296. *Optical Rotatory Dispersion in the Carbo-hydrate Group. Part I.*

By Thomas L. Harris, Edmund L. Hirst, and
Charles E. Wood.

NOTWITHSTANDING the important part played by the measurement
of optical rotatory powers in the study of the carbohydrates com-
paratively little attention has been given to the examination of
rotatory dispersion in this group. Observations have been made
chiefly for wave-lengths 5893 Å. or 5461 Å. and because the ratio
$[\alpha]_D/[\alpha]_{5461}$ has been found in most of the cases examined to be
approximately 0·85 it has often been assumed that sugar derivatives
show in general simple dispersion. It is well known, however, that
the character of the dispersion cannot be gauged with sufficient
exactness from measurements over a small number of wave-lengths
in a restricted spectral region. Adequate information is obtainable
only by a systematic study of the rotation over a wide range of
the spectrum. Such measurements have been carried out by Lowry
and Richards (*J.*, 1924, **125**, 2522) in the case of sucrose, which
was found to have simple rotatory dispersion over the whole spectral
range examined (λ 6708—3826).

The object of the present experiments is to investigate over the
maximum available range of wave-lengths the rotation dispersion
of a representative series of carbohydrate derivatives. The sub-
stances used in Part I have been selected on the ground that their
specific rotations are of special importance in connexion with the
application of Hudson's iso-rotation rules (*J. Amer. Chem. Soc.*,
1926, **48**, 1424; 1930, **52**, 1680, 1707). Since these rules are
founded upon rotational values for one arbitrary wave-length and
for a single solvent (water or chloroform according to the solubility
of the substance in question), it is obviously a matter of importance
to decide whether the rules hold for other wave-lengths and in
particular whether the breakdown of Hudson's rules in the case of

α-mannose and its derivatives is to be attributed to differences in the type of rotation dispersion shown by glucose and mannose derivatives, or to the complete failure of the rules in the case of substances which possess the particular configuration present in α-mannose. The alternative explanation, put forward by Hudson to account for the observed discrepancies, that α-mannose ($[\alpha]_D$ + 30° in water) has a different ring structure from α-glucose ($[\alpha]_D$ + 114°) has been shown by conclusive chemical evidence to be untenable (Haworth and Hirst, J., 1930, 2615).

In order to gain information on this point the rotatory dispersions in aqueous solutions of α-methylglucopyranoside (I; R = H), α-methylglucofuranoside (II; R = H), α-methylmannopyranoside (III; R = H), and α-methylmannofuranoside (IV; R = H) were compared. A detailed examination extending over the range λ 6708—2380 revealed that neither α-methylglucopyranoside nor α-methylmannopyranoside showed simple dispersion. With the former the maximum deviation from the simple type ($\lambda_0^2 = 0.022$) was less than 1% of the observed α. In the case of α-methyl-mannopyranoside ($\lambda_0^2 = 0.02235$) the maximum deviation was in the same sense and was less than 2%. The similarity between the rotatory dispersions is so great and their deviations from the simple type are so small that the failure of the iso-rotation rules in the case of α-methylmannopyranoside cannot be accounted for by dispersion differences.

(I.)   (II.)   (III.)   (IV.)

Greater complications were encountered in the comparison of the two methylfuranosides. α-Methylglucofuranoside showed little departure from the simple type ($\lambda_0^2 = 0.018$) down to λ 3226, but below this wave-length marked deviations occurred amounting to 9% of the observed value at λ 2410. The specimen of α-methyl-mannofuranoside, despite the utmost care in purification, was transparent only to λ 3100 (in concentrated solution only to λ 3300). Between λ 6708 and λ 3330 the dispersion was to all intents and purposes simple. There appeared to be a very slight tendency to deviate between λ 3330 and λ 3018, but unfortunately a direct comparison with α-methylglucofuranoside in the interesting region below λ 3000 was experimentally impracticable. It may be remarked

here that the difference between the molecular rotation of α-methyl-glucofuranoside ($[\alpha]_D$ + 118°) and α-methylmannofuranoside ($[\alpha]_D$ + 108°) is widely at variance with Hudson's calculated epimeric difference.

The difference in behaviour between the α-methylglucoside of pyranose structure and that of furanose structure is striking, but at present sufficient data are not available to allow of conclusions being drawn concerning the influence of the furanose ring on the dispersion. As stated above, the methylmannoside of furanose structure shows little or no deviation from simplicity over the range of wave-lengths examined and it is to be remarked also that sucrose, which contains a pyranose ring in one half of its molecule and a furanose ring in the other half, shows simple dispersion from λ 6708 to 2356. The observations now recorded prove that the simple formula given by Lowry and Richards (*loc. cit.*) may be used with accuracy over a range of wave-lengths extending for at least 1500 Å. below the limit reached by these authors.

