 (2) | 2016 (2) | 2.74 (7) |
| C(4) | 9343 (2) | 2702 (2) | 1227 (2) | 2.72 (7) |
| C(5) | 10634 (2) | 3686 (2) | -261 (2) | 3.39 (8) |
| C(6) | 10798 (3) | 4525 (2) | 946 (3) | 3.76 (9) |
| C(7) | 9934 (3) | 5217 (2) | -970 (2) | 3.81 (9) |
| C(8) | 8912 (3) | 5076 (2) | -300 (2) | 3.51 (9) |
| C(9) | 8770 (2) | 4249 (2) | 418 (2) | 2.98 (7) |
| C(10) | 9599 (2) | 3540 (2) | 446 (2) | 2.74 (7) |
| C(11) | 8202 (2) | 1852 (2) | 2954 (2) | 3.21 (7) |
| C(12) | 9218 (3) | 1151 (2) | 2888 (3) | 3.45 (8) |
| C(13) | 9715 (2) | 1057 (2) | 1517 (2) | 3.05 (7) |
| C(14) | 10773 (3) | 422 (2) | 1444 (4) | 4.06 (9) |
| C(15) | 9091 (4) | 731 (3) | -728 (3) | 5.4 (1) |
| C(16) | 8021 (2) | 2161 (2) | 4392 (2) | 3.10 (9) |
| C(17) | 8766 (3) | 2781 (2) | 4982 (3) | 4.7 (1) |
| C(18) | 8634 (4) | 3023 (3) | 6329 (4) | 5.6 (1) |
| C(19) | 7776 (4) | 2634 (3) | 7051 (3) | 5.5 (1) |
| C(20) | 7031 (3) | 2010 (3) | 6479 (3) | 6.1 (1) |
| C(21) | 7150 (3) | 1794 (3) | 5156 (3) | 5.0 (1) |

Table 4. Positions ($\times 10^4$) and B_{eq} 's for (3)

E.s.d.'s in parentheses.

| | <i>x</i> | <i>y</i> | <i>z</i> | $B_{eq}(\text{\AA}^2)$ |
|-------|-----------|-----------|----------|------------------------|
| O(1) | 6697 (3) | 8601 (2) | 7143 (2) | 3.88 (7) |
| O(2) | 7586 (3) | 10437 (3) | 7310 (2) | 4.73 (7) |
| O(3) | 9980 (3) | 6999 (3) | 6230 (2) | 3.62 (6) |
| O(4) | 11498 (3) | 7807 (3) | 7194 (2) | 4.12 (7) |
| O(18) | 8824 (3) | 13924 (3) | 4224 (3) | 5.48 (8) |
| C(2) | 7732 (4) | 9369 (4) | 7041 (3) | 3.31 (9) |
| C(3) | 8861 (4) | 8860 (4) | 6653 (3) | 2.78 (8) |
| C(4) | 8935 (4) | 7593 (4) | 6501 (3) | 2.89 (9) |
| C(5) | 7814 (5) | 5505 (4) | 6411 (3) | 4.1 (1) |
| C(6) | 6693 (5) | 4857 (4) | 6476 (3) | 4.7 (1) |
| C(7) | 5621 (5) | 5434 (5) | 6753 (4) | 4.9 (1) |
| C(8) | 5621 (4) | 6683 (4) | 6977 (3) | 4.2 (1) |
| C(9) | 6729 (4) | 7342 (4) | 6898 (3) | 3.32 (9) |
| C(10) | 7842 (4) | 6795 (4) | 6613 (3) | 3.02 (9) |
| C(11) | 9961 (4) | 9731 (4) | 6457 (3) | 3.02 (9) |
| C(12) | 10966 (4) | 9015 (4) | 5926 (3) | 3.8 (1) |
| C(13) | 11184 (4) | 7702 (4) | 6293 (3) | 3.35 (9) |
| C(15) | 9595 (4) | 10895 (4) | 5914 (3) | 3.01 (8) |
| C(16) | 8719 (5) | 10850 (4) | 5229 (4) | 4.5 (1) |
| C(17) | 8478 (5) | 11858 (5) | 4680 (4) | 5.0 (1) |
| C(18) | 9142 (4) | 12960 (4) | 4801 (3) | 3.6 (1) |
| C(19) | 10029 (5) | 13032 (4) | 5463 (3) | 4.3 (1) |
| C(20) | 10256 (4) | 12002 (4) | 6015 (3) | 3.9 (1) |
| C(21) | 9652 (6) | 14953 (5) | 4169 (4) | 5.7 (1) |
| C(22) | 12097 (5) | 6927 (4) | 5745 (3) | 4.5 (1) |

