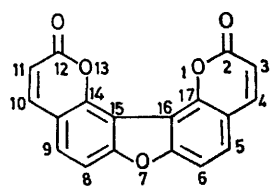
Structure of Gnidicoumarin, a Novel Pentacyclic Dicoumarin from *Gnidia lamprantha*

By S. MORRIS KUPCHAN,* J. G. SWEENY, T. MURAE, M.-S. SHEN, and R. F. BRYAN
(*Department of Chemistry, University of Virginia, Charlottesville, Virginia* 22901)

Summary The isolation, spectral properties, and *X*-ray structure determination of gnidicoumarin(**1**), a novel pentacyclic dicoumarin, are reported.

GNIDICOUMARIN, which is demonstrated herein to possess the 2*H*,12*H*-furo[2,3-*h*:5,4-*h*']bis[1]benzopyran-2,12-dione structure (**1**), is the first reported example of a compound having this ring system. The compound was isolated from a 95% ethanol extract of the roots of *Gnidia lamprantha* Gilg (Thymelaeaceae). Partition of the residue between $CHCl_3$–H_2O and column chromatography of the $CHCl_3$-soluble fractions on SilicAR CC-7 (8% MeOH–$CHCl_3$ elution) gave (**1**), $C_{18}H_8O_5$, 0·011%, m.p. 355—365° (decomp.; from $HCONMe_2$); λ_{max} (EtOH) 225 (ϵ 20,100), 268 (23,400), 279 (27,000), 292 (s, 14,300) and 325 (6350) nm; ν_{max} (KBr) 5·75, 5·83, 6·17, and 6·25 μm; *m/e* 304 (M^+), 276, 248, 220, 192, 164, 124, and 96.



(1)

From the marked insolubility of (**1**) (< 1 mg/100 ml) in common organic solvents, its high m.p., its spectral properties, and its lack of alcohol or ketonic functionalities, a

highly aromatic structure was inferred. Further evidence from the i.r. (5·75, 5·83 μm) and mass spectra (5 consecutive losses of CO) suggested that the molecule was a biscoumarin.[1]

The structure of gnidicoumarin was established by single-crystal *X*-ray analysis. Crystals belong to the monoclinic system, space group $P2_1/n$, with $a = 7{\cdot}599(1)$, $b = 18{\cdot}829(2)$, $c = 8{\cdot}969(1)$ Å, $\beta = 91{\cdot}07(1)°$, and $Z = 4$. The structure was solved by direct methods[2] and refined by least-squares methods to $R = 0{\cdot}039$ for 1682 independent reflections whose intensities were measured by counter diffractometry with Cu-K_α radiation.

The molecule is non-planar but has effective C_2 symmetry about an axis bisecting the planar furan ring. C(17), O(1), C(2), and O(2) are 0·06, 0·12, 0·32, and 0·45 Å, respectively, above the plane of the furan ring while the corresponding atoms C(14), O(13), C(12), and O(12) are 0·07, 0·13, 0·29, and 0·45 Å below that plane. The O(1) $\cdots$ O(13) separation is 2·85 Å.

We thank Dr. Robert E. Perdue, jun., U.S. Department of Agriculture, for the plant material (collected in Kenya in June, 1972), and the National Cancer Institute for financial support.

(*Received*, 10*th September* 1974; *Com.* 1151.)

[1] *Cf.*, *e.g.*, S. C. Das, S. Sengupta, and W. Herz, *Chem. and Ind.*, 1973, 792.
[2] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1970, B **26**, 274.