Another case of a similar nature is tetra-acetyl α-methylmanno-furanoside (IV; R = $CH_3 \cdot CO$). Here in chloroform solution the dispersion is simple between λ 6708 and λ 3196, the lowest wave-length at present attainable. Tetra-acetyl β-methylmannopyranos-ide (VI) also appears to have simple dispersion in chloroform (range λ 7520—2614).
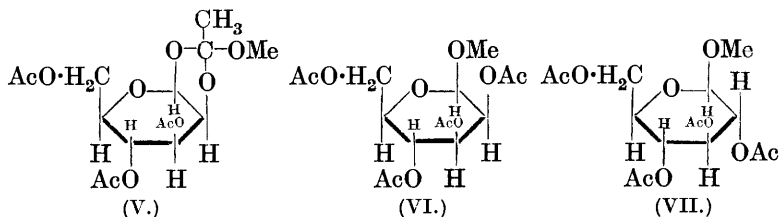
Apart from these two cases all the acetylated glycosides examined revealed marked departures from simple dispersion. With tetra-acetyl α-methylglucopyranoside (I; R = $CH_3 \cdot CO$) the deviation at λ 3185 amounted to 3% of the observed α; with tetra-acetyl β-methylglucopyranoside (VII) it was 12·5% at λ 2975; with tetra-acetyl α-methylmannopyranoside (III; R = $CH_3 \cdot CO$) it was 13% at λ 2983, and with the so-called " γ "-tetra-acetyl methylmannoside [3 : 4 : 6-triacetyl β-mannopyranose 1 : 2-orthomethyl acetate (V)], which contains two ring systems, the deviation was 4% at λ 2888.

As further examples of substances which are epimeric and so differ from one another only in the configuration of the groups attached to the second carbon atom of the sugar chain, octa-acetyl 4-β-glucosido-α-mannose and octa-acetyl α-cellobiose were chosen.

There can be no question here of any difference in ring structure, yet as in the case of many other fully acetylated derivatives, the rotations show marked departures from the requirements of Hudson's iso-rotation rules. In chloroform they both showed complex dispersion, the deviations from simplicity being very similar to one another and amounting to 4—5% of α at λ 2953 and λ 2976 respectively.

It should be emphasised that in every case examined the deviations from simple dispersion throughout the visual region were so small that the character of the rotatory dispersion will not account for the failure of many of the substances to conform with Hudson's iso-rotation rules. Further evidence is thus obtained that the iso-rotation rules as developed by Hudson cannot be used with certainty when the stereochemical arrangement of the groups round the first three carbon atoms of the sugar molecule is similar to that present in α-mannose (compare Haworth and Hirst, *loc. cit.*; Freudenberg and Kuhn, *Ber.*, 1931, **64**, 703).

In connexion with the influence of *cis-* and *trans-*groupings on the character of the rotation it is of interest to note that tetra-acetyl α-methylmannopyranoside and tetra-acetyl β-methylgluco-pyranoside, which have the OMe group on carbon atom 1 *trans* to the acetyl group on carbon atom 2, show marked deviations from simple rotatory dispersion, whilst tetra-acetyl α-methylgluco-pyranoside and tetra-acetyl β-methylmannopyranoside, in which the corresponding groups occupy *cis-*positions, show only small deviations.

A further point of interest is that for the substances now examined the deviations from simplicity are all of the same sign. This applies equally to tetra-acetyl α-methylglucoside and to tetra-acetyl β-methylglucoside. In the latter, owing to the preponderating influence of the first carbon atom, the sign of the observed rotation is reversed as compared with the α-derivative, but the sign of the deviation from simplicity is not reversed. It may be suggested, therefore, that optically active bands belonging to that portion of the molecule other than the reducing carbon atom are mainly responsible for the departure from simplicity. It will be apparent, however, that the calculation of a two (or more) term equation from the data available presents almost insuperable difficulties, whilst the strong general absorption of the substances in the extreme ultra-violet renders impossible the direct observation of absorption bands. In any case the absorption effect responsible for the rotation might be expected to be exceedingly minute (compare Kuhn, *Trans. Faraday Soc.*, 1930, **26**, 293; *Ber.*, 1930, **63**, 191).

The observations are summarised in the accompanying table.

In those cases where no single-term equation could be used to express the whole of the observed rotations, the simple equation which approximates most closely to the observed values has been given.   The values of λ_0^2 are of the order 0·025 and correspond to an absorption band situated far in the ultra-violet at about λ 1500.

The results now communicated show that in this series of substances complex dispersion is more usual than simple.   In subsequent papers the rotatory dispersion of other carbohydrates will be discussed, including the interesting series of sugar lactones in which a remarkable variation of rotation with solvent has been described by Haworth, Hirst, and Smith (J., 1930, 2659).   In many cases these display anomalous rotatory dispersion expressible by means of two-term equations of the Drude type.

Substance.	Range of wave-lengths examined (λ in Å.).	Type of dispersion.	λ_0^2.	Maximum deviation from simple formula, %.
Sucrose	6708—2356	Simple	0·0213	nil
α-Methylglucopyranoside	6708—2396	Complex	0·022	0·9
α-Methylglucofuranoside ...	6708—2410	Complex	0·018	9
α-Methylmannopyranoside	6708—2380	Complex	0·022	1·8
α-Methylmannofuranoside	6708—3018	Simple	0·019	—
Tetra-acetyl α-methyl-glucopyranoside	6708—3185	Complex	0·026	3
Tetra-acetyl α-methyl-mannopyranoside	6708—2983	Complex	0·030	13
Tetra-acetyl α-methyl-mannofuranoside	6708—3196	Simple	0·030	—
Tetra-acetyl β-methyl-glucopyranoside	6708—2975	Complex	0·030	12·5
Tetra-acetyl β-methyl-mannopyranoside	7520—2614	Simple	0·022	—
" γ "-Tetra-acetyl methyl-mannopyranoside	6708—2888	Complex	0·025	4
Octa-acetyl α-cellobiose ...	6708—2976	Complex	0·017	4·5
Octa-acetyl 4-β-glucosido-α-mannose	6708—2953	Complex	0·024	5

EXPERIMENTAL.

