Carbohydrate Research, 133 (1984) 25–32
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

INFRARED-SPECTRAL CHARACTERISTICS OF SOME ACETYLATED, ANOMERIC GLYCOSIDES*

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(Received March 22nd, 1984; accepted for publication, April 14th, 1984)

ABSTRACT

Barker and co-workers had described the C-1–H deformation bands in the ranges 844 ±8 cm^{-1} and 891 ±7 cm^{-1} as characteristic bands for the α and β anomers, respectively, of hexo- and pento-pyranoses and -pyranosides, and their derivatives. Later, Audichya and co-workers reported the presence of the 844 ±8-cm^{-1} band for both anomers of some aryl D-glucoside derivatives, making the applicability of the earlier findings doubtful. Examination by us of the i.r. spectra of some aryl glycoside derivatives suggested that the origin of the band at 844 ±8 cm^{-1} for the β anomers of the *p*-substituted-aryl glycoside derivatives studied by Audichya *et al.* could be a C–H, out-of-plane deformation-mode of the substituted aromatic ring. Also, their further claim of a characteristic band in the region 961–957 cm^{-1} for α anomers is shown to be of little diagnostic value. The relative intensities of bands in the C–O–C stretching region, 1100–1000 cm^{-1}, and a band near 300 cm^{-1} in the C–O–C deformation region, found only for the β anomers, are shown to be helpful in differentiating the anomers of some peracetylated alkyl and aryl glycosides.

INTRODUCTION

Infrared spectra of acetylated anomeric glycosides have been studied in the past to differentiate between α and β anomers[1–3], but the emphasis seems to have been on derivatives of methyl glycosides. Doss and Muller[4] showed that the α and β anomers have characteristic absorptions in the ranges of 844 ±8 cm^{-1} and 891 ±10 cm^{-1}, respectively. Audichya and co-workers[5] studied the spectra of some acetylated aryl D-glucosides and showed that this generalization, which is only a modification of the ranges suggested by Barker *et al.*[3], was not applicable to the compounds they studied, as both anomers showed absorption in the region 847–839 cm^{-1}. They further claimed that such a distinction is possible from an absorption band in the region 961–957 cm^{-1}, which is present in the i.r. spectra of α anomers only.

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*NCL Communication No. 3502.

0008-6215/84/$ 03.00

Tipson[6] pointed out in his excellent review that the fingerprint region is valuable for differentiating between anomers. However, it is noteworthy that the absorptions in the C–O–C stretching (1100–1000 cm^{-1}) and deformation (~300 cm^{-1}) regions have not thus far been explored for this differentiation. We have therefore studied the infrared spectra of a number of per-*O*-acetylated anomeric glycosides in these regions, and have concluded that these two regions are also useful in assigning the α- or β-anomeric structure to the glycosides. The assignments made by the earlier investigators were also examined by us for the compounds we studied.

EXPERIMENTAL

Materials. — Samples of acetylated α- and β-anomeric glycosides prepared in connection with other work were purified, and their purity was verified by melting point, microanalysis, and specific rotation.

Instrumentation. — Infrared spectra from 1200 to 200 cm^{-1} were recorded with a Perkin–Elmer infrared spectrophotometer, Model 599B, equipped with double gratings. A Perkin–Elmer infrared spectrophotometer, Model 137E, having a sodium chloride prism was used with the normal slit and a scan time of 12 min in order to study the region of 1100–1000 cm^{-1} . The relative intensities of the groups of bands in the regions 1100–1050 cm^{-1} and 1050–1000 cm^{-1} were integrated by weighing the band areas. All of the spectra were recorded by use of the Nujol-mull technique.

RESULTS AND DISCUSSION

Table I summarises the absorption bands at 845, 890, and 960 cm^{-1} that were used by Barker *et al.*[3], Doss and Muller[4], and Audichya *et al.*[5] for differentiating the α and β anomers of acetylated glycosides. It may be seen that, including the *p*-chlorophenyl and *p*-biphenylyl D-glucosides, the acetates of other aryl, as well as alkyl, glycosides showed bands at 844 ±8 and 891 ±10 cm^{-1} for the α and β anomers, respectively, as suggested by Doss and Muller[4] in an extension of the findings of Barker *et al.*[3]. In the spectra of the *p*-substituted-phenyl glucosides, the 844-cm^{-1} band was found for the β anomers also. Audichya *et al.*[5], whose studies included three *p*-substituted-aryl D-glucosides, had found a band at 844 ±8 cm^{-1} for the β anomers, and they concluded that this band could not, therefore, be used to differentiate the α and β anomers of aryl D-glucosides. Our analysis showed that the band observed at 844 ±8 cm^{-1} for the β anomer has its origin in the C–H out-of-plane deformation mode of the adjacent C–H groups of the *p*-substituted, aromatic aglycon. Furthermore, the β anomers *did* show the band at 891 ±10 cm^{-1}, as expected, although Audichya *et al.* had made no mention thereof.

