

THE STRUCTURE OF PEDERONE

A NOVEL SUBSTANCE FROM PAEDERUS (COLEOPTERA STAPHYLINIDAE).

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Re-examination of the early vesicatory ethereal fractions effluent from countercurrent distribution (against water) of the total extract of Paederus fuscipes ⁽¹⁾, allowed us to separate (by a new countercurrent distribution) small quantities (25-30 mg from 1 Kg of insects) of a novel substance (vitreous solid $\left[\alpha \right]_{364}^{20^\circ} + 107.7^\circ$ c 0.2 ethanol) the IR spectrum of which (capillary film : OH, NH 3350 broad; =CH₂ 3060 ; CONH 1685 , 1515 ; CO 1720 ; OH and O-ether series of bands 1130-1040) is very like to those of pederin and ψ -pederin and shows moreover a strong carbonyl band at 1720 cm⁻¹.

For this characteristic the new substance was named pederone [⊙] .

Pederone reacts with *p*-nitrophenylhydrazine, but it is not affected by barium methoxide. By hydrogenation on Adams's catalyst, a dihydroderivative (vitreous solid) is obtained. Its IR is substantially identical to that of the parent substance, but it does not show any longer the =CH₂ stretching band.

The MS of pederone does not show the molecular ion (at m/e 501) but it contains the peaks at m/e 469 (M - CH₃OH) and at m/e 437 (M - 2 CH₃OH) both having 2 mass units less than the corresponding ions of pederin (pederin shows a very weak molecular ion only).

Pederone by reduction with LiAlH₄ in ethereal solution at room temperature affords pederin. This behaviour, along with the IR and MS data is consistent with the hypothesis that pederone differs from pederin for its containing a >CO in the place of a >CHOH group.

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⊙ By TLC on Kieselgel G (ethyl acetate; sprayed with 70% H₂SO₄ and heated 5 min. at 70 °C) it was possible to recognize the presence of pederone, along with pederin, also in P. columbinus (collected in Venezuela) and in melamurus (collected in Northern Italy).

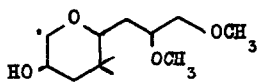
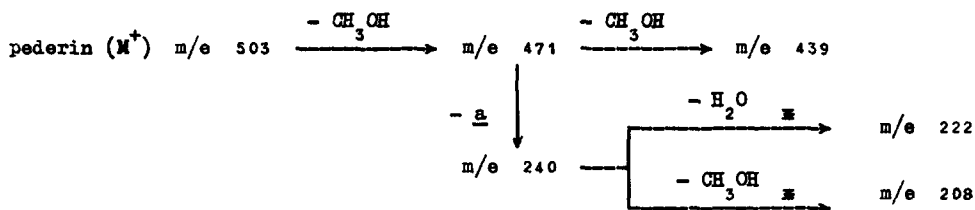
R_p pederone 1.3 ; R_p ψ -pederin 1.6 . (R_p = R_f relative to those of pederin).

TABLE I
Mass Spectrum of pederone †

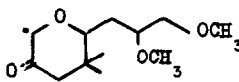
m/e	469	452	437	425	406	392	374	366	360	334	312
I %	0.01	0.01	13	1.5	0.5	2	4	1	1	0.5	2.5
m/e	305	294	273	258	240	229	227	222	208	194	180
I %	1	2	8	7	28	3	3	11	32	7	6
m/e	164	155	137	123	95	89	81	71	60	45	43
I %	18	65	15	27	60	43	28	65	100	65	54

The study of the pederone MS compared with pederin MS allowed us to decide which one of the two alcoholic groups remains inalterate.

We could demonstrate † that in the MS of pederin the peaks at m/e 240, 222 and 208 contain only one of the two alcoholic functions, the second being eliminated with the radical a according to the schema ‡ :



a (from pederin)



a' (from pederone)

The finding of the same ion tern (and their relative metastable ions) in the pederone MS is consistent with the presence of CO in that moiety of the molecule which is eliminated as a' radical.

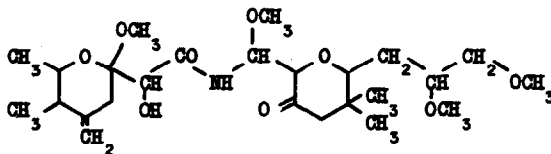
† Measured with Hitachi-Perkin-Elmer RMU-6D instrument (single focus); ionizing current 60 μ A, potential 70 eV. Samples were directly introduced in the ion source heated at 250°.

† A detailed study of the MS of pederin and some of their derivatives will be shortly published by A. Selva on Gazz. Chim. It.

‡ The asteriskate transitions are confirmed by the presence of proper metastable ions.

As expected, in the dihydropederone MS the tern of peaks at m/e 240, 222 and 208 is shifted of two units towards the highest masses, exactly like in the case of the dihydropederin.

The chemical and spectroscopical evidences are consistent with the structure (I) we propose for pederone



I pederone

Pederone posses a strong vesicatory action. Detailed studies on the biological proprieties of pederone will be shortly published by M. Pavan on another Journal.

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REFERENCES

1. G. Cardani, D. Ghiringhelli, R. Mondelli and A. Quilico, Tetr. Lett., 2537 (1965);
Gazz. Chim. It., 96, 3, (1966).