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THE STRUCTURE OF LUCIDONE AND METHYL-LUCIDONE

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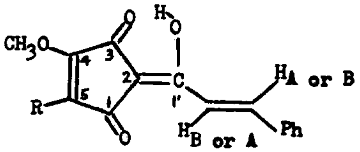
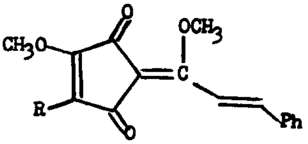
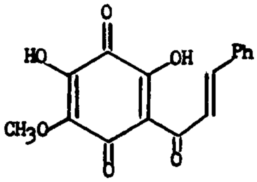
Linderone and methyl-linderone,[1] two pigments isolated from the root of Lindera pipericarpa have been shown to have structures (I) and (II) respectively, and their total synthesis from a possible biogenetic precursor (III) has recently been reported.[2]



(I, R = OCH_3)
(IV, R = H)



(II, R = OCH_3)
(V, R = H)



(III)

In examining the chloroform extracts of the fruit of a related plant Lindera lucida,[3] three yellow crystalline compounds were obtained. One of these was readily identified as methyl-linderone (II), while the other two, designated lucidone and methyl-lucidone are assigned structures (IV) and (V) respectively based on evidence described below.

Lucidone, $C_{15}H_{12}O_4^{*}$ (M^+ 256), m.p. 164-165°, $\nu_{max}^{CHCl_3}$ 1720, 1650, 1610 and 1595 cm^{-1}, λ_{max} (acidic EtOH) 244 and 355 mµ (log ϵ 4.40 and 4.51), λ_{max} (basic EtOH) 238, 290 sh. and

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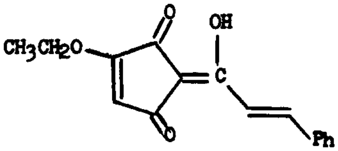
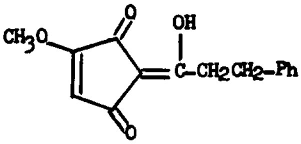
[*] Satisfactory elemental analyses have been obtained for all new compounds reported.

344 mμ (log ε 4.32, 4.17 and 4.27), is enolic, forms a monobenzoate $C_{22}H_{17}O_5$,* m.p. 245-247° and a brown-green copper chelate $C_{30}H_{22}O_8Cu$,* m.p. 305-309° (dec.). It is converted by dimethyl sulphate in acetone solution in the presence of anhydrous potassium carbonate to the naturally occurring methyl-lucidone, $C_{16}H_{14}O_4$* (M^+ 270), m.p. 115-116° (resolidified, m.p. 126-127°), $\nu_{max}^{CHCl_3}$ 1720, 1670 and 1620 cm^{-1}, λ_{max} (EtOH) 240 and 359 mμ (log ε 4.34 and 4.46), which in turn can be hydrolyzed to lucidone by oxalic acid in methanol. More vigorous hydrolysis of lucidone with ethanolic hydrochloric acid gave instead an ethyl ether, $C_{16}H_{14}O_4$,* m.p. 126-128°, $\nu_{max}^{CHCl_3}$ 1715, 1645, 1625 and 1590 cm^{-1}, λ_{max} (acidic EtOH) 241 and 359 mμ (log ε 4.35 and 4.53), λ_{max} (basic EtOH) 244, 292 and 349 mμ (log ε 4.35, 4.19 and 4.30). Comparison of the IR and UV data of lucidone, methyl-lucidone and lucidone ethyl ether with that of (I) and its derivatives and of other known acylcyclopentenediones[4,5] allowed, *a priori*, assumption of structures (IV), (V) and (VI) for the three pigments respectively.


(VI)


(VII)

Chemical evidence in support of a cinnamoyl side chain for (IV) was obtained from its alkaline degradation which yielded cinnamic acid, and from hydrogenation of (IV) over palladium-strontium carbonate which resulted in a dihydro-derivative (VII), $C_{15}H_{14}O_4$,* m.p. 106-108°, $\nu_{max}^{CHCl_3}$ 1720, 1673 and 1635 cm^{-1}, λ_{max} (acidic EtOH) 254-275 mμ (log ε 4.36), λ_{max} (basic EtOH) 251 and 279 mμ (log ε 4.32 and 4.38). Basic hydrolysis of (VII) gave hydrocinnamic acid. Analogous reactions were also observed in the structural studies of linderone (I).

The NMR spectra of (IV), (V), (VI) and (VII) are also consistent with the structural assignments (see Table):

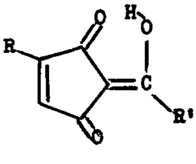
TABLE. NMR Spectral Data ($CDCl_3$, 100 Mc.) In p.p.m. From TMS.

	(IV)+	(V)	(VI)	(VII)
5-H	5.82	5.92, 5.91++	5.81	5.75
4-OCH_3	3.93	3.91, 3.90++		3.89
Aromatic-H	7.35 (m)	7.35 (m)	7.35 (m)	7.35 (m)
H_A or H_B	7.69, 7.72 (d) (J_{AB} 16 c/s)	8.00, 7.69 (d) 7.93++, 7.62++	7.66, 7.74 (d) (J_{AB} 16 c/s)	
1'- OCH_3		4.18, 4.20++		
4-OCH_2CH_3			4.15(q), 1.49(t)	
-CH_2-CH_2-				3.0 (m)

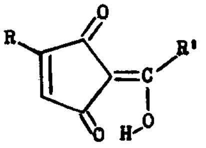
+ An enolic proton was indicated by a broad signal near 12 p.p.m.; d = doublet, m = multiplet, t = triplet, q = quartet.

++ Signals from minor isomer.

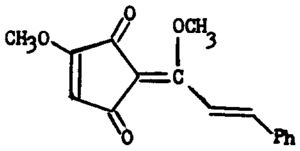
In addition, the NMR spectra of (IV), (V), (VI) and (VII) show a small splitting of the ring 5-proton and the adjacent 4-methoxyl (or 4-OCH_2CH_3) indicative of the presence of "external tautomers" such as (VIIIa) or (VIIIb) and (IX) or (X). Although the proportion of the minor isomer is quite low in (IV), (VI) and (VII) it is appreciable in (V) with approximate ratio of 3 : 2, albeit the assignment of proton signals to each tautomer is uncertain. The



(a)



(b)

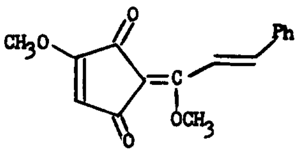


(IX)

[VIII, R = OCH_3 or OCH_2CH_3
R' = PhCH=CH or $PhCH_2CH_2$]

[XI, R = R' = CH_3]

[XII, R = Cl, R' = CH_3]



(X)

existence of such "external tautomers" and their interconversion in analogous enolized acylcyclopentenediones (XI) and (XII) has earlier been amply demonstrated and discussed by Forsén, Merényi and Nilsson.[4]

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