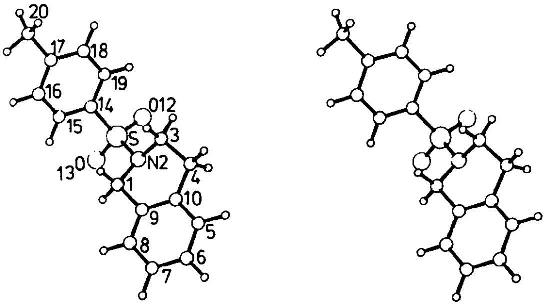

Fig. 1. Stereodrawing of the molecule (*PLUTO*; Motherwell & Clegg, 1978).

(1971). The C—S distance [1·778 (8) Å] is longer than the 1·753 (2) Å in *p*-toluenesulfonic acid and the 1·755 (3) Å found by Singh, Tiwari & Singh (1985), but similar to the 1·766 (7) Å found by Barrans & Cotrait (1976).

The N—S bond length [1·666 (6) Å] is comparable with the values in the above cited structures. The O—S—O angle in the present structure is 120·8 (4)°. In *p*-toluenesulfonic acid and in a number of sulfonate derivatives (Arora & Sundarlingam, 1971) it ranges from 111 to 114°. In N^1-(2,6-dimethyl-4-pyrimidinyl)-sulfanilamide (Singh *et al.*, 1985) it equals 115·0 (4)° while in tosyl-L-arginine methyl ester (Barrans & Cotrait, 1976) it is widened to 121·2 (4)°.

There are no unusual intermolecular contacts in the structure.

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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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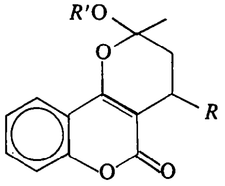
Abstract. Derivatives of 2-methyl-3,4-dihydro-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-one. (1) Racemic *trans*-2-methoxy-4-phenyl, $M_r = 322·4$, monoclinic, $P2_1/n$, $a = 5·858$ (1), $b = 16·732$ (9), $c = 16·383$ (9) Å, $\beta = 94·82$ (3)°, $V = 1600·1$ Å^3, $Z = 4$, $D_x = 1·338$ g cm^{-3}, λ(Mo *K*α) = 0·71073 Å, $\mu = 0·866$ cm^{-1}, $F(000) =$

0108-2701/86/121809-05$01.50

680, $T = 298$ K, final $R = 0{\cdot}047$ 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, $M_r = 322{\cdot}4$, orthorhombic, $P2_12_12_1$, $a = 11{\cdot}521$ (1), $b = 14{\cdot}061$ (2), $c = 10{\cdot}055$ (2) Å, $V = 1628{\cdot}9$ Å^3, $Z = 4$, $D_x = 1{\cdot}314$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}851$ cm^{-1}, $F(000) = 680$, $T = 298$ K, final $R = 0{\cdot}056$ 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), $M_r = 338{\cdot}4$, orthorhombic, $P2_12_12_1$, $a = 10{\cdot}584$ (1), $b = 10{\cdot}621$ (5), $c = 14{\cdot}778$ (2) Å, $V = 1661{\cdot}2$ Å^3, $Z = 4$, $D_x = 1{\cdot}353$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}908$ cm^{-1}, $F(000) = 712$, $T = 298$ K, final $R = 0{\cdot}044$ 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···O = 2·79 Å. (4) Racemic *trans*-2-hydroxy-4-(2-methyl-6-methoxyphenyl), $M_r = 372{\cdot}4$, monoclinic, $P2_1/n$, $a = 9{\cdot}637$ (2), $b = 14{\cdot}345$ (4), $c = 13{\cdot}224$ (2) Å, $\beta = 91{\cdot}09$ (1)°, $V = 1827{\cdot}8$ Å^3, $Z = 4$, $D_x = 1{\cdot}353$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}961$ cm^{-1}, $F(000) = 784$, $T = 298$ K, final $R = 0{\cdot}048$ for 2339 unique intensities. A synthetic derivative of warfarin, it crystallizes as the hydrate $C_{20}H_{18}O_6.H_2O$ and has a dihydropyran ring with a half-chair conformation and intermolecular H bonds with O···O distances between 2·67 and 2·77 Å. (5) Racemic *trans*-2-hydroxy-4-(4-dimethylaminophenyl), $M_r = 369{\cdot}4$, triclinic, $P\bar{1}$, $a = 9{\cdot}066$ (3), $b = 9{\cdot}509$ (2), $c = 12{\cdot}681$ (3) Å, $\alpha = 98{\cdot}50$ (2), $\beta = 91{\cdot}25$ (3), $\gamma = 116{\cdot}96$ (2)°, $V = 958{\cdot}8$ Å^3, $Z = 2$, $D_x = 1{\cdot}279$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}854$ cm^{-1}, $F(000) = 392$, $T = 298$ K, final $R = 0{\cdot}045$ on 2773 unique intensities. A synthetic derivative of warfarin, it also crystallizes as a hydrate, $C_{21}H_{21}NO_4.H_2O$, and has a dihydropyran ring with a half-chair conformation and intermolecular H bonds with O···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 ketals 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 rings near their ground state. A companion study of 4-aliphatic warfarin analogs is in preparation.



