JOURNAL OF RESEARCH of the National Bureau of Standards — A. Physics and Chemistry
Vol. 71A, No. 1, January–February 1967

Infrared Absorption Spectra of Some Aldofuranoid, Aldopyranoid, and Acyclic 1-Acylamido Derivatives of Sugars

R. Stuart Tipson, Alberto S. Cerezo,[1] Venancio Deulofeu,[1] and Alex Cohen

Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234

(October 17, 1966)

The infrared absorption spectra of two glycofuranosylacetamides and their perbenzoates, and of eleven glycopyranosylacylamides and eight esters thereof, are presented and discussed. For comparison, the spectra of thirteen 1,1-bis(acylamido)-1-deoxyalditols and eight esters thereof are also given and discussed.

The useful correlations between structure and infrared absorption made by Barker and co-workers for certain carbohydrates, and by Nanasi and co-workers for some *N*-arylglycosylamines, cannot be extended to the 1-acylamido compounds we have studied. Certain of Verstraeten's correlations may have some diagnostic value.

Key Words: Absorption spectra, acyclic sugars, 1-acylamido sugars, aldofuranoid sugars, aldopyranoid sugars, infrared spectra.

1. Purpose and Scope of the Project

The main object of the present project was to record the infrared absorption spectra of a variety of 1-acylamido derivatives of sugars (having furanoid, pyranoid, or acyclic structures), in order to find whether previously reported correlations between the structure and specific bands in the infrared spectra of certain derivatives of sugars are also applicable to this group of compounds. In essence, the study consisted of answering two questions: (a) Do compounds having certain structural features show, in their infrared spectra, the bands previously described as characteristic of such features, and (b) do compounds that lack these structural features show or fail to show these bands in their infrared spectra? No infrared band can be regarded as unique for any feature, of course; and interpretation must be substantiated by other evidence.

The spectra have been recorded for two glycofuranosylacetamides and their perbenzoates; eleven glycopyranosylacylamides and eight esters thereof; and thirteen 1,1-bis(acylamido)-1-deoxyalditols and eight esters thereof. For this purpose, we used one of the small instruments now commercially obtainable, because such low-cost instruments are now customarily employed routinely as an analytical tool in practical organic chemistry.

2. Compounds Investigated

Table 1 gives a list of the compounds, their code numbers [1],[2] and an index to the spectrograms; the serial number of a compound is the same as the number of its spectrogram.

In addition, a discussion is given of the spectra previously published [2] for five *N*-glycopyranosylacetamides and six acetates thereof, and for a 1,1-bis(acetamido)-1-deoxyalditol and its tetraacetate; the serial number given each of these compounds is that originally assigned [2], with the letter A suffixed thereto. Also, the spectra previously published [3] for three derivatives of D-ribosylamine have received consideration; the serial numbers for them are those originally given [3], with the letter B added.

The spectra were measured in the region of 4000 to 667 cm^{-1}. The spectrograms of compounds 1 to 44 are given (see fig. 1), together with a discussion of (a) the structure of the compounds and (b) some of the outstanding features of their spectra.

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[1] Departamento de Química Orgánica, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Perú 222, Buenos Aires, Argentina.

[2] Figures in brackets indicate the literature references at the end of this paper. The references for table 1 are given at the end of the table.

TABLE 1. *Compounds measured and index to spectrograms*

Code [a]	Compound	mp (°C)	[α]$_D$, degrees	References	Spectrogram
	A. *N*-GLYCOFURANOSYLACETAMIDES				
	1. *Unsubstituted*				
	N-Acetyl-				
10.116(82)	α-D-xylosylamine	147–148	+100.0(H_2O)	1	1
10.216(82)	α-D-glucosylamine	195–197	+87.6(H_2O)	2	2
	2. *Esters*				
	N-Acetyl-				
15.116(82)	2,3,5-tri-*O*-benzoyl-α-D-xylosylamine	139–141	+31.8($CHCl_3$)	1	3
15.216(82)	2,3,5,6-tetra-*O*-benzoyl-α-D-glucosylamine	153–155	−20.1($CHCl_3$)	3	4
	B. *N*-GLYCOPYRANOSYLACYLAMIDES				
	1. *Unsubstituted*				
	N-Acetyl-				
10.11?(82)	β-D-xylosylamine	213–214	−0.7(H_2O)	[b] 4, 5	(1A)
10.21?(82)	β-D-glucosylamine	230–260(dec.)	−22.8(H_2O)	[b] 4, 5	(2A)
10.12?(82)	β-D-lyxosylamine	166–167	−47.0(H_2O)	6	5
10.22?(82)(99)	β-D-mannosylamine, monohydrate	203–204	−47.4(H_2O)	[b] 4	(3A)
10.22?(80)(82)	6-deoxy-β-L-mannosylamine	210–211	+65.7(H_2O)	6	6
10.13?(82)	α-L-arabinosylamine	222–224	+69.1(H_2O)	[b] 7	(4A)
10.23?(82)	α-D-galactosylamine	179–180	+194.9(H_2O)	6,8	7
10.23?(82)	β anomer	233 236–238	+9.8(H_2O) +10.2(H_2O)	[b] 8	(5A), 8
10.14?(82)	α-D-ribosylamine	198–200	+17.8(H_2O)	[c] 9	(5B)
10.14?(82)	β anomer	195–197	−23.4(H_2O)	[c] 9	(6B)
10.21?(83)	*N*-Propionyl-β-D-glucosylamine	193–194	−23.2(H_2O)	3	9
	N-Benzoyl-				
10.12?(84)	β-D-lyxosylamine	234–235	−22.0(H_2O)	6	10
10.13?(84)	α-D-arabinosylamine	209–211	−53.2(H_2O)	6	11
10.21?(84)	β-D-glucosylamine	231–233	−12.2(H_2O)	3	12
10.22?(84)	β-D-mannosylamine	251–252	+5.8(py)	10	13
10.22?(80)(84)	6-deoxy-β-L-mannosylamine	235–237	+18.9(H_2O)	11	14
10.23?(84)	β-D-galactosylamine	188–190	+17.3(H_2O)	6	15
	2. *Esters*				
	N-Acetyl-				
12.11?(82)	2,3,4-tri-*O*-acetyl-β-D-xylosylamine	172–173	+28.5($CHCl_3$)	[b] 4	(6A)
12.21?(82)	2,3,4,6-tetra-*O*-acetyl-β-D-glucosylamine	163–164	+17.4($CHCl_3$)	[b] 4	(7A)
12.22?(82)	2,3,4,6-tetra-*O*-acetyl-β-D-mannosylamine	188–189	−16.5($CHCl_3$)	[b] 4	(8A)
12.22?(80)(82)	2,3,4-tri-*O*-acetyl-6-deoxy-β-L-mannosylamine	135–137	+6.2($CHCl_3$)	6	16
12.13?(82)	2,3,4-tri-*O*-acetyl-α-L-arabinosylamine	177–178	+89.6($CHCl_3$)	[b] 7	(9A)
15.13?(82)	2,3,4-tri-*O*-benzoyl-α-D-arabinosylamine	121–123	−270.6($CHCl_3$)	— [d]	17
12.23?(82)	2,3,4,6-tetra-*O*-acetyl-α-D-galactosylamine	172–173	+117.4($CHCl_3$)	[b] 8	(10A)
12.23?(82)	β anomer	173	+34.7($CHCl_3$)	[b] 8	(11A)
12.14?(82)	2,3,4-tri-*O*-acetyl-β-D-ribosylamine	128–130	+35.3($CHCl_3$)	[c] 9	(4B)
	N-Propionyl-				
14.21?(83)	2,3,4,6-tetra-*O*-propionyl-β-D-glucosylamine	103–104	+19.3($CHCl_3$)	3	18
15.21?(83)	2,3,4,6-tetra-*O*-benzoyl-β-D-glucosylamine	151–152	+68.7($CHCl_3$)	3	19
	N-Benzoyl-				
12.13?(84)	2,3,4-tri-*O*-acetyl-α-D-arabinosylamine	162–163	−40.1($CHCl_3$)	— [d]	20
15.11?(84)	2,3,4-tri-*O*-benzoyl-β-D-xylosylamine	173–175	+1.9($CHCl_3$)	6	21
15.13?(84)	2,3,4-tri-*O*-benzoyl-α-D-arabinosylamine	214	−174.2($CHCl_3$)	— [d]	22
15.21?(84)	2,3,4,6-tetra-*O*-benzoyl-β-D-glucosylamine	113–115	+23.0($CHCl_3$)	3	23
15.21?(84)	ditto	184	+22.9($CHCl_3$)	3	23a
	C. 1,1-BIS(ACYLAMIDO)-1-DEOXYALDITOLS				
	1. *Unsubstituted*				
	1,1-Bis(acetamido)-				
10.027(52)(82)	1-deoxy-D-erythritol	210–211	+8.7(H_2O)	12	24
10.137(52)(82)	1-deoxy-L-arabinitol	189–191	+9.8(H_2O)	[b] 13	(15A)
10.217(52(82)	1-deoxy-D-glucitol	165–167	+4.0(H_2O)	3	25
10.227(52)(80)(82)	1,6-dideoxy-L-mannitol	238–240	+22.7(H_2O)	11	26
10.237(52)(82)	1-deoxy-D-galactitol	194–196	+8.4(H_2O)	14	27
10.217(56)(83)	1-Deoxy-1,1-bis(propionamido)-D-glucitol	154–156	+6.6(H_2O)	3	28
	1,1-Bis(benzamido)-				
10.027(57)(84)	1-deoxy-L-erythritol	217–219	+13.5(py)	15	29
10.137(57)(84)	1-deoxy-L-arabinitol	194–196	−5.3(py)	15	30
10.147(57)(84)	1-deoxy-D-ribitol	190–192	−8.1(py)	15	31
10.217(57)(84)	1-deoxy-D-glucitol	199–201	+1.3(py)	10	32
10.217(57)(80)(84)	1,2-dideoxy-D-*arabino*-hexitol	208–210	+12.0(py)	— [e]	33
10.227(57)(84)	1-deoxy-D-mannitol	222–224	+2.9(py)	10, 16	34
10.227(57)(80)(84)	1,6-dideoxy-L-mannitol	220–222	+14.1(py)	11	35
10.237(57)(84)	1-deoxy-D-galactitol	207–208	−6.8(py)	14	36

	2. *Esters*				
	1,1-Bis(acetamido)-1-deoxy-				
12.137(52)(82)	2,3,4,5-tetra-*O*-acetyl-L-arabinitol	218–219	−72.5(CHCl$_3$)	[b] 5	(16A)
12.217(52)(82)	2,3,4,5,6-penta-*O*-acetyl-D-glucitol	188–190	+22.3(CHCl$_3$)	3	37
	1,1-Bis(benzamido)-1-deoxy-				
10.217(22)(57)(84)	6-*O*-benzoyl-D-glucitol	208–209	+5.2(py)	17	38
12.127(22)(57)(84)	2,3,4-tri-*O*-acetyl-5-*O*-benzoyl-D-lyxitol	184–186	+35.1(CHCl$_3$)	18	39
12.137(22)(57)(84)	2,3,4-tri-*O*-acetyl-5-*O*-benzoyl-D-arabinitol	192–193	+68.1(CHCl$_3$)	18	40
15.137(57)(84)	2,3,4,5-tetra-*O*-benzoyl-D-arabinitol	134–136	+62.0(CHCl$_3$)	15	41
12.027(57)(84)	2,3,4-tri-*O*-acetyl-L-erythritol	181–183	+9.2(CHCl$_3$)	15	42
12.147(57)(84)	2,3,4,5-tetra-*O*-acetyl-D-ribitol	175–176	−10.2(CHCl$_3$)	15	43
12.217(57)(84)	2,3,4,5,6-penta-*O*-acetyl-D-glucitol	189–191 (needles) 199–200 (plates)	−39.4(CHCl$_3$)	19	44

[a] In the coding system [1], certain numbers were left blank to permit later assignment to structural features as the need arose. The following additions have now been made: table 1, column 2, code No. 4, propionated; column 2, code No. 5, benzoylated; table 2, code No. 56, propionamido; code No. 57, benzamido; code No. 83, deoxypropionamido; code No. 84, benzamidodeoxy. [b] Spectrum given in reference 5. [c] Spectrum given in reference 9. [d] Prepared by A. S. Cerezo. [e] We thank J. O. Deferrari and I. Mastronardi (Buenos Aires) for providing a sample of this compound.

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3. Correlations Made by Barker and Co-workers

3.1. Description of the Correlations for Certain Aldopyranose Derivatives

In a series of articles [4, 5, 6], Barker and co-workers sought to identify, in the range of 960 to 730 cm^{-1}, infrared bands characteristic of several aldopyranoses and their derivatives.

They expressed the frequency of a band as the mean and the standard deviation; although indication of a range is customary, their expression was used for *defining* the probable frequency of an absorption band shown by each of a set of compounds. However, it is not practical in the reverse process, namely, in *searching* for this band within a range of wavelengths in the spectrum of a single compound. For example, the value given for the type 1a band was 917 ± 13 cm^{-1}; this *includes* the interval of 930 to 904 cm^{-1}, but it does not *exclude* the possibility that, for any one compound of this kind, the band might occur above 930 cm^{-1} or below 904 cm^{-1}. Therefore, for each band sought in an individual spectrum, subsequent authors have, for practical purposes, apparently confined their attention to the interval obtained by adding the standard deviation to, and subtracting it from, the mean value as given by these workers [4, 5, 6].

a. (D or L)-*gluco* Group Configuration

In their first article [4], they recorded (in tables) the frequencies of various types of bands shown by D-glucopyranose derivatives; these bands are listed in table 2. From these results, they identified [4] "three principal sets of bands, for which the average values (cm.$^{-1}$) and standard deviations" were (for α anomers) type 1a, 917 ± 13; type 2a, 844 ± 8; and type 3a, 766 ± 10; (for β anomers) type 1b, 920 ± 5; type 2b, 891 ± 7; and type 3b, 774 ± 9. They found that the type 2a band can be used with considerable confidence for diagnosing the α anomeric form, particularly in polymers of glucopyranose. The type 2b band was not found useful for diagnosing the β anomeric form, but the *absence* of the type 2a band was considered very useful for diagnosing the β anomeric form. They regarded the bands of types 1 and 3 as only useful for determining points of linkage in polymers of α-glucopyranose.

TABLE 2. *Frequencies* [a] *(cm^{-1}) of various types of bands for* D-*glucopyranose derivatives, as recorded in the tables in Ref.* [4]

Linkage	Type 1	Type 2a	Type 2b	Type 3
α Anomeric				
Monosaccharides	915 ± 5	847 ± 6		767 ± 8
	900 ± 8	842 ± 7		751 ± 8
Higher saccharides	930 ± 9	843 ± 10		761 ± 8
	917 ± 2	839 ± 1		768 ± 1
β Anomeric				
Monosaccharides	914 ± 6		896 ± 6	
	[b] 918 ± 5		891 ± 8	[c] 772 ± 9
Higher saccharides	921 ± 4		890 ± 5	[d] 774 ± 9

[a] Mean and standard deviation. [b] Six of ten compounds did not show this band. [c] Eleven of sixteen compounds did not show this band. [d] Five of sixteen compounds did not show this band.

