

CRYPTOCARYONE: A REVISED STRUCTURE

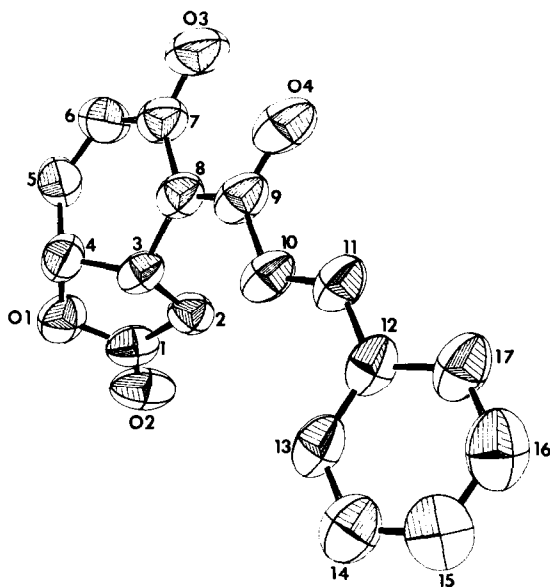
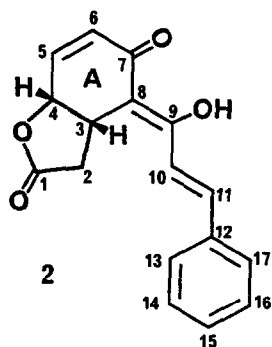
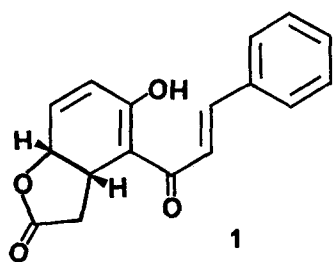
Joseph A. Maddry, Balawant S. Joshi, M. Gary Newton and S. William Pelletier*
Institute for Natural Products Research and the Department of Chemistry,
The University of Georgia, Athens, Georgia 30602, U.S.A.

P. C. Parthasarathy*
Hindustan CIBA-GEIGY Research Centre, Goregaon, Bombay 400063, India

Summary: Cryptocaryone, formulated earlier as the chalcone 1, has been shown to have structure 2 by an X-ray crystallographic analysis. Carbon-13 assignments are given.

A novel, orange dihydrochalcone cryptocaryone, $C_{17}H_{14}O_4$, was isolated from the roots of *Cryptocarya bourdillonii* Gamb. and its structure (1) was derived from spectral and degradative evidence.¹ This structure was also supported by transformation of cryptocaryone into 5-carbomethoxymethylflavone in three steps and a synthesis of the same.

The 1H nmr spectrum and the decoupling experiments leave no doubt about the environment of the protons in cryptocaryone. However, since it is the only example of a natural flavonoid



ORTEP drawing of cryptocaryone, 2

having a partially reduced ring A, except for ceroptin², and since the assigned structure has been questioned³, we wished to establish the structure of cryptocaryone by an X-ray analysis.

Cryptocaryone was crystallized from diethyl ether. A crystal approximately 0.5 mm on a side was mounted on a glass fiber, and preliminary examination and data collection were performed on an Enraf-Nonius CAD4 diffractometer system employing CuK α radiation ($\lambda = 1.542\text{\AA}$). The crystals belonged to the orthorhombic space group $P2_12_12_1$ with $a = 7.480(2)$, $b = 10.921(1)$, $c = 17.485(2)\text{\AA}$, $z = 4$, and $d_{\text{calc}} = 1.31\text{ g/cm}^3$. Data were collected out to $2\theta = 150^\circ$ using $\omega - 2\theta$ scans of width $(0.8 + 0.14 \tan \theta)^\circ$ and variable scan speed. Of the 1730 reflections measured, 1341 unique reflections were judged observed ($I > 3\sigma(I)$) after application of Lorentz and polarization corrections and were used in the least squares refinement.

The structure of cryptocaryone (**2**) was solved by direct methods. Using 250 reflections (minimum E of 1.40) 20 atoms were located from the E-map. Remaining non-hydrogen atoms were found on a difference map after partial full-matrix least squares refinement. After anisotropic refinement of the non-hydrogen atoms the hydrogens were not discernable from a difference synthesis; thirteen of these were located using stereochemical criteria and refined isotropically (the hydroxy proton was not located). The quantity minimized in refinement was $w(\Delta F)^2$ where the weight $w = 1/\sigma(F)^2$. The final R factor was 0.052, and $R_w = 0.064$.⁴

An ORTEP plot of cryptocaryone is shown. Except for the five-membered saturated lactone ring which is *cis*-fused to ring A, the molecule exists in an extended, planar conformation, the least squares plane of the phenyl ring being inclined 14.1° to that of the skeletal carbons C(3) through C(11). Bond length considerations clearly indicate that ring A exists as an α, β -unsaturated ketone and not as an enolic dihydrobenzene as depicted in **1**. The C(9)-O(4) bond possesses largely single-bond character.

The ¹³C-nmr spectrum (SFORD) indicated five singlets, nine doublets and one triplet. The chemical shifts and assignments are as follows: C(1)174.7^a, C(2)35.4, C(3)34.0, C(4) 76.1, C(5)139.7, C(6)130.1, C(7)185.1, C(8)103.6, C(9)174.2^a, C(10)117.1, C(11) 142.5, C(12)135.1, C(13) and C(17)128.3, C(14) and C(16)129.2, C(15)130.5 (a. these assignments may be interchanged). The elusive problem of deciding between the keto-enol tautomeric structures of cryptocaryone could not have been solved without an X-ray analysis or in solution employing carbon-carbon connectivity 2D ¹³C-nmr techniques.

REFERENCES

1. T.R. Govindachari and P.C. Parthasarathy, *Tetrahedron Letters*, 3419 (1972); T.R. Govindachari, P.C. Parthasarathy, H.K. Desai and M.N. Shanbhag, *Tetrahedron*, **29**, 3091 (1973).
2. B.A. Bohm in *The Flavonoids, Advances in Research*, Eds. J.B. Harbourne and T.J. Mabry, Chapman and Hall, London, 1982, p. 313.
3. J. Gosteli, private communication to P.C.P during a seminar in Basle in 1980.
4. Tables of atomic coordinates, bond distances and angles and thermal parameters, all with standard deviations are deposited with the Cambridge Crystallographic Data Centre.

(Received in USA 13 August 1985)