

THE IDENTIFICATION OF *TRANS*-4-KETOHEX-2-ENAL BY ITS PROTON MAGNETIC RESONANCE SPECTRUM*

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The defensive secretions of a number of insects are known to contain a hitherto unidentified dicarbonyl compound. This substance was isolated by gas chromatography from the contents of the scent reservoir of the green vegetable bug, *Nezara viridula* (L.), as part of a comprehensive investigation of the chemical composition of the scent of that insect.¹ The ultraviolet and infrared absorption spectra and the mass spectrum of the compound¹ were consistent with it being *trans*-4-ketohex-2-enal but they did not constitute unambiguous proof of this structure. The proton magnetic resonance spectrum presented here shows that the compound is *trans*-4-ketohex-2-enal. The spectrum is of special interest because it illustrates an unusual interaction between some of the protons.

The proton magnetic resonance spectrum of the compound is illustrated in Figure 1. This shows a triplet of three-proton intensity centred at 1.17 p.p.m. and a quartet of two-proton intensity centred at 2.74 p.p.m. These have equal spacings of 7.3 c/s and are assigned to an ethyl ketone group. Less straightforward are the multiplets centred at 6.78 p.p.m. (two-proton intensity) and at 9.85 p.p.m. (one-proton intensity) assigned to olefinic and aldehydic protons respectively. The multiplicities of these signals do not lend themselves to first-order analysis. In fact they form an example of the so-called deceptive spectra,^{2,3} with the unexpected multiplicity of the aldehydic resonance due to virtual coupling.⁴ However, the line positions and intensities were matched satisfactorily by a computed spectrum (shown in Fig. 1, inset) calculated using the parameters shown in the legend to Figure 1. Since the root mean square deviation between the computed and the observed lines in the spectra is 0.097 c/s, it is suggested that the assignment is correct. This conclusion is further supported by the fact that the two weak lines resembling side bands in the computed spectrum of the vinylic protons can be distinguished in the observed spectrum.

The assignment of the vinylic resonances at 6.89 p.p.m. to the proton labelled A in Figure 1 rests upon the relative magnitudes of the vicinal and allylic coupling constants. It is interesting that the latter (J_{BX}) is negligible, as noted previously for

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¹ Gilby, A. R., and Waterhouse, D. F., unpublished data.

² Abraham, R. J., and Bernstein, H. J., *Canad. J. Chem.*, 1961, **39**, 216.

³ Anet, F. A. L., *Canad. J. Chem.*, 1961, **39**, 2262.

⁴ Musher, J. I., and Corey, E. J., *Tetrahedron*, 1962, **18**, 791.

other α,β -unsaturated aldehydes.⁵ The magnitude of the coupling between olefinic protons (J_{AB}) proves unequivocally that they are in a *trans* configuration.⁶

There appear to be no previous literature references to *trans*-4-ketohex-2-enal. Clauson-Kaas and Limborg⁷ isolated the lower homologue, 4-ketopent-2-enal, but not in a pure form.

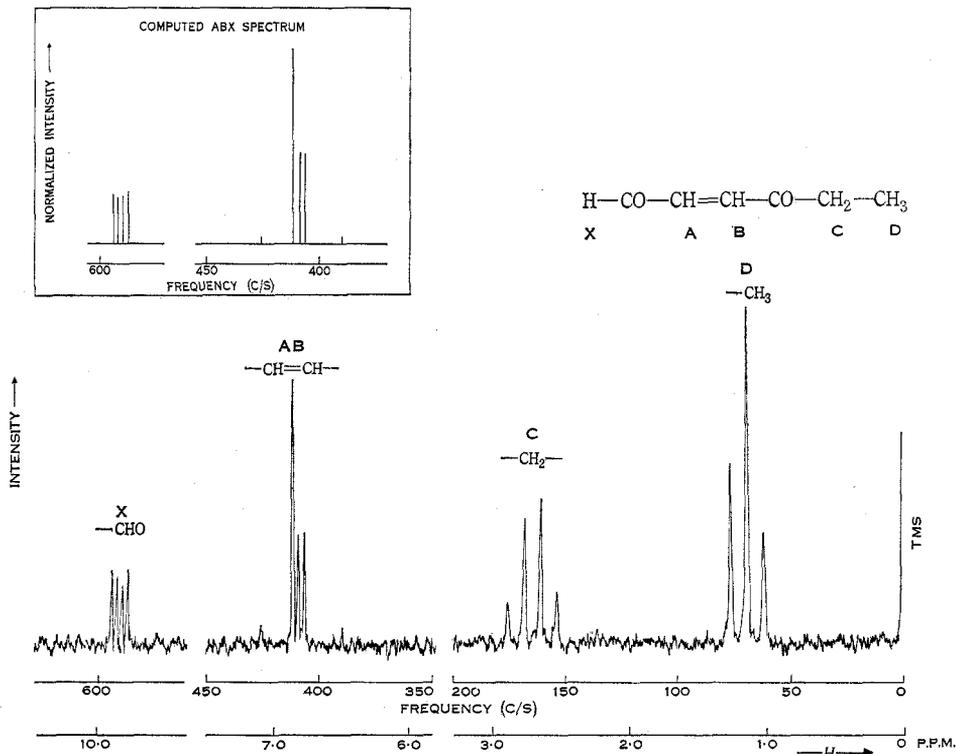


Fig. 1.—60 Mc/s proton magnetic resonance spectrum of *trans*-4-ketohex-2-enal in carbon tetrachloride. The computed spectrum (inset) with the following parameters: δ_X 9.85, δ_A 6.89, δ_B 6.78 p.p.m., J_{AB} 16.62, J_{AX} 7.14, J_{BX} 0.04 c/s, was obtained by an iterative technique.

Experimental

The contents of the scent glands of *Nezara viridula* adults were collected as in other work.¹ The compound identified as *trans*-4-ketohex-2-enal was separated and trapped by gas chromatography on a preparative Pye Argon Chromatograph. On a 1 by 120 cm column of 10% Apiezon L on Celite it had a retention time of 20.5 min at 100° with an argon flow of 50 ml/min.

The proton magnetic resonance spectrum was obtained on a Varian A60 spectrophotometer with an approximately 1% solution in carbon tetrachloride. Chemical shifts are quoted from tetramethylsilane as internal standard.

⁵ Sternhell, S., *Rev. Pure Appl. Chem.*, 1964, **14**, 15.

⁶ Jackman, L. M., "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," p. 85. (Pergamon Press: London 1959.)

⁷ Clauson-Kaas, N., and Limborg, F., *Acta Chem. Scand.*, 1947, **1**, 619.

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