248. *Optical Rotatory Dispersion in the Carbohydrate Group. Part III. Tetramethyl α-Methylglucopyranoside and Tetramethyl α-Methylmannopyranoside.*

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In Part I (J., 1932, 2108) it was shown that the rotatory dispersions of α-methyl-glucopyranoside and -mannopyranoside were slightly complex. The present paper describes experiments carried out during an attempt to investigate more closely the nature and character of the divergences from simplicity. For this purpose, specially purified specimens of the tetramethyl derivatives were prepared and their rotations were measured in various solvents over the maximum attainable range of wave-lengths. The results display several interesting features. In the first place, tetramethyl α-methylmannopyranoside in contrast with the unmethylated pyranoside shows simple dispersion in each of the solvents water, alcohol, and chloroform. From Table II it will be seen that the rotation appears to be controlled by an absorption band in the Schumann region situated in the neighbourhood of λ 1600. This is in agreement with the observation that the absorption spectrum of the substance in aqueous solution shows no trace of selective absorption down to the minimum attainable wave-length (λ 2100). It appears, therefore, that methylation of the free hydroxyl groups has resulted in the removal of the tendency to complexity shown by α-methylmannopyranoside. This could be brought about either by suppression of the optically active absorption band responsible for the complexity in the unmethylated methylmannoside or by such alteration of the numerical value of the contributions from the various centres that cancellation occurs with respect to the disturbing factors situated on the low-frequency side of the dominating band. A similar case, in which, however, the high-frequency terms completely cancel out, has been investigated by Hudson, Wolfrom, and Lowry in connexion with the rotatory dispersion of the aldehydic form of sugars (J., 1933, 1179).
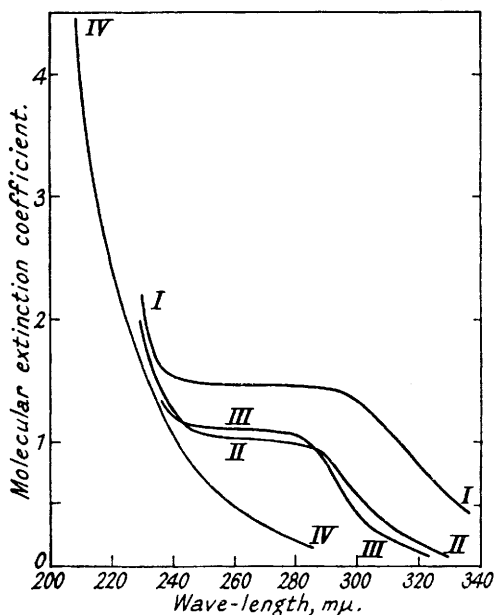
An interesting contrast is provided by the experiments with tetramethyl α-methylglucopyranoside. Here, the complexity displayed by the unmethylated glucoside is

considerably enhanced by methylation, and the rotation of the tetramethyl ether can now be represented by a two-term Drude equation with terms of opposite sign, k_1 of the high-frequency term being greater than k_2 of the low-frequency term.

TABLE I.

Solvent.	c.	Tetramethyl α-methylglucopyranoside.				Tetramethyl α-methylmannopyranoside.		
		$[\alpha]_D^{20°}$	λ_1^2.	λ_2^2.	k_2/k_1.	c.	$[\alpha]_D^{20°}$.	λ_1^2.
H_2O	16·7	150°	0·0226	0·065	−0·0198	15·05	43·4°	0·024
EtOH	16·62	157	0·0233	0·0492	−0·0484	15·0	76·7	0·0247
$CHCl_3$	16·4	146	0·021	0·065	−0·0248	16·1	79·3	0·026
(Homogeneous)	—	159·2	0·025	—	—			

