

The measurements were carried out with a Varian V-4300 High Resolution Spectrometer operating at 40 Mc; chloroform was chosen as the inner reference and the band positions were read by the side-band method. It is seen in Fig. 1 that instead of the doublet "d" and "e" (propenyl methyl) and multiplet around "g", the spectrum of the dihydro-compound (Fig. 2) shows a triplet "j" which corresponds to the α -methylene of the propyl chain. Signals "a" and "b" are due to the n -alkyl chain and "c" arises from an uncoupled methyl group. Signal "i" corresponds in position to a proton adjacent to the pyronoid oxygen⁴⁾ and this is supported by chemical evidence¹⁾. The other two low-field signals, "g" and "h", undoubtedly arise from the remaining two nuclear protons. The shape and intensity of signal "f" is similar to "j" which has been assigned to a methylene group, and therefore in structure II it could be correlated with the $-\text{CH}_2\text{CO}-$ protons of the $n\text{-C}_7\text{H}_{15}\text{CO}-$ side-chain. On the other hand, in structure I the $-\text{CH}_2\text{CO}-$ protons belong to the ABX type and thus a complicated pattern would be expected. The signal for the bridgehead proton of the ethereal ring in I can not be detected in the expected 100~200 cps region, but this could be due to extensive coupling with adjacent protons. The coupling of signals "h" and "i" (ca. 1.2 cps) presumably correspond to that observed between meta-oriented protons on benzene nuclei⁵⁾. Thus, although no clear-cut differentiation between structures I and II is possible, the present measurements appear to be slightly in favor of the latter; however, chemical and ultraviolet spectroscopic evidence can be accounted for more smoothly

NMR Spectra of the Metabolites of *Monascus*.

II. Monascorubrin*

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Structures I¹⁾ and II²⁾ have been tentatively proposed for monascorubrin³⁾, $\text{C}_{23}\text{H}_{26}\text{O}_5$, the orange pigment produced by *Monascus purpureus* Wentii. The NMR spectra of monascorubrin and dihydromonascorubrin have been measured in order to check the gross character of this complicated pigment, and if possible to differentiate between the two structures.

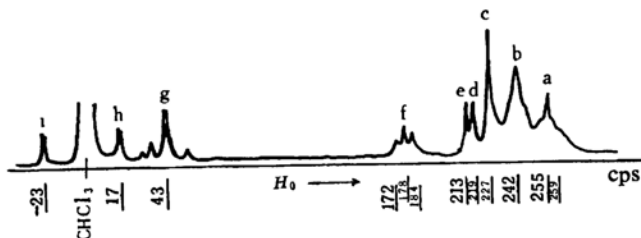


Fig. 1. Monascorubrin.

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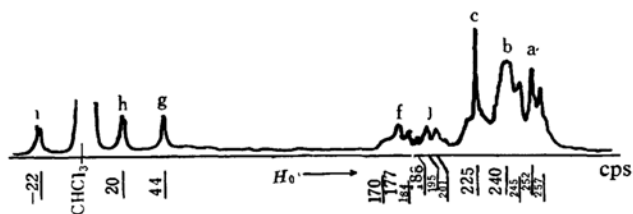


Fig. 2. Dihydromonascorubin.

by structure I and this point will be reported shortly.

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