[CONTRIBUTION FROM THE AGRICULTURAL EXPERIMENT STATION AND DEPARTMENT OF PHYSICS, UNIVERSITY OF FLORIDA]

The Infrared Absorption Spectra of Some Sugars and Furans

BY LEWIS H. ROGERS AND DUDLEY WILLIAMS

In a previous paper,[1] the authors reported a study of the infrared absorption spectrum of Vitamin C. At that time a band was observed at 4 μ which, it was suggested, may have arisen from the lactone linkage. Additional studies on similar compounds are reported in this paper.

The infrared absorption spectra between 2 and 12 μ have been mapped for the following furans: furfural, tetrahydrofurfuryl alcohol, furfuryl alcohol and hydrofuramide. Spectra between 3 and 12 μ have been studied for the following sugars: *d*- and *l*-arabinose, *d*-lyxose, *l*-xylose, *d*-galactose, *d*-mannose, levulose and dextrose. Several studies of the Raman spectra of the furans have been reported,[2] while Coblentz[3] studied the infrared spectra of levulose and dextrose in approximately the same region as that studied here.

The spectrometer and experimental details have been described elsewhere;[1] the only change which has been made consists of the addition of a current amplifier employing two photocells. With the furans, rock salt absorption cells were used, which were of approximately 0.05 mm. thickness. The liquid furans were introduced directly into the cells; hydrofuramide, however, was melted onto the rock salt plates. The data are corrected for the absorption of the rock salt. The furans were contributed by the Quaker Oats Company.

Saturated water solutions of the sugars were used and fluorite cells of approximately 0.02 mm. thickness, together with a comparison cell of fluorite containing water. The sugars were obtained from Eastman Kodak Co.

In Fig. 1 are presented the transmission curves for the furans. Table I summarizes these data. In Table II, data are given on the sugars.

Discussion

The furans show considerable similarity in their absorption spectra in the region studied. In Fig. 1, it will be noted that the bands which occur in the 3–3.5 μ region are more pronounced in the alcohols than in the other two furans, a result which is to be expected, since no OH groups appear in furfural and hydrofuramide. From 5.6 to 6.6 μ there are several bands which arise from C=O, C=C or C=N. Tetrahydrofurfuryl alcohol, which contains none of these groups, exhibits no distinct bands in this region. Furfural contains a band at 5.9 μ which is characteristic of the C=O linkage. Again, in the 10 to 11 μ region, a band known to arise from the C—C linkage is found in all the furans.

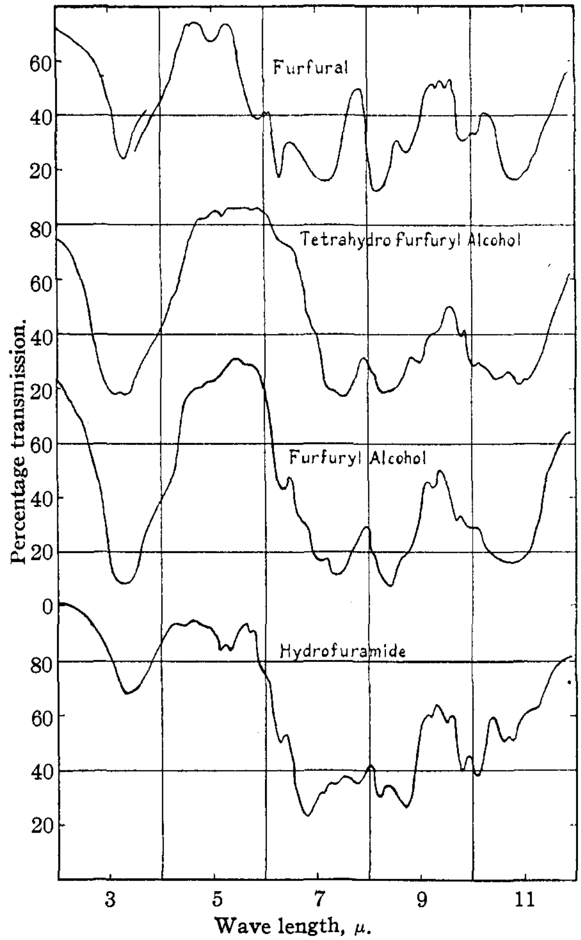

Fig. 1.

It will be seen that at 4 μ no band was observed in any of the furans. This would seem to indicate that the band observed at this wave length in Vitamin C was not due to a vibration involving the lactone linkage, as was previously suggested.[1]

---

(1) D. Williams and L. H. Rogers, THIS JOURNAL, **59**, 1422 (1937).

