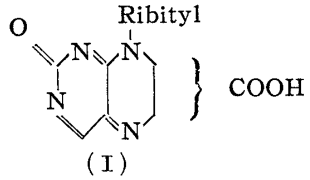
Communications to the Editor

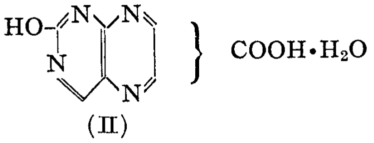
UDC 547.854.1'861.1 : 582.284

Structure of V-Compound produced by *Eremothecium Ashbyii*

In a paper published earlier,[1] the writers assigned the structures (I) and (II) respectively, to the V-compound and its photodecomposition product based on the results of various experiments.



(I)
V-Compound

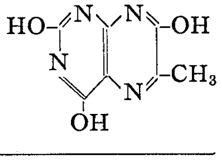


(II)
Photodecomposition product

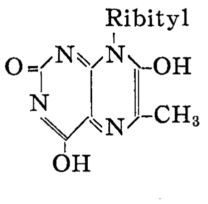
The photodecomposition product does not agree with 2,4-dihydroxypteridine-6-carboxylic acid or -7-carboxylic acid in ultraviolet spectrum, decomposition point, or distance of migration in paper ionophoresis.

If the photodecomposition product is assumed to have the above structure, it must be oxidized by potassium permanganate to 2,4-dihydroxypteridinecarboxylic acid, for in this case the 4-position of the pteridine ring would be oxidized as stated by Brown *et al.*,[2] but the result of the experiment was negative. On the other hand, while 2,4,7-trihydroxypteridine-6-acetic acid and -6-carboxylic acid are decarboxylated only on heating at 280°,[3] and 2,4-dihydroxypteridine-6-carboxylic acid is also readily decarboxylated on boiling with copper powder in quinoline, the photodecomposition product is not affected in the least by either method. From these negative results the authors hesitated to draw a definite conclusion about the structure of the photodecomposition product. However, the same result obtained by repeated experiments made the existence of a carboxyl group in this compound doubtful, and moreover since existence of a hydroxyl group at the 4-position became obvious from the fact that the compound forms a chelate compound with Cu^{2+}, the idea that it may be a trihydroxyl compound came to gain ground.

Therefore a comparison was made between the photodecomposition product and 2,4,7-trihydroxy-6-methylpteridine, prepared by the condensation of 2,4-dihydroxy-5,6-diaminopyrimidine with pyruvic acid at pH 5 in the presence of hydrazine, and it was observed that they are in complete agreement in ultraviolet and infrared spectra, and in Rf value in paper chromatography obtained with various solvent systems. In addition, they give the same decomposition point, color of fluorescence, behavior to sodium hydrogen carbonate solution, distance of migration in paper ionophoresis, and color reaction with silver nitrate. The photodecomposition product was also compared with its isomer, 2,4,6-trihydroxy-7-methylpteridine, but they were different



(III)



(IV)

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[1] T. Masuda, T. Kishi, M. Asai : This Bulletin, **5**, 598(1957).
[2] D. J. Brown, S. F. Mason : J. Chem. Soc., **1956**, 3443.
[3] R. Tschesche, F. Korte : Chem. Ber., **84**, 801(1951).

in various properties. From these results the structure of the photodecomposition product was established as 2,4,7-trihydroxy-6-methylpteridine (III) and consequently it is more likely that the V compound has the structure (IV).

The writers wish to express their grateful thanks to Prof. A. Albert, who recently visited this laboratory and gave valuable advices. Incidentally, the present work was reported by S. Kuwada, who is a member in charge of this series, at the Vitamin Commitee meeting held on December 7, 1957.

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Characteristic Infrared Absorption Band of Organic Sulfate Esters

Oragnic sulfate esters are being taken up with increasing interest in medicine, biochemistry, and other fields but their characteristic absorption bands in the infrared region have not been clarified as yet.

The present writer measured the infrared absorption spectrum of monopotassium methyl sulfate in the region of 4000～350 cm^{-1}. By the consideration of Raman spectral data for alkyl sulfites of Simon and others,[1] the absorptions at 1252 and 1215 cm^{-1} were assigned to $\nu(\mathrm{SO})_{\mathrm{deg.}}$, at 1183 and 1156 cm^{-1} to $\rho(\mathrm{CH}_3)$. at 1063 cm^{-1} to $\nu(\mathrm{SO})_{\mathrm{sym.}}$, at 1022 to $\nu(\mathrm{CO})$, at 750 cm^{-1} to $\nu(\mathrm{S}\overset{|}{\mathrm{O}})$ of $\mathrm{S{-}\overset{|}{O}{-}C}$ bond, at 617 cm^{-1} to $\delta(\mathrm{SO})$, at 576 and 562 cm^{-1} to $\delta(\mathrm{SO})_{\mathrm{deg.}}$, and that at 440 cm^{-1} to $\delta(\mathrm{OSO})$.

Further, infrared absorption spectra of monopotassium salts of ethyl, butyl, propyl, isopropyl, isoamyl, cyclohexyl,. benzyl, *p*-cresyl, and *p*-nitrophenyl sulfates were compared with the absorption of corresponding alcohols and phenols, and it was confirmed that the characteristic absorption bands of organic sulfate monoesters appeared at 1240～1260 $\mathrm{cm}^{-1}(\nu_{\mathrm{S\text{-}O}})_{\mathrm{deg.}}$, 1200～1220 $\mathrm{cm}^{-1}(\nu_{\mathrm{SO}})_{\mathrm{deg.}}$, 1040～1070 $\mathrm{cm}^{-1}(\nu_{\mathrm{SO}})$, 750～800 $\mathrm{cm}^{-1}(\nu_{\mathrm{SOC}})$, 615～650 $\mathrm{cm}^{-1}(\delta_{\mathrm{SO}})_{\mathrm{sym.}}$, and at 550～590 $\mathrm{cm}^{-1}(\delta_{\mathrm{SO}})_{\mathrm{deg.}}$(two bands).

Infrared absorption spectra in the region of 4000～350 cm^{-1} were also measured of sulfate esters of polysaccharides such as those of glucose, cellulose, hydroxycellulose, starch, and of heparin, charoninsulfuric acid, and chondroitinsulfuric acid. The presence of an organic sulfate monoesters in the urine, as a result of detoxication, was also detected by spectral measurements. Detailed reports on this work will be published in the near future.

The writer expresses his deep gratitude to Prof. S. Shibata and Dr. M. Ishimoto for their encouragement during this work, and to Mr. T. Omura, Drs. K. Nakanishi, T. Sato, and H. Terayama, and to Miss N. Takahashi for the donation of samples. The present work is being financed by the Grant in Aid for Scientific Research from the Ministry of Education which is gratefully acknowledged.

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[1] A. Simon, H. Kriegsmann : Chem. Ber., **89**, 1718, *et seq.* (1956).