The spectropolarimeter was of the type devised by Lowry (*Proc. Roy. Soc.*, 1908, **81**, 472).   A Hilger polarimeter, capable of accommodating 4 dm. tubes, was fitted with Foucault prisms and quartz-fluorite lenses in such a way that a real image of the horizontal triple field could be focused on the vertical slit of a spectrograph.   The polarimeter was fixed on a rotatable table and two spectrographs were so mounted that by a slight movement of the table the image of the triple field could be centred on the slit of either instrument.   For observations in the visual region a Hilger constant-deviation spectrometer was used and the same instrument fitted with a camera was employed for readings in the violet region.   Measurements in the ultra-violet were made by means of a Hilger medium quartz spectrograph.

The visual readings were obtained in the ordinary way by turning the

polarimeter circle until the three fields visible in the telescopic eyepiece of the spectrometer were evenly matched for the spectral line selected. The photographic observations necessitated a different procedure. In this case the polarimeter circle was set at a definite reading and the exposure was made with the image of the triple field in one section of a Hartmann diaphragm. The next division of the diaphragm was then moved into place over the slit and a photograph of an iron arc spectrum was taken, the vertical iron electrodes being placed between the polarimeter and the spectrograph. The iron spectrum was in this way registered in exact juxtaposition with the previous spectrum. With the aid of a low-power travelling microscope it was then possible to determine exactly the wave-length at which the three fields of the polarimetric photograph had the same intensity. The process was repeated with other settings of the polarimeter until the desired range of wave-lengths had been covered.

In the following tables the visual readings are for fixed wave-lengths and any experimental errors occur in the observed value of a. With a half-shadow angle of $5°$, which was chosen after numerous preliminary experiments as the most convenient, the experimental errors do not in general exceed $\pm 0.02°$. The photographic readings on the other hand have a definite a and the errors of observation occur in the measurement of λ. With the instruments mentioned above there is sufficient dispersion of the spectral lines to render possible the measurement of the end-point to within ± 1 Å. in the region of λ 2500, ± 2 Å. in the region λ 3000—3500 Å., and ± 3—5 Å. in the neighbourhood of λ 4000. At the limit of transparency of a substance, when long exposures were necessary, fogging of the plates occasionally tended to impair the accuracy of reading and in such cases a range of wave-lengths is given between which the end-point certainly occurs. The accuracy of the photographic method is higher for large values of a owing to the increased sharpness of the change-over at the end-point. Whenever possible, observations have been made with solutions having a large rotation. In certain cases, however, this was impossible, but an examination of the results given below will show that here also highly accurate measurements are obtained by the photographic method.

The experiments were greatly facilitated by the use of an extremely intense light source (see below) in conjunction with very rapid photographic plates, e.g., Ilford Iso-Zenith (H. and D. 700) and Imperial Eclipse (H. and D. 650). In a few cases photographic readings in the extreme red were made by using a glass prism and Kodak Extreme-red sensitive plates supersensitised by means of ammonia. The plates were in all cases developed to give contrast in the negatives.

After experiments with various types of arc it was found that the most suitable light source was an arc between oppositely rotating vertical tungsten electrodes. The current used varied from 4—10 amps. according to the opacity of the solution at the spectral region under investigation. With Ilford Iso-Zenith plates, a slit 0.02 mm. wide, and a current of 4 amps., an exposure of about 1 min. was required in the region of λ 4500. The photographic readings were discontinued when a wave-length was reached at which exposures of more than 45 mins. with a heavy current were required.

The same light source was used for visual observations. The following lines were prominently displayed by the electrodes used and were selected for visual readings : λ 6292, 5805, 5515, 5225, 4887. In addition, visual readings

were obtained for λ 6708 and 6104 by feeding LiBr into the arc from an asbestos wick. Observations in sodium light were obtained by feeding the arc with NaNO₃. The complete list of visual lines is, therefore, in order of wave-length : λ 6708, 6292, 6104, 5893, 5805, 5515, 5225, 4887.

In the tables, observations for the above wave-lengths refer to visual measurements. All others were obtained photographically.

Early in the investigation it became apparent that for success in the polarimetric work it was not sufficient to control the purity of the substances used by m. p., specific rotation and analysis. On many occasions substances which were apparently pure and gave clear colourless solutions were found to be strongly absorbent in the ultra-violet. The proportion of the impurity was clearly extremely minute but was nevertheless sufficient to prohibit the taking of spectropolarimetric measurements in the very region most desired. Accordingly the process of purification was controlled by spectro-photometric methods, a Hilger sector photometer being employed. None of the substances described in this paper showed selective absorption in the ultra-violet. The elimination of the light-absorbing impurity was in many cases extremely tedious and in spite of efforts made it seems probable that in certain instances the state of maximum transparency has not been reached. For example, polarimetric observations with α-methylmannoside were possible at λ 2380, whereas with the purest specimen of α-methylmannofuranoside the limit was λ 3018. The opacity in this case seemed to be due rather to adventitious impurities than to the presence of the furanose ring structure, since α-methylglucofuranoside was transparent to λ 2410. Similar irregularities in opacity were encountered amongst the acetylated glucosides examined. The impurity responsible for the absorption had no effect on the rotation, precisely the same rotatory dispersion being observed with " opaque " and " transparent " specimens of the same substance over the spectral range common to both.

