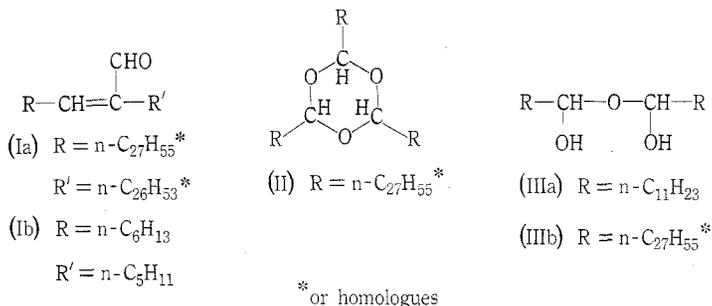


THE LONG-CHAIN ALDEHYDES OF SUGAR-CANE WAX*

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In an earlier study¹ of sugar-cane wax it was shown that about 85% of the wax could be readily distilled at low pressure. The distillate contained approximately 40% of long-chain aldehydes, n-octacosanal with higher and lower homologues, which were separated as sparingly soluble semicarbazones from the rest of the distillate. Infrared spectra indicated that free aldehydes were present in solutions of sugar-cane wax in chloroform, and, when the wax was heated with ethanolic potassium hydroxide under normal saponification conditions, a major product was thought to be the unsaturated aldehyde (Ia), produced by aldol condensation.



* or homologues

It was difficult, however, to obtain evidence regarding the form in which the aldehydes were present in the wax before distillation, and to establish beyond doubt that they were not artefacts arising from decomposition of more complex compounds. The low solubility of the wax in chloroform made it difficult to obtain quantitative spectroscopic estimates of the free aldehydes. Because of the instability of free aldehydes it was suggested that they probably occurred in the wax as a trioxan (II) or in some other polymeric form, thus being less susceptible to oxidation and decomposition on the plant surface and during the isolation of the wax. However, this suggestion was based on analogy with the structure then favoured for the polymeric form of dodecanal rather than on direct evidence. The recent demonstration by Klass *et al.*² that dodecanal in the presence of water exists not as a trioxan or other polymer but as a stable hemihydrate (IIIa), which readily dissociates into free aldehyde on melting or dissolving in benzene, suggests that the aldehydes of sugar-cane wax might have a similar hemihydrate structure (IIIb), or possibly a more highly polymeric structure of this type. Such ease of conversion into free aldehyde in solvents seemed to be consistent with the observed properties of sugar-cane wax and it may be that the aldehydes originally existed in the hemihydrate form (IIIb) on the plant but were wholly or partially converted into free aldehydes in the course of extraction with solvents.

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¹ Lamberton, J. A., and Redcliffe, A. H., *Aust J. Chem.*, 1960, **13**, 261.

² Klass, D. L., Jensen, W. N., Blair, J. S., and Martinek, T. W., *J. Org. Chem.*, 1963, **28**, 3029.

It has now been possible to obtain more direct and conclusive evidence for the presence of free aldehydes in solutions of sugar-cane wax from the n.m.r. spectra of solutions in deuteriochloroform, measured at 60° so that high concentrations could be obtained. The spectrum of the whole wax measured immediately after solution had occurred showed a clearly defined triplet, typical of aldehydic CHO, at δ 9.76. No significant amount of trioxan was present, as there were no discernible peaks in the region of the spectrum where the signals of trioxan ring protons might be expected to occur, from analogy with the published spectrum of paraldehyde³ which shows a quartet at δ 5.05. The n.m.r. spectrum of freshly distilled sugar-cane wax, known to contain at least 40% of long-chain aldehydes, also showed a distinct triplet at δ 9.76. The relative intensities of the CHO triplet with respect to other peaks and to the chloroform peak at δ 7.31 were similar in the spectra of distilled and undistilled wax. There may have been a slightly higher proportion of free aldehydes in the distilled wax, but the difference was so small that it could be explained by the fact that 15% of the wax, consisting largely of non-aldehydic material, did not distil. Preparation of semicarbazones directly from the undistilled wax in approximately 45% yield has now confirmed that the amount of aldehydes in both distilled and undistilled wax is similar.

