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CRYPTOCARYONE, A NOVEL 5',6'-DIHYDROCHALCONE, FROM CRYPTOCARYA BOURDILLONI GAMB.*

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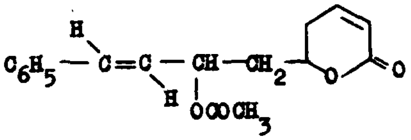
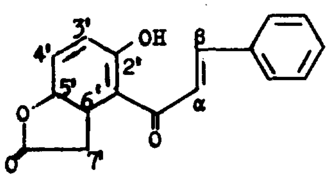
The isolation of cryptocaryalactone (I), a new Kawa-type lactone from the roots of Cryptocarya bourdilloni Gamb. (Lauraceae) has recently been reported by us[1]. From the same plant, we have now isolated cryptocaryone, a novel 5',6'-dihydrochalcone, the first of its kind to occur in Nature for which we wish to assign structure II based on the following evidence: Cryptocaryone, $C_{17}H_{14}O_4$, M^+ 282, m.p. 153°, $[\alpha]_D + 776.6°$, exhibits spectral properties suggestive of the presence of a 5-memb. sat. lactone, an extended cinnamoyl chromophore and an enolized β-diketonic function; UV: λ_{max} 237, 243, 287, 385 and 396 nm (log ε 4.00, 3.96, 4.00, 4.36 and 4.36), λ_{shl} 230 nm (log ε 3.97); IR (CH_2Cl_2): 1788 and 1634 cm^{-1}. The NMR spectrum[+] and the decoupling experiments described in Table lead to structure II for cryptocaryone.



I



II

Conclusive evidence for the structure has been obtained in the following manner: Brief exposure of cryptocaryone to SeO_2 in hot amyl alcohol gave the corresponding 5,6-dihydroflavone, $C_{17}H_{12}O_4$, M^+ 280, m.p. 181-183°, $[\alpha]_D + 376.21°$, which isomerised to a flavone carboxylic acid, $C_{17}H_{12}O_4$, m.p. 260-262° (d), in

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[+] NMR spectra were recorded with a Varian HA-100-D spectrometer; symbols s, d, m and d,d represent singlet, doublet, multiplet and doublet of a doublet, respectively. All shifts are reported as ppm in δ values.

refluxing diphenyl ether containing Pd/C through which a gentle stream of CO_2 was bubbled. The methyl ester of the acid, $C_{18}H_{14}O_4$, M^+ 294, m.p. 167-169°, was found to be identical in all respects (m.p., mixed m.p., TLC, IR and NMR) with an authentic specimen of the hitherto unknown methyl ester of 5-carboxymethylflavone prepared from the methyl ester of 2-acetyl-3-hydroxyphenylacetic acid (made from 4-methoxy-3-methylindene by oxidation accompanied by demethylation) by an Allan-Robinson reaction.

TABLE : NMR AND DECOUPLING DATA ON CRYPTOCARYONE (II)

Proton	Chemical shift ($CDCl_3$)	Multiplicity	Coupling Constant
C-7' $\underline{H}_2$	2,56, 2.80	d,d each	J = 12 and 17 Hz; 9 and 17 Hz
*C-6' $\underline{H}$	3.97	m	-
†C-5' $\underline{H}$	5.45	m	-
C-3' $\underline{H}$	6.16	d,d	J = 2 and 10 Hz
C-4' $\underline{H}$	6.52	m	-
**α-$\underline{H}$	6.78	d,d	J = 1 and 16 Hz
$C_6\underline{H}_5$	7.42	m	-
β-$\underline{H}$	7.75	d	J = 16 Hz
C-2' O$\underline{H}$	16.05	s (broad)	-

* Irradiation of C-6' $\underline{H}$ results in C-4' $\underline{H}$ becoming a doublet of a doublet with J=2 and 10 Hz; each of the C-7' protons appears as a doublet with J=17 Hz and the signal due to C-5' $\underline{H}$ has also simplified.

† Upon irradiation of C-5' $\underline{H}$, C-6' $\underline{H}$ becomes a broadened doublet of a doublet with J=9 and 12 Hz; C-4' $\underline{H}$ disintegrates to a broad doublet with J=10 Hz and C-3' $\underline{H}$ becomes a doublet with J=10 Hz.

** With D_2O α-$\underline{H}$ simplifies to a doublet with J=16 Hz.

Cryptocaryone is thus the first member of a new class of naturally occurring chalcones.

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Reference

1. T.R. Govindachari and P.C. Parthasarathy, Tetrahedron Letters, 3401 (1971).