During the observations the solutions were kept at a const. temp. by means of a cylindrical water jacket attached to the polarimeter and so shaped that it replaced the bed of the instrument. A rapid stream of water from a thermostat was passed through the jacket, which fitted closely round the polarimeter tube.

Matched end plates of crystalline quartz were used, cut respectively from d- and l-quartz. The matching of the pair used was not quite perfect, the residual rotation being about − 0·01° at λ 5893 and − 0·06° at λ 3000. The polarimeter reading required correction on this account and a further correction was necessary because the zero of the polarimeter was not the same for all wave-lengths. Below λ 3000 the absorption of ultra-violet light by the calcite prisms becomes noticeable with the result that when the polarimeter is set on the zero for wave-lengths above λ 3000 the two outer sections of the triple field transmit less light than the central section. The necessary corrections were obtained by taking a series of photographs with polarimeter settings at intervals of 0·02°, beginning with the zero setting for λ 5893. On each photograph the wave-length for which the three fields had even intensity was measured and the results were plotted on a graph from which the zero of the instrument for any wave-length could be determined.

| λ .... | 6000 | 5000 | 4000 | 3000 | 2800 | 2600 | 2400 | 2300 |
| Correction ... | 0·00° | 0·00° | 0·01° | 0·07° | 0·10° | 0·16° | 0·25° | 0·30° |

In practice the sum of the two corrections was determined experimentally by taking a series of photographs with small intervals (0·02°) between successive polarimeter settings, the polarimeter tube being in position fitted with end-plates but empty. The photographs were examined as before and a graph was drawn which gave the total correction to be applied to the observed value of a for any particular value of λ.

λ	6000	5000	4000	3500	3000
Total correction ...	+ 0·01°	+ 0·02°	+ 0·02°	+ 0·01°	− 0·01°
λ	2800	2600	2400	2300	
Total correction ...	− 0·04°	− 0·08°	− 0·15°	− 0·20°	

The accuracy of the above procedure was checked by plotting against wavelength the difference between the two corrections tabulated above. The resulting curve corresponded closely to the known rotation dispersion curve of quartz.

Sucrose.—Recryst. sucrose of A.R. quality, supplied by Messrs. British Drug Houses, was used, $[a]_D^{20°} + 66·5°$ in H_2O (c, 17·2). The observations of Lowry and Richards (*loc. cit.*) have been extended to λ 2356, where absorption of light both by the calcite prisms of the polarimeter and by the sucrose solution began to be pronounced. The dispersion is apparently simple throughout the range examined and the value for λ_0^2 given by Lowry and Richards applies exactly. The accuracy of the methods of measurement used was shown by the fact that over the range of wave-lengths examined by the earlier investigators our observed results differed from the calc. values by at most 0·05°. In view of this complete agreement with the previous results we have omitted from the following table all observations between λ 6708 and λ 4045 except that for λ 5893.

c, 17·218 in H_2O. t, 20°. l, 2 dm. $[a]_\lambda^{20°} = 2·9039a_\lambda$.
$$a_\lambda = 7·4645/(\lambda^2 - 0·0213).$$

λ.	$a_{obs.}$.	$a_{calc.}$.	Diff.	λ.	$a_{obs.}$.	$a_{calc.}$.	Diff.
5893	+ 22·90°	+ 22·90°	± 0	2736	139·37°	139·37°	± 0
4045	52·41	52·45	− 0·04°	2670	149·35	149·32	+ 0·03°
3981	54·41	54·41	± 0	2611 ⎫		159·25	+ 0·09
3833	59·41	59·42	− 0·01	2610 ⎭	159·34	159·43	− 0·09
3589	69·41	69·43	− 0·02	2557 ⎫		169·33	− 0·02
3396	79·40	79·39	+ 0·01	2558 ⎭	169·31	169·13	+ 0·18
3237	89·40	89·41	− 0·01	2464 ⎫		189·37	− 0·07
3105	99·40	99·38	+ 0·02	2465 ⎭	189·30	189·15	+ 0·15
2992	109·39	109·42	− 0·03	2468	188·58*	188·45	+ 0·13
2895	119·38	119·41	− 0·03	2390	208·50*	208·38	+ 0·12
2811	129·38	129·33	+ 0·05	2356	218·48*	218·21	+ 0·27

* These three observations were made with a tube of length 1 dm., the same solution being used. The observed a_λ has been doubled before inclusion in the table.

a-Methylglucoside.—This was repeatedly crystallised from EtOH containing some H_2O, the progress of the purification being controlled by measurement of the ultra-violet absorption spectrum. The pure substance, $[a]_D^{20°} + 158·2°$ in H_2O (c, 16·1), showed little or no absorption until λ 2300 for 16% aq.

solutions examined in 2 cm. tubes. Below λ 2300 strong general absorption set in (compare Marchlevski and Mayer, *Bull. Acad. Polonaise,* 1929, 111). The rotatory dispersion of a-methylglucoside is almost simple, but the devi·ations from the calc. values are considerably greater than the possible experi·mental errors and the dispersion must be classed definitely as complex.

$$c, \ 16\cdot104 \text{ in } H_2O. \quad t, \ 20°. \quad l, \ 1 \text{ dm.} \quad [a]_\lambda^{20°} = 6\cdot2112a_\lambda.$$
$$a_\lambda = 8\cdot2962/(\lambda^2 - 0\cdot0220).$$