Curtin *et al.*⁴ noted the usefulness of n.m.r. spectra in distinguishing between the semicarbazones of aldehydes and ketones, and they reported chemical shifts measured in methylene chloride solutions for these compounds. In agreement with their findings the spectra of the semicarbazones from sugar-cane wax, measured in CDCl₃ at 60° to obtain a concentrated solution, were characterized by a triplet at δ 7.12 (—CH=N—), and by a broad singlet at δ 8.97 (=N—NH—), which was downfield with respect to the corresponding peak in the spectra of ketone semicarbazones (δ 7.91 in the spectrum of the semicarbazone of methyl n-heptadecyl ketone). Semicarbazones of methyl ketones showed a sharp peak due to CH₃—C=N—, which occurred at δ 1.82 in the spectrum of the semicarbazone of methyl n-heptadecyl ketone, for example, while semicarbazones of both aldehydes and ketones showed a broad two-proton peak at about δ 5.55, attributed to —CO—NH₂. The n.m.r. spectra of the semicarbazones prepared from both sugar-cane wax and distilled sugar-cane wax were closely similar, and showed that the semicarbazones were derived from aldehydes, with no detectable amount from ketones.

Good evidence has thus been obtained for the presence in solutions of sugar-cane wax of an amount of free aldehydes comparable with that found in solutions of freshly distilled wax, showing that the wax consisted either of free aldehyde or more probably of an aldehyde hemihydrate which dissociates readily in solution.

The n.m.r. spectrum, also measured at 60°, of the "unsaponifiable fraction" obtained by heating sugar-cane wax with ethanolic potassium hydroxide provided conclusive evidence for the structure of the major product. The spectrum showed a sharp singlet at δ 9.27, assigned to the CHO group of the unsaturated aldehyde (Ia), and a well-defined triplet at δ 6.38 assigned to the single proton of the α,β

³ Bhacca, N. S., Hollis, D. P., Johnson, L. F., and Pier, E. A., "High Resolution NMR Spectra Catalog." Vol. 2, spectrum No. 474. (Varian Associates: Palo Alto, Cal., 1963.)

⁴ Curtin, D. Y., Gourse, J. A., Richardson, W. H., and Rinehart, K. L., *J. Org. Chem.*, 1959, **24**, 93.

double bond. This assignment was shown to be correct by comparison with the n.m.r. spectrum of the unsaturated aldehyde (Ib), prepared from n-heptanal, which showed a one-proton singlet at δ 9.35 and a one-proton triplet at δ 6.42. A similar spectrum was also obtained at 60° for a fraction previously isolated⁵ from a sugar-cane wax extracted from sugar mill filter "mud" and refined by solvent fractionation, showing that this fraction also consists essentially of the unsaturated aldehyde (Ib). This structure was suggested previously on the basis of spectroscopic evidence then available, but the survival of unsaturated aldehydes of this type in sugar mill "mud" was somewhat surprising and it seemed desirable to investigate this point further.

Experimental

All n.m.r. spectra were measured in CDCl₃ solution at 60° on a Varian A60 spectrometer fitted with a variable temperature probe. Chemical shifts are relative to tetramethylsilane, δ 0.00.

Preparation of Aldehyde Semicarbazones from Undistilled Sugar-Cane Wax

Semicarbazide reagent, prepared from semicarbazide hydrochloride (1.5 g) and sodium acetate (1.5 g) in ethanol (50 ml), was filtered into a warm solution of sugar-cane wax (10 g) in a mixture of benzene (200 ml) and ethanol (200 ml). On cooling most of the wax crystallized out and was filtered, washed in turn with water and ethanol, and then dried. After repeated extraction of the filtered material with warm chloroform, crystalline semicarbazones (3.6 g), m.p. 110–112°, remained. A further quantity was obtained by chromatographing on alumina the material which had dissolved in chloroform. The semicarbazone fraction was only eluted by a warm chloroform/ethanol mixture, and after crystallization from chloroform this yielded crystalline semicarbazones (1.5 g, m.p. 107–110°).

⁵ Lamberton, J. A., and Redcliffe, A. H., *Aust. J. Appl. Sci.*, 1960, **11**, 473.