In a review, Neely [7] summarized this and related work; without explanation, he arrived at further conclusions, presumably in the following way. It would seem that, as the range for type 1a encompasses that for type 1b, the range 917 ±13 cm^{-1} may be simply referred to as type 1 (as shown in table 3). Also, as there is an overlap (from 776 to 765 cm^{-1}) of 11 cm^{-1} for the ranges of types 3a (766 ±10) and 3b (774 ±9), only extreme values of each range will have diagnostic value for these respective types, and so, they were combined (as 770 ±14 cm^{-1}) and referred to as type 3 (see table 3).

TABLE 3. *Summary of the results of Barker and co-workers [4,5] for infrared bands characteristic of five* (D *or* L)*-aldopyranoses and their derivatives*

Type	Bands (cm^{-1}; mean and standard deviation, or range)				
	Xylose	Arabinose	Glucose	Mannose	Galactose
	Both anomers				
1	?	?	[a] 917 ±13	?	?
2c	–	–	[b] –	[b] 876 ±9	[b] 871 ±7
3		[c] 781–744	[a] 770 ±14 [b] 753 ±17	[b] 791 ±18	[b] 752 ±20
	α anomers only				
2a	[d] –	[c] –	[a, e] 844 ±8 [b] 843 ±4	[b] 833 ±8	[b] 825 ±11
3	[d] 749 ±10				
	β anomers only				
2a	[d] –	[d] 855–830 [c] 854–836			
2b			[a, e] 891 ±7 [b] 890 ±8	[b] 893 ±6	[b] 895 ±9

[a] Given in table 2 of ref. [7]; see present text for probable derivation. [b] Given in table 5 of ref. [5]. [c] Given in table 4 of ref. [5]. [d] Given in the text of ref. [5]. [e] Given in the text of ref. [4].

In summary, in the correlations of Barker and co-workers [4], the infrared spectra of α- and β-(D or L)-glucopyranose derivatives should show type 1 absorption (917 ±13 cm^{-1}) and type 3 absorption (770 ±14 cm^{-1}). In addition, the spectra of the α anomers should show type 2a absorption (844 ±8 cm^{-1}), and the spectra of the β anomers should show type 2b absorption (891 ±7 cm^{-1}). These values were given by Neely [7], in an article which will be discussed in section 3.2.

If the bands are to have diagnostic value for glucopyranose derivatives, α anomers should not show type 2b absorption, and β anomers should not show type 2a absorption. However, these workers [4] found that (a) some α anomers exhibited type 1 absorption in the range of type 2b bands, and (b) some β anomers showed "weak peaks of type 2a" which they believed were due to traces of the α anomers.

Barker and co-workers [4] then made tentative assignments for these glucopyranose derivatives. They suggested that: (1) type 1 bands might be due to a ring vibration including ring C-O-C antisymmetrical stretching; (2) type 2 bands might be connected with "one of the C-H deformation modes in which the hydrogen on C-1 is involved intimately"; and (3) type 3 bands might be correlated with ring breathing.

In a second article, Barker and co-workers [5] examined the infrared spectra of some more glucopyranose derivatives, and found slightly different positions for bands of type 2a and type 3 (see table 3). As before, some of the α anomers were found to show type 1 absorption in the range of type 2b bands. Also, they pointed out that derivatives containing a benzene ring may show absorption in the region of the type 2a band, and that acetates absorb in the region of the type 2b band.

b. Other Group Configurations

The results of Barker and co-workers [5] for infrared bands characteristic of four other pyranoid aldoses and their derivatives are also summarized in table 3.

No decision was made as to the presence or absence of bands of *type 1* in the spectra of these other compounds. It was found that, for manno- and galactopyranose, the *type 2a* band can be used for diagnosing the α anomeric form, although with slightly less confidence than for α-glucopyranose derivatives. Absence of the type 2a band was useful for diagnosing the β anomeric form.

These authors [5] also found that a band at 876 ±9 cm^{-1}, designated *type 2c*, was characteristic of mannopyranose derivatives; and that a band of type 2c, at 871 ±7 cm^{-1}, was characteristic of galactopyranose derivatives.

From these results (see table 3), it may be seen that the mean frequency for a given type of absorption may change with the group configuration; for example, the mean frequency for type 3 absorption is at 791 cm^{-1} for the *manno* configuration, but at 752 to 753 cm^{-1} for the *gluco* and *galacto* configurations. Furthermore, β-(D or L)-xylopyranose derivatives are not characterizable by any of the bands listed in table 3. In connection with the present study, it should be noted that many derivatives containing a benzene ring absorb [8] in the region of the type 3 band of the glucopyranose, galactopyranose, and α-xylopyranose derivatives.

Barker and co-workers suggested that *type 2a* bands may be associated with an equatorial C-1—H grouping, because the favored conformation [3] (CA) of the α-(D or L) anomers having the *gluco*, *manno*, and *galacto* configurations has an equatorially attached hydrogen atom on C-1. (However, for both the *manno* and *galacto* configurations, some β anomers showed type 2a absorption.) The type 2a absorption for β-(D or L)-arabinopyranose (see table 3) was related to the same structural feature, because the CE conformation (having an equatorially attached hydrogen atom on C-1 of the β anomer) is favored for the *arabino* configuration. Similarly, *type 2b* bands, shown by the β-(D or L) anomers of gluco-, manno-, and galactopyranose, were associated with the presence of an axial C-1—H grouping.

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[3] In the conformational nomenclature of Isbell and Tipson [9], the β anomer of a pyranoid aldose in the CA conformation has an *axial* C-1—H bond; in the CE conformation, it has an *equatorial* C-1—H bond.

Barker and co-workers [5] again made assignments for these bands. They suggested that the *type 2c* bands are due to deformations of the equatorial C—H bond at C-2 of (D or L)-mannopyranose-CA and at C-4 of (D or L)-galactopyranose-CA. In agreement with this conclusion, Ellis [10] has found that derivatives of (D or L)-arabinopyranose-CE show type 2c absorption. However, according to Ellis, "an equatorial C—H bond at C-3 may also give rise to the type 2c absorption," as in derivatives of (D or L)-ribopyranose-CA. Barker and co-workers indicated that β-(D or L)-xylopyranose derivatives show no absorption of *type 3*, and that, in the CA conformation, these derivatives have *all* of the exocyclic C—O bonds equatorial; β-(D or L)-glucopyranose derivatives showed weak absorption of type 3, and their CA conformation has an equatorial hydroxymethyl group on C-5. If type 3 absorption is a symmetrical ring-breathing frequency, such a band would not be expected to be strong for the more symmetrical molecules, such as β-D-xylo- and β-D-gluco-pyranose, but would be expected to be stronger for the corresponding α anomers (having a bulky group attached axially at C-1). Their *assignments* for the bands of *types 2a and 2b* have since been disproved [11], but the *correlations*, already mentioned, remain unaffected. It was "concluded that a vibration of the whole grouping at C-1 is responsible for type 2a and type 2b absorption. The frequency exhibited is dependent on the stereochemical configuration at C-1 (i.e., α or β)."

Barker and co-workers [6] next found that 2-deoxy and 3-deoxy derivatives of gluco-, manno-, and galacto-pyranose show absorption at 867 ± 2 cm^{-1}, attributed to a CH_2 rocking mode of a ring-methylene grouping *not* adjacent to the ring-oxygen atom (because xylopyranose derivatives, having a methylene grouping at C-5 do not show this band). In addition, they noted that seven 6-deoxy derivatives of mannopyranose or galactopyranose show a band near 967 cm^{-1}, tentatively attributed to a *C*-methyl (terminal) rocking mode, but they cautioned that this band might not have diagnostic value.

Application of the correlations of Barker and co-workers [4, 5, 6] has proved useful in the study of many related compounds, including oligo- and poly-saccharides; and, for the compounds they studied, none of their correlations are questioned in the present article.

TABLE 4. *Ranges*[a] (*cm*$^{-1}$) *for the bands of types 2a and 2b, as given by Spedding* [13] *from the work of Barker and co-workers* [12]

Type	Anomer	Glucopyranose	Mannopyranose	Galactopyranose
2a	α	[b]855–833 (844)	[b]843–818 (831)	[b]839–810 (825)
2b	β	[c]905–876 (891)	[d]898–888 (893)	[d]914–886 (900)

[a] The mean is given in parentheses. [b] Derivatives containing a benzene ring absorb here. [c] Must be confirmed by absence of absorption at 855–833 cm^{-1}. [d] But other types of vibration also occur here.

These results were collated by Barker and co-workers [12]. Some of them were summarized by Spedding [13], who gave slightly different figures for the ranges of absorption for the bands of types 2a and 2b, as shown in table 4. He also stated that β-arabinopyranose derivatives show a type 2a band at 855 to 830 cm^{-1} (mean, 843 cm^{-1}); and that α-xylopyranose derivatives show a band at 760 to 740 cm^{-1} (mean, 750 cm^{-1}), but that many derivatives containing a benzene ring absorb here.

3.2. Neely's Summation

In a review [7], Neely correctly described the results of Barker and co-workers in the text of his article, and he attempted to condense this information in his table II (reproduced in table 5) entitled "Frequencies Characteristic of the Sugar Pyranose Ring." Study of this table reveals that, of the seven vibrations listed in column 1, only the first two could be described as possibly being "frequencies characteristic of the sugar pyranose ring." The other bands are those indicated by Barker and co-workers [4, 5, 6] to be characteristic of certain structural features possessed by some compounds that have a pyranoid ring. Unfortunately, Neely's table II has since been copied in articles and books [14].

TABLE 5. *Frequencies characteristic of the sugar pyranose ring*[a]

Group	Frequency	References[b]
	cm^{-1}	
Antisymmetrical ring vibration	917 ± 13	[4]
Symmetrical ring breathing vibration	770 ± 14	[4]
α-Anomeric C—H deformational vibration	844 ± 8	[4]
β-Anomeric C—H deformational vibration	891 ± 7	[4]
Equatorial C—H deformational vibration, other than anomeric C—H	880 ± 8	[5]
Ring methylene rocking vibration	867 ± 2	[6]
Terminal methyl group rocking vibration	967 ± 6	[6]

[a] According to W. B. Neeley [7]. [b] The reference numbers have been changed to those used in the present article.

The 2a band was described in table 5 as due to an "α-anomeric C—H deformational vibration"; however, Spedding more correctly described it as caused by an "anomeric C—H equatorial deformation" [15], because Barker and co-workers [12] had indicated that, in the favored chair conformation (CE) of (D or L)-arabinopyranose derivatives, the β anomers have an equatorial C-1—H bond. As already mentioned, further work [11] has shown that all that can at present be said is that type 2a bands are in some way associated with structures having an equatorial C-1—H bond, and type 2b bands with those having an axial C-1—H bond.

It is evident that the bands of types *2a and 2b*, listed in table 5 as occurring at 844 ± 8 cm^{-1} and at 891 ± 7 cm^{-1}, were taken from the paper [4] which had been restricted to study of D-glucopyranose and its derivatives. However, Neely may have considered that these values also applied fairly well to other pyranoses; because, for the gluco-, manno-, and galacto-pyranose derivatives (see table 3), the ranges of 852 to 814 cm^{-1} (mean, 833 cm^{-1}) and 904 to 882 cm^{-1} (mean, 893 cm^{-1}) encompass the values given [5] for the 2a and 2b bands, respectively, of these three groups of sugars. Moreover, as pointed out by Barker and co-workers [5], the range of 855 to 830 cm^{-1} (mean, 843 cm^{-1}) for the β-arabinopyranose derivatives (see table 3) fits the value for the 2a band.

As regards the bands of *types 1 and 3*, we have already discussed (in sec. 3.1a) how Neely [7] must have derived the values that he lists as occurring at 917 ± 13 cm^{-1} and at 770 ± 14 cm^{-1}—namely, from the values given [4] for D-glucopyranose derivatives. Barker and co-workers [5] had reached no firm conclusion as to the presence of *type 1* bands in the spectra of any pyranoid sugar derivatives other than those of (D or L)-glucopyranose. However, it would appear that, without comment, Neely may have intended to include bands of mannopyranose and galactopyranose derivatives in these values. Inspection of columns 2 and 3 of table 3 in Ref. [5] reveals that all of the mannopyranose compounds show a type 1 band in the range of 947 to 905 cm^{-1} (mean, 926 cm^{-1}); similarly, twelve of the 14 galactopyranose compounds (columns 1, 2, and 3 of table 2 in Ref. [5]) show a band in the range of 943 to 905 cm^{-1} (mean, 924 cm^{-1}). For the *type 3* bands listed for these three hexopyranoses in our table 3, the range is 809 to 732 cm^{-1} (mean, 771 cm^{-1}); Neely [7] listed 770 ± 14 cm^{-1}, and presumably concluded that this value should serve for derivatives of the three hexopyranoses. As derivatives of β-(D or L)-xylopyranose do not show type 3 absorption [5], this band cannot be ascribed to the pyranoid ring *per se*.

The band of *type 2c*, given in table 5 as lying at 880 ± 8 cm^{-1}, was presumably derived by Neely [7] from the values given by Barker and co-workers [5] for manno- and galacto-pyranose derivatives, namely, 876 ± 9 cm^{-1} and 871 ± 7 cm^{-1}; it was indicated that this band is shown by conformers having an equatorial C—H bond (other than an equatorial, anomeric C—H bond).

Finally, Neely [7] indicated that the last two bands listed in his table II were taken from a paper by Barker and co-workers [6]. The band at 867 ± 2 cm^{-1} had been found for 2-deoxy derivatives of gluco- and galacto-pryanoses and for a 3-deoxy derivative of mannopyranose. The band at 967 ± 6 cm^{-1} had been found for 6-deoxy derivatives of manno- and galacto-pyranoses.

3.3. Description of the Correlations for Aldo- and Keto-furanose Derivatives

For aldo- and keto-furanose derivatives, Barker and Stephens [16] noted absorption bands as follows: type A, 924 ± 13 cm^{-1} ("not distinguished from types 1 or 2b" of aldopyranoses); and type D, 799 ± 17 $cm.^{-1}$. "In addition, most of these compounds also showed type B absorption at 879 ± 7 $cm.^{-1}$ and type C at 858 ± 7 $cm.^{-1}$." Type A absorption was assigned to the symmetrical ring-breathing frequency. The following tentative assignments were also made: type D, to a carbon-hydrogen deformation mode where the hydrogen atom is on a carbon atom directly attached to the ring-oxygen atom; and types B and C, to modes of vibration involving the skeletal stretching of the substituents, with type B possibly concerned with side chains and type C "with the OH group."

3.4. Attempted Application of These Correlations to 1-Acylamido Derivatives

In this part of our study, the objective was not to make assignments for the bands observed in the spectra, but to determine whether the bands of the types reported by Barker and co-workers [4, 5, 6, 16] have *diagnostic value* for sugar derivatives other than those studied by these investigators. That is, we wished to find out if, when a 1-acylamido group is present in the molecule, the presence or absence of these bands can still be correlated with those structural features mentioned by Barker and co-workers.

For example, absorption of type A has been assigned to the symmetrical ring-breathing frequency of the furanoid ring. Consequently, it is to be expected that the spectrum of every furanoid compound having ring-breathing should show a band of type A. If the spectrum of a furanoid compound does *not* show a band of type A, either the ring-breathing is disturbed (or suppressed) or the correlation is faulty. However, if the spectrum of a *non*furanoid compound *shows* a band of type A, the correlation is still valid, but its diagnostic value is impaired because it is no longer exclusive, but merely indicative of a possibility that must then be checked by some other test.