λ.	$a_{obs.}$.	$a_{calc.}$.	Diff.	λ.	$a_{obs.}$.	$a_{calc.}$.	Diff.
6708	+ 19·33°	+ 19·38°	− 0·05°	3183	105·43°	104·60°	+ 0·83°
6292	22·13	22·17	− 0·04	3042	118·42	117·61	+ 0·81
5893	25·47	25·51	− 0·04	2911	133·39	132·23	+ 1·16
5805	26·34	26·34	+ 0·00	2863	139·39	138·34	+ 1·05
5515	29·44	29·40	+ 0·04	2790	149·38	148·57	+ 0·81
5225	33·10	33·05	+ 0·05	2691	165·36	164·56	+ 0·80
4887	38·26	38·26	+ 0	2616	179·34	178·66	+ 0·68
4820	39·46	39·44	+ 0·02	2545	194·32	193·97	+ 0·35
4484	46·47	46·33	+ 0·14	2497	206·31	205·86	+ 0·45
4182	54·47	54·26	+ 0·21	2458	216·29	215·95	+ 0·34
3942	62·47	62·19	+ 0·28	2430	224·29	223·93	+ 0·36
3728	71·46	70·92	+ 0·54	2412	229·28	229·32	− 0·04
3532	81·45	80·74	+ 0·71	2405	231·27	231·48	− 0·21
3338	93·44	92·78	+ 0·66	2396	234·27	234·30	− 0·03

a-Methylglucofuranoside.—A specimen prepared by Haworth, Porter, and Waine (see paper No. 319) was used. This had m. p. 62—63° and $[a]_D^{20°}$ + 118·0° in water (*c*, 4·5). A solution of this concentration examined in a tube of length 2 cm. showed general absorption from λ 2500, but no specific absorption. The rotatory dispersion was complex.

$$c, \ 4\cdot544 \text{ in } H_2O. \quad t, \ 20°. \quad l, \ 1 \text{ dm.} \quad [a]_\lambda^{20°} = 22\cdot007a_\lambda.$$
$$a_\lambda = 1\cdot762/(\lambda^2 - 0\cdot018).$$

λ.	$a_{obs.}$.	$a_{calc.}$.	Diff.	λ.	$a_{obs.}$.	$a_{calc.}$.	Diff.
6708	+ 4·10°	+ 4·09°	+ 0·01°	3371	18·46°	18·42°	+ 0·04°
6292	4·61	4·66	− 0·05	3226	20·45	20·47	− 0·02
6104	5·05	4·97	+ 0·08	3100	22·45	22·56	− 0·11
5893	5·36	5·35	+ 0·01	2987	24·44	24·74	− 0·30
5805	5·47	5·52	− 0·05	2895	26·43	26·77	− 0·34
5515	6·16	6·16	± 0	2805	28·42	29·04	− 0·62
5525	6·91	6·91	± 0	2722	30·40	31·41	− 1·01
4887	7·99	7·98	+ 0·01	2668	31·89	33·13	− 1·24
4780	8·47	8·37	+ 0·10	2618	33·37	34·86	− 1·49
4324	10·47	10·43	+ 0·04	2570	34·86	36·67	− 1·81
4005	12·47	12·37	+ 0·10	2524	36·35	38·55	− 2·20
3747	14·47	14·40	+ 0·07	2462	38·32	41·35	− 3·03
3546	16·47	16·35	+ 0·12	2410	40·30	43·96	− 3·66

a·Methylmannopyranoside.—This was prepared by heating mannose with 2% methyl-alcoholic HCl. The crude product was crystallised several times from EtOH until spectrophotometric examination showed that an aq. solution was transparent down to λ 2300. At lower wave-lengths general absorption was observed. The specimen used had m. p. 190°, $[a]_D^{25°}$ + 78·6° in H_2O (*c*, 12·5). The rotatory dispersion was complex.

c, 12·489 in H_2O. t, 25°. l, 2 dm. $[a]_\lambda^{25°} = 4·0035a_\lambda$.
$$a_\lambda = 6·3913/(\lambda^2 - 0·02235).$$

λ.	$a_{obs.}$	$a_{calc.}$	Diff.	λ.	$a_{obs.}$	$a_{calc.}$	Diff.
6708	+ 14·94°	+ 14·95°	− 0·01°	3931	48·43°	48·35°	+ 0·08°
6292	17·16	17·10	+ 0·06	3711	55·43	55·40	+ 0·03
6104	18·26	18·25	+ 0·01	3510	63·43	63·38	+ 0·05
5893	19·64	19·67	− 0·03	3330	72·42	72·30	+ 0·12
5805	20·31	20·31	+ 0·00	3161	82·42	82·40	+ 0·02
5515	22·69	22·68	+ 0·01	3026	92·42	92·34	+ 0·08
5515*	22·64	22·68	− 0·04	3025*	92·36	92·42	− 0·06
5225	25·53	25·50	+ 0·03	2806	112·38	113·35	− 0·97
4887	29·63	29·52	+ 0·11	2608	138·94	139·95	− 1·01
4882	29·63	29·59	+ 0·04	2603*	139·76	140·76	− 1·00
4630	33·44	33·28	+ 0·16	2512*	155·48	156·84	− 1·36
4403	37·44	37·26	+ 0·18	2510	155·48	157·22	− 1·74
4208	41·44	41·40	+ 0·04	2432*	171·40	173·70	− 2·30
4039	45·44	45·40	+ 0·04	2380*	183·12	186·36	− 3·24

* Observations with a 1 dm. tube.

a-Methylmannofuranoside.—This, m. p. 119°, was prepared by Haworth, Hirst, and Webb's method (J., 1930, 651). Spectrophotometric measurements on a 4% aq. solution in 2 cm. tubes showed no specific absorption, but general absorption from λ 2800. The specific rotation of this substance has been given as + 113° in H_2O, c, 1·1 (Haworth and Porter, J., 1930, 649; Haworth, Hirst, and Webb, *loc. cit.*). This value is slightly too high, the figure recorded in the present experiments with highly purified material being $[a]_D^{25°}$ + 108·4° (c, 4·2). The rotatory dispersion is simple or at most very slightly complex over the range examined.

c, 4·169 in H_2O. t, 25°. l, 1 dm. $[a]_\lambda^{25°} = 23·99a_\lambda$. $a_\lambda = 1·486/(\lambda^2 - 0·019)$.