	R	*R'*
(1)	C_6H_5	CH_3 racemic (2*R*,4*R*;2*S*,4*S*)
(2)	C_6H_5	CH_3 resolved (2*R*,4*R*)
(3)	*p*-$C_6H_4OCH_3$	H resolved, spontaneous
(4)	*o,o*-$C_6H_3(OCH_3)(CH_3)$	H racemic
(5)	*p*-$C_6H_4N(CH_3)_2$	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*R*,4*R*)	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, $g = 2\cdot53\,(1)\times10^{-7}$. Structures were discovered with *MULTAN* (Germain, Main & Woolfson, 1971). Non-H-atom positions were refined with $U_{\rm iso}$'s by full-matrix least squares, then with their U_{ij}'s. H atoms were refined from calculated positions with their $U_{\rm iso}$'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); $p = 0\cdot05$. 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.
$B_{\rm eq} = \frac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j$.

	x	y	z	$B_{\rm eq}$(Å^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.

	x	y	z	$B_{\rm eq}$(Å^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.

	x	y	z	$B_{\rm eq}$(Å^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.

	x	y	z	$B_{\rm eq}$(Å^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}(Å^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)	3456 (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 Å^{-3}, no troughs were less than −0·207 e Å^{-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), O···O 2·795 (5) Å. 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, O···O 2·673 (3) Å, which H-bonds to a carbonyl oxygen and to a hemiketal hydroxyl oxygen in neighboring molecules, O···O 2·745 (3), 2·769 (3) Å, respectively. In (5), the hemiketal hydroxyl is also H-bonded to water, O···O 2·705 (2) Å, which H-bonds to a carbonyl oxygen and more weakly to a coumarin ring oxygen in neighboring molecules, O···O 2·927 (2), 3·067 (2) Å, respectively.

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 Å) than found in sugars (1·42–1·43 Å); 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.

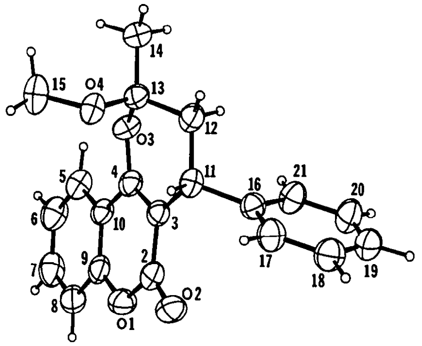


Fig. 1. An ellipsoid plot of (1), showing the numbering scheme.

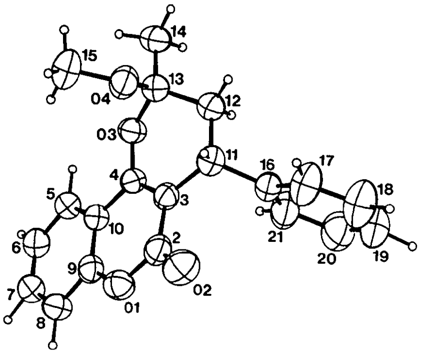


Fig. 2. An ellipsoid plot of (2).

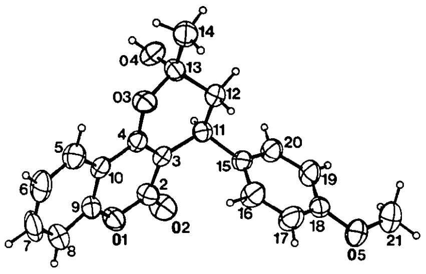


Fig. 3. An ellipsoid plot of (3).

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* 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.

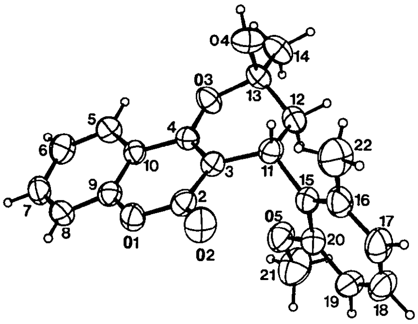


Fig. 4. An ellipsoid plot of (4).

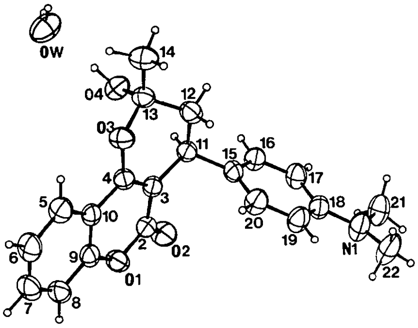
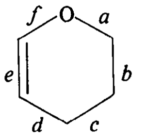


Fig. 5. An ellipsoid plot of (5).

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.

Table 7. *Torsion angles* (°) *in the dihydropyran rings*

E.s.d.'s are at most about 0·5°; common configuration.



	a	*b*	*c*	*d*	*e*	*f*
(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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Structure Redetermination of *m*-Nitroaniline and Structure Determination of *m*-Nitroaniline Hydrochloride

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Abstract. *m*-Nitroaniline, $C_6H_6N_2O_2$: $M_r = 138{\cdot}1$, orthorhombic, $Pbc2_1$, $a = 6{\cdot}499\,(1)$, $b = 19{\cdot}369\,(4)$, $c = 5{\cdot}084\,(1)$ Å, $V = 639{\cdot}9\,(4)$ Å^3, $Z = 4$, $D_m = 1{\cdot}430\,(1)$ by flotation, $D_x = 1{\cdot}434$ Mg m^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71069$ Å, $\mu = 12$ mm^{-1}, $F(000) = 288$, $T = 295$ K. $R = 0{\cdot}037$ for 769 reflexions. The *m*-nitroaniline molecules are held together by van der Waals forces. The benzene ring is planar; the two N atoms are out of

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