To make this study, we examined, in turn, the spectra of those cyclic 1-acylamido derivatives having the five configurations given in table 3, because these were the only configurations discussed by Barker and co-workers for pyranoid derivatives. For comparison, we also examined the spectra of related acyclic derivatives, where available.

Table 6 lists the bands for compounds having the *xylo* configuration, from which it may be seen that the furanoid compounds 1 and 3 show some bands that have been associated [16] with the furanoid (*f*) structure, but they also show some bands that have been ascribed to the pyranoid (*p*) structure. The type 3(α) band of compound 3 might be due to the benzene ring. The pyranoid compounds show some *p* bands, and also some *f* bands. Pyranoid compound 1A shows one *f* and one *p* band. The β compounds 1A and 21 lack type 2(β) absorption, and the β compound 6A shows type 3(α) absorption. The type 2(β) band shown by compound 6A (the only acetate ester) might be due to the acetate ester groups. The pyranoid compound 21 shows all of the *f* bands, and also a band in the 855 to 830 cm^{-1} region (a region where the xylopyranose compounds studied by Barker and co-workers [5] show no absorption) which could be due to the benzene ring. The three pyranoid compounds (1A, 6A, and 21) show type 1 absorption; this was not specifically recognized by Barker and co-workers [5] for xylopyranose compounds, although they recorded bands in this region (in table 4 of ref. [5]) for such compounds.

TABLE 6. *Bands* (cm^{-1})[a] *in the spectra of compounds having the* xylo *configuration*

Serial No.	Anomer	*f* bands				*p* bands			
		A	B	C	D	1	2(β)	No band	3(α)
		Range							
		937–911	886–872	865–851	816–782	930–904	896–886	855–830	759–739
Furanoid									
1	α	(938)	883	–	803	(903)	–	831	–
3	α	–	(887, 871)	860	810	–	[b] [887]	–	749
Pyranoid									
1A	β	(939)	–	–	–	(903)	–	–	–
6A	β	934	877	–	–	904	895	–	(738)
21	β	(939)[913]	(870)	[853]	805	913	–	853	–

[a] Enclosure of a wavenumber in parentheses indicates that it is located somewhat (usually not more than 3 cm^{-1}) beyond the upper or lower limit of the wavenumber range under consideration. [b] Enclosure of a wavenumber in brackets indicates that, from other evidence, an alternative and more likely assignment can be made. The wavenumber for the latter is not enclosed in brackets.

Table 7 lists six pyranoid compounds and five acyclic compounds having the *arabino* configuration. Four of the α anomers show type 2(β) absorption, and these four compounds have a benzene ring. All of the pyranoid compounds show type 1 absorption; this was not specifically recognized by Barker and co-workers [5] for arabinopyranose compounds, although they recorded bands in this region (in table 4 of ref. [5]) for such compounds. However, the pyranoid compounds also show some *f* bands; indeed, compounds 11, 20, and 22 show all of the *f* bands (as well as the *p* bands). The *acyclic* compounds show some *f* and *p* bands. Compounds 16A and 40 show all of the *f* and *p* bands; and compounds 30 and 41 show all of the *p* bands. Like many furanoid compounds studied by Barker and co-workers [16], the acyclic compounds 30 and 41 show types A and D absorption, but lack type B (compound 41) or type C (compound 30) absorption.

TABLE 7. *Bands* (cm^{-1})[a] *in the spectra of compounds having the* arabino *configuration*

Serial No.	Anomer	*f* bands				*p* bands		
		A	B	C	D	1	2(β)	3(α; β)
		Range						
		937–911	886–872	865–851	816–782	930–904	855–830	781–744
Pyranoid								
4A	α	936[913]	–	864	–	913	–	771
11	α	934[928]	880	[856]	803	928	(856)	780
9A	α	933	(870)	–	–	907	–	(741)
17	α	935[931]	–	862 [851]	806	(931)	851 (828)	774, 758
20	α	[931,917]	876	[851]	808	(931) 917	851	746
22	α	937	877	[851]	804	(901)	851	772, 752
Acyclic								
15A	–	–	877	–	–	904	–	775 (742)
30	–	919	(870)	–	800	919	845	770
16A	–	931, 922	873	856	784	(931) 922	(856)	(784)
40	–	(939) 932, 921, 911	873	855	808, 800	(932) 921, 911	855 (829)	772 (?)
41	–	(938) 933, 911	–	(867) 851	805, 801	(933) 911	851, 846, 840	(743)

[a] See footnotes to table 6.

In table 8 are listed the bands of furanoid and pyranoid compounds having the *gluco* configuration, together with those of seven related acyclic compounds. The *furanoid* compounds show the *f* bands, although the type B band could be interpreted as being a *p* band of type 2(β); hence, *these compounds fit the correlations of Barker and co-workers* [16]. With the possible exception of compound 2A, the *pyranoid* compounds do not show a type 3 band, but all of them show a type 1 band. Although all of the pyranoid compounds are β anomers, four of them do not show type 2 (β) absorption, and three show type 2(α) absorption; compound 18 shows both. Compound 23a, which is formed on melting compound 23 at 117–120° and allowing the melt to crystallize, shows only one *p* band, at 922 cm^{-1}; this could equally well be interpreted as being an *f* band of type A, in which case the compound shows no *p* bands, but all of the *f* bands; this could suggest the possibility that it is the furanoid isomer of compound 23, which shows the ease with which such bands could be misinterpreted. The pyranoid compound 2A shows no *f* bands, and compound 9 shows an *f* band of type 2A which might well be a *p* band of type 1; these are in agreement with the correlations. The rest of the pyranoid compounds show two or more *f* bands, and compounds 18 and 23a show all of them. The *acyclic* compounds show *f* and *p* bands. Compounds 32 and 38 show all of the bands of both sorts; compounds 33 and 44 show all of the *f* bands; and compound 37 shows all of the *p* bands.

For *pyranoid* compounds having the *manno* configuration (see table 9), all of the β anomers show type 1 and 2(β) bands. The β anomers 13 and 14 show a type 2(α) band at the extremes of the range, which could be due to the benzene ring (not present in the four others). Also, the pyranoid compounds show some *f* bands; however, some of the ranges given by Barker and co-workers [16] for *f* bands could also be interpreted as being *p* bands in the case of manno-

TABLE 8. *Bands (cm^{-1})*[a] *in the spectra of compounds having the* gluco *configuration*

Serial No.	Anomer	*f* bands				*p* bands				
		A	B	C	D	1(α; β)	2(β)	2(α)	3(α; β) or 3(α; β)	
		Range								
		937–911	886–872	865–851	816–782	930–904	898–882	852–836	784–756	770–736
Furanoid										
2	α	(942)	886	(867)	810, 794	–	[886]	–	–	–
4	α	(939)	885	857	803, 800	–	[885]	–	776	–
Pyranoid										
2A	β	–	–	–	–	(902)	–	–	(758?)	(758?)
9	β	[922]	–	–	–	922, 908	896	–	–	–
12	β	[917]	[(889)]	(866)	811	917	889	–	–	–
7A	β	[917]	(871)	–	–	917, 909	897	–	–	–
18	β	934	[886]	864	810	905	886	836	–	–
19	β	(940) [(910)]	–	858	803	910	–	847	–	–
23	β	(940) [(907)]	–	858	804	907	–	845	–	–
23a	β	(940) 922	874	855	806	[922]	–	–	–	–
Acyclic										
25	–	930	882	–	787	930, 909	882	–	756	756
28	–	926	–	864	795	926, 909	894	847	–	–
32	–	923	878	862	800	923	892	851	775	–
33	–	930	877	863, 853	810, 804	930	889	(853)	–	–
37	–	937, 925, 917	–	862 (850)	–	925, 917	897	850	760	760
38	–	929	(870)	(849)	810, 801	929	(901)	849, 842	760	760
44	–	935, 917	(887)	(868)	808	917	887	–	772	(772)

[a] See footnotes to table 6.

TABLE 9. *Bands (cm^{-1})*[a] *in the spectra of compounds having the* manno *configuration*

Serial No.	Anomer	*f* bands				*p* bands					
		A	B	C	D	5-*C*-CH$_3$	1	2(β)	2c(α; β)	2(α)	3(α; β)
		Range									
		937–911	886–872	865–851	816–782	973–961	930–904	899–887	885–867	841–825	809–773
Pyranoid											
3A	β	–	[876]	–	[808]	–	907	(900)	876	–	808
6	β	–	–	[(867)]	[(781)]	(958)	(902)	(902)	867	–	781
13	β	(938) [917 (909)]	–	[(866)] 856	[803]	(958)	917, 909	898	(866)	826	803, 776
14	β	937 [917]	–	–	[806]	(975, 957)	917	898	–	(845)	806, 773
8A	β	(940)	[880]	–	–	972, 965	905	(900)	880	–	–
16	β	[924, 914]	–	861	–	(978)	924, 914, 904	893	–	–	–
Acyclic											
26	–	919	–	856	–	(975) 966	919	899	–	–	–
34	–	935	884, 875	–	803, 784	966	928(?)	896	884, 875	–	803, 784
35	–	930	877	–	803	(958)	930	895	877	–	803 (772)

[a] See footnotes to table 6.

pyranose derivatives. Thus, for compounds 13, 14, and 16, some of the *f* bands of type A could be interpreted as being *p* bands of type 1. Similarly, for compound 3A, the type B and D bands, and, for compound 6, the type C and D bands, could be interpreted as being bands of types 2c and 3. The three 5-*C*-methyl compounds (6, 14, and 16) show a band in the range of 978 to 957 cm^{-1}, but compounds 13 and 8A, which lack this grouping, also show a band in this range. The *acyclic* compounds show *f* and *p* bands.

Table 10 lists the bands of five pyranoid compounds having the *galacto* configuration. All of them show type 2c absorption. None of the unsubstituted compounds show type 3 absorption. The α anomers 7 and 10A show type 2(α) absorption, and the β anomers do not. The α anomer 10A also shows type 2(β) absorption. All of the β anomers show type 2(β) absorption. All of the pyranoid compounds show some *f* bands, but some of these bands could equally well be interpreted as being *p* bands. For example,

TABLE 10. *Bands (cm^{-1})*[a] *in the spectra of compounds having the* galacto *configuration*

Serial No.	Anomer	*f* bands				*p* bands				
		A	B	C	D	1	2(*β*)	2*c*(*α*; *β*)	2(*α*)	3(*α*; *β*)
		Range								
		937–911	886–872	865–851	816–782	930–904	904–886	878–864	836–814	772–732
Pyranoid										
7	*α*	[930]	[873]	–	791	930	–	873	833	–
5A; 8	*β*	–	–	[(868)]	786	–	896	868	–	–
		–	–	[(867)]	786	–	895	867	–	–
15	*β*	(939)	[(888) 876]	858	808, 784	–	896, 888	876	–	–
10A	*α*	[921]	–	[862]	–	921, 907	(907) 899	(862)	834	757
11A	*β*	[914]	[(870)]	–	–	914, 907	(907) 894	870	–	734
Acyclic										
27	–	–	879	(867) 856	–	–	–	(879) 867	–	759
36	–	929	875	–	803	929	894	875	–	745

[a] See footnotes to table 6.

for compound 11A, the bands of types A and B could be types 1 and 2c bands, respectively; the bands for this compound then *show complete agreement* with the *p* bands for a *β*-galactopyranose. Similarly, for compound 10A, if the *f* bands of types A and C are actually *p* bands of types 1 and 2c, the bands *agree with those for a galactopyranose*, but the presence of types 2(*α*) and 2(*β*) bands does not permit a conclusion as to the anomeric configuration. The *acyclic* compounds listed show *f* and *p* bands. The bands for compound 36 correspond with those for a *β*-galactopyranose, which shows that use of these bands without other evidence could give an erroneous conclusion.

To be of general usefulness in structural analysis, the correlations made by Barker and co-workers [12] should be applicable to the furanoid and pyranoid forms, respectively, of sugar derivatives of all kinds, provided that allowance is made for bands attributable to such other features as benzene rings or acetate ester groups present in the molecule. However, from the above study, it is apparent that the correlations made by Barker and co-workers [12] are, in most instances, restricted to the compounds they studied, and that the correlations cannot be extended to have a wider diagnostic applicability to related compounds. This conclusion confirms our previous reports that, for cyclic acetals of sugars, "distinctive absorption bands are not apparent for pyranose or furanose rings" [17], and that, for 1-acetamido derivatives of sugars, "no bands were noted which could be correlated with the absence or presence of the pyranoid ring" [2].

4. Correlations Made by Verstraeten for Furanoid and Pyranoid Forms of Aldoses and Ketoses

In 1962, the infrared spectra of most of the readily available aldo- and keto-pentoses and aldo- and keto-hexoses were published [18], but no correlations of bands according to the type-system of Barker and co-workers [4, 5, 6, 16] were given.

However, in 1964, Verstraeten [19] made a study of these spectra, together with those of some additional 2-ketoses, and obtained evidence that "all of the common sugars having a cyclic structure, and their derivatives, display" absorption at 929 ±15 cm^{-1} (which he designated "type 1"). Exceptions noted were *α*-D-lyxose, showing a band at 965 cm^{-1}, and *α*-D-galactose, at 960 cm^{-1}. He assigned "type 1" absorption to a symmetrical ring-stretching frequency, and apparently regarded his "type 1" absorption as being the same as the type 1 absorption described by Barker and co-workers [4] for glucopyranose derivatives.

Verstraeten found that only furanoses give "type 2" absorption at 850 ±6 cm^{-1} (provided that the ring is free to vibrate). He stated that his type 2 absorption is the same as the type C absorption of Barker and Stephens [16].

The same author observed that some ketoses, as well as aldoses, show a band at 781 ±5 cm^{-1}. He designated this band "type 3" and regarded it as being the same as the type 3 absorption mentioned, for several aldoses, by Barker and co-workers [4, 5]. He indicated that type 3 absorption was shown provided that two conditions were met: (a) the sugar must have a pyranoid ring, and (b) this pyranoid form must assume a conformation having at least one axial hydroxyl group. He noted that, if the number of axial hydroxyl groups is increased (thereby decreasing the conformational stability), type 3 absorption becomes manifest. For example, *β*-(D or L)-xylopyranose-CA, which shows no type 3 absorption, is devoid of axial hydroxyl groups, whereas the *α* anomer in the CA conformation, which has an axial hydroxyl group at C-1, shows absorption at 760 cm^{-1}. Type 3 absorption was tentatively ascribed to ring-breathing. It was concluded that, if the total structure was suitable, as with compounds having the *β-xylo* or *β-ribo* configuration in the CA conformation, intramolecular

TABLE 11. *Summary of the results of Verstraeten [19] for infrared bands characteristic of various kinds of sugars and derivatives*

Type	Aldoses and ketoses			Ketoses	
	Furanoid	Certain pyranoid [a]	Furanoid and pyranoid	Furanoid [b]	Furanoid and pyranoid
1 [c]			929 ± 15 (944–914)		
2 [d]	850 ± 6 (856–844)	——			
3 [e]	——	781 ± 5 (786–776)			
I [f]					874 ± 9 (883–865)
IIA [g]					817 ± 7 (824–810)
IIB				834 ± 4 (838–830)	

[a] See text.