The equations which represent the rotation in water, alcohol, and chloroform respectively are all similar in type (anomalous) and contain a positive term contributed by an absorption band in the Schumann region ⫣(λ 1500 approx.) and a negative term corresponding to a band in the neighbourhood of λ 2500 (for water and chloroform; λ 2300 for alcohol). The deviations from simplicity are slight, and on this account it will be understood that the small negative term may be composite and the constants derived by calculation may represent approximately the sum of several terms, the frequency constants of which differ only slightly from one another. Not only the optical rotatory dispersion, but also the absorption spectrum (see fig.), of tetramethyl α-methylglucopyranoside differs markedly from that of the corresponding mannose derivative. Measurements with tetramethyl α-methylglucopyranoside in the three solvents water, alcohol, and chloroform show an absorption curve characterised by a definite step-out in the region λ 2600. The absorption is weak in comparison with that of the majority of substances which display selective absorption, but with the evidence at present available it is not unreasonable to suppose that the step-out is associated with a region of absorption (*ca.* λ 2600) connected

I. *Tetramethyl α-methylglucoside in water.*
II. *Tetramethyl α-methylglucoside in alcohol.*
III. *Tetramethyl α-methylglucoside in chloroform.*
IV. *Tetramethyl α-methylmannoside in water.*

with the low-frequency term of the dispersion equations. This point is of special interest in that the linkages present in the molecule of tetramethyl methylglucopyranoside are not of the types normally associated with selective absorption in this region, inasmuch as C–C, C–O–C, and C–H linkages are connected with absorption in the Schumann region (see Kuhn, *Trans. Faraday Soc.*, 1930, **26**, 293). Absorption in the neighbourhood of λ 2600 is occasioned by various unsaturated linkages, none of which is, however, present in the molecule of methylated methylglucoside. Nevertheless, the first carbon atom differs from the others in that it is connected with the ring oxygen atom and is included in a semi-acetal grouping. It might be suggested that absorption frequencies associated with this part of the molecule are responsible for the polarimetric effects now observed. In spite of the attractiveness of this idea, it should be pointed out that these properties are not observed with other semi-acetals of closely related structure, and the occurrence or non-occurrence of the phenomenon of complex rotatory dispersion seems to be dependent in some way upon the stereochemistry of the molecule. For instance, the corresponding fully methylated mannose derivative, which differs structurally only in the disposition of the groups round the second carbon atom, shows no sign of selective absorption or complex dispersion. Similarly, as shown by our previous work (Part I), sucrose and α-

methylmannofuranoside, which possess semi-acetal ring structures of the kind now under consideration, display simple rotatory dispersion. On the other hand, the majority of the sugar derivatives hitherto examined give definitely complex rotatory dispersions, and it would appear most probable that where simplicity occurs it is due either to an effect of the molecular structure on the absorption which renders negligible the effective value of the corresponding dispersion constant k, or to the elimination of an effective contribution to the rotation by mutual cancellation of terms (see above).

There is some evidence that the solvent may play an important part. For example, tetramethyl α-methylglucopyranoside in the homogeneous condition shows such small deviation from simplicity over the range λ 6708—3316 that its rotation may be represented within the limits of experimental error by a one-term equation. The absorption spectra of the substance in alcohol, chloroform, and water are all of the same type and, as may be expected, the corresponding values of λ_1^2 and λ_2^2 in the two-term Drude equations representing the rotatory dispersion in the different solvents vary only slightly from solvent to solvent. The solvent effect is more evident when the values of the ratio k_2/k_1 are considered. These are $-0 \cdot 0198$ for water, $-0 \cdot 0484$ for alcohol, and $-0 \cdot 0248$ for chloroform, the value for the substance in the homogeneous condition being so small that calculation of a two-term equation is not possible. It is of interest to find that this function of the solvent in altering the magnitude of the contribution of an optically active band to the total rotation is prominently displayed by tetramethyl methylglucopyranoside, the specific rotation of which is nearly independent of solvent. On the other hand, the rotation of tetramethyl methylmannopyranoside differs widely from solvent to solvent, but in each solvent the rotatory dispersion is now simple. The very different behaviour of this pair of closely related epimeric substances shows in a striking manner the extreme difficulty of correlating chemical structure with such sensitive phenomena as optical rotatory dispersion and absorption.

Experimental.

