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Note

Laser-Raman spectroscopy of carbohydrate derivatives. The C=N absorption of some carbohydrate oximes[*][†]

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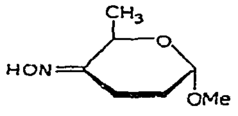
The C=N bond in organic molecules normally gives rise to a strong absorption band near 1660 cm^{-1} in the infrared spectrum, although this band is of only moderate intensity with certain oximes of aldehydes and ketones[2]. However, several oximes of sugar derivatives synthesized in this laboratory[1,3–7] have been found to exhibit negligible absorption in this region of their i.r. spectra, as determined by use of a simple i.r. spectrophotometer (see Fig. 1). These examples include methyl 2,3,6-trideoxy-α-D-*glycero*-hexopyranosid-4-ulose oxime[5] (**1**), 1,6-anhydro-2,3-*O*-isopropylidene-β-D-*lyxo*-hexopyranos-4-ulose oxime[3] (**2**), and 1,6-anhydro-4-*C*-formyl-2,3-*O*-isopropylidene-β-D-talopyranose oxime[1,6,7] (**3**). As the intensity of an absorption band in the i.r. spectrum is related to the extent of polarization of the bond, and is zero when the bond is not polarized, it had been proposed[5] that inductive effects of the substituents at each end of the C=N bond coincidentally give rise to little net polarization of the bond, so that absorption in the i.r. region is weak or absent with these oximes.



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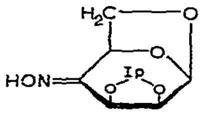

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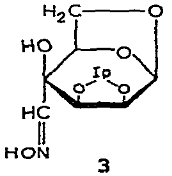

3

In the three examples noted (**1**, **2**, and **3**), there is little reason to suppose that these molecules have structures other than those given, as there is no possibility for intramolecular addition of hydroxyl groups to the double bond, and each compound shows a strong i.r. absorption band for the OH group. By use of a high-resolution,

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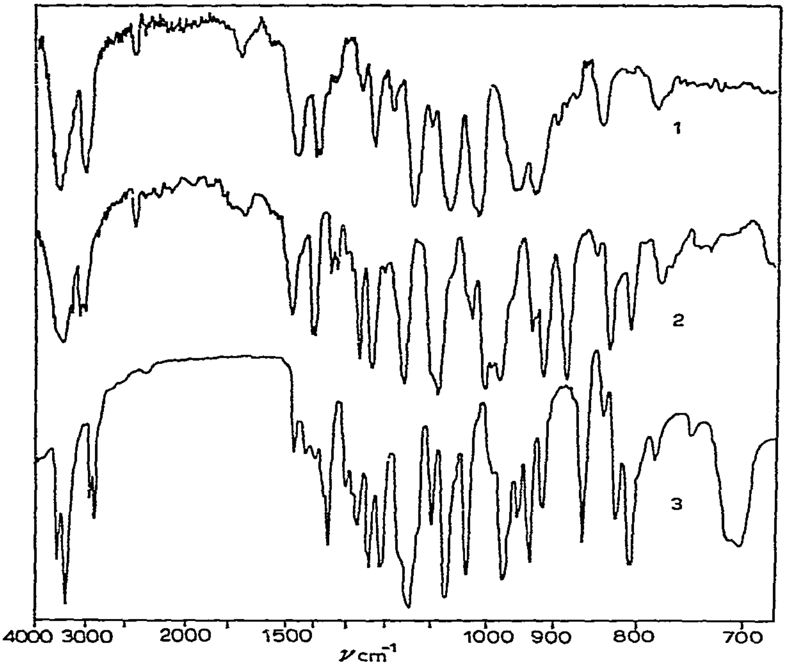

Fig. 1. The infrared spectra of methyl 2,3,6-trideoxy-α-D-*glycero*-hexopyranosid-4-ulose oxime (**1**) as a liquid film, 1,6-anhydro-2,3-*O*-isopropylidene-β-D-*lyxo*-hexopyranos-4-ulose oxime (**2**) as a KBr pellet, and 1,6-anhydro-4-*C*-formyl-2,3-*O*-isopropylidene-β-D-talopyranose oxime (**3**) as a KBr pellet (Perkin–Elmer 137 spectrophotometer).

