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COUMURRAYIN, A NEW COUMARIN FROM Murraya paniculata (L.) JACK

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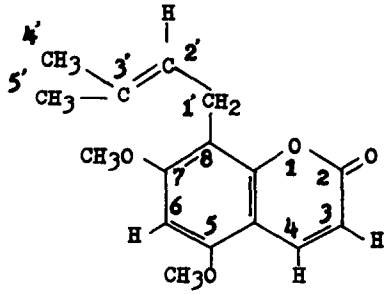
We have isolated from the ripe fruits of Murraya paniculata (L.) Jack (Rutaceae) a new compound, coumurrayin, $C_{16}H_{18}O_4$. It forms colorless prisms, m.p. 157°. On the basis of the following data the constitution of coumurrayin has been established as 5,7-dimethoxy-8-(2-isopentenyl)coumarin.



The compound is a neutral lactone that dissolves in methanolic sodium hydroxide with a light yellow color and can be recovered in unchanged form upon acidification of this solution; infrared band at 1710 cm^{-1}.

$\lambda_{max}^{ethanol}$: 329 mμ (log ε 4.09), 263 mμ (log ε 3.99), 239 mμ (log ε 3.77), 221 mμ (log ε 4.19). λ_{max} 329 mμ and λ_{min} 274 mμ (log ε 3.25) provide evidence of the presence of a 7-oxygenated coumarin [1].

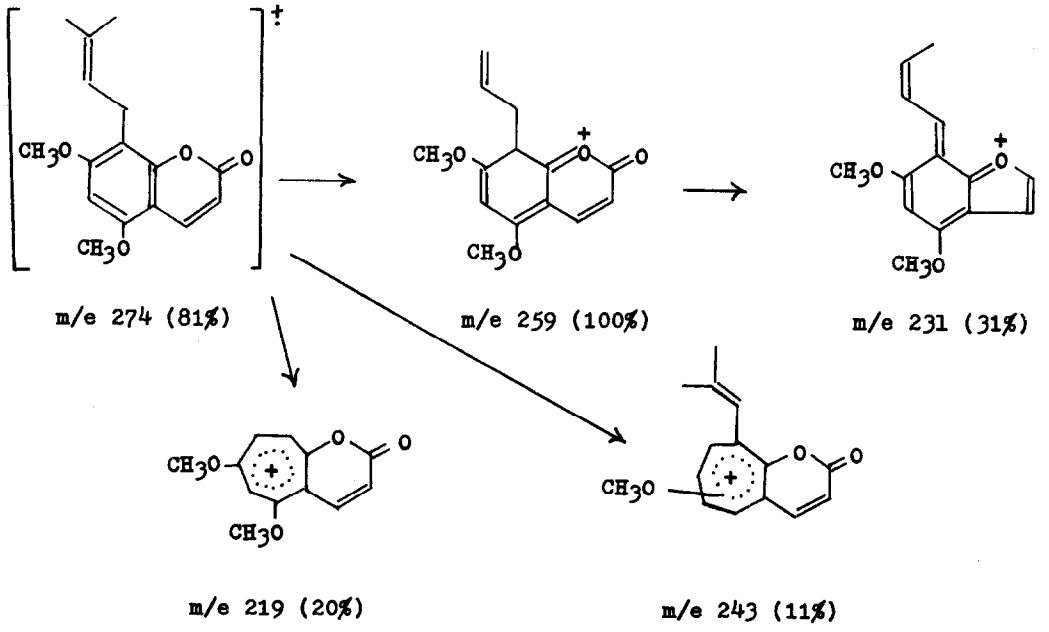
The I.R. spectrum (KBr) is characterized by bands at 1710 (s) (lactone), 1600 (s), 1500 (m), 1450 (m), 860 (w), 830 (w) and 813 (s) cm^{-1} (substituted benzene ring) and 1375-1380 (w) cm^{-1} ($=C(CH_3)_2$).

A positive Gibbs reaction indicates the presence of a free proton at position C-6 [2] The relatively low-field position of this proton, which appears as a sharp peak at δ 6.33,

is in agreement with its being flanked by two methoxy groups [3] as shown below.

The NMR spectrum (60 Mc, $CDCl_3$) displays two doublets at δ 6.08 and at δ 7.93, each equivalent to one proton and both having J=9.5 cps. These two doublets have the characteristics of protons at positions 3 and 4 of coumarin derivatives that have an alkyl or an alkoxyl group at position 5 [3]. A sharp peak at δ 3.98, equivalent to 6 protons, is indicative of 2 aromatic OCH_3 groups at positions C-5 and C-7. The coincident position of the methoxy protons supports their assignments to these positions.

The side chain attached to the remaining position of C-8 is represented in the coumurrayin by the following features: (a) two broad peaks at δ 1.64 and δ 1.80, each of three-proton content and each showing faint secondary splittings (J=1.7 cps), evidence for the presence of two sterically unequal CH_3 groups (positions C-4' and C-5') coupled through a double bond to a single proton (position C-2'); (b) a broad triplet of one-proton content around δ 5.28, each peak of which shows multiple fine secondary splittings from distant coupling with the methyl protons at C-4' and C-5'; (c) a broad two-proton-strong doublet centered around δ 3.44 (J=7 cps) and indicative of methylene protons of a benzyl group coupled to a single proton (at C-2'). The shapes, positions and proton-contents of the peaks described under (a), (b) and (c) pinpoint the side chain at position C-8 as being $(CH_3)_2$-C=CH-CH_2-, a grouping occurring in many natural products.



The mass-spectral evidence support the conclusions from the above findings:

The base peak, m/e 259 (100%), would result from the loss of terminal CH_3 of the side chain of coumurrayin (m/e 274, 81%) and the formation of the peak at m/e 231 (31%) can be rationalized by an expected [4] loss of CO from the former. Mass at m/e 206 (23%) would result from the loss of a dimethylallyl from coumurrayin. Other prominent peaks are at m/e 243 (11%), which can be rationalized as the loss of one OCH_3 group with simultaneous rearrangement to a tropolium structure. Loss of $(CH_3)_2$-C=CH and ring enlargement would give rise to the peak at m/e 219 (20%).

Toddaculin, 5,7-dimethoxy-6-(2-isopentenyl)coumarin, is an isomer of coumurrayin and occurs in Toddalia aculeata Pers. of the same family [5].

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