(2) W. E. Catlin and H. A. Wilhelm, *Iowa State Coll. J. Sci.*, **10**, 135 (1936). A complete bibliography is given in this paper.

(3) W. W. Coblentz, *Carnegie Inst. of Wash.*, Pub. No. 65 (1906).

TABLE I

FREQUENCIES OF THE OBSERVED ABSORPTION MAXIMA OF SOME FURAN DERIVATIVES

Frequencies cm.$^{-1}$	Probable origin	Raman frequencies[2] cm.$^{-1}$
	Furfural	
3030	ν(C—H)	3142
2000		
1700	ν(C=O)	1691
1590	ν(C=C)	1569
1390		1395
1220		1223
1140		1156
1020		1024
925	ν(C—C)[a]	931
	Tetrahydrofurfuryl alcohol	
3120	ν(C—H), ν(O—H)	
1330		
1190		
1110		
1020		
1000		
950		
915	ν(C—C)[a]	
	Furfuryl alcohol	
3030	ν(C—H), ν(O—H)	3110
1590	ν(C=C)	1599
1430	δ(CH$_2$)	
1350		
1190		
1090		1091
1000		1015
925	ν(C—C)[a]	
	Hydrofuramide	
3030	ν(C—H)	
1960		
1890		
1590	ν(C=N)	
1470		
1280		
1220		
1150		
1020		
990		
933	ν(C—C)[a]	

[a] Barnes [*Rev. Sci. Instruments,* **7**, 265 (1936)] gives ν(C—C) as 980 cm.$^{-1}$; therefore the frequencies of 1000 cm.$^{-1}$ possibly should be assigned to ν(C—C) instead of those given.

TABLE II

FREQUENCIES OF OBSERVED ABSORPTION MAXIMA OF SOME PENTOSES AND HEXOSES

Frequencies cm.$^{-1}$	Probable origin	Frequencies cm.$^{-1}$	Probable origin
	d-Arabinose		*d*-Mannose
3030	ν(C—H), ν(O—H)	3030	ν(C—H), ν(O—H)
2040		2080	
1700	ν(C=O)	1725	ν(C=O)
1560		1350	δ(CH$_2$)
1390	δ(CH$_2$)	1040	
1220			
1090			
	l-Arabinose		*d*-Galactose
3030	ν(C—H), ν(O—H)	3030	ν(C—H), ν(O—H)
2040		2040	
1700	ν(C=O)	1725	ν(C=O)
1370	δ(CH$_2$)	1590	
1220		1370	δ(CH$_2$)
1110		1125	
	l-Xylose		Dextrose
3030	ν(C—H), ν(O—H)	3030	ν(C—H), ν(O—H)
2080		2080	
1725	ν(C=O)	1670	ν(C=O)
1350	δ(CH$_2$)	1590	
1100		1370	δ(CH$_2$)
960		1100	
		1000	
	d-Lyxose		Levulose
3030	ν(C—H), ν(O—H)	3030	ν(C—H), ν(O—H)
2080		1890	
1750	ν(C=O)	1350	δ(CH$_2$)
1590		1100	
1350	δ(CH$_2$)		
1100			

In column 4 of Table I are given some of the Raman frequencies reported by Catlin and Wilhelm.[2] The agreement in the case of furfural is good with the exception of the 3030 cm.$^{-1}$ frequency. This discrepancy is to be expected, since the high frequency OH vibration is active in the infrared, but is inactive in the Raman effect. On account of the low resolution obtainable in the 3 μ region with a rock salt prism the C–H and O–H bands could not be separated. The other frequencies reported here are apparently not active in the Raman effect. Similarly, certain Raman frequencies do not appear in the infrared.

The data in Table II for the eight sugars studied are strikingly similar for each compound. Charlton, Haworth and Peat[4] have discussed the possibility of a lactone linkage occurring in some of these sugars; since no band was observed at 4 μ in these materials, there is no evidence indicating that a lactone linkage gives rise to a band at this point.