[b] Substituted, or joined to a pyranoid ring.

[c] Equated with Barker's type 1 for glucopyranose derivatives (917 ± 13 cm^{-1}); Barker and Stephens [16] had pointed out that this is in the same range as their type A for aldo- and keto-furanose derivatives (924 ± 13 cm^{-1}).

[d] Equated with Barker's type C (858 ± 7 cm^{-1}) for aldo- and keto-furanose derivatives.

[e] Equated with Barker's type 3 for certain aldopyranose derivatives.

[f] In the same range as Barker's type B for aldo- and keto-furanose derivatives (879 ± 7 cm^{-1}).

[g] In about the same range as Barker's type D for aldo- and keto-furanose derivatives (799 ± 17 cm^{-1}).

TABLE 12. *Types of bands shown by aldoses and ketoses [19]*

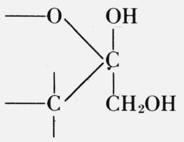
Aldoses		Ketoses	
Furanose	Pyranose	Furanose	Pyranose
1	1	1	1
2	–	2	–
–	[a] 3	–	[a] 3
–	–	I	I
–	–	IIA	IIA
–	–	[b] IIB	–

[a] Not shown if the favored conformation has no axial groups.

[b] Shown if the hydroxyl groups of the ketofuranose are substituted (or if C–2 of the ketofuranose is joined to a pyranoid or furanoid structure).

linkages (such as van der Waals contact or hydrogen bonds) might be formed, resulting in modification of the ring-breathing, so that absorption at this frequency would not be shown.

Verstraeten also found that 2-ketoses display "type I" bands at 874 ±9 cm^{-1} and "type IIA" bands at 817 ±7 cm^{-1}, regardless of whether the sugars are pyranose or furanose. These bands were ascribed to the presence of the following structural feature:



and tentatively assigned to a skeletal vibration. He pointed out that α- and β-D-lyxose, α- and β-D-talose, α-D-mannose, and α-L-fucose (which are not ketoses) also show these bands.

He found that if the ketofuranose ring is substituted, or joined to a pyranoid ring, a type IIB band appears at 834 ±4 cm^{-1}, in addition to or instead of the type IIA band. Verstraeten's results are summarized in tables 11 and 12.

4.1. Attempted Application of These Correlations to 1-Acylamido Derivatives

None of the compounds in table 1 are derivatives of ketoses. Hence, we wished to find out (a) whether the spectra of our furanoid compounds showed Verstraeten's *f*-band of type 2 and the band of type 1; and (b) whether the pyranoid compounds showed Verstraeten's *p*-band of type 3 and the band of type 1. If the bands of types I, IIA, and IIB are usefully diagnostic of *ketoses*, they should *not* be shown by the compounds in table 1.

a. Unsubstituted Derivatives

The bands in the spectra of 13 unsubstituted furanoid and pyranoid 1-acetamido derivatives are listed in table 13. The *furanoid* compounds 1 and 2 do not show an *f* band of type 2, but both show a type 1 band. Both show the *ketose* band of type I. Compound 1 shows the ketofuranose band of type IIB and the *p* band of type 3; and compound 2 shows the ketose band of type IIA.

Of the 11 *pyranoid* compounds, seven do not show the *p* band of type 3; for the five compounds (1A, 5B, 6B, 2A, and 9) having the *xylo*, *ribo*, or *gluco* configuration, this is in agreement with Verstraeten's correlations. Six do not show the type 1 band. None of them show a type IIA band, so this band may be characteristic of ketoses. Only one of the pyranoid compounds shows a type 2 band, but the two furanoid compounds do not show the band, either. Only two of the eleven pyranoid compounds show a type IIB band, so this band, also, may have some value for diagnosis of ketoses. However, eight of these aldose derivatives show the "type I band of ketoses." Except for the type IIB band shown by compound 7, none of the *N*-acetylaldohexopyranosylamines show bands of types 2, IIA, and IIB, in agreement with Verstraeten's correlations. The β-xylopyranose compound 1A and the β-glucopyranose compounds (2A and 9) show no bands of types 2, I, IIA, or IIB, in agreement with Verstraeten's correlations.

TABLE 13. *Bands (cm^{-1}) in the spectra of unsubstituted, furanoid and pyranoid, 1-acetamido derivatives*

Serial No.	Bands of aldoses (and ketoses)			Bands of ketoses		
	1(*f*, *p*)	2(*f*)	3(*p*)	I	IIA	IIB
	Range					
	944–914	856–844	786–776	883–865	824–810	838–830
Furanoses						
1	938	—	778	883	—	831
2	942	—	—	867	810	—
Pentopyranoses						
1A	939	—	[a]—	—	—	—
5	—	856	776	881	—	—
4A	936 (913)	—	(771)	(864)	—	—
5B	—	—	[b]—	882	—	838
6B	—	—	[b]—	880	—	—
Hexopyranoses						
2A	—	—	[c]—	—	—	—
[9 [d]	922	—	[c]—	—	—	—]
3A	—	—	—	876	—	—
6	—	—	781	867	—	—
7	930	—	—	873	—	833
5A,8	942	—	786	867	—	—

[a] *xylo.* [b] *ribo.* [c] *gluco.* [d] 1-Propionamido derivative.

Table 14 lists the bands in the spectra of six unsubstituted, pyranoid, 1-benzamido derivatives. Only two do not show the *p* band of type 3, and for one of these (compound 12), this agrees with Verstraeten's correlations. All of them show the band of type 1. Four of these pyranoid compounds show the *f* band of type 2; this impairs the diagnostic value of the band. Only one of the compounds shows a type IIA band and only one shows a type IIB band; this strengthens the possibility that these bands have some diagnostic value for ketoses. All but one of the compounds show a "type I band of ketoses," as do ten aldose derivatives listed in table 13; hence, the type I band has no value for diagnosing the presence of the 2-ketose structure.

TABLE 14. *Bands (cm^{-1}) in the spectra of unsubstituted, pyranoid, 1-benzamido derivatives*

Serial No.	Bands of aldoses (and ketoses)			Bands of ketoses		
	1(*f*, *p*)	2(*f*)	3(*p*)	I	IIA	IIB
	Range					
	944–914	856–844	786–776	883–865	824–810	838–830
Pentopyranoses						
10	933, 918	—	—	870	—	830
11	934, 928	856	780	880	—	—
Hexopyranoses						
12	917	—	[a]—	866	811	—
13	938, 917	856	776	866	—	—
14	937, 917	845	(773)	—	—	—
15	939	(858)	784	876	—	—

[a] *gluco.*

From a study of tables 13 and 14, it may be seen that only two of these aldose derivatives show the type IIA band of ketoses, and only four of them show the type IIB band of ketofuranoses. Of the five compounds showing the type 2 absorption of furanoses, four are 1-benzamido pyranoid derivatives. Also, from a comparison of the spectra of the β-glycopyranose compounds 2A and 12, it would seem that, for compound 12, the 1-benzamido group must, in some way, be responsible for the bands of types 1, I, and IIA.

Table 15 lists bands in the spectra of five unsubstituted 1,1-bis(acetamido)-1-deoxyalditols. None of them show the types IIA and IIB bands of ketoses, indicating that these bands may have some diagnostic value. All of these acyclic compounds show the type 1 band of aldoses and ketoses, and all but one show the type I band of ketoses. Two of the five compounds show the type 2 band of furanoses, and two of the five show the type 3 band of certain pyranoid aldoses and ketoses.

TABLE 15. *Bands (cm^{-1}) in the spectra of unsubstituted 1,1-bis(acylamido)-1-deoxyalditols*

Serial No.	Bands of aldoses (and ketoses)			Bands of ketoses		
	1(*f*, *p*)	2(*f*)	3(*p*)	I	IIA	IIB
	Range					
	944–914	856–844	786–776	883–865	824–810	838–830
1,1-Bis(acetamido)						
24	936	—	—	882	—	—
15A	(947)	—	(775)	877	—	—
25	930	—	(787)	882	—	—
26	919	856	—	—	—	—
27	943	856	—	879, 867	—	—
1,1-Bis(propionamido)						
28	926	847	—	(864)	—	—
1,1-Bis(benzamido)						
29	937, 926	(843)	—	880	—	—
30	919	845	—	870	—	—
31	932, 916	—	—	881	—	838
32	923	851	(775)	878	—	—
33	930	853	—	877	810	—
34	935	—	784	(884)875	—	—
35	930	846	(772)	877	—	—
36	929	847	—	875	—	—

In table 15 are also listed the bands of unsubstituted 1,1-bis(benzamido)-1-deoxyalditols. Only one compound (33) shows type IIA absorption, and only one compound (31) shows type IIB absorption, confirming that these bands have some diagnostic value. However, like the compounds shown in table 14, all of these acyclic compounds show the type 1 band of aldoses and ketoses, and all show the type I band of ketoses. Only two of the eight acyclic compounds do not show the type 2 band of furanoses, and three show the type 3 band of certain pyranoid aldoses and ketoses.

b. Esters

Verstraeten did not study the infrared spectra of esters. The bands in the spectra of esters of furanoid and pyranoid 1-acetamido derivatives are listed in table 16. The *furanoid* compounds 3 and 4 show the *f* band of type 2 and the band of type 1, in agreement with Verstraeten's correlations. However, they both show the ketose band of type I. In agreement with Verstraeten's correlations, compound 3 does not show the *p* band of type 3; however, compound 4 shows this band. Compound 3 shows the type IIA band of ketoses, and compound 4 shows the type IIB band of ketoses.

TABLE 16. *Bands* (*cm*$^{-1}$) *in the spectra of esters of (pyranoid) 1-propionamido and (furanoid and pyranoid) 1-acetamido derivatives*

Serial No.	Ester	Bands of aldoses (and ketoses)			Bands of ketoses		
		1(*f*, *p*)	2(*f*)	3(*p*)	I	IIA	IIB
		Range					
		944–914	856–844	786–776	883–865	824–810	838–830
		1-PROPIONAMIDO					
18	*O*-Pr.	934	–	[a]–	(886, 864)	810	836
19	*O*-Bz	940	(858)847	[a]–	–	–	830
		1-ACETAMIDO					
Furanoses							
3	*O*-Bz	943	(860)	–	(887)871	824, 810	–
4	*O*-Bz	939	(857)	776	(885)	–	830
Pentopyranoses							
17	*O*-Bz	944, 935	851	774	(862)	–	(828)
6A	*O*-Ac	934	–	[b]–	877	–	–
9A	*O*-Ac	944, 933	–	–	870	–	–
4B	*O*-Ac	936	–	[c]–	870	–	–
Hexopyranoses							
7A	*O*-Ac	917	–	[a]–	871	–	–
8A	*O*-Ac	940	–	–	880	–	–
16	*O*-Ac	(945) 924, 914	–	–	(861)	–	–
10A	*O*-Ac	943, 921	–	–	(862)	–	834
11A	*O*-Ac	914	–	–	870	–	–

[a] *gluco.* [b] *xylo.* [c] *ribo.*

Of the eight *pyranoid* acetates, none show the *f* band of type 2, and all show the band of type 1, in agreement with Verstraeten's correlations. However, none of them show the type 3 band, although only three (compounds 6A, 4B, and 7A) would be expected not to show it. In agreement with Verstraeten's correlations, none of them show the type IIA band, and all but one (compound 10A) do not show the type IIB band. However, all of them show the type I band of ketoses.

The *pyranoid* benzoates (compounds 17 and 19) show the band of type 1 and do not show the type IIA band, in agreement with Verstraeten's correlations. However, they both show the *f* band of type 2 and the ketose band of type IIB. Compound 17 shows the *p* band of type 3, but compound 19 does not, in agreement with Verstraeten's correlations. Like the acetates in table 16, the propionate (18) and the benzoate (17) show the type I absorption of ketoses, but benzoate 19 does not. The 1-propionamido compounds (18 and 19) show absorption of type 1 but not type 3 absorption, in agreement with Verstraeten's correlations; however, they both show the type IIB absorption of ketofuranoses. Of the pyranoid compounds in table 16, compounds 6A, 4B, 7A, 18, and 19 would be expected not to show type 3 absorption and they do not, in agreement with Verstraeten's correlations. However, compounds 9A, 17, 8A, 10A, and 11A would be expected to show type 3 absorption, but only compound 17 shows it.

Table 17 lists the bands of esters of pyranoid 1-benzamido derivatives. All of them show the type 1 band, in agreement with Verstraeten's correlations. However, they all show the *f* band of type 2 and the type I band of ketoses. Compounds 21, 23, and 23a do not show the *p* band of type 3, whereas compound 22 does, in agreement with Verstraeten's correlations. However, compound 20 does not show this band. Three of the five compounds show the type IIA band of ketoses, and two show the type IIB band of ketofuranoses.

TABLE 17. *Bands* (*cm*$^{-1}$) *in the spectra of esters of pyranoid, 1-benzamido derivatives*

Serial No.	Bands of aldoses (and ketoses)			Bands of ketoses		
	1(*f*, *p*)	2(*f*)	3(*p*)	I	IIA	IIB
	Range					
	944–914	856–844	786–776	883–865	824–810	838–830
***O*-Acetyl**						
20	(947)931, 917	851	–	876	(808)	–
***O*-Benzoyl**						
21	939(913)	853	[a]–	870	824	–
22	(945)937	851	(772)	877	824	–
23	940	(858)845	[b]–	870	–	831
23a	940, 922	855	[b]–	874	–	830

[a] *xylo.* [b] *gluco.*

In table 18 are listed the bands of nine esters of 1,1-bis(acylamido)-1-deoxyalditols. All of these acyclic compounds show types 1 and I bands. All of the acetates, but none of the benzoates or acetate-benzoates, show a band of type 3. All of the benzamido compounds show a band of type IIA. Only two of the compounds do *not* show an *f* band of type 2. Three of the compounds show the type IIB band of ketofuranoses, and they possess both *O*-benzoyl and 1,1-bis(benzamido) groups.

c. Summation

The results are summarized in table 19, which lists, by the categories in tables 13 to 18, the compounds in this study that fit Verstraeten's correlations. For this purpose, an agreement score of unity is given if the spectrum of a compound (a) shows a predicted band or (b) does not show a band predicted to be absent; a score of zero is given if the spectrum (a) does not show a predicted band or (b) shows a band predicted to be absent. From these results, an estimate of diagnostic value (see table 20) of each type of band was made, on the assumption that an agreement of 50 percent or less has no diagnostic value, but an agreement near 100 percent has diagnostic value. An agreement lying between 50 and 100 percent may have some value as being indicative of a possibility that must be further explored. Table 21 lists the results for six separate compounds, for comparison.

Verstraeten [19] pointed out that the *type 1* band is shown by the cyclic aldoses *and* ketoses that he studied; as may be seen from tables 20 and 21, this is now confirmed, except for some of the 1-acetamido pyranoses (see table 13). Consequently, to have diagnostic value, the band should *not* be shown by the acyclic derivatives; however, the type 1 band is shown by them (see tables 15 and 18). As may be seen from tables 20 and 21, the type 1 band has no diagnostic value for the acyclic derivatives. Hence, it has no diagnostic value at all in distinguishing between cyclic and acyclic structures for the compounds in this study.

