Revised Structure for Cassiollin: Identity with Pinselin

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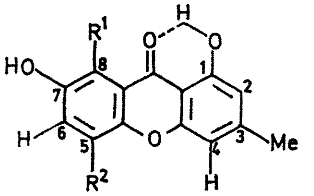
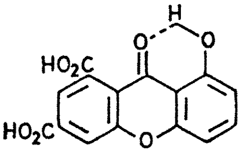
Summary Cassiollin is 1,7-dihydroxy-8-methoxycarbonyl-3-methylxanthone *i.e.* pinselin, and not 1,7-dihydroxy-5-methoxycarbonyl-3-methylxanthone as previously reported.

THE isolation of a new xanthone, cassiollin, from the acid-hydrolysed extractives of *Cassia occidentalis* Linn was reported recently.[1] It was formulated as 1,7-dihydroxy-5-methoxycarbonyl-3-methylxanthone (II). However, consideration of the data of Kulkarni *et al.*, and those presented below leads to the conclusion that cassiollin must be reformulated as (I) the structure previously suggested for pinselin.[2] The latter is one of two metabolites produced by *Penicillium amarum*.†

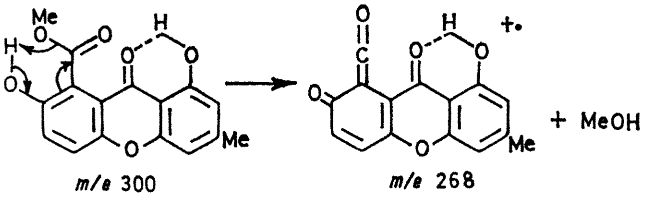


(I) $R^1 = CO_2Me; R^2 = H$
(II) $R^1 = H; R^2 = CO_2Me$
(III) $R^1 = CO_2H; R^2 = H$
(IV) $R^1 = H; R^2 = H$



(V)

High-resolution mass spectrometry‡ established the molecular formula of (I) as $C_{16}H_{12}O_6$, and the base peak ($M - 32$, m^* 239·41) of the spectrum corresponds to the loss of methanol. Such a dominant loss is highly characteristic of salicylate esters[3,4] (see Scheme). Other prominent peaks at 240 (m^* 214·93), 212 (m^* 187·27), 184 (m^* 159·7), and 156 (m^* 132·2) are derived by four successive expulsions of carbon monoxide. Cleavage with loss of methoxyl ($M - 31$) is significant and again the fragment produced undergoes four consecutive losses of carbon monoxide, as would be expected for (I).



SCHEME

The 60 MHz n.m.r. spectrum§ of pinselin (I) displays, in addition to the two OH protons,¶ the following signals: δ 2·37 (3H, m), 3·87 (3H, s), 6·52 (1H, m), 6·71 (1H, m), and 7·45 (2H, *singlet*). It is readily apparent from the 100 MHz n.m.r. spectrum[5] run with a sweep width of 50 Hz (see Figure) that the two proton *singlet* at δ 7·45 constitutes an AB quartet (J_{AB} 9·1 Hz, $\Delta\nu_{AB}$ 3·63 Hz, $\Delta\nu_{AB}/J_{AB}$ 0·40).

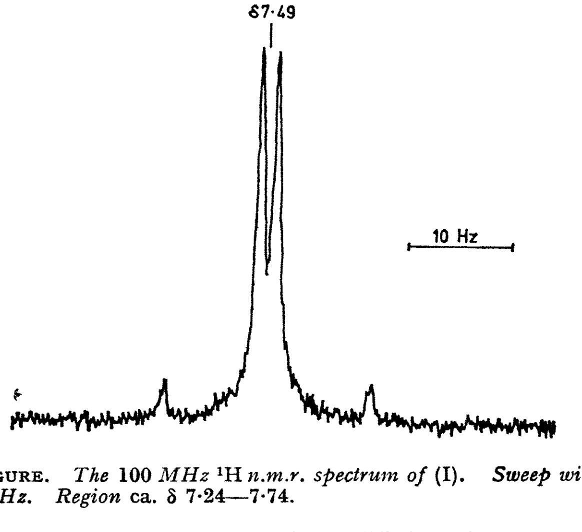


FIGURE. *The* 100 *MHz* ^1H *n.m.r. spectrum of* (I). *Sweep width* 50 *Hz. Region ca.* δ 7·24—7·74.

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† Pinselin and cassiollin were identical by spectral comparisons (u.v., i.r., n.m.r., and m.s.) and t.l.c. in differing solvent systems. We thank Dr. A. B. Kulkarni for a sample of cassiollin and Dr. H. Munekata for a sample of pinselin. In view of the identity of cassiollin with pinselin we shall from here on refer to (I) as pinselin.

‡ The mass spectrum was obtained on an CEC 21-110B mass spectrometer. Metastable transitions were determined by the defocusing technique.

§ Because of the limited solubility of (I), its n.m.r. spectrum was determined in $(CD_3)_2SO$ at 85°. Chemical shifts are expressed in p.p.m. relative to internal tetramethylsilane (δ = 0).

¶ These readily exchange with deuterium oxide.

This requires an *ortho*-relationship for these protons (C-5 and C-6), leaving (I) as the unique structure for pinselin.

The further chemistry of pinselin, in particular the marked difficulty of its hydrolysis to pinselic acid (III)[2] and the ready thermal loss of carbon dioxide from the latter to give 1,7-dihydroxy-3-methylxanthone (IV), is readily explicable in terms of the formulation (I).

This appears to be the second occasion[1] that a xanthone has been isolated from a *Cassia* species. Recently Nair and co-workers[6] have deduced structure (V) for the pale yellow crystalline material first isolated in 1949[7] from a bicarbonate extract of the leaves of *Cassia reticulata* Willdenow. This same compound has also been isolated from *Cassia alata*.[8]

To our knowledge this is the first time that one and the same xanthone (*i.e.*, I) has been isolated from both a fungus and a plant.

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[2] H. Munekata, *J. Agric. Chem. Soc. Japan*, 1943, **19**, 343; *J. Biochem.* (*Japan*), 1953, **40**, 451.
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[5] We thank Dr. D. T. Dix of this laboratory for these spectra.
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