λ.	$a_{obs.}$	$a_{calc.}$	Diff.	λ.	$a_{obs.}$	$a_{calc.}$	Diff.
6708	+ 3·43°	+ 3·45°	− 0·02°	4681	7·44°	7·43°	+ 0·01°
6292	3·92	3·94	− 0·02	4424	8·44	8·41	+ 0·03
6104	4·20	4·20	± 0	4045	10·44	10·28	+ 0·16
5893	4·52	4·53	− 0·01	3745	12·43	12·29	+ 0·14
5805	4·65	4·67	− 0·02	3504	14·43	14·38	+ 0·05
5515	5·22	5·21	+ 0·01	3306	16·42	16·55	− 0·13
5525	5·87	5·86	+ 0·01	3145	18·42	18·59	− 0·17
5003	6·43	6·42	+ 0·01	3018	20·42	20·67	− 0·25
4868	6·84	6·82	+ 0·02				

The simple nature of the dispersion over the range λ 6708—3353 was confirmed by the following series of measurements made with a conc. solution.

$[a]_D^{25°} = 108·1°$ (c, 13·169) in H_2O. $t = 25°$. $l = 2$ dm. $[a]_\lambda^{25°} = 3·797a_\lambda$.
$$a_\lambda = 9·3432/(\lambda^2 - 0·0190).$$

λ.	$a_{obs.}$	$a_{calc.}$	Diff.	λ.	$a_{obs.}$	$a_{calc.}$	Diff.
6708	+ 21·65°	+ 21·68°	− 0·03°	4887	42·47°	42·50°	− 0·03°
6292	24·78	24·77	+ 0·01	4434	52·63	52·61	+ 0·02
5805	29·39	29·38	+ 0·01	3989	66·68	66·68	± 0·00
5225	36·83	36·78	+ 0·05	3353	100·00	100·01	− 0·01

Tetra-acetyl a-Methylglucoside.—This was prepared by the acetylation of a-methylglucoside. The specimen used had m. p. 101°, $[a]_D^{25°}$ + 134·4° in $CHCl_3$ (c, 14·6). Spectrophotometric observations with a 15% solution in $CHCl_3$ (l, 2 cm.) showed strong general absorption below λ 3000. The rotatory dispersion was complex.

$$c,\ 14\cdot5904 \text{ in } CHCl_3.\quad t,\ 25°.\quad l,\ 1\ dm.\quad [a]_\lambda^{25°} = 6\cdot854a_\lambda.$$
$$a_\lambda = 6\cdot298/(\lambda^2 - 0\cdot026).$$

λ.	$a_{obs.}$.	$a_{calc.}$.	Diff.	λ.	$a_{obs.}$.	$a_{calc.}$.	Diff.
6708	+ 14·83°	+ 14·86°	− 0·03°	4523	35·44°	35·27°	+ 0·17°
6292	17·03	17·02	+ 0·01	4353	38·44	38·52	− 0·08
6104	18·18	18·17	+ 0·01	4171	42·43	42·56	− 0·13
5893	19·61	19·60	+ 0·01	4011	46·43	46·69	− 0·26
5805	20·25	20·25	+ 0·00	3872	50·43	50·82	− 0·39
5515	22·62	22·64	− 0·02	3748	54·43	55·02	− 0·59
5225	25·48	25·50	− 0·02	3625	59·03	59·75	− 0·72
4887	29·60	29·59	+ 0·01	3462	66·03	67·10	− 1·07
4887*	29·61	29·59	+ 0·02	3252	77·02	78·97	− 1·95
4691	32·44	32·45	− 0·01	3185	81·02	83·48	− 2·46

* Here and in the following tables, an asterisk denotes photographic measurement.

Tetra-acetyl β-Methylglucoside.—This was prepared from acetobromoglucose by Hudson and Dale's method (*J. Amer. Chem. Soc.*, 1915, **37**, 1264). The specimen used had m. p. 104°, $[a]_D^{25°}$ − 18·7° in $CHCl_3$ (*c*, 12·9) and a 13% solution in $CHCl_3$ showed strong general absorption below λ 2800. The rotatory dispersion was complex, the deviations from the simple formula being in the same direction but considerably greater than those found in the case of tetra-acetyl α-methylglucoside.

$$c,\ 12\cdot921 \text{ in } CHCl_3.\quad t,\ 25°.\quad l,\ 2\ dm.\quad [a]_\lambda^{25°} = 3\cdot870a_\lambda.$$
$$a_\lambda = -\ 1\cdot538/(\lambda^2 - 0\cdot03).$$