The data in Table II for dextrose are in partial agreement with Coblentz' data,[3] since he reported a broad absorption maximum between 3 and 4 μ and another maximum at 4.8 μ. Beyond 7 μ, however, Coblentz was unable to detect any transmission. In the present study, thinner

---

(4) W. Charlton, W. N. Haworth and S. Peat, *J. Chem. Soc.,* 89–101 (1926).

cells permitted the extension of the data to longer wave lengths. Also, it should be noted that Coblentz made his measurements with melted samples while in the present study sugar solutions were used. Furthermore, small bands were found at 6.0 μ and 6.3 μ which were not reported by Coblentz. In the case of levulose, agreement between Coblentz' data and those reported here is still less satisfactory. There is agreement on the 3.3 μ band, but Coblentz reports a band at 5.85 μ which is not noted here, and another at 5.3 μ reported here is not shown by Coblentz. Again, thinner cells permitted the extension of this study to longer wave lengths.

The effect of the solvent on the absorption of the sugars is very slight; also, no variation of the spectra of the solutions with time was detected.

Summary

The infrared absorption spectra for four furan derivatives, four pentoses and four hexoses between 2 and 12 μ have been mapped and the results compared with Raman and infrared data from other sources. Several bands were common to all the furans. Data on sugar solutions are in fair agreement with earlier results obtained in studies of melted compounds. No pronounced differences occurred between the spectra of any of the sugars studied.

GAINESVILLE, FLA. RECEIVED JULY 28, 1938

[CONTRIBUTION FROM NAVAL STORES RESEARCH DIVISION, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

The Dihydroabietic Acids from So-called Pyroabietic Acids

BY E. E. FLECK AND S. PALKIN

In a previous paper it has been shown that so-called "α-pyroabietic acid" prepared from *l*-abietic acid by the catalytic method, was a mixture of dehydro-, dihydro- and tetrahydroabietic acids.[1] It was pointed out, however, with regard to the *di*hydro acid ($[\alpha]^{20}\text{D}$ $-3°$) isolated, that while the combustion data were in good agreement with those calculated for the dihydro compound, the rotation did not conform to that indicated by the Biot relationship[2] in that the latter pointed to a dihydroabietic acid of high positive rotation.

This compound ($[\alpha]^{20}\text{D}$ $+108°$) has now been isolated by first removing the tetrahydroabietic acid as the insoluble ammonium salt and then the dehydroabietic acid as the crystalline methyl ester. The non-crystalline residue of methyl esters was saponified with 10% n-butyl alcoholic potassium hydroxide to obtain the new dihydroabietic acid.

Another dihydroabietic acid ($[\alpha]^{20}\text{D}$ $+$ 9.0°, m. p. 193–194°) from α-pyroabietic acid mixture prepared by heat, without catalyst has been reported recently by Ruzicka *et al.*[3]

Further work on the previously reported dihydro compound ($[\alpha]^{20}\text{D}$ $-3°$, m. p. 130–131°), which was isolated by partial sulfonation of the non-crystalline portion of the mixed methyl esters and subsequent hydrolysis of the unsulfonated part, has now been found to be a lactone, as it took up no alkali on direct titration. This lactone was found to be identical with that reported by Hasselstrom, *et al.*,[4] who also obtained it as a sulfonation by-product, and with that reported earlier by Ruzicka, *et al.*,[5] who prepared it by the action of hydrobromic acid on dihydroabietic acid.

By treatment with butyl alcoholic potassium hydroxide, the lactone yielded hydroxytetrahydroabietic acid, m. p. 164–165°, identical with that reported by the above authors.

Experimental Part

Fifty grams of *l*-abietic acid was converted into "pyroabietic" acid mixture at 225° as previously described.[1] The yield was 47 g. of a product that melted at 166–168° and showed $[\alpha]^{20}\text{D}$ $+62°$ in absolute alcohol. This mixture was dissolved in 180 cc. of alcohol and 425 cc. of 0.4 N ammonium hydroxide. On standing overnight at room temperature fine needles separated which consisted chiefly of tetrahydroabietic acid. These were removed by filtration. A second and third crop of crystals was obtained from the mother liquor at intervals of several days. The crystalline ammonium salts were recrystallized and the mother liquors were united with the original filtrate. The combined mother liquors were evaporated to dryness on the

---

[1] Fleck and Palkin, THIS JOURNAL, **60**, 921 (1938).

[2] *Ibid.*, citation 11, p. 924.

[3] Ruzicka, Bacon, Sternbach and Waldmann, *Helv. Chim. Acta*, **21**, 595–596 (1938).

[4] Hasselstrom, Brennan and McPherson, THIS JOURNAL, **60**, 1267 (1938).

[5] Ruzicka, Meier, Waldmann and Hösli, *Helv. Chim. Acta*, **5**, 333 (1922); **16**, 139 (1933).