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# Gnidicoumarin

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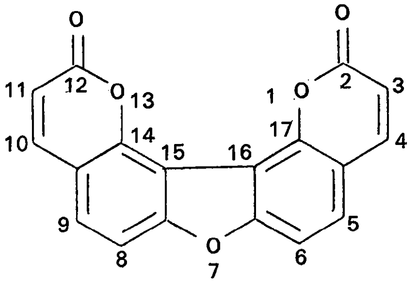
**Abstract.** $C_{18}H_8O_5$, monoclinic, $P2_1/n$, $a=7{\cdot}599$ (1), $b=18{\cdot}829$ (2), $c=8{\cdot}969$ (1) Å, $\beta=91{\cdot}07$ (1)° ($\lambda=1{\cdot}5418$ Å), $U=1283$ Å$^3$, $D_m=1{\cdot}56$ g cm$^{-3}$, $Z=4$, $D_x=1{\cdot}574$ g cm$^{-3}$. The structure was solved by direct methods and refined by least-squares methods to an $R$ of 0·039 for 1682 unique reflections measured by counter diffractometry. Gnidicoumarin is the first reported compound having the 2*H*,12*H*-furo[2,3-*h*:5,4-*h'*]bis-[1]benzopyran-2,12-dione ring system. The molecule is non-planar with approximate $C_2$ symmetry.

**Introduction.** In the course of a continuing search for compounds of plant origin showing tumor-inhibitory activity Kupchan and his coworkers have subjected plants of the *Gnidia* family (Thymelaeaceae) to phytochemical study. From the roots of *Gnidia lamprantha* Gilg the novel pentacyclic dicoumarin, gnidicoumarin (I), was isolated and its structure established by X-ray analysis (Kupchan, Sweeny, Murae, Shen & Bryan, 1975).



(I)

**Experimental.** Systematic absences from precession photographs are $h0l$ with $h+l$ odd and $0k0$ with $k$ odd. The density determination was made by flotation (aq. $ZnI_2$). Intensity measurements were made by single-crystal diffractometry of a single quadrant of reciprocal space ($2\theta \le 120°$). The $\theta$–$2\theta$ scan method was used with monochromatic (HOG) Cu $K\alpha$ radiation, scintillation counting, and pulse-height analysis. The intensities of

Table 1. *Heavy atom parameters and their standard deviations*

Values in the table have been multiplied by $10^4$. The temperature factor has the form

$$\exp\,[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]\,.$$

E.s.d.'s in parentheses are applicable to the least significant figures given.

| | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| O(1) | 5808 (2) | 6642 (1) | 10421 (2) | 152 (3) | 12 (1) | 116 (2) | 8 (1) | −9 (2) | −3 (1) |
| C(2) | 5129 (3) | 7251 (1) | 11082 (3) | 141 (5) | 13 (1) | 142 (4) | −1 (1) | −8 (3) | −11 (1) |
| O(2) | 5245 (2) | 7286 (1) | 12421 (2) | 246 (4) | 19 (1) | 134 (3) | 9 (1) | −30 (3) | −16 (1) |
| C(3) | 4367 (3) | 7771 (1) | 10079 (3) | 162 (5) | 12 (1) | 163 (4) | 7 (1) | −24 (4) | −7 (1) |
| C(4) | 4262 (3) | 7665 (1) | 8614 (3) | 142 (5) | 12 (1) | 160 (4) | 1 (1) | −26 (4) | 6 (1) |
| C(4a) | 4882 (3) | 7020 (1) | 7953 (3) | 124 (5) | 12 (1) | 128 (4) | −4 (1) | −4 (3) | 5 (1) |
| C(5) | 4726 (3) | 6868 (1) | 6426 (3) | 153 (5) | 19 (1) | 128 (4) | −8 (2) | −12 (3) | 12 (1) |
| C(6) | 5242 (3) | 6227 (1) | 5834 (3) | 175 (5) | 22 (1) | 107 (4) | −8 (2) | −5 (3) | 4 (1) |
| C(6a) | 5921 (3) | 5741 (1) | 6855 (3) | 139 (5) | 15 (1) | 118 (4) | −7 (1) | 15 (3) | −4 (1) |
| O(7) | 6437 (2) | 5061 (1) | 6462 (2) | 183 (4) | 16 (1) | 111 (2) | −1 (1) | 13 (2) | −7 (1) |
| C(7a) | 7045 (3) | 4751 (1) | 7755 (3) | 125 (5) | 15 (1) | 117 (4) | −5 (1) | 19 (3) | −2 (1) |
| C(8) | 7727 (3) | 4066 (1) | 7814 (3) | 160 (5) | 14 (1) | 144 (4) | −2 (1) | 27 (4) | −11 (1) |
| C(9) | 8328 (3) | 3841 (1) | 9180 (3) | 141 (5) | 11 (1) | 170 (4) | 2 (1) | 23 (4) | −3 (1) |
| C(9a) | 8293 (3) | 4275 (1) | 10456 (3) | 107 (4) | 11 (1) | 136 (4) | −3 (1) | 16 (3) | 3 (1) |
| C(10) | 8950 (3) | 4059 (1) | 11893 (3) | 138 (5) | 12 (1) | 159 (4) | 1 (1) | 3 (3) | 9 (1) |
| C(11) | 8964 (3) | 4501 (1) | 13052 (3) | 171 (5) | 16 (1) | 135 (4) | 1 (2) | −6 (4) | 11 (1) |
| C(12) | 8315 (3) | 5223 (1) | 12898 (3) | 143 (5) | 15 (1) | 109 (3) | −6 (1) | 8 (3) | 8 (1) |
| O(12) | 8370 (2) | 5680 (1) | 13841 (2) | 239 (4) | 18 (1) | 111 (2) | −1 (1) | 4 (3) | −2 (1) |
| O(13) | 7579 (2) | 5410 (1) | 11531 (2) | 151 (3) | 11 (1) | 105 (2) | 3 (1) | 2 (2) | 0 (1) |
| C(14) | 7596 (3) | 4963 (1) | 10330 (3) | 99 (4) | 10 (1) | 112 (3) | −5 (1) | 19 (3) | −1 (1) |
| C(15) | 6943 (3) | 5207 (1) | 8971 (3) | 105 (4) | 11 (1) | 113 (3) | −4 (1) | 15 (3) | 0 (1) |
| C(16) | 6176 (3) | 5860 (1) | 8373 (3) | 108 (4) | 12 (1) | 105 (3) | −4 (1) | 9 (3) | 3 (1) |
| C(17) | 5635 (3) | 6516 (1) | 8925 (3) | 112 (4) | 13 (1) | 104 (3) | −6 (1) | 5 (3) | −1 (1) |

1682 independent reflections were observed as significantly above background [$I > 3\sigma(I)$] and structure amplitudes derived from them used in the analysis. No correction for absorption was made.

The structure was solved by the multi-solution tangent formula method (Germain, Main & Woolfson, 1971) from the 226 $E(hkl) > 1{\cdot}45$. The $E$ map based on the solution of highest FOM revealed the positions of all 23 heavy atoms. Refinement of the parameters was carried out by block-diagonal least-squares methods (3 × 3 and 6 × 6 blocks) by minimizing the quantity $\sum w(kF_o - F_c)^2$, a Hughes (1941) weighting scheme being used. Hydrogen atoms were located from a $(\varrho_o - \varrho_c)$ synthesis and refined with individual isotropic thermal parameters. At convergence [$\Delta(p) < 0{\cdot}1\sigma(p)$] the conventional unweighted and weighted residuals were 0·039 and 0·040.* A final $(\varrho_o - \varrho_c)$ synthesis clearly showed significant residual electron density, attributable to neglect of bonding interactions, between all bonded pairs of atoms other than the two C=O groups. No effort was made to take account of this density. Tables 1 and 2 give the atom parameters.