i.r. spectrophotometer, it is possible to observe weak $C=N$ absorption near 1660 cm^{-1} for the oximes **1** and **3** (see Experimental). Because the vibrational transitions of electronically symmetrical bonds are inactive in the i.r., but give rise to strong absorptions in the Raman spectra, it is to be expected that the $C=N$ group of the oximes **1**, **2**, and **3** should be readily detectable by Raman spectroscopy. The present report confirms that this is the case.

The technique of Raman spectroscopy has, until recently, been restricted in its application because of severe experimental difficulties in obtaining sufficient scattered light, perpendicular to an incident light-beam, to permit accurate spectral measurements, especially with small samples of material[8]. Some early measurements by Raman spectroscopy have been made with free sugars[9] and with simple dioxolane derivatives related to carbohydrates[10], but no further applications of Raman spectroscopy to carbohydrates and their derivatives appear to have been reported. With the advent of Raman spectrometers equipped with a laser-beam light-source, it has become feasible to obtain well-resolved Raman spectra from small samples of complex organic compounds[8], and the technique has now been applied with the three oximes **1**, **2**, and **3**.

The i.r. spectrum of methyl 2,3,6-trideoxy-α-D-*glycero*-hexopyranosid-4-ulose oxime (**1**), as a liquid film (see Fig. 1), shows strong absorption maxima at

3390 cm^{-1} for the hydroxyl group and at 1385 and 1371 cm^{-1} for the C–CH_3 group, but there is negligible absorption near 1660 cm^{-1} for the C=N group. In contrast, the Raman spectrum of compound **1**, measured neat, shows a band of moderate intensity at $\Delta\nu$ 1665 cm^{-1}, indicative of the C=N group.

The other 4-oxime studied, namely, **2**, which is a crystalline *syn*, *anti* mixture, similarly shows strong hydroxyl absorption in its i.r. spectrum (see Fig. 1) at 3140 cm^{-1} and absorption for the CMe_2 group at 1380 cm^{-1}, but negligible C=N absorption. A strong C=N absorption in the Raman spectrum was observed, at $\Delta\nu$ 1648 cm^{-1}. The third oxime, **3**, gave data closely similar to those for compound **2**, with very weak i.r. absorption, but strong Raman absorption, for the C=N group. The i.r. and the Raman spectra for compounds **2** and **3** were obtained with solid samples.

The ease of obtaining Raman spectra by use of a laser-energized spectrometer suggests that Raman spectroscopy should be a useful tool, as a routine complement to i.r. spectroscopy, in structural studies of carbohydrates and their derivatives, especially in the study of functional groups containing multiple bonds. The structures of the oximes examined in the present study were not open to serious question, but there are numerous instances of carbohydrate derivatives for which it is possible to write tautomeric structures by intramolecular addition of a hydroxyl group to a C=N function, to give products no longer containing the C=N group. The absence of a strong absorption band for a C=N bond in the i.r. spectrum might indeed be taken as evidence for such a tautomeric structure; however, if based on i.r. spectroscopy alone, such an interpretation is clearly unsound, as shown by the present examples. The presence or absence of a C=N bond can, however, be firmly established if the complementary evidence from Raman spectroscopy is also available.

The technique of laser-Raman spectroscopy, used in conjunction with i.r. spectroscopy, should have considerable utility for gaining additional structural information for a wide range of carbohydrate derivatives containing alkene and imine groups, including numerous derivatives containing the azomethine (Schiff base) structure, as in hydrazones, osazones, and related derivatives.