λ.	$a_{obs.}$.	$a_{calc.}$.	Diff.	λ.	$a_{obs.}$.	$a_{calc.}$.	Diff.
6708	− 3·69°	− 3·66°	− 0·03°	4466	9·06°	9·08°	+ 0·02°
6292	4·20	4·20	± 0	4119	11·06	11·01	− 0·05
6104	4·50	4·49	− 0·01	3866	13·06	12·87	− 0·19
5893	4·84	4·85	+ 0·01	3670	15·07	14·69	− 0·38
5805	5·02	5·01	− 0·01	3510	17·07	16·50	− 0·57
5515	5·58	5·61	+ 0·03	3397	19·07	18·01	− 1·06
5225	6·31	6·33	+ 0·02	3285	21·08	19·74	− 1·34
5069*	6·76	6·78	+ 0·02	3197	23·08	21·30	− 1·78
4887	7·34	7·36	+ 0·02	3126	25·08	22·71	− 2·37
4887*	7·36	7·36	± 0	3057	27·08	24·24	− 2·84
4700	8·06	8·06	± 0	2975	30·09	26·29	− 3·80

Tetra-acetyl α-Methylmannoside.—This, m. p. 65°, $[a]_D^{25°}$ + 49·2° in $CHCl_3$ (*c*, 6·5), was prepared by Dale's method (*J. Amer. Chem. Soc.*, 1924, **46**, 1046). In $CHCl_3$ solution strong general absorption was observed below λ 2800. The rotatory dispersion was complex.

$$c,\ 6\cdot4879 \text{ in } CHCl_3.\quad t,\ 25°.\quad l,\ 2\ dm.\quad [a]_\lambda^{25°} = 7\cdot707a_\lambda.$$
$$a_\lambda = 2\cdot026/(\lambda^2 - 0\cdot03).$$

λ.	$a_{obs.}$.	$a_{calc.}$.	Diff.	λ.	$a_{obs.}$.	$a_{calc.}$.	Diff.
6708	+ 4·82°	+ 4·82°	± 0	4640	10·94°	10·93°	+ 0·01°
6292	5·54	5·53	+ 0·01°	4376	12·44	12·55	− 0·11
6104	5·92	5·91	+ 0·01	4107	14·44	14·61	− 0·17
5893	6·39	6·39	± 0	3872	16·44	16·89	− 0·45
5805	6·61	6·60	+ 0·01	3688	18·43	19·11	− 0·68
5515	7·38	7·39	− 0·01	3531	20·43	21·40	− 0·97
5225	8·32	8·34	− 0·02	3390	22·43	23·86	− 1·43
5348*	7·94	7·91	+ 0·03	3269	24·42	26·36	− 2·12
5067*	8·94	8·94	± 0	3120	27·42	30·08	− 2·66
4843*	9·94	9·90	+ 0·04	2983	30·43	34·35	− 3·92

Tetra-acetyl β-Methylmannoside.—This, m. p. 161°, $[a]_D^{25°}$ — 50·4° in $CHCl_3$ (*c*, 11·4), was prepared by the method of Bott, Haworth, and Hirst (J., 1930, 2655). In $CHCl_3$ solution (*c*, 11·4) it showed greater transparency to ultra-violet light than did most of the acetates examined. Strong general absorption was observed below λ 2600. The rotatory dispersion was apparently simple.

c, 11·415 in $CHCl_3$.   *t*, 25°.   *l*, 2 dm. $[a]_λ^{25°} = + 4·3802a_λ$.

$$a_λ = - 3·748/(λ^2 - 0·0215).$$

λ.	$a_{obs.}$	$a_{calc.}$	Diff.	λ.	$a_{obs.}$	$a_{calc.}$	Diff.
*7520—30	− 6·80°	− 6·88°	+ 0·08°	4887	17·23°	17·24°	+ 0·01°
*7010	8·05	7·98	− 0·07	4404	21·77	21·73	− 0·04
6708	8·73	8·75	+ 0·02	3784	30·77	30·80	− 0·03
6292	10·01	10·00	− 0·01	3101	50·00	50·20	+ 0·20
5805	11·87	11·88	+ 0·01	2789	66·62	66·59	− 0·03
5225	14·87	14·90	+ 0·03	2614	79·97	80·03	+ 0·06

Tetra-acetyl a-Methylmannofuranoside.—A sample, m. p. 63°, $[a]_D^{25°}$ + 108·5° in $CHCl_3$ (*c*, 11·0), was prepared by Haworth, Hirst, and Webb's method (J., 1930, 655). When examined spectrophotometrically in $CHCl_3$ solution, it showed no selective absorption. Marked general absorption commenced at λ 3000. The rotatory dispersion was approximately simple.

c, 11·0407 in $CHCl_3$.   *t*, 25°.   *l*, 1 dm. $[a]_λ^{25°} = 9·0576a_λ$.

$$a_λ = 3·80/(λ^2 - 0·030).$$

λ.	$a_{obs.}$	$a_{calc.}$	Diff.	λ.	$a_{obs.}$	$a_{calc.}$	Diff.
6708	+ 9·08°	+ 9·05°	+ 0·03°	4235	25·44°	25·44°	± 0
6292	10·39	10·38	+ 0·01	4045	28·43	28·44	− 0·01°
6104	11·08	11·09	− 0·01	3883	31·43	31·46	− 0·03
5893	11·98	11·98	± 0	3748	34·43	34·40	+ 0·03
5805	12·34	12·38	− 0·04	3628	37·43	37·39	+ 0·04
5515	13·86	13·87	− 0·01	3557	39·43	39·36	+ 0·07
5225	15·63	15·64	− 0·01	3490	41·43	41·39	+ 0·04
4887	18·24	18·20	+ 0·04	3428	43·42	43·42	± 0
4887*	18·24	18·20	+ 0·04	3371	45·42	45·43	− 0·01
4874	18·35	18·31	+ 0·04	3321	47·42	47·33	+ 0·09
4674	20·18	20·16	+ 0·02	3248	50·42	50·33	+ 0·09
4467	22·44	22·41	+ 0·03	3196 †	52·42	52·67	− 0·25

† This value is subject to a possible error ± 3 Å.