Tetramethyl α-methylmannopyranoside, m. p. 40°, was prepared by methylation of α-methylmannoside (see Tipson, Haworth, and Hirst, J., 1930, 2658). Before use, it was crystallised several times from cold ($-10°$) light petroleum and finally distilled under diminished pressure. Tetramethyl α-methylglucopyranoside was prepared by methylating specially purified α-methylglucoside with methyl sulphate in the usual manner, and purified by repeated distillation under diminished pressure, b. p. 108°/0·1 mm. It was a colourless liquid, $n_D^{20°}$ 1·4455. The measurements of the rotatory dispersion were made by the methods described in Part I (*loc. cit.*).

Table II.

Tetramethyl α-Methylmannopyranoside.

(A) *In water.* $t = 20°$. $l = 1$ dm. $c = 15 \cdot 05$. $[a]_\lambda^{20°} = 6 \cdot 645 a_\lambda$. $a_\lambda = 2 \cdot 11178/(\lambda^2 - 0 \cdot 024)$.

λ.	$a_{obs.}$.	$a_{calc.}$.	Diff.	λ.	$a_{obs.}$.	$a_{calc.}$.	Diff.
6708	$+4 \cdot 97°$	$+4 \cdot 96°$	$+0 \cdot 01°$	3646	$19 \cdot 44°$	$19 \cdot 39°$	$+0 \cdot 05°$
6137	$6 \cdot 00$	$5 \cdot 99$	$+0 \cdot 01$	3329	$24 \cdot 44$	$24 \cdot 32$	$+0 \cdot 12$
5893	$6 \cdot 53$	$6 \cdot 53$	± 0	3209	$26 \cdot 92$	$26 \cdot 80$	$+0 \cdot 12$
5616	$7 \cdot 24$	$7 \cdot 25$	$-0 \cdot 01$	3102	$29 \cdot 40$	$29 \cdot 24$	$+0 \cdot 16$
5406	$7 \cdot 90$	$7 \cdot 87$	$+0 \cdot 03$	2932	$34 \cdot 39$	$34 \cdot 08$	$+0 \cdot 31$
5270	$8 \cdot 33$	$8 \cdot 32$	$+0 \cdot 01$	2786	$39 \cdot 36$	$39 \cdot 38$	$-0 \cdot 02$
4957	$9 \cdot 54$	$9 \cdot 52$	$+0 \cdot 02$	2676	$44 \cdot 35$	$44 \cdot 36$	$-0 \cdot 01$
4563	$11 \cdot 44$	$11 \cdot 46$	$-0 \cdot 02$	2630	$46 \cdot 83$	$46 \cdot 75$	$+0 \cdot 08$
4183	$13 \cdot 94$	$13 \cdot 97$	$-0 \cdot 03$	2585	$49 \cdot 33$	$49 \cdot 32$	$+0 \cdot 01$
3903	$16 \cdot 44$	$16 \cdot 46$	$-0 \cdot 02$	2505	$54 \cdot 31$	$54 \cdot 50$	$-0 \cdot 19$

(B) *In alcohol.* $t = 20°$. $l = 1$ dm. $c = 15 \cdot 007$. $[a]_\lambda^{20°} = 6 \cdot 664 a_\lambda$. $a_\lambda = 3 \cdot 72968/(\lambda^2 - 0 \cdot 02467)$.