**Discussion.** Gnidicoumarin is the first compound reported as having the 2*H*,12*H*-furo[2,3-*h*:5,4-*h'*]bis[1]-benzopyran-2,12-dione ring system. Bond lengths and angles in the dibenzofuran moiety are in good agreement with those found for dibenzofuran itself (Dideberg, Dupont & André, 1972) where the exocyclic

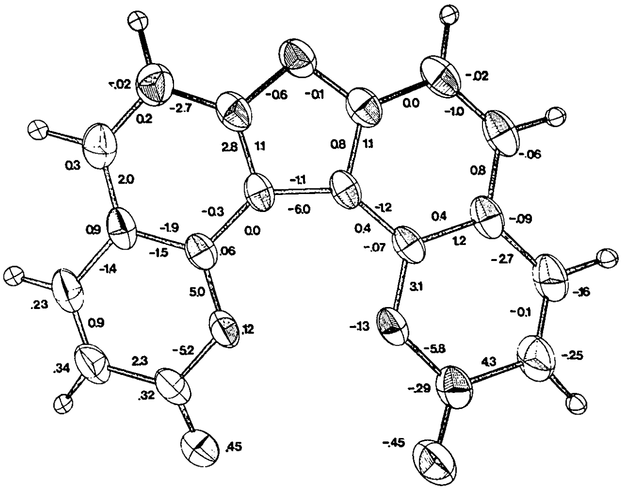


Fig. 1. *ORTEP* plot with boundary surfaces for C and O drawn at the 50% probability level and arbitrarily for H. Displacements (Å) of atoms from the plane of the furan ring are given as are torsion angles (°).

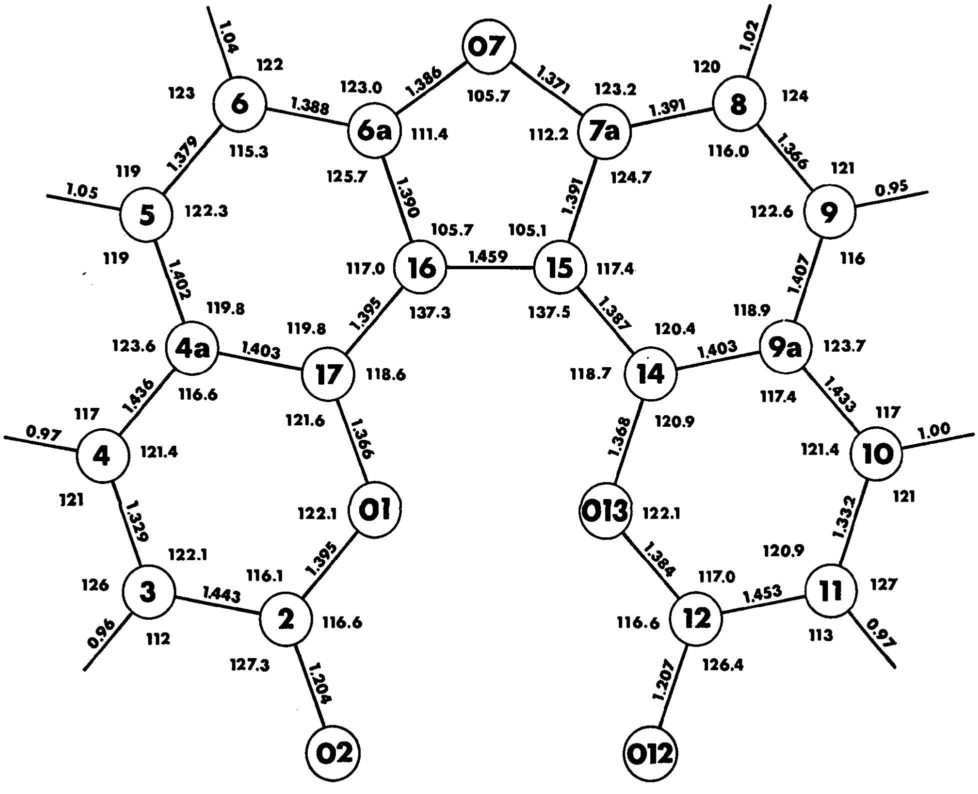


Fig. 2. Bond lengths and angles and numbering scheme for gnidicoumarin. E.s.d.'s are 0·002 Å for C–O, 0·003 Å for C–C, and 0·025 Å for C–H; for angles not involving hydrogen 0·2° and for those involving hydrogen 1·5°.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31266 (12 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Positional parameters* ($\times 10^3$) *for the hydrogen atoms and isotropic thermal parameters*