Table 5. Positions ($\times 10^4$) and B_{eq} 's for (4)

E.s.d.'s in parentheses.

| | <i>x</i> | <i>y</i> | <i>z</i> | $B_{eq}(\text{\AA}^2)$ |
|-------|-----------|-----------|----------|------------------------|
| O(1) | 4915 (2) | -379 (1) | 3331 (1) | 3.63 (4) |
| O(2) | 4008 (2) | 278 (1) | 1975 (2) | 4.93 (5) |
| O(3) | 8735 (2) | 785 (1) | 2817 (1) | 3.31 (3) |
| O(4) | 9121 (2) | 657 (1) | 1107 (1) | 3.95 (4) |
| O(5) | 5580 (2) | 2492 (1) | 3122 (1) | 4.38 (4) |
| O(W) | 1694 (2) | 58 (2) | 756 (2) | 7.81 (6) |
| C(2) | 5030 (3) | 208 (2) | 2514 (2) | 3.21 (5) |
| C(3) | 6325 (2) | 679 (2) | 2362 (2) | 2.73 (5) |
| C(4) | 7445 (2) | 442 (2) | 2936 (2) | 2.67 (4) |
| C(5) | 8427 (3) | 453 (2) | 4415 (2) | 3.24 (5) |
| C(6) | 8197 (3) | -998 (2) | 5251 (2) | 3.82 (6) |
| C(7) | 6880 (3) | -1308 (2) | 5460 (2) | 3.77 (6) |
| C(8) | 5789 (3) | -1101 (2) | 4816 (2) | 3.67 (5) |
| C(9) | 6019 (2) | -556 (2) | 3969 (2) | 2.95 (5) |
| C(10) | 7328 (2) | -203 (2) | 3771 (2) | 2.61 (4) |
| C(11) | 6423 (2) | 1392 (2) | 1520 (2) | 3.17 (5) |
| C(12) | 7788 (3) | 1930 (2) | 1656 (2) | 3.64 (6) |
| C(13) | 9005 (2) | 1304 (2) | 1883 (2) | 3.02 (5) |
| C(14) | 10347 (3) | 1809 (2) | 2099 (2) | 4.16 (6) |
| C(15) | 5223 (3) | 2076 (2) | 1419 (2) | 3.21 (5) |
| C(16) | 4522 (3) | 2192 (2) | 490 (2) | 3.88 (6) |
| C(17) | 3536 (3) | 2902 (2) | 392 (2) | 4.79 (7) |
| C(18) | 3214 (3) | 3462 (2) | 1197 (3) | 4.96 (7) |
| C(19) | 3867 (3) | 3342 (2) | 2117 (2) | 4.51 (6) |
| C(20) | 4873 (3) | 2652 (2) | 2223 (2) | 3.60 (5) |
| C(21) | 5558 (4) | 3206 (2) | 3871 (3) | 6.19 (9) |
| C(22) | 4812 (3) | 1587 (3) | 405 (2) | 5.70 (8) |

Table 6. Positions ($\times 10^4$) and B_{eq} 's for (5)

