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FERULENOL A NEW COUMARIN DERIVATIVE FROM FERULA COMMUNIS

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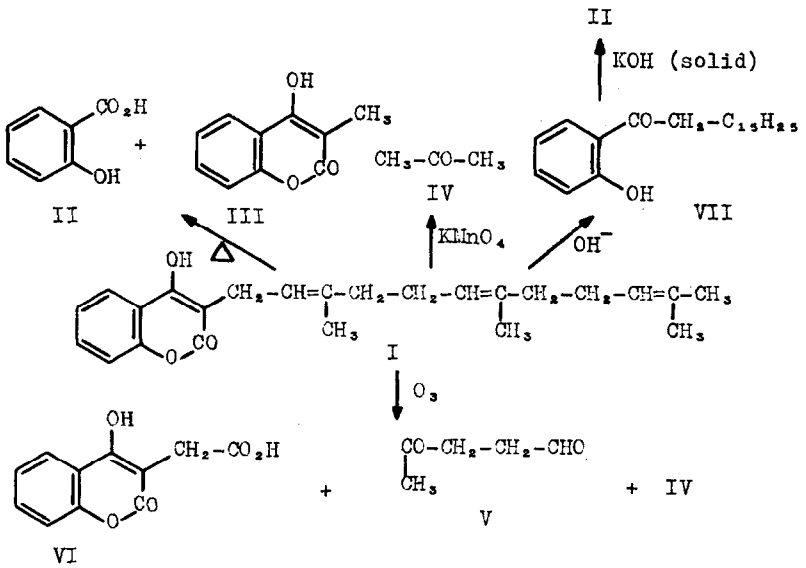
A substance, m.p.64-65°, with a hemorrhagic action, isolated from the acidic fraction of the latex of Ferula communis L. (Umbelliferae) of Sardinia, was previously described [1].

New chemical and spectrophotometric examinations allow us now to propose for this substance structure I, corresponding to 3-(1-farnesyl)-4-hydroxycoumarin.



The results are summarized as follows (all known products obtained from I by chemical degradations were compared with authentic samples by m.p.'s, mixed m.p.'s and infra-red spectra): analysis: found C 78,76; H 8,28; O 13,30; $C_{24}H_{30}O_5$ requires: C 78,65; H 8,25; O 13,10.

Molecular weight: 338 (Rast, camphor); 344 (acetic acid); $C_{24}H_{30}O_5$ requires: 366,48; determinations in benzene gave almost double values, because of association.

The product absorbed three moles of hydrogen over palladium-calcium carbonate (three aliphatic double bonds).

Pyrolysis at 300° afforded, as solid products, salicylic acid (II) and 4-hydroxy-3-methylcoumarin (III), m.p.230°[2].

Oxidation with potassium permanganate in basic solution and steam-distillation, gave mainly acetone (IV).

By ozonization in ethyl acetate and decomposition of the ozonide with steam, an excellent yield of levulinaldehyde (V) was obtained, characterized as the bis-(2,4-dinitrophenylhydrazone), m.p.236-240°[3]; acetone was also formed but no formaldehyde was isolated.

When the oily ozonide was precipitated by adding hexane to the ethyl acetate solution and the mixture kept four months in a refrigerator, a solid was formed: this, freed from oily by-products by mixing with a little chloroform, was identified as 4-hydroxycoumarin-3-acetic acid (VI), m.p.228°(dec.)[4].

By refluxing I with concentrated aqueous or methanolic potassium hydroxide, the hydroxy ketone VII (b.p.220°/1,5 mm; n_D^{30} 1,5312; 2,4-dinitrophenylhydrazone, m.p.83-84°) was obtained, in addition to some salicylic acid. A similar transformation is known for dicoumarol[5].

The hydroxy ketone gave salicylic acid on heating at 300° with solid potassium hydroxide.

Finally, the N.M.R. spectrum of I presents signals between 8,76 and 8,22 τ (total intensity 20 H) that may be assigned to the four CH_3 and to the four CH_2 groups far from the coumarin nucleus. Two signals near 6,70 τ (2 H) may be assigned to the CH_2 group linked to the coumarin nucleus. Two series of signals, between 4,95 and 4,61 τ (3 H) and between 2,69 and 2,27 τ (4 H) may be assigned to the olefinic and, respectively, to the aromatic protons. A signal at 6,28 τ (1 H) may be assigned to the enolic OH.

Compound I, for which the name ferulenol is proposed, differs from ammoresinol [6] only for the lack of the 7-hydroxyl group.

It is an important term of the very small class of natural coumarins which are not derived from umbelliferone [7].

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