*NMR Spectra of the Metabolites of Monascus. III. Monascoflavin and Reduction Products**

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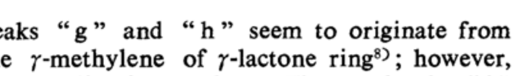
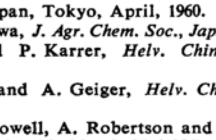
The structure of monascoflavin¹⁾, $C_{21}H_{26}O_5$, m. p. 143°C, the yellow metabolite of *Monascus purpureus Wentii* has still not been elucidated. Its chemical properties showed that it was related to γ-pyrones²⁾, and the close relationship with monascorubrin has also been suggested³⁾; structure I was provisionally proposed in 1959 as a working hypothesis⁴⁾. The NMR spectra of I, dihydro-I, hexahydro-I, and octahydro-I⁵⁾ have been measured with a Varian V-4300 model Spectrometer at 56.4 Mc, in order to correlate the chemical transformations with appropriate changes in the spectra (Figs. 1—4) and thus gain an insight into its structure. Chloroform was employed as an inner reference, and toluene was used for calculating line separation. Unlike monascorubrin⁶⁾, the present monascoflavin showed no peak in the -30 cps region corresponding to the α-hydrogen of γ-pyrones⁷⁾. Instead of the "d" doublet (J: 6 cps, area for three protons) and the weak "k" multiplet in Fig. 1, the spectrum of II revealed a triplet "l" (J: 8 cps); this can be ascribed to the hydrogenation of the propenyl side-chain. The "a" and "b" peaks arise from the methyl and methylene groups, respectively, of the n-C_5H_{11} side-chain. The peaks at "c" is due to an uncoupled methyl group, and peaks "i" and "j" (Figs. 1 and 2) suggest that three protons attached to an unsaturated system are present besides the propenyl group. In Fig. 3, only a diffuse absorption "i" is left in this region; instead there appears two ill-defined peaks "m" and "n" which could be assigned to protons attached to α-carbons of an ethereal linkage. The hydrogenation stages can be represented by the following scheme:



(I) (II) (III)

Peaks "g" and "h" seem to originate from the γ-methylene of γ-lactone ring⁸⁾; however, the coupling is not clear. The quadraplet "i" (Figs. 1 and 2) seems to arise from an AB type of coupling (J: 10 cps) and is absent in Fig. 3. Although it is apparent that the quadraplet is



(I)

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* Presented at the 13th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1960.

1) A. Nishikawa, *J. Agr. Chem. Soc., Japan*, **8**, 1007 (1932); H. Salomon and P. Karrer, *Helv. Chim. Acta*, **15**, 18 (1931).

2) P. Karrer and A. Geiger, *Helv. Chim. Acta*, **25**, 289 (1941).

3) A. D. G. Powell, A. Robertson and W. B. Whalley, *Chem. Soc. Special Publ.*, No. 5, 27 (1956).

4) K. Nakanishi, M. Ohashi, A. Terahara, S. Kumasaki, S. Yamamura, Y. Hirata and H. Koike, the 3rd Symposium on the Organic Chemistry of Natural Products, Tokyo, 1959, Abstract, p. 55.

5) Chemical and spectroscopic results indicate that this is not a straight-forward reduction product. Accordingly, the spectrum will not be discussed at present.

6) Part II of this series.

7) Part I of this series.

8) L. M. Jackman, "Applications of NMR Spectroscopy in Organic Chemistry", Pergamon Press, London (1959), p. 55.

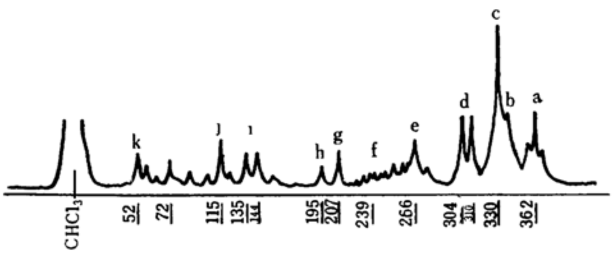


Fig. 1. Monascoflavin.

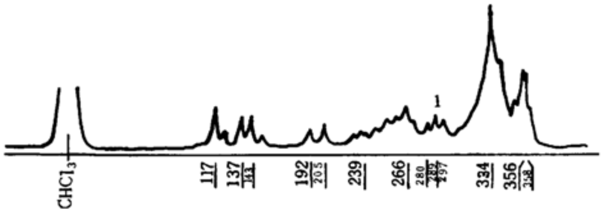


Fig. 2. Dihydromonascoflavin.

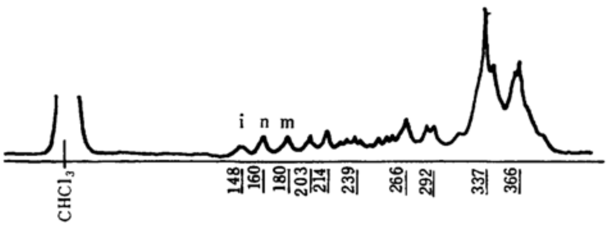


Fig. 3. Hexahydromonascoflavin.

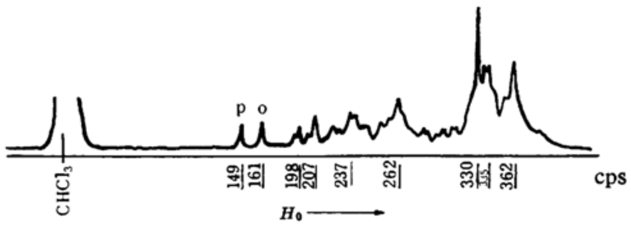
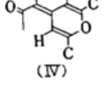
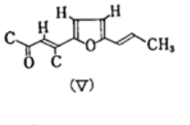


Fig. 4. " Octahydromonascoflavin ".

due to protons on an unsaturated system, it is questionable that any two protons shown in the partial structure IV should couple so extensively.



(IV)



(V)

Structure V appears to be more appropriate to account for the coupling but this, in turn, can not be reconciled with ultraviolet spectral data[4]. Model compounds are being synthesized in order to check this point further. Peak "e" is presumably due to the $-COCH_2-$ protons but the reason that it is not split into a triplet is not clear. The diffuse "f" signal could arise from the bridgehead proton(s) of the β-keto-γ-lactone moiety.

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