| | E.s.d.'s in parentheses. | | | |
|-------|--------------------------|-----------|-----------|------------------------|
| | x | y | z | $B_{eq}(\text{\AA}^2)$ |
| O(1) | 7744 (1) | 1980 (1) | 6217 (1) | 3.52 (3) |
| O(2) | 9068 (2) | 4574 (2) | 6290 (1) | 4.20 (4) |
| O(3) | 3526 (1) | 2164 (1) | 7153 (1) | 3.35 (3) |
| O(4) | 3455 (2) | 3960 (1) | 6125 (1) | 3.70 (3) |
| O(W) | 625 (2) | 2817 (2) | 4805 (1) | 5.55 (4) |
| N(1) | 12479 (2) | 9545 (2) | 10041 (2) | 4.67 (5) |
| C(2) | 7804 (2) | 3465 (2) | 6475 (2) | 3.12 (4) |
| C(3) | 6413 (2) | 3573 (2) | 6918 (1) | 2.77 (4) |
| C(4) | 4975 (2) | 2203 (2) | 6905 (1) | 2.77 (4) |
| C(5) | 3474 (2) | -807 (2) | 6600 (2) | 3.70 (5) |
| C(6) | 3519 (3) | -2241 (2) | 6277 (2) | 4.40 (5) |
| C(7) | 4952 (3) | -2248 (2) | 5932 (2) | 4.32 (5) |
| C(8) | 6364 (2) | -838 (2) | 5919 (2) | 3.82 (5) |
| C(9) | 6318 (2) | 589 (2) | 6256 (2) | 3.14 (4) |
| C(10) | 4896 (2) | 641 (2) | 6589 (1) | 2.86 (4) |
| C(11) | 6548 (2) | 5219 (2) | 7280 (2) | 3.01 (4) |
| C(12) | 4979 (2) | 5019 (2) | 7810 (2) | 3.52 (4) |
| C(13) | 3430 (2) | 3678 (2) | 7165 (2) | 3.23 (4) |
| C(14) | 8102 (2) | 6350 (2) | 8024 (2) | 3.00 (4) |
| C(15) | 8627 (3) | 5896 (2) | 8883 (2) | 3.96 (5) |
| C(16) | 10043 (3) | 6939 (2) | 9559 (2) | 4.09 (5) |
| C(17) | 11006 (2) | 8512 (2) | 9400 (2) | 3.44 (4) |
| C(18) | 10437 (3) | 8982 (2) | 8557 (2) | 3.58 (5) |
| C(19) | 9025 (2) | 7916 (2) | 7883 (2) | 3.34 (4) |
| C(20) | 13351 (3) | 11186 (3) | 9892 (2) | 5.18 (6) |
| C(21) | 12793 (3) | 9204 (3) | 11057 (2) | 5.99 (7) |
| C(22) | 1830 (2) | 3388 (3) | 7638 (2) | 4.52 (5) |

International Tables for X-ray Crystallography (1974) except for H (Stewart, Davidson & Simpson, 1965). In all cases final $\Delta/\sigma_{\text{ave,max}}$ were less than 0.05, 0.20 respectively and positive excursions were less than 0.3 e \AA^{-3} , no troughs were less than $-0.207 \text{ e \AA}^{-3}$.

Discussion. Final atom positions and vibrational parameters are given in Tables 2–6.*

No close intermolecular contacts are seen in (1) and (2). Structure (1) is the racemic compound (2*R*,4*R*;2*S*,4*S*), (2) is chiral (2*R*,4*R*). The racemate has a lower cell volume, higher density but a lower melting point compared with the resolved compound, pointing to differences in the crystal packing between them. Intermolecular hydrogen bonding is found in (3)–(5). Hemiketal hydroxyls and coumarin carbonyls are H-bonded in (3), $\text{O}\cdots\text{O}$ 2.795 (5) \AA. The water of crystallization in each of (4) and (5) donates two H bonds and accepts one H bond. In (4), the hemiketal hydroxyl is H-bonded to water, $\text{O}\cdots\text{O}$ 2.673 (3) \AA, which H-bonds to a carbonyl oxygen and to a hemiketal hydroxyl oxygen in neighboring molecules, $\text{O}\cdots\text{O}$ 2.745 (3), 2.769 (3) \AA, respectively. In (5), the hemiketal hydroxyl is also H-bonded to water, $\text{O}\cdots\text{O}$ 2.705 (2) \AA, which H-bonds to a carbonyl oxygen and more weakly to a coumarin ring oxygen in neighboring molecules, $\text{O}\cdots\text{O}$ 2.927 (2), 3.067 (2) \AA, respectively.

* Lists of structure factors, anisotropic vibrational amplitudes and H-atom positions have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43210 (109 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

All five structures have the 2-oxygen *trans* to the 4-aryl substituent, and the hydroxyl or methoxyl is axial (anomeric effect). Hemiketal hydroxyl H's and ketal methyls are *gauche* synclinal to the dihydropyran oxygen and directed *exo* to the ring (exoanomeric effect). Ring (hemi)ketal C–O bonds are longer (1.45–1.47 \AA) than found in sugars (1.42–1.43 \AA); the ring unsaturation widens two intraring angles and modifies closure geometry relative to a saturated heterocycle. Phenyl ring substituents are pseudo-equatorially disposed on the dihydropyran ring and phenyl rings are inclined relative to coumarin ring planes to avoid close contacts. Extent of the inclination ranges from 71° (dihedral angle) in (3) to 98° in (4). See Figs. 1 to 5 for ellipsoid plots of the molecular structures.