TABLE 18. *Bands* (cm^{-1}) *in the spectra of esters of 1,1-bis(acylamido)-1-deoxyalditols*

Serial No.	Bands of aldoses (and ketoses)			Bands of ketoses		
	1(*f*, *p*)	2(*f*)	3(*p*)	I	IIA	IIB
	Range					
	944–914	856–844	786–776	883–865	824–810	838–830
	ACETATES					
Acetamido						
16A	929, 921	855	784	871	–	–
37	937, 925, 917	850	778(?)	(862)	–	–
Benzamido						
42	941, 935	847	778(?)	879	821	–
43	935	847	(775)	870	820(?)	–
44	935, 917	–	(772)	868	824	–
	BENZOATES					
Benzamido						
38	940, 929	849	–	870	810	–
41	938, 933, (911)	851, 846	–	867	822	(840)
	ACETATE–BENZOATES					
39	926, 917	–	–	871	(809)	837
40	939, 932, 921	855	–	873	(808)	(829)

TABLE 19. *Number of compounds of each category that fit Verstraeten's correlations*

Compounds studied			No. of compounds fitting band of type					
In table No.	Structural type	No.	1	2	3	I	IIA	IIB
Furanoses								
13	*N*-Ac	2	2	0	1	0	1	1
16	*N*-Ac, *O*-Bz	2	2	2	1	0	1	1
	Total	4	4	2	2	0	2	2
Pyranoses								
13	*N*-Ac	10	4	9	8	2	10	8
	N-Pr	1	1	1	1	1	1	1
14	*N*-Bz	6	6	2	5	1	5	5
16	*N*-Ac, *O*-Ac	8	8	8	3	0	8	7
	N-Pr, *O*-Pr	1	1	1	1	0	0	0
	N-Ac, *O*-Bz	1	1	0	1	0	1	0
	N-Pr, *O*-Bz	1	1	0	1	1	1	0
17	*N*-Bz, *O*-Ac	1	1	0	0	0	0	1
	N-Bz, *O*-Bz	4	4	0	4	0	2	2
	Total	33	27	21	24	5	28	24
Acyclic								
15	*N*-Ac	5	0	3	3	1	5	5
	N-Pr	1	0	0	1	0	1	1
	N-Bz	8	0	2	5	0	7	7
18	*N*-Ac, *O*-Ac	2	0	0	0	0	2	2
	N-Bz, *O*-Ac	3	0	1	0	0	0	3
	N-Bz, *O*-Bz	2	0	0	2	0	0	1
	N-Bz, *O*-Ac, *O*-Bz	2	0	1	2	0	0	0
	Total	23	0	7	13	1	15	19
	Grand total	60	31	30	39	6	45	45

TABLE 20. *Diagnostic value of Verstraeten's correlations for the various categories of compounds*

Compounds studied			Diagnostic value [a] of band of type					
In table No.	Structural type	No.	1	2	3	I	IIA	IIB
Aldofuranoses								
13	*N*-Ac	2	[++]	0	0	0	0	0
16	*N*-Ac, *O*-Bz	2	[++]	++	0	0	0	0
Aldopyranoses								
13	*N*-Ac	10	[0]	+	+	0	++	+
14	*N*-Bz	6	[++]	0	+	0	+	+
16	*N*-Ac, *O*-Ac	8	[++]	++	0	0	++	+
17	*N*-Bz, *O*-Bz	4	[++]	0	++	0	0	0
Acyclic								
15	*N*-Ac	5	0	+?	+?	0	++	++
	N-Bz	8	0	0	+?	0	+	+
18	*N*-Ac, *O*-Ac	2	0	0	0	0	++	++
	N-Bz, *O*-Ac	3	0	0	0	0	0	++
	N-Bz, *O*-Bz	2	0	0	++	0	0	0
	N-Bz, *O*-Ac, *O*-Bz	2	0	0	++	0	0	0

[a] Key: ++, 100% agreement: +, nearly 100% agreement: +?, above 50%, but much less than 100% agreement: 0, agreement of 50% or less.

TABLE 21. *Diagnostic value of Verstraeten's correlations applied to single compounds of various categories*

Compounds studied			Diagnostic value [a] of band of type					
In table No.	Serial No.	Structural type	1	2	3	I	IIA	IIB
Pyranoses								
13	9	*N*-Pr.	[+]	+	+	+	+	+
16	18	*N*-Pr, *O*-Pr.	[+]	+	+	0	0	0
	19	*N*-Pr, *O*-Bz	[+]	0	+	+	+	0
	17	*N*-Ac, *O*-Bz	[+]	0	+	0	+	0
17	20	*N*-Bz, *O*-Ac	[+]	0	0	0	0	+
Acyclic								
15	28	*N*-Pr.	0	0	+	0	+	+

[a] Key: +, agrees with correlation; 0, does not agree with correlation.

From line 1 of table 20, it may be seen that none of the bands (including type 1, for the reasons just given) have diagnostic value for the two aldofuranoses studied (table 13); but, on benzoylation (table 16), the *f* band of *type 2* becomes manifest. Similarly, the diagnostic value of the type 2 band for the 1-acetamido pyranoses (table 13) is increased by acetylation (table 16); but the band has no diagnostic value for the 1-benzamido pyranoses (table 14), and benzoylation (table 17) has no effect on the value. The type 2 band has no diagnostic value for distinguishing furanoses from the acyclic compounds (tables 15 and 18).

Except for the furanoses (tables 13 and 16), the *type 3* band has diagnostic value for all of the benzoates (tables 16, 17, and 18), but not for the acetates (tables 16, 17, and 18); it may have value for the unesterified compounds (tables 13, 14, and 15).

From table 20, it may be seen that the band of *type I* has no diagnostic value for any of the compounds; for this band, the results in table 21 have no statistical significance.

Except for the furanoses (tables 13 and 16) and the esters of 1-benzamido compounds (tables 17 and 18), the *type IIA* band has excellent diagnostic value. The same is true for the *type IIB* band, which also has diagnostic value for the acetylated 1,1-bis(acetamido) alditols.

Consequently, for the compounds discussed in this study, the bands of types 1 and I have no diagnostic value. Secondly, before a spectrum is checked for the presence or absence of bands of types 2, 3, IIA, and IIB, it should be examined for the presence or absence of the group frequencies characteristic of the *O*-acetyl and *O*-benzoyl groups. *If no ester group is present*, the spectrum should be examined for the group frequencies characteristic of the *N*-acetyl and *N*-benzoyl groups. (a) If the *N*-acetyl group is present, the Verstraeten bands have no diagnostic value for the furanoid compounds 1 and 2. If these structures are eliminated from consideration by the results of some other kind of test, the bands of types 2, 3, IA, and IIA *may* have diagnostic value. (b) Should the *N*-benzoyl group be present, the type 2 band has no diagnostic value, but the bands of types 3, IA, and IIA should be useful.

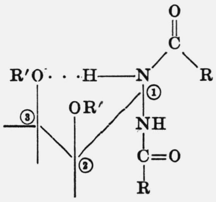
If an ester group is present, it may be seen (from table 20) that, for the *N*-acetyl-*O*-acetyl compounds, the bands of types IIA and IIB differentiate between Verstraeten's ketoses and our nonketoses, but cyclic compounds cannot be distinguished from acyclic compounds. Insufficient evidence is available for the *N*-acetyl-*O*-benzoyl compounds; compounds 3 and 4 show the *f* band of type 2, but this band has no diagnostic value for compound 17. As regards the *N*-benzoyl-*O*-acetyl compounds, only the type IIB band has diagnostic value. For the *N*-benzoyl-*O*-benzoyl compounds, only the type 3 band has diagnostic value.

5. Correlations Made by Nanasi and Co-workers

Nanasi and co-workers [20] have made some correlations for infrared spectra of *N*-*p*-tolyl-α-and-β-D-glucopyranosylamines and their tetraacetates, and for tetramethyl ethers of the *N*-*p*-tolylglycosylamines having the α-D-glucofuranosyl, α-D-glucopyranosyl, and β-D-galactopyranosyl structures. They also made correlations for the *N*-*p*-bromophenylglycosylamines having the 2-deoxy-β-D-*arabino*-hexopyranosyl, β-D-glucopyranosyl, and β-D-galactopyranosyl structures, and for the tetraacetates of the last two. In the range of wavelengths we have discussed, most of their correlations agreed with those of Barker and co-workers [12], and so, detailed comment is not necessary. We have found that their correlations cannot be extended to the compounds described in the present article.

6. Other Absorption Bands

All of the compounds in this study are secondary amides, and all of them show at least one band at 3460 to 3226 cm^{-1} (N-H stretching); in this region, the completely esterified compounds (group 1a, table 22) could not be distinguished from those having free hydroxyl groups (group 1b) that would show O-H stretching in the same region. All of the compounds show a band at 1681–1626 cm^{-1} (amide I) and at 1575 to 1504 cm^{-1} (amide II). The bis(acylamido) compounds (group 1d) show two amide II bands, suggesting that the two acylamido groups on C-1 of these compounds are not equivalent. They may have a hydrogen-bonded structure, possibly of the following type.



where R is Me, Et, or Ph; and R′ is H, Ac, EtCO, or Bz.

TABLE 22. *Structural groups studied*

Group	Structural feature	Compounds (serial numbers) in group
1	Amide, secondary	
a	no hydroxyl group	3, 4, 16–23a, 37, 39–44, 6A–11A, 16A, 4B
b	free hydroxyl groups	1, 2, 5–15, 24–36, 38, 1A–5A, 15A, 5B, 6B
c	mono(acylamido)	1–23a, 1A–11A, 4B–6B
d	bis(acylamido)	24–44, 15A, 16A
2	Esters	
a	acetates	16, 20, 37, 42–44, 6A–11A, 16A, 4B
b	propionate	18
c	benzoates	3, 4, 17, 19, 21–23a, 38, 41
d	mixed acetate-benzoates	39, 40
3	Phenyl group	
a	*N*-benzoyl, *O*-benzoyl, or both	3, 4, 10–15, 17, 19–23a, 29–36, 38–44
b	no phenyl group	1, 2, 5–9, 16, 18, 24–28, 37, 1A–11A, 15A, 16A, 4B–6B

All of the compounds show a band at 1311 to 1258 cm^{-1} ("amide III"). All of the acyclic compounds having a benzoyl group show the amide V band at 712 to 689 cm^{-1}, and this band is shown by many of the other compounds in this study.

The acetates and the tetrapropionate (groups 2a and 2b) show a band at 1761 to 1742 cm^{-1} (C=O stretching), except for compound 4B, which shows a band at 1718 cm^{-1}. The benzoates (group 2c) show a band at 1745 to 1727 cm^{-1}, except for the monobenzoate (compound 38) which shows a band at 1698 cm^{-1}. The mixed esters (group 2d) show two bands in this region: compound 39 at 1742 and 1715 cm^{-1}, and compound 40 at 1761 and 1745 cm^{-1}.

All of the compounds containing a phenyl group (group 3a) show bands at 1613 to 1600 cm^{-1}, 1587 to 1567 cm^{-1}, and 1506 to 1477 cm^{-1}. All of the compounds containing a phenyl group also show a band at 811 to 798 cm^{-1}; a band (*f* band of type D) in this region is also shown by the furanoid compounds 1 and 2, which lack a phenyl group. Consequently, this band has no diagnostic value for the furanoid ring if benzoyl groups are present. The propionate (compound 18) shows a band at 810 cm^{-1}, and the bis(propionamido) compound 28 shows a band at 807 cm^{-1}, but the propionamido compound 9 shows no band in this region. Compounds 38, 39, and 40, which are 1,1-bis(benzamido) compounds having a lone, terminal, *O*-benzoyl group, show two distinct bands in this region (810 to 798 cm^{-1}).

7. Experimental Procedures

7.1. Preparation and Purification of the Compounds

The compounds listed in table 1 were prepared by the methods given in the references cited. Each compound was recrystallized from an appropriate solvent until further recrystallization caused no change in melting point or optical rotation.

7.2. Measurement of Infrared Absorption

The spectrograms were recorded with a Perkin-Elmer Model 137 spectrophotometer[4] which was calibrated against a polystyrene standard (found value and deviation in parentheses): 3030 (3096; +66), 2924 (2976; +52), 2849 (2865; +16), 1946 (1953; +7), 1802 (1808 to 1805; +6 to +3), 1603 (1605 to 1600; +2 to −3), 1495 (1495 to 1493; 0 to −2), 1155 (1155 to 1153; 0 to −2), 1029 (1029 to 1028; 0 to −1), and 906 (907; +1) cm^{-1}, and against polyethylene: 720 (720 to 719; 0 to −1) cm^{-1}.

The spectrograms (see fig. 1) were recorded for Nujol mulls of the samples, and the bands of Nujol were used as an internal reference standard. In this study, the bands in the range of 4000 to 1800 cm^{-1} were of little interest, and the bands observed were corrected by reference to the above calibration and to the Nujol band at 2861 cm^{-1}. For bands in the range of 1800 to 667 cm^{-1}, the observed bands were not corrected. As, in some instances, the bands of interest occurred inside a range of as much as 26 cm^{-1}, and as (in the range of 1000 to 730 cm^{-1}) this instrument gave results to ±2 cm^{-1}, the instrument was considered to be sufficiently accurate for our purposes. For example, for compound 15A, the bands in the region of 1000 to 730 cm^{-1} were compared with those recorded for the same specimen with a Beckman Model IR4 (double beam) spectrophotometer[4] (latter results in parentheses) as follows: 966 (964), 948 (947), 906 (904), 879 (877), 775 (775), 741 (742), and 714 (714) cm^{-1}. For compound 5A, the bands were compared with those obtained with a Perkin-Elmer Model 21 (double beam) spectrophotometer[4] (latter results in parentheses): *ca.* 995 (*ca.* 995), 968 (967), 948 (947), 943 (942), 896 (895), 868 (867), and 786 (786) cm^{-1}.

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[4] Certain commercial instruments are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the equipment identified is necessarily the best available for the purpose.

