

Short Communications

Pakistan J. Sci. Ind. Res., Vol. 18, No. 5, October 1975

STUDIES ON THE QUANTITATIVE DETERMINATION AND PHOTODEGRADATION OF EPHEDRINE

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(Received May 14, 1975, revised July 1, 1975)

Ephedrine, in aqueous solution, on exposure to sunlight and UV light in the presence of air deteriorate and forms coloured products.^{1,2} The nature of photodegradation products and the mode of reaction is not known. The ease with which ephedrine and pseudoephedrine give benzaldehyde on oxidation, suggests that as soon as the benzaldehyde is formed it condenses with unchanged ephedrine to form a compound which was named benzalephedrine by Schmidt³ who deduced its structure on the basis of chemical studies as 2,5-diphenyl-3,4-dimethyltetrahydrooxazole.

In the present investigation the spectral characteristics of 2,5-diphenyl-3,4-dimethyltetrahydrooxazole have been reported and the structure of the photoproduct has been confirmed as 2,5-diphenyl-3,4-dimethyltetrahydrooxazole. It is suggested that the oxazole derivative plays an intermediate role in the photodegradation of ephedrine leading to the formation of the coloured products.

Experimental

Preparation of 2,5-Diphenyl-3,4-dimethyltetrahydrooxazole. Ephedrine base was obtained by treating ephedrine hydrochloride with 20% NaOH, the solution saturated with NaCl and extracted with ether. Ephedrine base (0.6470 g; 1 mole) was mixed with benzaldehyde (0.42 ml; 5% excess of 1 mole) in a conical flask and heated over flame for a few seconds until the water suddenly separated. The product was heated on a water bath for about 15 min and after cooling colourless needle-shaped crystals, m.p. 72–73°, were obtained from dilute alcohol. The crystals were completely dried in vacuum and used for spectral studies.

Photodegradation and Separation of 2,5-Diphenyl-3,4-dimethyltetrahydrooxazole. A 1% aqueous solution of ephedrine base was placed in a beaker and directly exposed to UV light, (30 W Phillips UV tube fixed at a distance of 30 cm), in a dark chamber. The solution changed through yellow to brown colour with the simultaneous formation of colourless needle-shaped crystals and subsequent disappearance resulting in a more intense brown solution. The colourless needle-shaped crystals so formed were separated from the coloured solution, washed with dilute alcohol to remove any traces of colour and finally dried in vacuum.

The confirmation of the identity of the colourless needle-shaped crystalline photoproduct with the

authentic laboratory-prepared specimen was achieved by mixed melting point determination and comparison of the IR spectra.

Determination of Spectra of the Photoproduct and 2,5-Diphenyl-3,4-Dimethyltetrahydrooxazole. IR spectra were determined in KBr disc, and UV in EtOH on the Hitachi recording spectrometer. NMR spectra were recorded on Varian A-60 spectrometer in CDCl₃ and mass spectra on Hitachi RMU-6 mass spectrometer.

Results and Discussion

Schmidt³ showed that ephedrine base on reaction with benzaldehyde forms colourless needle-shaped crystals of benzalephedrine which on the basis of chemical studies were identified as 2,5-diphenyl-3,4-dimethyltetrahydrooxazole (Fig. 1). So far no physicochemical studies have been reported to confirm the structure of 2,5-diphenyl-3,4-dimethyltetrahydrooxazole.

2,5-Diphenyl-3,4-dimethyltetrahydrooxazole was prepared according to the method of Schmidt and the various spectra were determined (Table 1.) In the UV spectrum the band at 258 nm was attributed to B-bands ($\pi \rightarrow \pi^*$) of benzene rings. The IR spectrum shows the characteristic bands of monosubstituted phenyl group. In NMR spectrum the assignment of all the protons is shown in Table 1. The spin-spin coupling constant (J) of the vicinal two protons H(4) and H(5) is about 8.0 Hz. On the basis of Karplus equation, this J value implies *cis*-configuration of the vicinal two protons. However, there may not be justification for the application of Karplus equation to the oxazolidine ring. The NMR spectrum proves that the prepared samples contain small amounts of stereoisomeric impurity. Mass spectrum shows that 2,5-diphenyl-3,4-dimethyltetrahydrooxazole (2,5-diphenyl-3,4-dimethyltetrahydrooxazolidine) exhibits M-1 ion peak at m/e 252 instead of M⁺ (molecular) ion peak, because M-1 ion appeared by loss of one atom of hydrogen is more stable than intact M⁺ ion. The intense peaks at m/e 105, 146 and 147 in the mass spectrum are explained in Fig. 2.

All these spectral data indicate that the sample prepared according to the method of Schmidt³ has the structure of 2,5-diphenyl-3,4-dimethyltetrahydrooxazole.

The formation of colourless needle-shaped crystalline photoproduct on UV irradiation of the aqueous solution of ephedrine base and its disappearance on continued irradiation in the solution as well as the identification of the photoproduct as 2,5-diphenyl-3,4-dimethyltetrahydrooxazole, suggest that the later compound plays an intermediary role in the

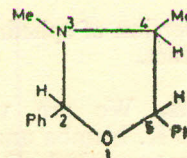


Fig. 1.