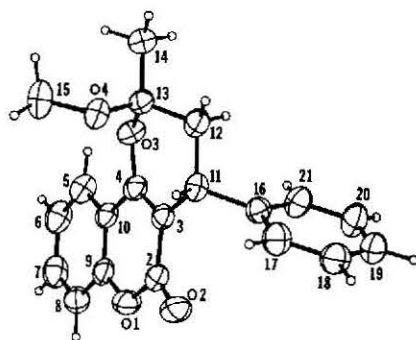


Fig. 1. An ellipsoid plot of (1), showing the numbering scheme.

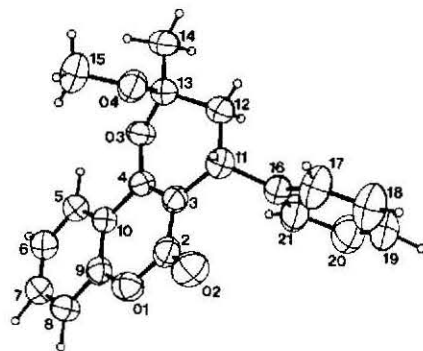


Fig. 2. An ellipsoid plot of (2).

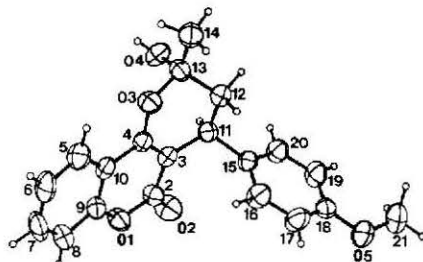


Fig. 3. An ellipsoid plot of (3).

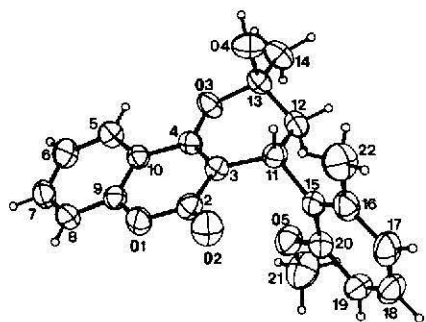


Fig. 4. An ellipsoid plot of (4).

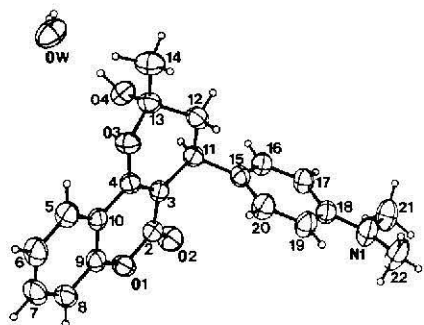


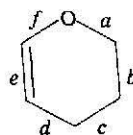
Fig. 5. An ellipsoid plot of (5).

A 3,4-dihydro-2*H*-pyran ring is embedded in each structure. The unsaturation is part of the coumarin ring and other ring substituents are 2-methyl, 2-hydroxyl or methoxyl, and 4-aryl. Rings in both (1) and (2) are half chairs strongly distorted toward the *d,e*-diplanar forms, (3)–(5) are essentially half-chairs. Intraring torsion angles are given in Table 7.

Thanks go to B. D. Santarsiero and A. Aruffo for experimental assistance early in this project. We

Table 7. Torsion angles ($^{\circ}$) in the dihydropyran rings

E.s.d.'s are at most about 0.5° ; common configuration.



| | <i>a</i> | <i>b</i> | <i>c</i> | <i>d</i> | <i>e</i> | <i>f</i> |
|-----|----------|----------|----------|----------|----------|----------|
| (1) | -50.2 | 59.5 | -36.6 | 5.7 | 3.5 | 20.0 |
| (2) | -51.9 | 60.4 | -35.3 | 2.0 | 6.3 | 20.1 |
| (3) | -45.2 | 60.3 | -42.9 | 10.7 | 4.6 | 13.9 |
| (4) | -42.1 | 59.3 | -45.4 | 15.2 | 1.4 | 12.8 |
| (5) | -44.3 | 63.6 | -48.3 | 16.0 | 3.6 | 11.3 |

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