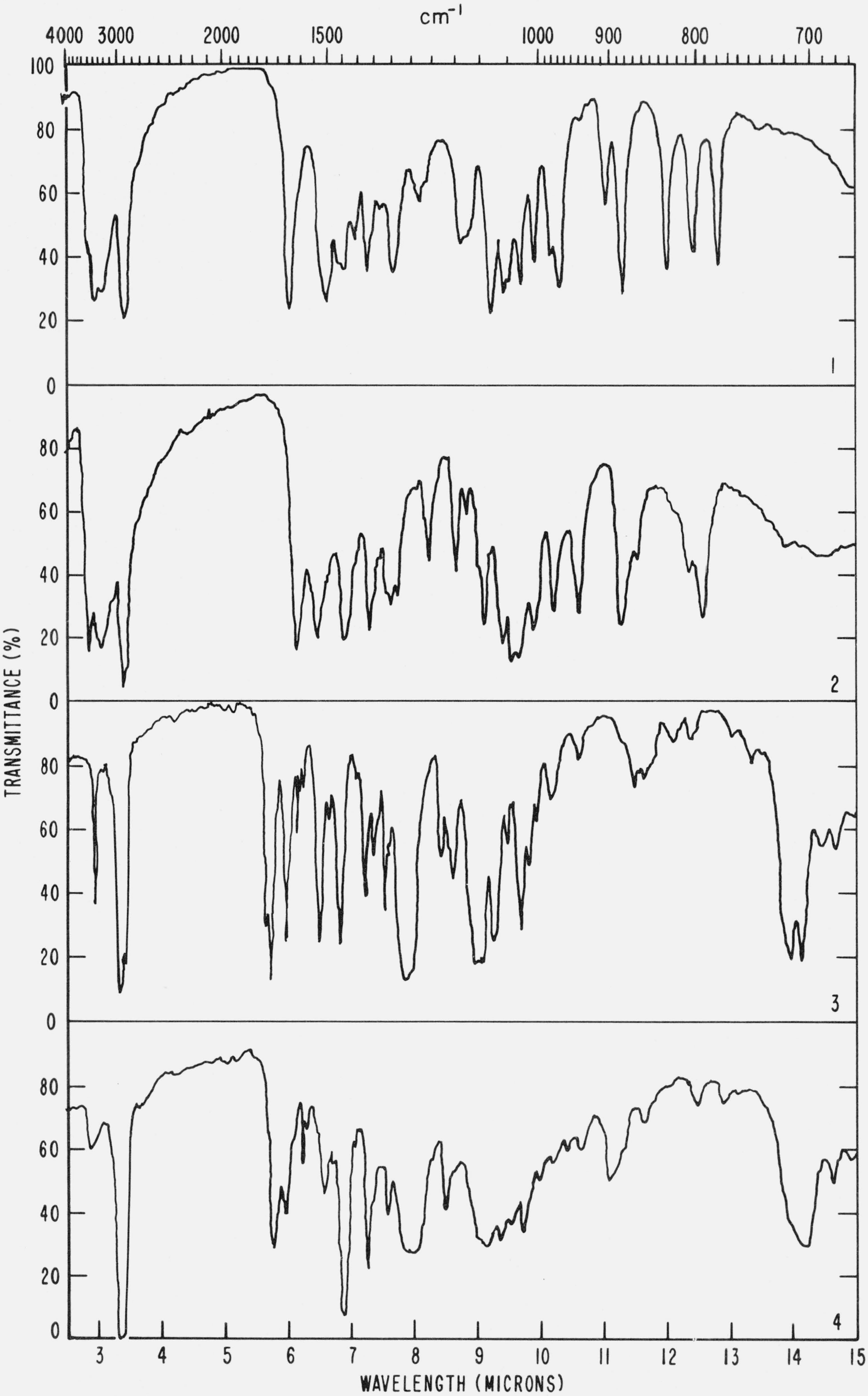

FIGURE 1. *Spectrograms of compounds in Nujol mulls.*

1, *N*-Acetyl-α-D-xylofuranosylamine; **2,** *N*-acetyl-α-D-glucofuranosylamine; **3,** *N*-acetyl-2,3,5-tri-*O*-benzoyl-α-D-xylofuranosylamine; **4,** *N*-acetyl-2,3,5,6-tetra-*O*-benzoyl-α-D-glucofuranosylamine.

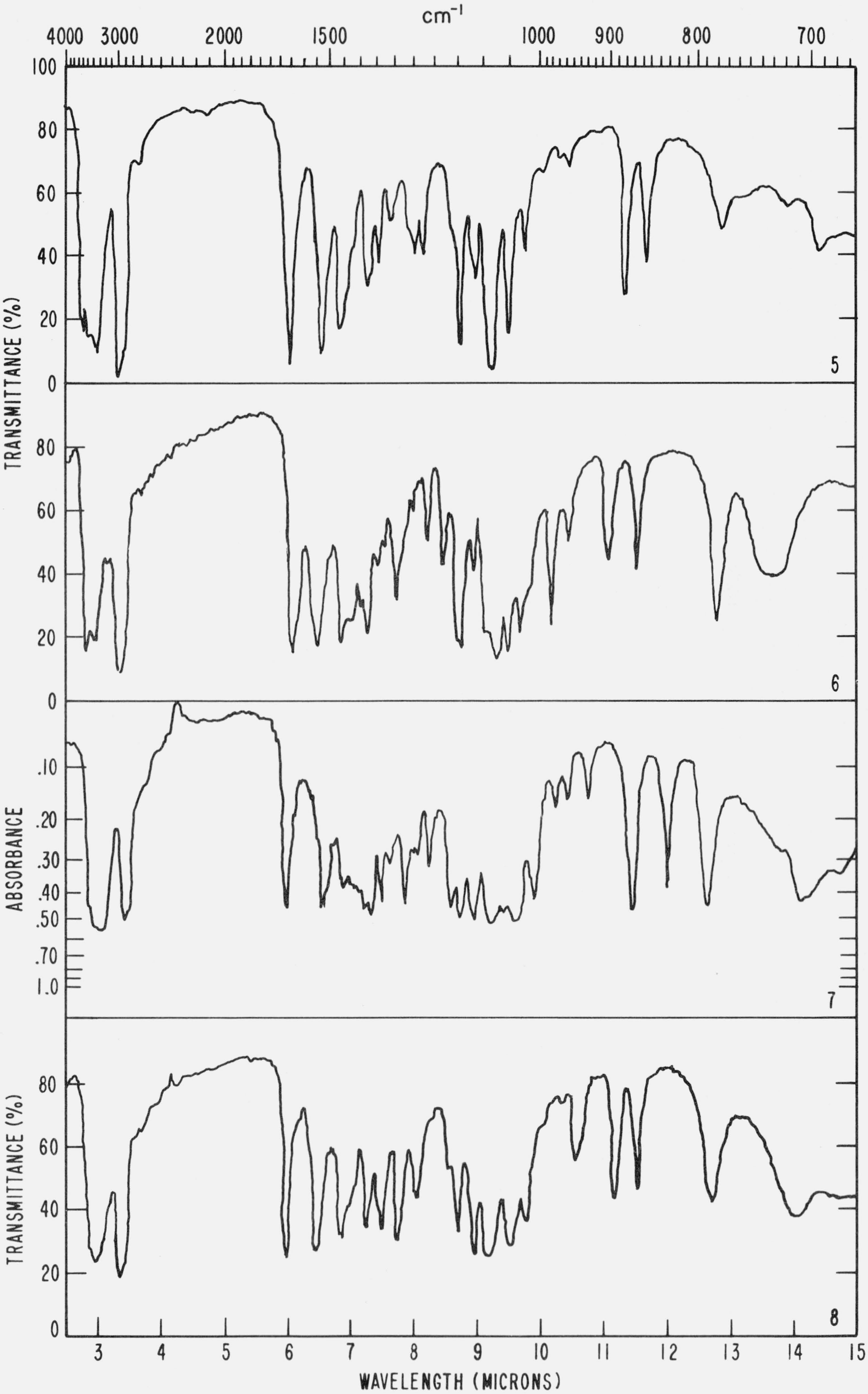

FIGURE 1. *Spectrograms of compounds in Nujol mulls.*—Continued

5, *N*-acetyl-β-D-lyxopyranosylamine; **6,** *N*-acetyl-6-deoxy-β-L-mannopyranosylamine; **7,** *N*-acetyl-α-D-galactopyranosylamine; **8,** *N*-acetyl-β-D-galactopyranosylamine.

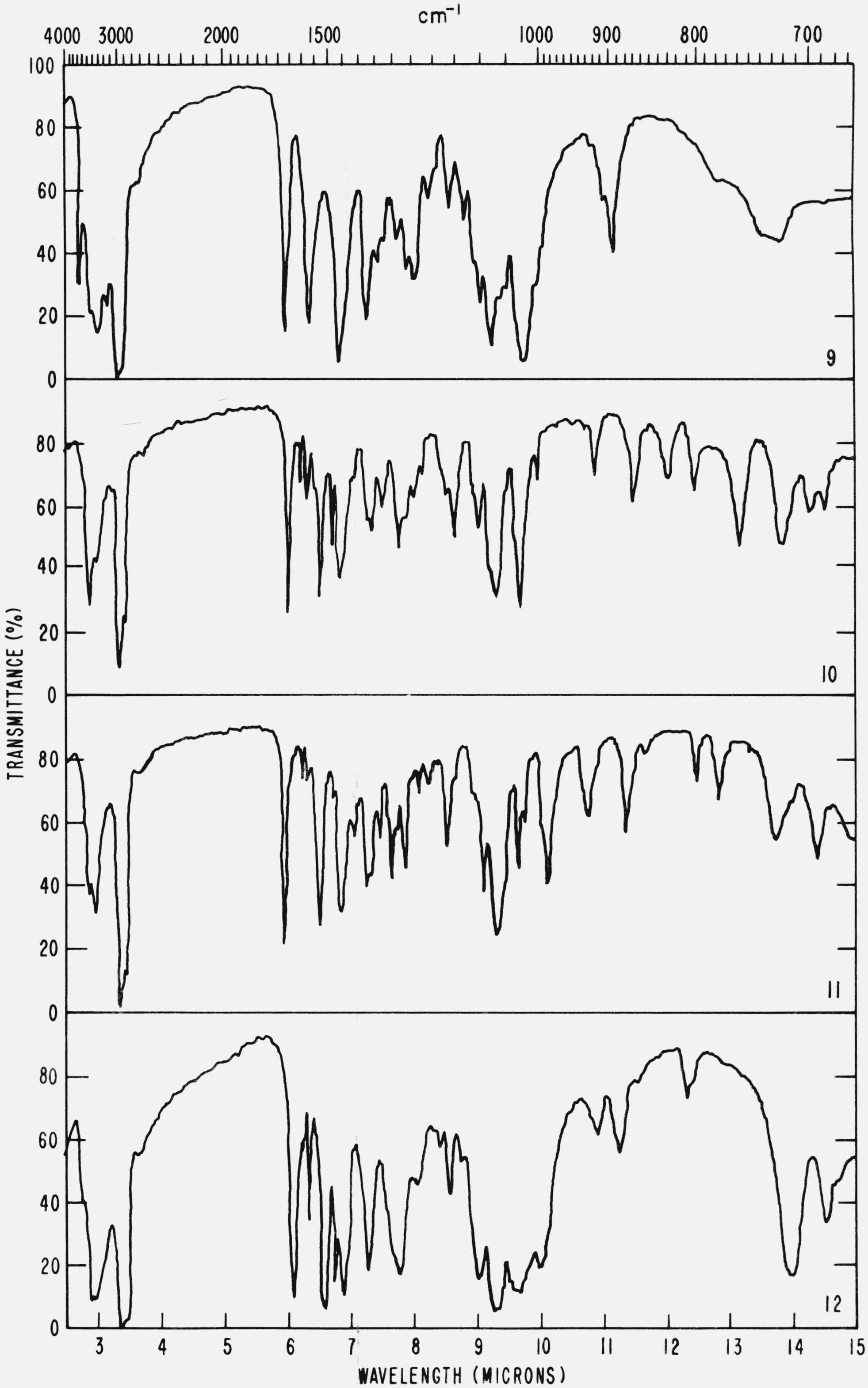

FIGURE 1. *Spectrograms of compounds in Nujol mulls.* – Continued

9, *N*-propionyl-β-D-glucopyranosylamine; **10,** *N*-benzoyl-β-D-lyxopyranosylamine; **11,** *N*-benzoyl-α-D-arabinopyranosylamine; **12,** *N*-benzoyl-β-D-glucopyranosylamine.

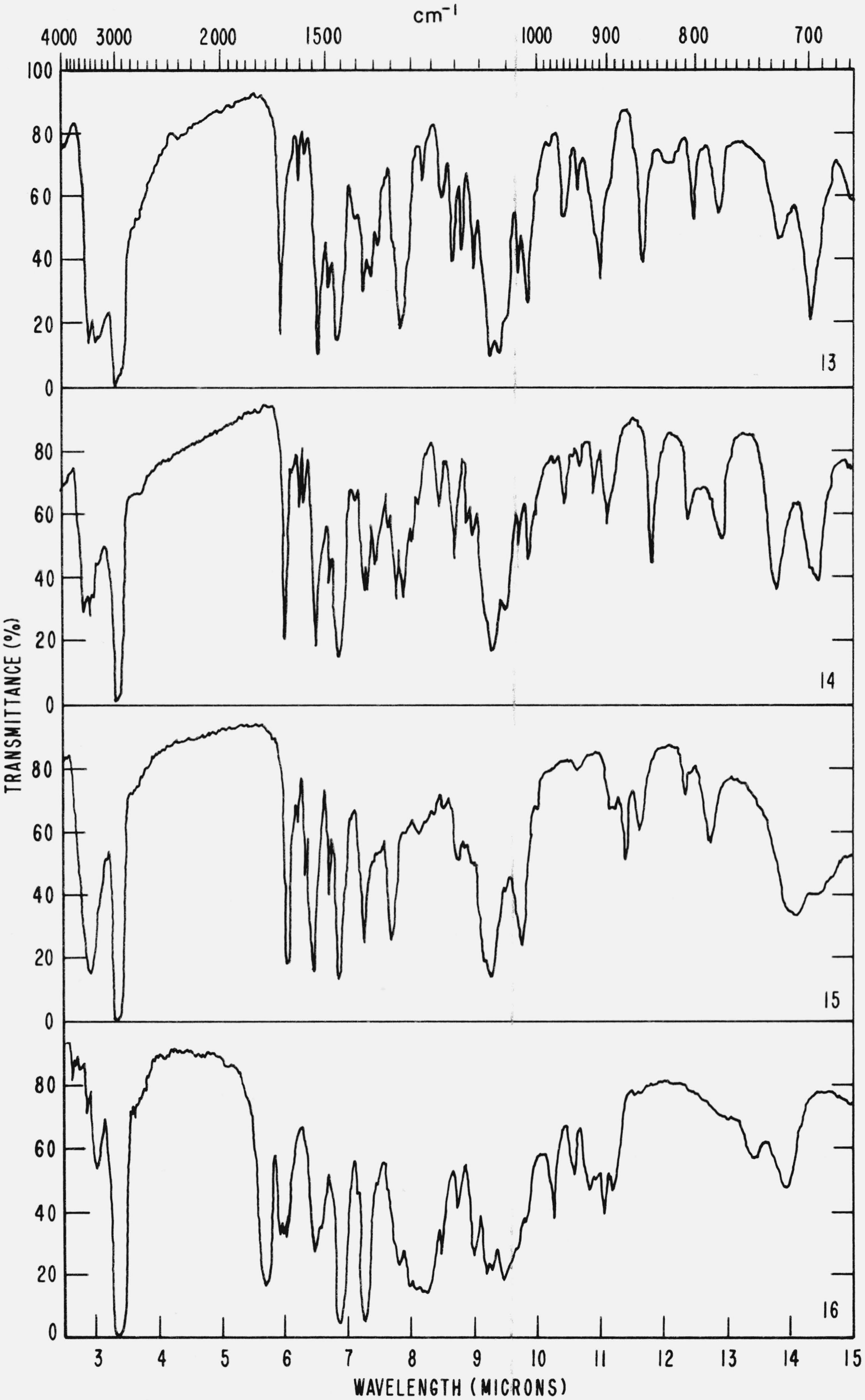

FIGURE 1. *Spectrograms of compounds in Nujol mulls.*—Continued

13, *N*-benzoyl-β-D-mannopyranosylamine; **14,** *N*-benzoyl-6-deoxy-β-L-mannopyranosylamine; **15,** *N*-benzoyl-β-D-galactopyranosylamine; **16,** *N*-acetyl-2,3,4-tri-*O*-acetyl-6-deoxy-β-L-mannosylamine.

