*The Partial Structure of Pederin**

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In 1949, one of the present authors (A. U.)[1] reported the isolation of a toxic principle, m. p. 114°C, from *Paederus fuscipes*. Reinvestigation of this material has now revealed that it is identical with pederin, $C_{25}H_{45}O_6N$, isolated from the same insect by Pavan and Bo[2] in 1953 and recently studied chemically by Quilico et al. and Cardani.[3,4] The infrared spectrum of pederin exhibits bands at 3480, 3380 (OH, NH), 1665, 1510 (NHCO), 3060 and 900 cm^{-1} ($\rangle C{=}CH_2$). Contrary to the opinion of the Italian workers, however, the latter two bands indicate the presence of at least one double bond in pederin. Since no other band is observable in the olefinic C–H stretching vibration region,[5] the only additional double bond that could possibly be present would be tetrasubstituted. The double bond is not conjugated ($\varepsilon_{200\,m\mu}$ 1400). On being treated with acetic anhydride and pyridine, pederin affords a diacetate, $C_{29}H_{49}O_{11}N$[6], m. p. 106°C, which shows bands at 3500 (broad, OH), 3360 (NHCO), 1740, 1720 (CH_3CO_2), 1700, 1520 (CONH), 3060 and 1650 cm^{-1} ($\rangle C{=}CH_2$). The NMR spectrum of pederin[7] exhibits its main peaks at the following positions (these peaks are assignable to the following groups by comparison with the spectrum of its diacetate): τ 9.11, 9.04 (each s, CH_3–$\underset{|}{C}$–), 8.98, 8.82 (each d, J 7 c. p. s., $\underline{CH_3}$–$\underset{|}{C}$–H), 7.55 (s, –$\underset{|}{C}$–CH_2–CO), 6.67 (s, 2 OCH_3), 6.61 (s, 2 OCH_3 and –O–CH_2–$\underset{|}{C}$–)[8], 6.20 (broad, 2 $\underline{H}$–$\underset{|}{C}$–OCH_3), 5.65 (s, $\underline{H}$–$\underset{|}{C}$–OH), 5.26, 5.18 (each broad s, $\rangle C{=}CH_2$) and 4.66 (m, $\underset{H}{C}\rangle C\langle\overset{OR}{OR}$). Since the peak due to the –$\underset{|}{C}$–CH_2–O– group in pederin does not shift appreciably to a lower field in the spectrum of diacetate, the oxygen atom in this group must be ethereal. Thus, out of the nine oxygen atoms of pederin, four are present as methoxyl groups, one as an amide, one as a C–O–CH_2–$\underset{|}{C}$– group and three as hydroxyl groups, two of which are acylable. A dimethyl acetal group is absent, since the *m/e* 75 peak is negligibly weak in the mass spectrum of both pederin and its diacetate. The spectroscopic evidence described above, coupled with the chemical findings[3] that preudopederin yields oxamic acid upon oxidation and that pederin

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1) A. Ueta, *Kyushu Igaku Zasshi* (*Journal of Kurume Medical College, Kyushu*), **1949**, 249.

2) M. Pavan and G. Bo, *Phys. Com. et Oecol.*, **3**, 307 (1953); M. Pavan, "Richerche biologiche e mediche su pederina e su estratti purifficatti di *Paederus fuscipes* Curt.," M. Ponzio, Pavia (1963).

3) A. Quilico, C. Cardani, D. Chiringhelli and M. Pavan, *La Chim. e l'Ind.*, **43**, 1434 (1961); C. Cardani, D. Chiringhelli and A. Quilico, "Abstracts of Papers, International Symposium on the Chemistry of Natural Products," Kyoto (1964), p. 139.

4) The identity of the two substances was confirmed by a direct comparison of m. p.'s and infrared spectra. We wish to express our sincere thanks to Professor Cardani for his generous gift of a sample of pederin.

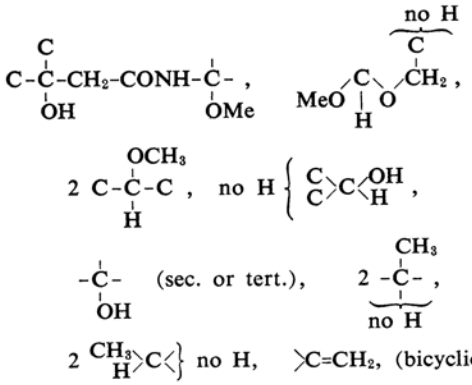
5) The infrared spectrum was obtained by means of a JASCO 401G grating spectrometer.

6) The molecular formulas of diacetate and pederin itself were confirmed by elemental analysis and mass spectrometry. The mass spectra were measured by Mr. Hiroshi Sato of the Hitachi Naka works, to whom our sincere thanks are due.

7) Measured in a $CDCl_3$ solution containing a small amount of pyridine as a stabilizer for pederin; pederin is very sensitive to acids.

8) In the spectrum of diacetate, the peak due to the -OCH_2-$\underset{|}{C}$- group appears at 6.52 as a broad singlet while the peaks due to methoxyl groups appear at 6.60 (3H), 6.64 (6H) and 6.83 (3H); the singlet line at 5.65 ($\underline{H}$-$\underset{|}{C}$-OH) in the spectrum of pederin is shifted to 4.70. The intensity of the broad absorption centered at 6.20 indicates the presence of two -$\underset{|}{C}$H-OCH_3 groups in acetate.

readily splits off ammonia upon treatment with acid, suggest the presence of the following moieties in pederin:



The molecular formula indicates that pederin is bicyclic if the tetrasubstituted double bond is absent.

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