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CRYPTOCARYALACTONE, A NOVEL 5,6-DIHYDRO-2H-PYRAN-2-ONE FROM CRYPTOCARYA BOURDILLONI GAMB.*

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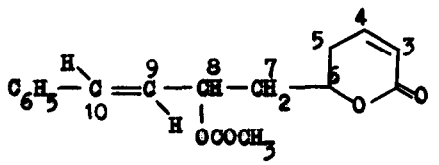
A new lactone has been isolated from the roots of Cryptocarya bourdilloni Gamb. (Lauraceae), for which we wish to assign structure I based on the following evidence: Cryptocaryalactone, $C_{17}H_{18}O_4$, M^+ 286, m.p.124-126°, $[\alpha]_D^{25}$ + 15.55° (C = 2.52 in $CHCl_3$) exhibits spectral properties suggestive of the presence of an acetoxyl group, a styryl moiety and an α,β-unsaturated 6-membered lactone. IR: CH_2Cl_2 1740 ($OCOCH_3$) and 1705 cm^{-1} (6-memb. α,β-unsat. lactone). Strong infrared absorptions at 690 and 750 cm^{-1} and a 5-proton multiplet in NMR† spectrum at 7.23 indicate the presence of a monosubstituted benzene ring. Strong infrared absorption at 965 cm^{-1} is assigned to the trans-disubstituted double bond while the UV spectrum (λ_{shl} 216 nm (ϵ 22,800); λ_{max} 250-3, 283 and 292 nm (ϵ 19,000, 1,600 and 1,200) showed it is conjugated with the benzene ring as a styryl residue. The NMR spectrum† and the decoupling experiments described in Table I support the structure I assigned for cryptocaryalactone.



(I)

a, $C_5H_5O_2$ (m/e 97) b, C_4H_5O (m/e 69) c, C_4H_4O (m/e 68)

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† NMR spectra were recorded with a Varian HA-100-D spectrometer in $CDCl_3$; Symbols s, m and q represent singlet, multiplet and quartet, respectively. All shifts are reported as ppm in δ values.

TABLE I : NMR and Decoupling data on Cryptocaryalactone

Proton	Chemical shift in $CDCl_3$ (ppm)	Multiplicity	Coupling constant
$OCOCH_3$	2.05	s	-
*C-7 H_2	2.15	m	-
**C-5 H_2	2.38	m	-
†C-6 H	4.55	m	-
††C-8 H	5.65	m	-
C-3 H	5.99	sextet	J = 2 and 10 Hz
C-9 H	6.10	q	J = 7 and 16 Hz
C-10 H	6.67	d	J = 16 Hz
C-4 H	6.83	sextet	J = 4.5 and 10 Hz
C_6H_5	7.23	m	-

* On irradiation of C-7 H_2, C-8 H becomes a doublet with J = 7 Hz; C-6 H multiplet has also simplified.

** Upon irradiation of C-5 H_2, C-4 H degenerate to a doublet with J = 10 Hz; C-6 H multiplet has also simplified.

† On irradiation of C-6 H, both C-5 H_2 and C-7 H_2 have simplified.

†† Irradiation of C-8 H results in the appearance of C-9 H as a doublet with J = 16 Hz

In consonance with structure I, cryptocaryalactone exhibits in the mass spectrum peaks at m/e 97 (a, $C_5H_5O_2$, 49.4%), 69 (b, C_4H_5O, 18.1%), 68 (c, C_4H_4O, 21.7%), 77 (phenyl, C_6H_5, 16.9%), 91 (tropylium, C_7H_7, 21.7%), 115 (indenyl, C_9H_7, 30.1%) and 131 (benzopyrilium, C_9H_7O, 81.9%). It is pertinent to note that cryptocaryalactone represents the first example of a naturally occurring Kawa-type lactone arising by the condensation of three acetate units to cinnamic acid. Work to resolve the absolute stereochemistry of cryptocaryalactone is in progress.

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