| | $x$ | $y$ | $z$ | $B$ (Å$^2$) |
|---|---|---|---|---|
| H(3) | 390 (3) | 817 (1) | 1061 (3) | 4·6 (6) |
| H(4) | 374 (3) | 801 (1) | 795 (2) | 3·3 (5) |
| H(5) | 423 (3) | 726 (1) | 571 (3) | 4·7 (6) |
| H(6) | 519 (3) | 612 (1) | 469 (3) | 4·2 (6) |
| H(8) | 779 (3) | 377 (1) | 687 (3) | 4·3 (6) |
| H(9) | 886 (3) | 339 (1) | 930 (3) | 4·3 (6) |
| H(10) | 945 (3) | 357 (1) | 1198 (3) | 4·5 (6) |
| H(11) | 940 (3) | 440 (1) | 1406 (3) | 4·7 (6) |

C–C–C and C–C–O angles at the furan ring are 135·3 (2) and 124·6 (2)°, the endocyclic furan C–C–C and C–C–O angles 105·4 (2) and 112·4 (2)°. The dimensions of the pyran rings are likewise in good agreement with those found in comparable structures such as xanthotoxin (Stemple & Watson, 1972) and 3-(1-phenylpropyl)-4-hydroxycoumarin (Bravic, Gaultier & Hauw, 1971).

In the crystal structure there are small but significant deviations from the formal symmetry expected for such a molecule. Agreement between bond lengths and angles related by the near diad axis passing through O(7) and the mid-point of C(15)–C(16) is good with r.m.s. deviations from the mean values for those not involving hydrogen of 0·004 Å and 0·35°. In terms of the e.s.d.'s quoted there are apparently significant differences between O(7)–C(6a) and O(7)–C(7a), C(5)–C(6) and C(8)–C(9), and O(1)–C(2) and O(13)–C(12). It seems more reasonable to assume that the e.s.d.'s are underestimated than that these differences are real.

The significant deviations from exact $C_2$ symmetry are in the slightly differing conformations of the pyran rings. The furan ring is rigorously planar, the maximum deviation of any of its atoms from their least-squares mean plane being 0·006 Å. The deviations of individual atoms in the rest of the molecule from this plane are shown in Fig. 1 which also gives various torsion angles. The C(15) phenyl ring is also planar but the C(17) phenyl ring shows minor distortions from planarity. Each pyran ring is significantly non-planar and the pattern of torsion angles is different in each with the angles at the junction with the phenyl ring being of opposite sign though small. Bond lengths and angles are in Fig. 2.

The O(1)···O(13) separation is 2·852 (2) Å and the overall non-planarity of the molecule presumably arises from lone-pair interactions involving these two atoms. The dihedral angle between the planes of the two phenyl rings is 3°, that between the least-squares mean planes for the pyran rings is 10°.

Intermolecular contacts are of normal van der Waals type with no unusually close approaches.

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# Thiomorpholin-3-thione-pentacarbonyltungsten

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**Abstract.** $(CO)_5WS=C{-}NH{-}CH_2{-}CH_2{-}S{-}CH_2$, monoclinic, $P2_1/n$, $a=5{\cdot}64$ (1); $b=23{\cdot}17$ (3); $c=10{\cdot}25$ (2) Å; $\beta=91{\cdot}7$ (3)°; $D_m=2{\cdot}24$ g cm$^{-3}$; $Z=4$, $D_c=2{\cdot}26$ g cm$^{-3}$. The compound was prepared by ultraviolet irradiation of a dry ethyl ether solution of $W(CO)_6$ and the ligand. The coordination is octahedral, with the heterocyclic ligand bonded through the thioketonic S atom.

**Introduction.** Crystals suitable for X-ray analysis were obtained by slow evaporation of a methylene chloride–ligroin solution. Cell constants were determined by a least-squares fit of 17 values of $\theta, \chi, \varphi$, accurately measured by use of a very narrow counter aperture. Weissenberg photographs showed systematic absences corresponding to space group $P2_1/n$ ($h0l$ with $h+l$ odd and $0k0$ with $k$ odd). The intensities were obtained from a crystal of approximate dimensions 0·01 × 0·02 ×