With regard to the alternative assignment of the 961–957-cm^{-1} band,

TABLE I

ABSORPTION BANDS IN THE REGIONS OF 844 ±8, 891 ±10, AND 961–957 cm^{-1} FOR SOME PERACETYLATED GLYCOSIDES

Sl. No.	*Compound*	*Region*			
		844 ±8	*891 ±10*	*961–957 cm^{-1}*	
		Anomer			
		α	β	α	β
	A. 2,3,4,6-Tetra-O-acetyl-D-glucopyranoside				
1	Methyl	851 m	895 s	960 m	959 w
2	Ethyl	845 m	890 s	960 m	955 s
3	Propyl	840 w	900 w	960 m	959 m
4	Butyl	850 w	895 w	960 w	960 s
5	*tert*-Butyl	872 m	880 m	no band	no band
6	Phenyl	848 w	895 w	960 m	no band
7	Benzyl	840 m	898 w	960 w	no band
8	*p*-Chlorophenyl	851 m	840 s 880 m	950 s	no band
9	*p*-Biphenylyl	840 m	840 s 895 w	960 s	no band
10	Phenyl 1-thio	850 m	880 s	no band	no band
	B. 2,3,4,6-Tetra-O-acetyl-D-galactopyranoside				
1	Phenyl	848 s	900 s	958 s	960 s
2	2-Phenylethyl	850 w	890 m	961 m	955 m
	C. 1,2,3,4,6-Penta-O-acetyl-D-glucopyranose				
		845 m	900 m	no band	no band

suggested for α anomers by Audichya *et al.*[5], it was found that, although the aryl glycosides showed this band for the α anomers, both anomers of the alkyl D-glucosides, with the exception of the *tert*-butyl D-glucosides, exhibited this band. In the spectra of *tert*-butyl D-glucosides and phenyl 1-thio-D-glucosides, there were no bands at 961–957 cm^{-1} in the spectrum of either anomer. For the D-galactosides, although differentiation of α and β anomers was possible on the basis of bands at 844 ±8 cm^{-1} and 891 ±10 cm^{-1}, respectively, both anomers absorbed in the 961–957-cm^{-1} region. These results thus confirm the applicability of the original assignment of Barker *et al.*[3] to aryl glycosides also, provided that the absorption bands due to the C–H out-of-plane deformation-pattern of the aromatic substitution is taken into account. It also establishes the limited applicability of the band at 961–957 cm^{-1} for differentiating the anomers of the glycosides.

1. Region of 600–200 cm^{-1}. — In Table II, the bands observed for α and β anomers in the region 320–280 cm^{-1} are given for some anomeric pairs. It may be seen that acetates of β anomers of alkyl D-glucosides exhibited a band at 300–280 cm^{-1}, and a band for the aryl glucosides was observed at a slightly higher frequency, *i.e.*, 320–300 cm^{-1}. None of the α anomers absorbed in these regions, except for the α anomer of the benzyl D-glucoside.

TABLE II

ABSORPTION BANDS IN THE REGION OF 320–280 cm^{-1} FOR SOME PERACETYLATED GLYCOSIDES

Sl. No.	*Compound*	*Region* 300–280 cm^{-1} *Anomer* α	β	320–300 cm^{-1} α	β
	*A. 2,3 4,6-Tetra-O-acetyl-*D*-glucopyranoside*				
1	Methyl	—[a]	300 m	315 w	—[a]
2	Ethyl	—	295 m	—	310 m
3	Propyl	—	295 w	—	—
4	Butyl	—	290 m	—	315 m
5	*tert*-Butyl	—	280 m(b)	—	320 s
6	Phenyl	—	—	—	318 s
7	*p*-Chlorophenyl	—	—	—	315 s
8	*p*-Biphenylyl	—	—	—	320 m
9	Phenyl 1-thio	—	—	—	320 s
10	Benzyl	290 m	—	—	—
	*B. 2,3 4,6-Tetra-O-acetyl-*D*-galactopyranoside*				
1	Phenyl	285 w	—	—	302 m
2	2-Phenylethyl	285 s	280 m(b)	—	320 m
	*C. 1,2,3,4,6-Penta-O-acetyl-*D*-glucopyranose*				
		—	290 m	—	—

[a] The symbol — denotes "no band"