Tetra-acetyl " γ "-Methylmannoside (Triacetyl β-mannopyranose 1 : 2-orthomethyl acetate).—This acetate, m. p. 104°, $[a]_D^{25°}$ − 30·1° (*c*, 32·0) in $CHCl_3$, was prepared by Dale's method (*J. Amer. Chem. Soc.*, 1924, **46**, 1046). In $CHCl_3$ it showed strong general absorption below λ 2700. Its rotatory dispersion was complex.

c, 31·98 in $CHCl_3$.   *t*, 25°.   *l*, 1 dm. $[a]_λ^{25°} = 3·127a_λ$.

$$a_λ = - 3·1083/(λ^2 - 0·025).$$

λ.	$a_{obs.}$	$a_{calc.}$	Diff.	λ.	$a_{obs.}$	$a_{calc.}$	Diff.
7490*	− 5·81°	− 5·80°	− 0·01°	4880	14·49°	14·58°	+ 0·09°
7300*	6·14	6·12	− 0·02	4014	22·73	22·83	+ 0·10
6708	7·32	7·31	− 0·01	3738	27·04	27·09	+ 0·05
6292	8·40	8·37	− 0·03	3444	33·33	33·20	− 0·13
5805	9·97	9·96	+ 0·01	3247	39·04	38·65	− 0·39
5515	11·10	11·13	+ 0·03	3068	45·99	44·97	− 1·02
5225	12·49	12·53	+ 0·04	2987	49·97	48·40	− 1·57
4887	14·49	14·54	+ 0·05	2888	55·53	53·22	− 2·31

Octa-acetyl Cellobiose.—This, m. p. 224°, $[a]_D^{25°} + 41·6°$ in $CHCl_3$ (c, 15·4), was prepared from cellulose by Haworth and Hirst's method (J., 1921, **119**, 193). In $CHCl_3$ it showed strong general absorption below λ 2750. The rotatory dispersion was complex.

c, 15·39 in $CHCl_3$.   t, 25°.   l, 2 dm. $[a]_\lambda^{25°} = 3·249a_\lambda$.
$$a_\lambda = 4·225/(\lambda^2 - 0·017).$$

λ.	$a_{obs.}$.	$a_{calc.}$.	Diff.	λ.	$a_{obs.}$.	$a_{calc.}$.	Diff.
6708	+ 9·79°	+ 9·76°	+ 0·03°	4273	25·45°	25·52°	− 0·07°
6292	11·12	11·14	− 0·02	4110	27·70	27·81	− 0·11
6104	11·88	11·88	± 0·00	4011	29·24	29·36	− 0·12
5893	12·81	12·79	+ 0·02	3857	31·85	32·06	− 0·21
5805	13·21	13·20	+ 0·01	3700	34·97	35·24	− 0·27
5515	14·73	14·71	+ 0·02	3549	38·31	38·78	− 0·47
5225	16·54	16·50	+ 0·04	3398	42·19	42·91	− 0·72
4887	19·06	19·05	+ 0·01	3239	46·95	48·06	− 1·11
4892 *	19·06	19·00	+ 0·06	3076	52·36	54·43	− 2·07
4694	20·83	20·78	+ 0·05	2976	56·50	59·04	− 2·54
4498	22·83	22·80	+ 0·03				

Octa-acetyl 4-Glucosidomannose.—This substance (Brauns, *J. Amer. Chem. Soc.*, 1926, **48**, 2776) was prepared by acetylation of 4-glucosidomannose (J., 1930, 2643). The material used was crystallised several times from EtOH; m. p. 202—203°, $[a]_D^{25°} + 36·0°$ in $CHCl_3$ (c, 14·7). In $CHCl_3$ it showed strong general absorption below λ 2800. The rotatory dispersion was complex.

c, 14·72 in $CHCl_3$.   t, 25°.   l, 2 dm. $[a]_\lambda^{25°} = 3·396a_\lambda$.
$$a_\lambda = 3·427/(\lambda^2 - 0·024).$$

λ.	$a_{obs.}$.	$a_{calc.}$.	Diff.	λ.	$a_{obs.}$.	$a_{calc.}$.	Diff.
6708	+ 8·07°	+ 8·05°	+ 0·02°	4891	15·95°	15·92°	+ 0·03°
6292	9·22	9·21	+ 0·01	4580	18·53	18·45	+ 0·08
6104	9·83	9·83	± 0	4185	22·73	22·67	+ 0·06
5805	10·91	10·95	− 0·04	3789	28·63	28·66	− 0·03
5515	12·21	12·23	− 0·02	3450	35·73	36·06	− 0·33
5225	13·75	13·76	− 0·01	3122	45·47	46·65	− 1·18
4887	15·95	15·95	+ 0	2953 †	51·60	54·22	− 2·62

† Observation with 1 dm. tube.

UNIVERSITY OF BIRMINGHAM,
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