## SHORT COMMUNICATIONS

# *NMR Spectra of the Metabolites of Monascus. I. NMR Spectra of Several Authentic Pyrones**

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As with the C-2 and C-5 protons of furans1) it may be expected that the protons alpha to the pyronoid oxygen will absorb at characteristically low frequencies and thus assist in the identification of the substitution pattern, which is not so facile by other physico-chemical methods. A Varian model V-4300 spectrometer was employedat 56.4 Mc; the band separations were estimated from the toluene peaks and chloroform was used as internal reference. The measurements were carried out in 10~20 percent solutions of 1 : 1 mixtures of chloroform and carbon tetrachloride. The results are summarized in Table I2). It can be seen qualitatively that the $\alpha$-protons of both $\alpha$- and $\gamma$-pyrones absorb at lower fields than the chloroform proton, and that they can be clearly differentiated from the other unsaturated protons. The coupling constant of the $\alpha$- and $\beta$-protons, ca. 6 cps, is larger than the 1.3 cps value reported for furans3). The C-2 and C-6 methyl groups absorb in the range of 280~300 cps (II, III and VII). One of the nuclear protons of the extended pyronoid compound VII had its peak at an exceptionally low field, and this interesting phenomenon is presumably caused by the strong long range shielding effect of the nearby nitrile group. It is to be noted that this shift is opposite to that encountered in the well-known acetylenic protons4) and this can be attributed to the directional difference of the triple bond5). Citrinin has been chosen

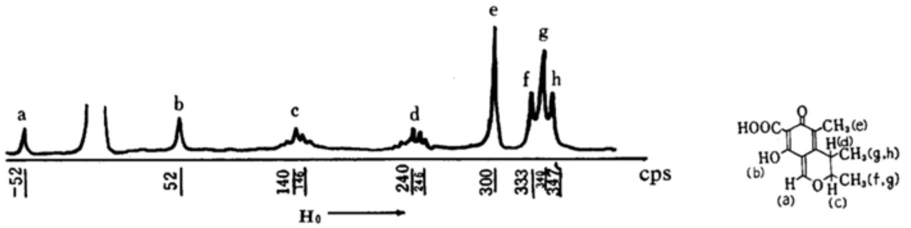
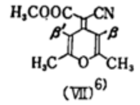


Fig. 1. NMR spectra of citrinin.

TABLE I. NMR SPECTRA OF PYRONES

| Compound | $\alpha$-H | $\beta$-H | Other H |
|---|---|---|---|
| $\gamma$-Pyrone(I) | −15, −9 | 71, 76 | |
| 2,6-Dimethyl-$\gamma$-pyrone(II) | | 73 | 289 ($CH_3$) |
| 2-Methoxy-6-methyl-$\gamma$-pyrone(III) | | 87, 116 | 205 ($OCH_3$), 294 ($CH_3$) |
| 2,6-Dimethoxycarbonyl-$\gamma$-pyrone(IV) | | 12 | 188 ($OCH_3$) |
| $\alpha$-Pyrone(V) | −15 | 53, 60 | |
| 6-Methoxycarbonyl-$\alpha$-pyrone(VI) | | 12 | 194 ($OCH_3$) |
|  (VII)6) | | −42, 52 | 200 ($OCH_3$), 284 ($CH_3$) |

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1) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, 37, 1056 (1959).

2) No corrections for the bulk susceptibilities were carried out.

3) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance", McGraw-Hill Book Company, New York (1959), p. 193.

4) We are grateful to Dr. N. Nakagawa, University of Electro-Communications, for this explanation.

5) L. M. Jackman, "Applications of NMR Spectroscopy in Organic Chemistry", Pergamon Press, London (1959), p. 114.

6) M. Ohta and H. Kato, This Bulletin, 32, 707 (1959).

as an appropriate model to clarify the spectra of the more complicated natural products, and its spectrum is analyzed in Fig. 1. The qualitative results obtained from the spectra of the pyrones are hoped to assist in handling related compounds.

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