TABLE III

MODES OF VIBRATIONS OF ETHER AND ESTER LINKAGES ABSORBING IN THE RANGE 325–270 cm^{-1}

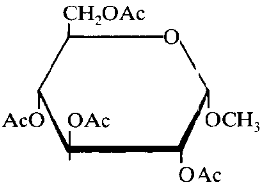
Compound	*Type of vibration*	*Frequency* cm^{-1}	*Reference*
$CH_3OCH_2OCH_3$	COCOC sym. deform.	320	7
CH_3OCH_3	CH_3 torsion	270	8
$CH_3OCH_2OCH_3$	COC bending	304	9
CH_3COOCH_3	COC bending	303	10
Aliphatic acetates	no assignment	323–306	11
	no assignment	321	12

Table III lists the assignments of absorptions near 300 cm^{-1} given by various investigators[7–12]. F. F. Bentley and coworkers[11] reported that a band in the range of 323–306 cm^{-1} is observed for many aliphatic acetates, with the exception of isopropyl and *sec*-butyl acetate. However, its absence for the α anomers of all of these glycoside derivatives, with the exception of methyl 2,3,4,6-tetra-*O*-acetyl-α D-glucopyranoside, proves that the band at ~300 cm^{-1} in the spectra of these acetylated derivatives is not ascribable to the acetyl-group vibrations.

A band near 300 cm^{-1} is also found for many alkyl ethers[7–9], and it has been ascribed to the C–O–C deformation mode. It is readily seen that such a vibration would be affected by 1,3-diaxal interactions of the hydrogen atoms on C-3 and C-5 of certain sugars. For the β anomers, where the C-O-CH$_3$ group is equatorial, the 1,3-diaxial interaction at H-3 and H-5 of such sugars would be absent, whereas, for the α anomer, where C-O-CH$_3$ is axial, it would be large. It is worth noting that the band in the 900–800-cm^{-1} region, used to differentiate between the anomers, has been ascribed to a C–H deformation mode similarly affected[3b] by the axial hydrogen atom on C-5. Because, in bending vibrations, the frequency increases with restriction to bending, it might be inferred that α anomers would give rise to a higher frequency for this mode than the β anomers.

The bulk of the aglycon moiety also seems to be critical, as this bending-mode vibration absorbs for both anomers of methyl 2,3,4,6-tetra-*O*-acetyl-D-glucopyranoside.

II. Region of 1100–1000 cm^{-1}. — With a view to ascertaining whether the C–O stretching vibrations of the ether group[13] can be used to differentiate the anomeric forms of acetylated glycosides, we first examined the spectra of 1,2,3,4,6-

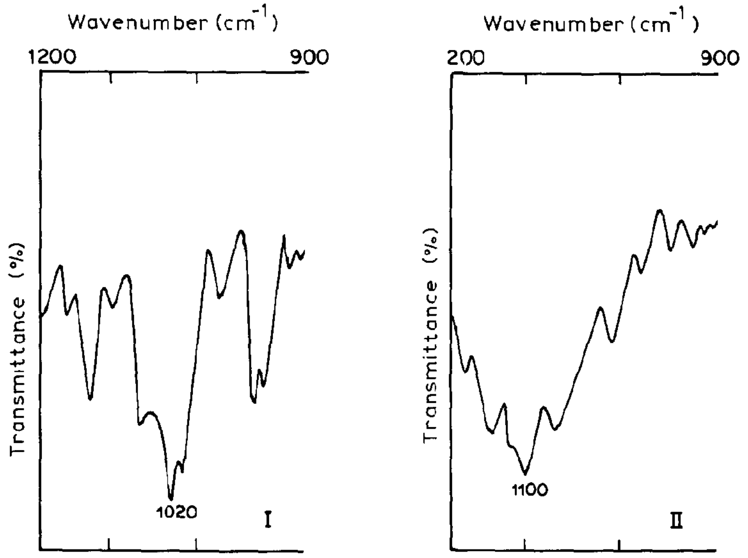


Fig. 1. Infrared spectra, in the range 1200–900 cm^{-1}, of I, 1,2,3,4,6-Penta-*O*-acetyl-α-D-glucopyranose[1] and II, methyl 2,3,4,6-tetra-*O*-methyl-α-D-glucopyranoside[14].