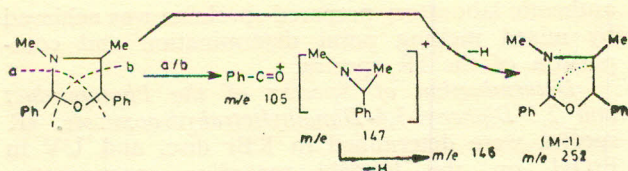


Fig. 2.

TABLE 1. SPECTRAL CHARACTERISTICS OF 2, 5-DIPHENYL-3, 4-DIMETHYL-TETRAHYDROXAZOLE.

UV EtOH λ_{max} nm(log ϵ)	IR KBr ν_{max} cm $^{-1}$	NMR δ p.p.m.(CDCl $_3$)	Mass m/c
258 (2.651)	1825	C(4)-Me 0.78 (3H, doublet; J=6.7 Hz)	252 (M $^{+}$)
251.5 (2.565)	1900	N(3)-Me 2.16 (3H, singlet)	147 (M $^{+}$ -105)
264 (2.530)	1970	C(4)-H 2.98 (1H, ABq; J=6.7-8.0 Hz)	146 (M $^{+}$ -106)
267 (2.354) Shoulder	1996	C(2)-H 4.71 (1H, singlet)	105 (M $^{+}$ -147)
	Monosubstituted phenyl groups	C(5)-H 5.16 (1H, doublet; J=8.0 Hz)	
		C $_6$ H $_5$ (2, 5) 7.28-7.70 (10H, multiplet)	
		Integrated intensity ratio : 3 : 3 : 1 : 1 : 1 : 10	

photochemical conversion of ephedrine to the final coloured photoproduct.

Acknowledgements. We are very grateful to Dr. H. Kaneko, Mr. K. Namba and Mr. S. Naruto of Dainippon Pharmaceutical Co. Ltd., Osaka

(Japan) for the determination of spectra and for helpful suggestions.

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Pakistan J. Sci. Ind. Res., Vo. 18, No. 5, October 1975

IMPORTANT INSECT PESTS OF SUMMER LEGUMES IN THE PUNJAB*

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(Received November 7, 1974; revised September 10, 1975)

The edible legumes are well known for their importance as human food due to their high protein contents and as additives of soil fertility through nitrogen fixation. In order to supplement animal protein with plant protein components, efforts are underway to improve the yields of pulse crops in Pakistan. But a heavy toll is taken by insect pests. As a modest beginning, the present investigation was initiated to identify the insect pest problems of summer-edible legumes viz., 'mungbean' (*Vigna radiata*), 'urdbean' (*V. mungo*), 'mothbean' (*V. aconitifolia*), cowpea (*V. unguiculata*) and soyabean (*Glycine max*) grown in the Punjab province during the summers of 1973 and 1974.

As a result of the surveys carried throughout pulse growing areas of the Punjab and the regular observations made at the University of Agriculture, Lyallpur, the following insect pests were mainly found infesting these legumes: whiteflies (Homoptera; Aleyrodidae), *Bemisia tabaci* Genn; aphids (Homoptera; Aphididae) (a) *Aphis craccivora* Koch, (b) *Acyrtosiphon pisum* (Harris); leafhoppers (Homoptera; Cicadellidae), *Empoasca devastans* Dist. and others; thrips (Thysanoptera; Thripidae), (a) *Caliothrips indicus* (Bagnall) (b) *Thrips tabaci* Lind; surface grasshoppers (Orthoptera; Acrididae) (a) *Chrotogonus* spp., (b) *Aiolopus* spp., (c) *Acrida* spp., (d) *Atractomorpha* spp., and storage pulse beetles (Coleoptera; Bruchidae), (a) *Callosobruchus maculatus* (F.) (b) *Callosobruchus analis* (F.), (c) *Callosobruchus chinensis* (L).

*Research supported in Part by funds, provided by the U.S. Department of Agriculture A.R.S., under a PL-480 grant FG-PA-175

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From the above list, 3 insects viz., *A. craccivora*, *A. pisum* and *C. indicus* were recorded for the first time in Pakistan.

The cotton whitefly, *B. tabaci*, ranks as the most destructive pest of pulse crops because it acts as a vector of yellow mosaic virus affecting 'urdbean', 'mungbean' 'mothbean' and soyabean in Pakistan.¹ Both the aphid species, although not very devastating at present, must be given serious attention as they have the potential to become very important pests as well as vectors of legume viruses. In Iran, these two aphids have been found associated with the transmission of serious viruses of pulse crops.² Leafhoppers, although infested all the summer legumes, were most destructive to cowpeas, which can be attributed to less hair on the leaf surface of cowpeas. Due to their severe feeding, a characteristic toxicogenic effect was discernible in the field in the form of curling, downward cupping, vein clearing, chlorosis and yellowing of cowpea leaves. Similar disease-like injury caused by leaf-

hoppers has long been reported in legumes.^{3,4} *C. indicus* was very serious in the seedling stage during August. As much as 67% loss in the yield of pea crop has been recorded due to its infestation at Indore, India.⁵ It was interesting to note that the eggs laid by bruchids on the mature pods and grains of partially opened pods in the field provided an inherent source of initial infestation in the store.

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