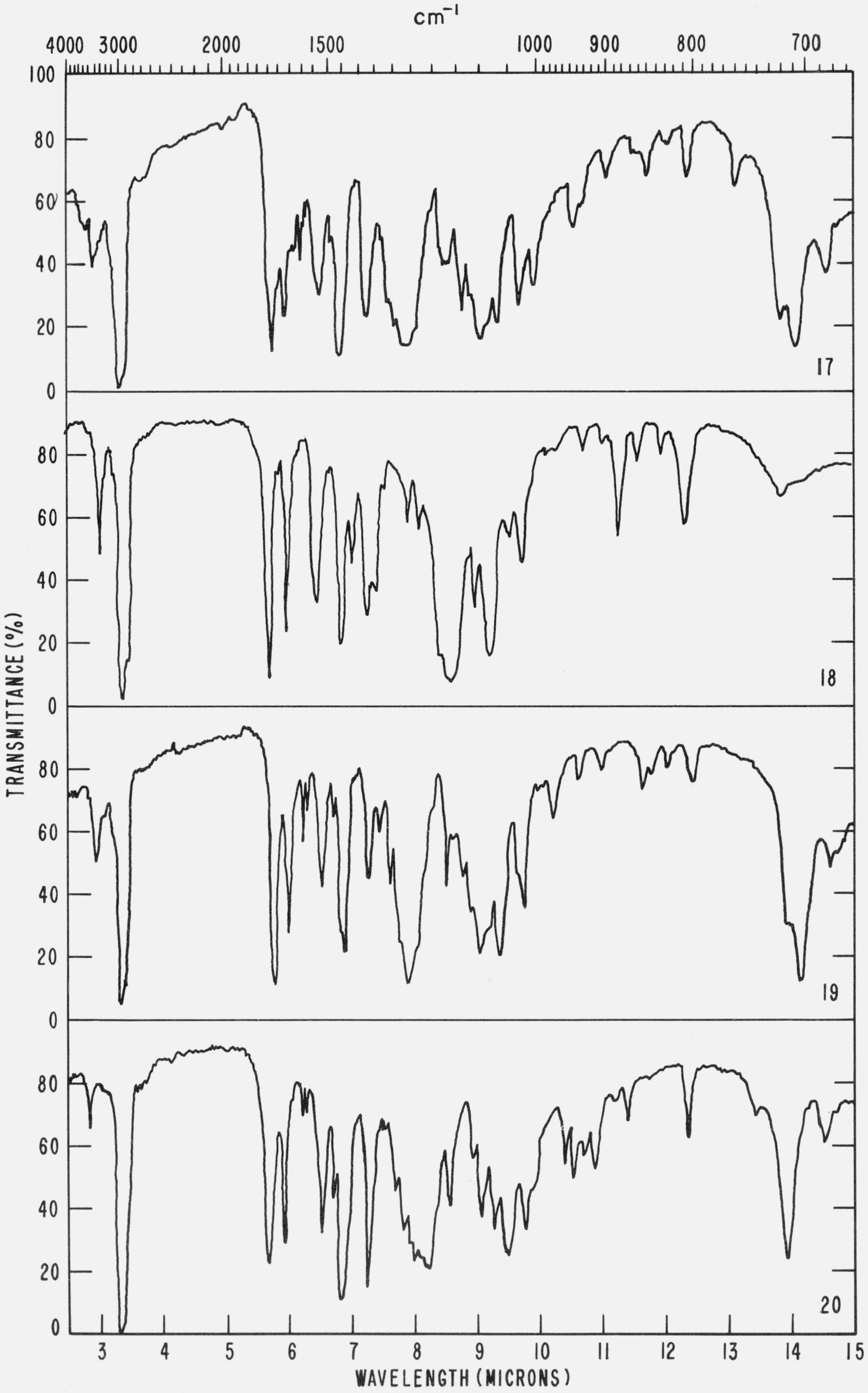

FIGURE 1. *Spectrograms of compounds in Nujol mulls.*—Continued

17, *N*-acetyl-2,3,4-tri-*O*-benzoyl-α-D-arabinosylamine; **18,** *N*-propionyl-2,3,4,6-tetra-*O*-propionyl-β-D-glucosylamine; **19,** 2,3,4,6-tetra-*O*-benzoyl-*N*-propionyl-β-D-glucosylamine; **20,** 2,3,4-tri-*O*-acetyl-*N*-benzoyl-α-D-arabinosylamine.

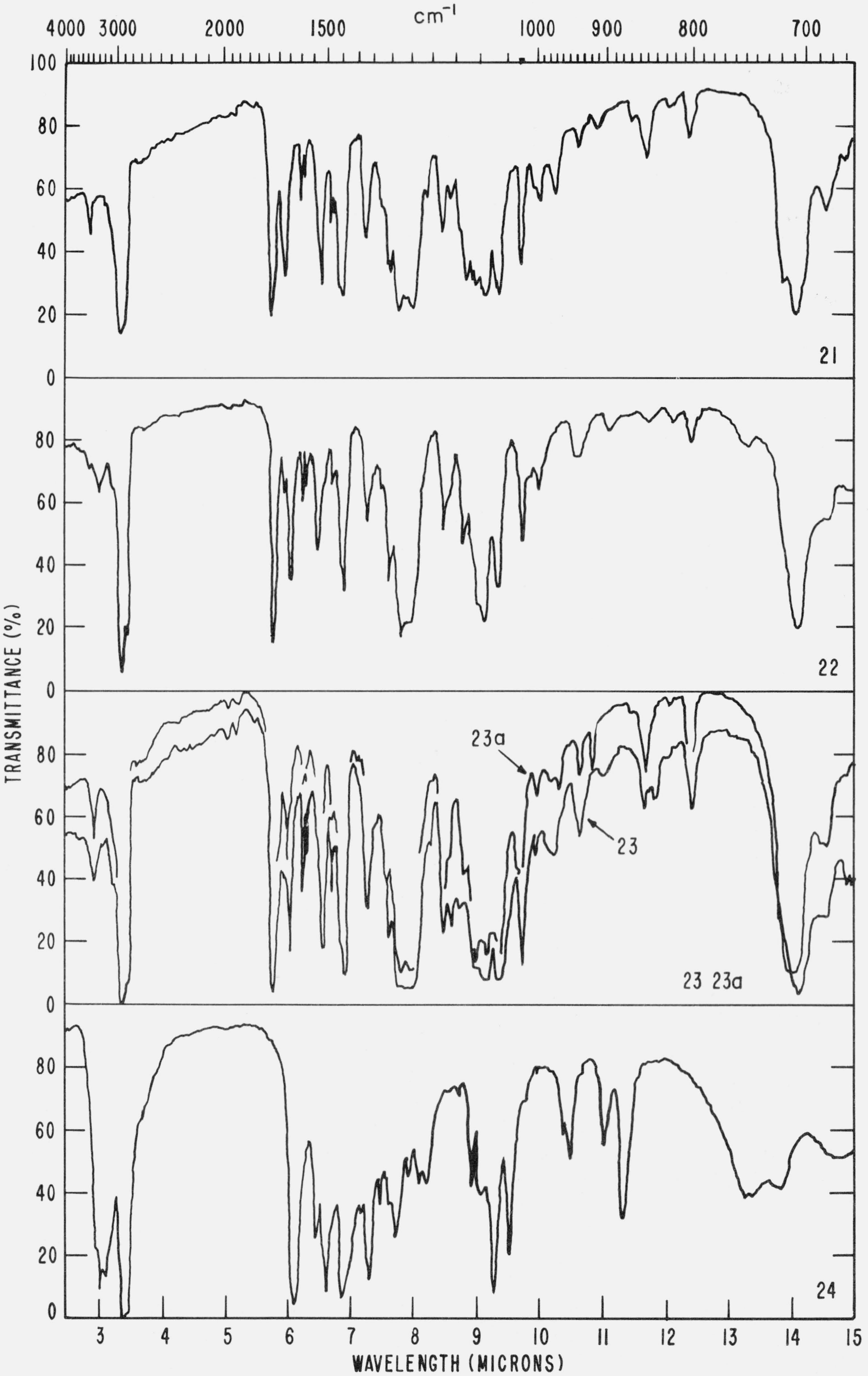

FIGURE 1. *Spectrograms of compounds in Nujol mulls.*—Continued

21, *N*-benzoyl-2,3,4-tri-*O*-benzoyl-β-D-xylosylamine; **22,** *N*-benzoyl-2,3,4-tri-*O*-benzoyl-α-D-arabinosylamine; **23,** *N*-benzoyl-2,3,4,6-tetra-*O*-benzoyl-β-D-glucosylamine (mp 113–115°); **23a,** *N*-benzoyl-2,3,4,6-tetra-*O*-benzoyl-β-D-glucosylamine (mp 184°); **24,** 1,1-bis(acetamido)-1-deoxy-D-erythritol.

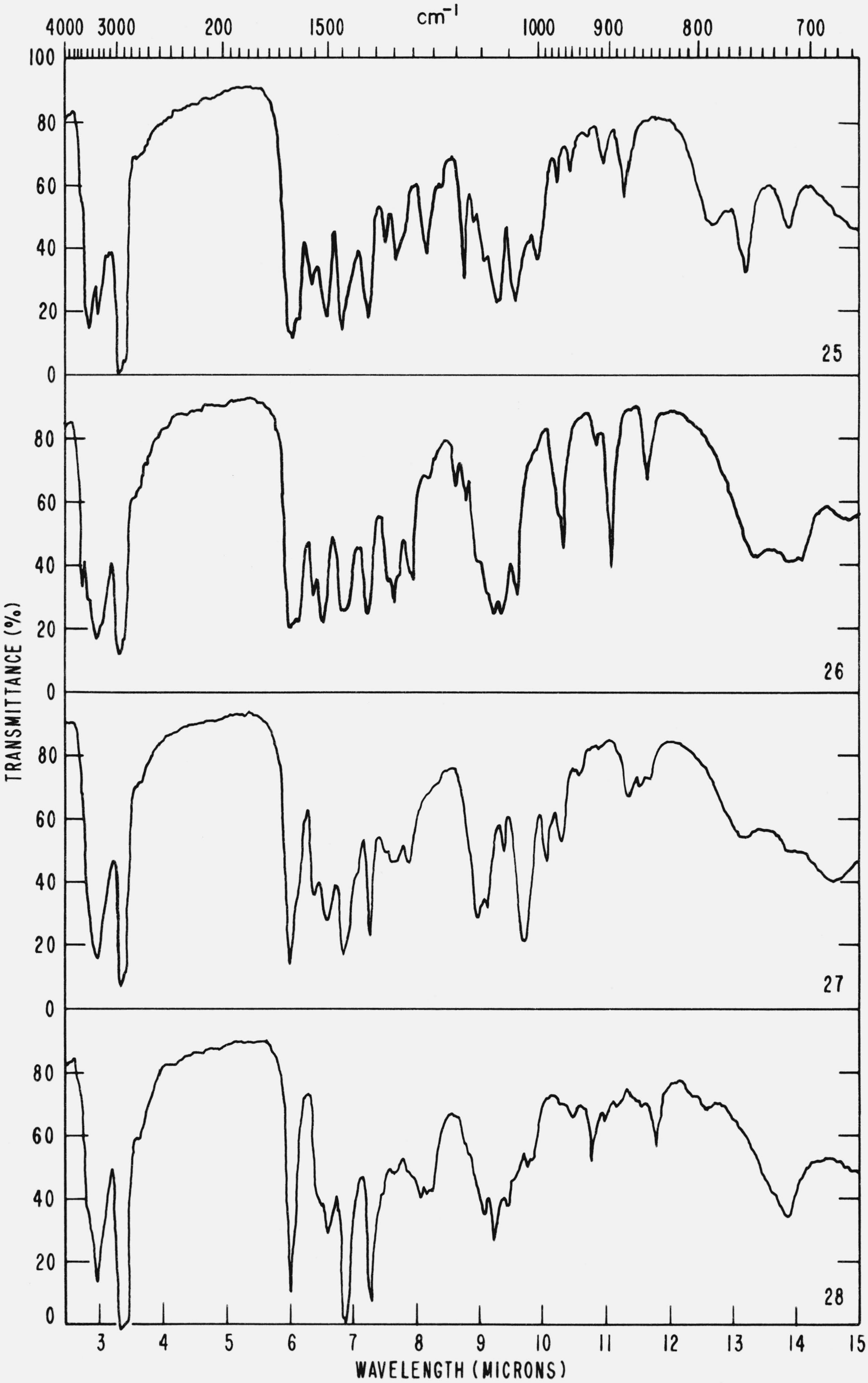

FIGURE 1. *Spectrograms of compounds in Nujol mulls.* – Continued

25, 1,1-bis(acetamido)-1-deoxy-D-glucitol; **26**, 1,1-bis(acetamido)-1,6-dideoxy-L-mannitol; **27**, 1,1-bis(acetamido)-1-deoxy-D-galactitol; **28**, 1-deoxy-1,1-bis(propionamido)-D-glucitol.