TABLE IV

RATIO OF THE INTENSITIES OF THE ABSORPTION BANDS IN THE REGION 1100–1000 cm^{-1} IN I R SPECTRA OF ACETYLATED GLYCOSIDES

Sl. No.	*Compound*	*Anomer*	*A*[a]	*B*[b]	*Ratio A/B*
	*2,3,4,6-Tetra-O-acetyl-*D*-glucopyranoside*				
1	Methyl	α	4.4	6.3	0.7
		β	5.2	6.0	0.9
2	Ethyl	α	4.5	7.4	0.6
		β	5.3	4.3	1.2
3	Propyl	α	4.7	6.2	0.8
		β	3.9	5.1	0.8
4	Butyl	α	5.3	7.0	0.8
		β	4.6	5.8	0.8
5	*tert*-Butyl	α	6.1	10.0	0.6
		β	8.1	7.6	1.1
6	Phenyl	α	5.7	9.3	0.6
		β	7.4	9.0	0.8
7	*p*-Chlorophenyl	α	3.6	7.9	0.5
		β	9.0	8.9	1.0
8	*p*-Biphenylyl	α	3.2	7.9	0.4
		β	7.7	8.4	0.9
9	Phenyl 1-thio	α	2.8	6.6	0.4
		β	5.0	4.2	1.2
10	Benzyl	α	5.1	8.2	0.6
		β	2.8	3.8	0.7
11	Cetyl	α	4.9	7.0	0.7
		β	4.0	3.5	1.1
	*2,3,4,6-Tetra-O-acetyl-*D*-galactopyranoside*				
12	Phenyl	α	7.1	4.9	1.5
		β	7.6	6.5	1.2
13	2-Phenylethyl	α	7.4	7.0	1.1
		β	7.1	7.2	1.0
	*1,2,3,4,6-Penta-O-acetyl-*D*-glucopyranose*				
14		α	5.6	5.4	1.0
		β	7.3	4.4	1.7

[a] A, Region 1100–1050 cm^{-1}. [b] B, Region 1050–1000 cm^{-1}.

penta-*O*-acetyl-α-D-glucopyranose and methyl 2,3,4,6-tetra-*O*-methyl-α-D-glucopyranoside[14], shown in Fig. 1. It may be seen that, whereas a strong peak at 1020 cm^{-1} was found for the pentaacetate, the pentamethyl ether showed a strong band at 1100 cm^{-} . These absorptions would thus correspond to the C–O stretching modes of the ester (alcohol part) and the ether linkages, respectively.

Hence, a comparison of the intensities of the bands at 1100 cm^{-1} and 1050 cm^{-1} could give rise to different ratios for the α and β anomers, provided that there is a difference in intensity between the C–O–C stretching modes in the two orientations of the ether group.

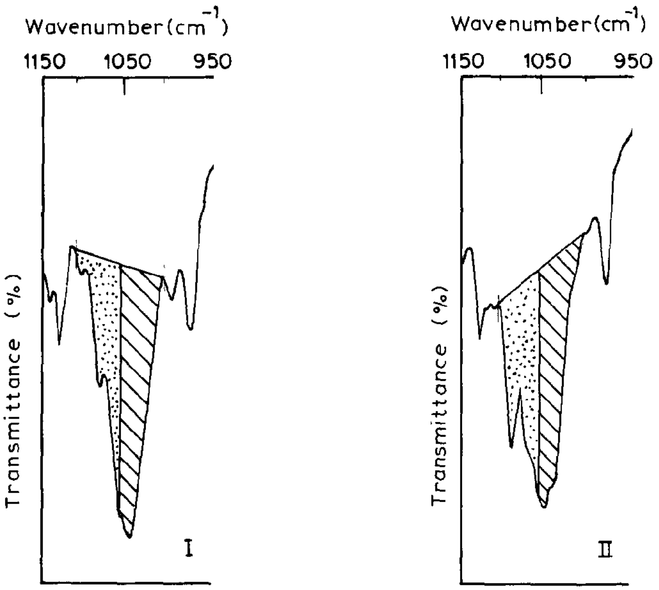


Fig. 2. Infrared spectra of *tert*-butyl 2,3,4,6-tetra-*O*-acetyl-D-glucopyranosides (I, α anomer and II, β anomer. Regions: ░, A; ▨, B.)

In Table IV are summarized the values of the intensity ratio A/B, where A and B correspond to the intensities of the bands at 1100–1050 cm^{-1} and 1050–1000 cm^{-1}, respectively, observed in the i.r. spectra of the solid state of various glycoside derivatives. It may be seen from these data that the intensity ratios for all of the β anomers of the D-glucoside derivatives is higher than those of the corresponding α anomers. (Fig. 2 shows a typical case, namely, that of the *tert*-butyl 2,3,4,6-tetra-*O*-acetyl-D-glucopyranoside anomers.) Whereas the value of β/α exceeds 2 in some cases (2, 7, 8, and 9), it is as low as 1 for two (3 and 4). However, the magnitude of the ratios is reversed for the D-galactosides, perhaps due to the stereochemistry at C-4 (12 and 13). It is, therefore, necessary to apply this observation to unknown glycoside derivatives only after ascertaining the identity of the sugar moiety and studying the behavior of model compounds. The ratio of intensities of the bands at 1100 and 1050 cm^{-1} can thus be used as supporting evidence to differentiate the anomeric forms of acetates of glycosides.

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