EXPERIMENTAL

Raman spectra. — The spectra were measured with a Jarrell–Ash 25-300, Raman spectrometer equipped with a Spectra Physics Model 125A, 50 milliwatt, CW helium–neon laser operating at 632.8 nm, with detection of scattered light by means of a photomultiplier. Solid samples (10 mg) in glass capillary-tubes (0.9 mm inside diameter) were fused and allowed to resolidify. Liquid samples were examined neat in half-silvered, glass capillary-tubes. Spectra were obtained with a parallel-polarized, incident beam at a slit width of 6 cm^{-1} and the time constants of 2 sec for both solid and liquid samples. The liquid sample was measured at a scan speed of 50 $cm^{-1}.min^{-1}$, and the two solid samples were measured at a scan speed of 100 $cm^{-1}.min^{-1}$. An interference filter with a 10-nm band-pass was used to eliminate the He I emission line at $\Delta\nu$ 1650 cm^{-1} (706.6 nm).

I.r. spectra. — The spectra were recorded with Perkin–Elmer Models Nos. 137 and 457 i.r. spectrophotometers. Solid samples (~5 mg) were examined as pellets in potassium bromide, and liquid samples as films between sodium chloride plates. Qualitative peak intensities are given: m, moderate; s, strong; v, very; and w, weak.

Samples. — Methyl 2,3,6-trideoxy-α-D-*glycero*-hexopyranosid-4-ulose oxime (**1**) was a single isomeric form, prepared by the method of Albano and Horton[5] as a distilled liquid, b.p. 95–98° (bath)/0.1 torr, $[\alpha]_D$ +223° (chloroform). Raman spectrum: $\Delta\nu$ (neat) 1665 (moderate, C=N), 1701 cm^{-1} (weak). I.r. spectrum (see Fig. 1): ν_{max}^{film} (Model 457 spectrophotometer) 3390 vs (broad, OH); 2990 vs, 2945 vs, 2910 vs, 2840 vs (CH); 1661 vw (C=N); 1448 s; 1385 s, 1371 s (CMe_2); 1550 m (shoulder), 1325 w, 1312 w, 1250 m, 1216 s, 1172 m, 1130 vs, 1092 s, 1060 vs, 1009 vs, 946 vs, 920 vs, 891 s, 879 m, 864 m, 834 s, 774 m, 720 w, 684 s, and 647 m cm^{-1}.

1,6-Anhydro-2,3-*O*-isopropylidene-β-D-*lyxo*-hexopyranos-4-ulose oxime (**2**) was prepared, as described by Horton and Jewell[3], as a crystalline mixture of *syn* and *anti* isomers, m.p. 110–119°, $[\alpha]_D$ −65° (chloroform). Raman spectrum: $\Delta\nu$ (fused solid) 1648 cm^{-1} (strong, C=N); i.r. spectrum (see Fig. 1): ν_{max}^{KBr} (Model 137 spectrophotometer) ~3140 vs (broad, OH), ~1660 vw (C=N), and 1380 s cm^{-1} (CMe_2).

1,6-Anhydro-4-*C*-formyl-2,3-*O*-isopropylidene-β-D-talopyranose oxime (**3**) was obtained by the procedure of Horton and Just[1,6,7] as a crystalline solid, m.p. 153–154° $[\alpha]_D^{20}$ −87.2 ±2° (chloroform). Raman spectrum: $\Delta\nu$ (fused solid) 1648 cm^{-1} (strong, C=N); i.r. spectrum (see Fig. 1): ν_{max}^{KBr} (Model 457 spectrophotometer) 3555 s, 3490 s, 3405 vs, 3287 s (OH); 3015 w, 2990 s, 2930 s, 2920 m (CH); 1657 vw (C=N); 1482 m, 1462 w, 1445 w, 1415 w, 1387 s, 1380 m, 1370 vs (CMe_2); 1350 w, 1314 m, 1298 m, 1283 s, 1251 vs, 1221 vs, 1175 s (shoulder), 1158 vs, 1107 s, 1099 s, 1080 vs, 1041 vs, 1001 m, 995 m, 979 vs, 953 s, 939 vs, 920 s, 913 m, 870 vs, 841 m, 828 s, 812 vs, 785 w, 750 w, 718 m, 710 m, 687 w, 668 w, 653 w, 590 vs, and 575 w cm^{-1}.

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