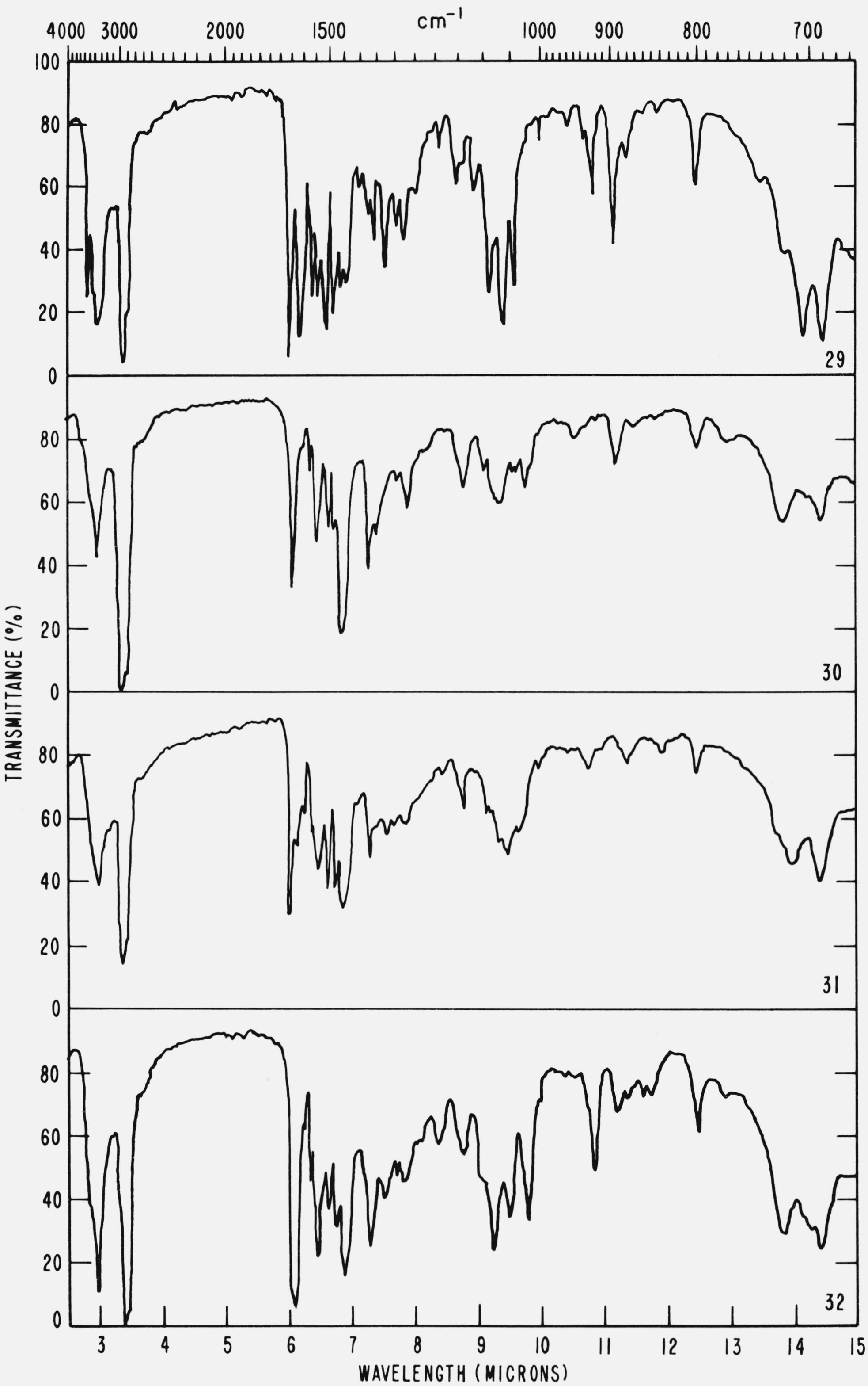

FIGURE 1. *Spectrograms of compounds in Nujol mulls.*—Continued

29, 1,1-bis(benzamido)-1-deoxy-L-erythritol; **30**, 1,1-bis(benzamido)-1-deoxy-L-arabinitol; **31**, 1,1-bis(benzamido)-1-deoxy-D-ribitol; **32**, 1,1-bis(benzamido)-1-deoxy-D-glucitol.

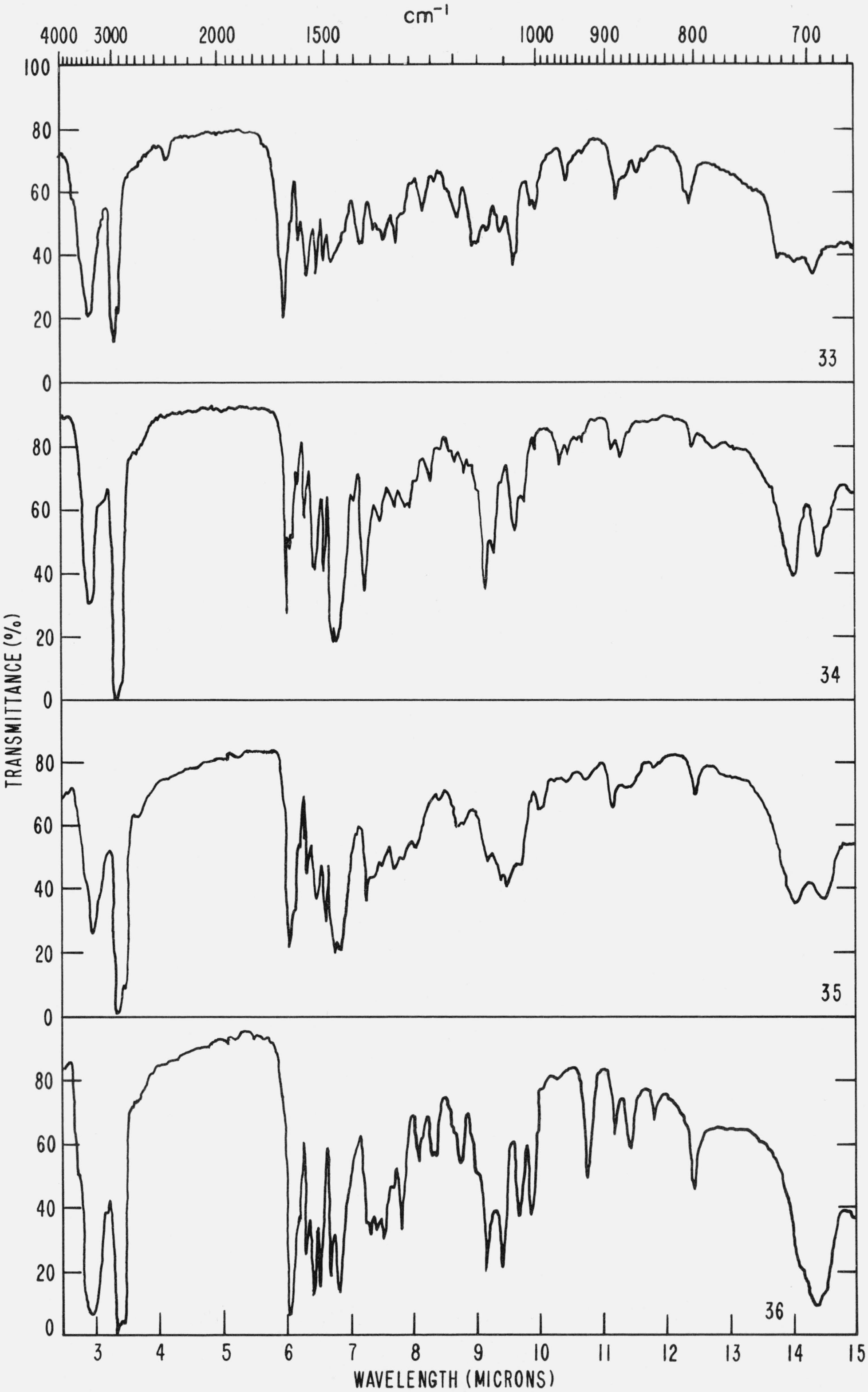

FIGURE 1. *Spectrograms of compounds in Nujol mulls.*—Continued

33, 1,1-bis(benzamido)-1,2-dideoxy-D-*arabino*-hexitol; **34,** 1,1-bis(benzamido)-1-deoxy-D-mannitol; **35,** 1,1-bis(benzamido)-1,6-dideoxy-L-mannitol; **36,** 1,1-bis(benzamido)-1-deoxy-D-galactitol.

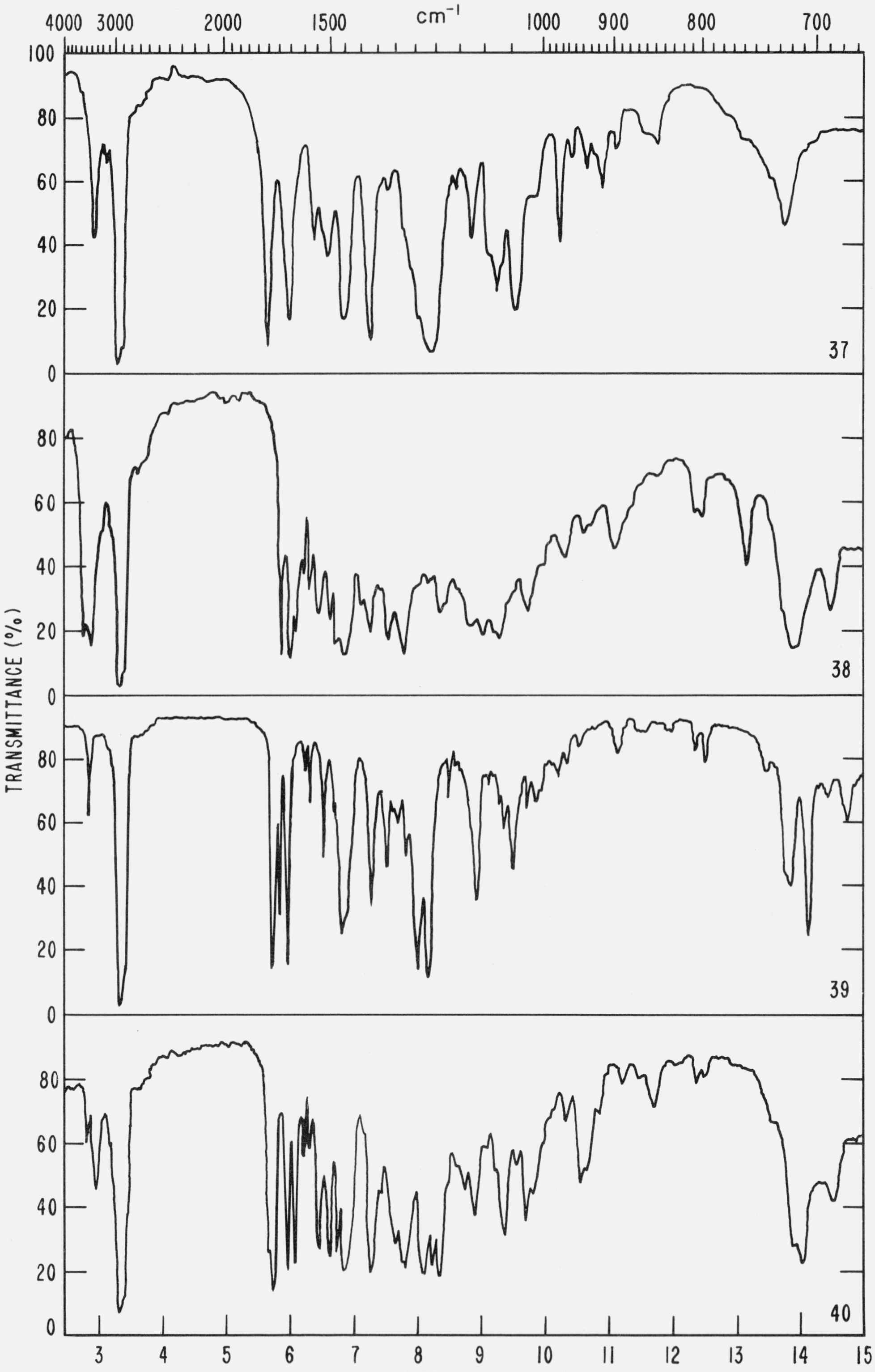

FIGURE 1. *Spectrograms of compounds in Nujol mulls.*—Continued

37, 1,1-bis(acetamido)-2,3,4,5,6-penta-*O*-acetyl-1-deoxy-D-glucitol; **38,** 1,1-bis(benzamido)-6-*O*-benzoyl-1-deoxy-D-glucitol; **39,** 2,3,4-tri-*O*-acetyl-1,1-bis(benzamido)-5-*O*-benzoyl-1-deoxy-D-lyxitol; **40,** 2,3,4-tri-*O*-acetyl-1,1-bis(benzamido)-5-*O*-benzoyl-1-deoxy-D-arabinitol.

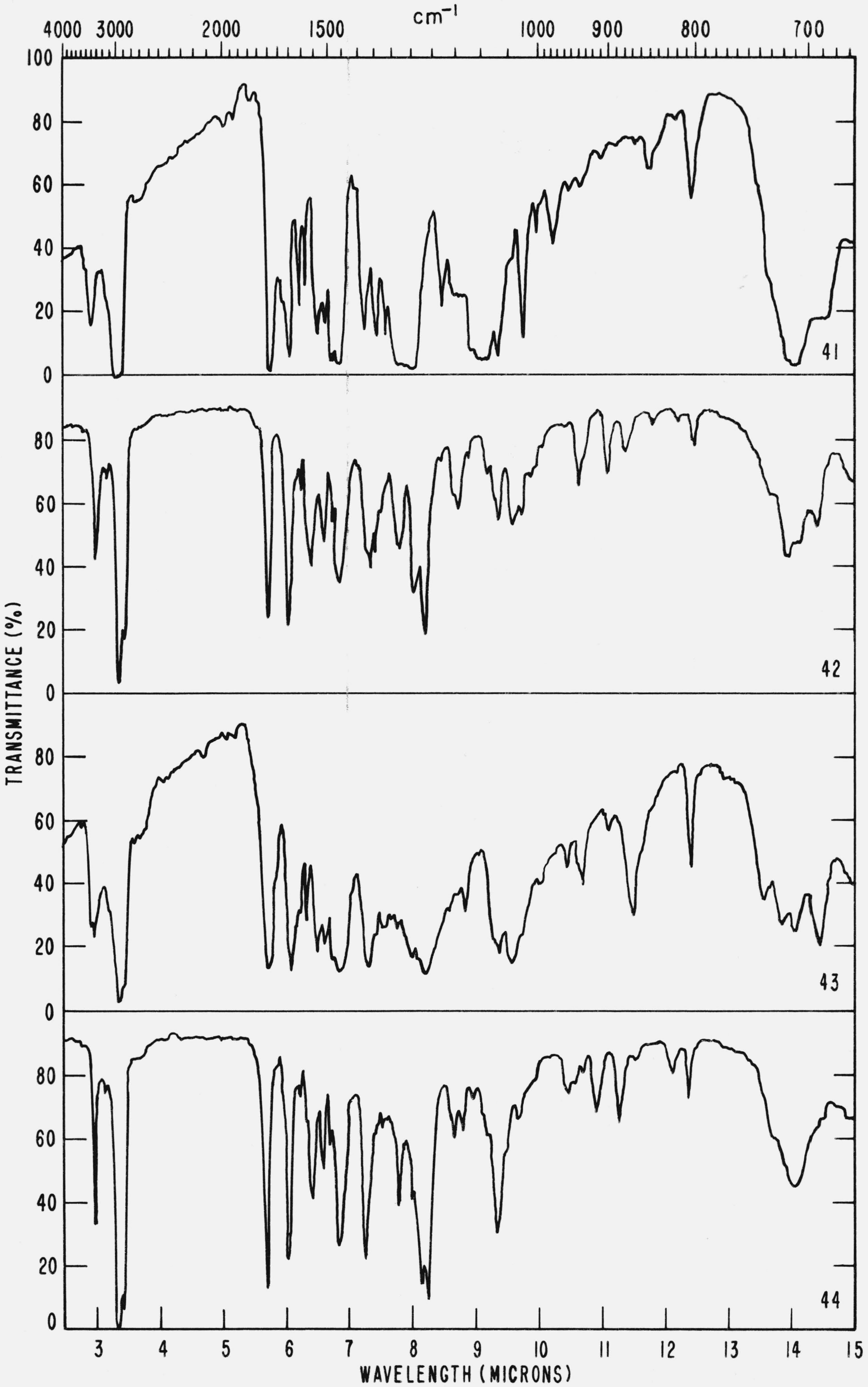

FIGURE 1. *Spectrograms of compounds in Nujol mulls.*—Continued

41, 1,1-bis(benzamido)-2,3,4,5-tetra-*O*-benzoyl-1-deoxy-D-arabinitol; **42,** 2,3,4-tri-*O*-acetyl-1,1-bis(benzamido)-1-deoxy-L-erythritol; **43,** 2,3,4,5-tetra-*O*-acetyl-1,1-bis(benzamido)-1-deoxy-D-ribitol; **44,** 2,3,4,5,6-penta-*O*-acetyl-1,1-bis(benzamido)-1-deoxy-D-glucitol.

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