λ.	$a_{obs.}$.	$a_{calc.}$.	Diff.	λ.	$a_{obs.}$.	$a_{calc.}$.	Diff.
6708	$+8 \cdot 72°$	$+8 \cdot 77°$	$-0 \cdot 05°$	3860	$29 \cdot 94°$	$30 \cdot 00°$	$-0 \cdot 06°$
6292	$10 \cdot 00$	$10 \cdot 05$	$-0 \cdot 05$	3743	$32 \cdot 44$	$32 \cdot 31$	$+0 \cdot 13$
6104	$10 \cdot 72$	$10 \cdot 72$	± 0	3356	$42 \cdot 44$	$42 \cdot 40$	$+0 \cdot 04$
5893	$11 \cdot 51$	$11 \cdot 56$	$-0 \cdot 05$	3216	$47 \cdot 42$	$47 \cdot 36$	$+0 \cdot 06$
5805	$11 \cdot 84$	$11 \cdot 94$	$-0 \cdot 10$	3100	$52 \cdot 41$	$52 \cdot 21$	$+0 \cdot 20$
5515	$13 \cdot 32$	$13 \cdot 35$	$-0 \cdot 03$	2999	$57 \cdot 41$	$57 \cdot 14$	$+0 \cdot 27$
5225	$15 \cdot 01$	$15 \cdot 02$	$-0 \cdot 01$	2912	$62 \cdot 40$	$62 \cdot 03$	$+0 \cdot 37$
4887	$17 \cdot 41$	$17 \cdot 42$	$-0 \cdot 01$	2829	$67 \cdot 37$	$67 \cdot 30$	$+0 \cdot 07$
4650	$19 \cdot 44$	$19 \cdot 47$	$-0 \cdot 03$	2759	$72 \cdot 36$	$72 \cdot 49$	$-0 \cdot 13$
4370	$22 \cdot 44$	$22 \cdot 43$	$+0 \cdot 01$	2696	$77 \cdot 35$	$77 \cdot 68$	$-0 \cdot 33$
4005	$27 \cdot 44$	$27 \cdot 48$	$-0 \cdot 04$	2645	$82 \cdot 35$	$82 \cdot 35$	± 0

(C) *In chloroform.* $t = 20°$. $l = 1$ dm. $c = 16·134$. $[\alpha]_\lambda^{20°} = 6·198a_\lambda$. $a_\lambda = 4·1118/(\lambda^2 - 0·026)$.

λ.	$a_{obs.}$.	$a_{calc.}$.	Diff.	λ.	$a_{obs.}$.	$a_{calc.}$.	Diff.
6708	+9·70°	+9·70°	±0°	3689	37·44°	37·35°	+0·09°
6292	11·10	11·12	−0·02	3507	42·44	42·39	+0·05
6104	11·87	11·86	+0·01	3358	47·44	47·39	+0·05
5893	12·79	12·80	−0·01	3234	52·44	52·32	+0·12
5805	13·20	13·22	−0·02	3123	57·44	57·48	−0·04
5515	14·81	14·84	−0·03	3032	62·40	62·37	+0·03
5225	16·68	16·65	+0·03	2949	67·39	67·44	−0·05
4887	19·33	19·32	+0·01	2878	72·38	72·35	+0·03
4667	21·44	21·44	±0	2813	77·37	77·39	−0·02
4444	23·94	23·98	−0·04	2755	82·36	82·40	−0·04
4266	26·44	26·36	+0·08	2678	89·86	89·94	−0·08
3966	31·44	31·32	+0·12	2605	97·33	98·23	−0·90

In these three solvents the rotatory dispersion was simple.

Tetramethyl α-Methylglucopyranoside.

(A) *In water.* $t = 20°$. $l = 1$ dm. $c = 16·693$. $[\alpha]_\lambda^{20°} = 5·9904a_\lambda$. $a_\lambda = 8·30103/(\lambda^2 - 0·0226) - 0·1645/(\lambda^2 - 0·065)$.

λ.	$a_{obs.}$.	$a_{calc.}$.	Diff.	λ.	$a_{obs.}$.	$a_{calc.}$.	Diff.
6708	+18·99°	+19·00°	−0·01°	4105	55·45°	55·30°	+0·15°
6495	20·25	20·33	−0·08	3945	60·45	60·59	−0·14
6137	22·93	22·92	+0·01	3821	65·45	65·24	+0·21
5893	25·00	24·99	+0·01	3695	70·45	70·56	−0·11
5805	25·79	25·80	−0·01	3591	75·45	75·48	−0·03
5616	27·71	27·69	+0·02	3497	80·45	80·40	+0·05
5515	28·82	28·79	+0·03	3370	87·95	87·86	+0·09
5225	32·37	32·36	+0·01	3258	95·44	95·36	+0·08
4887	37·45	37·44	+0·01	3151	102·93	103·44	−0·51
4667	41·45	41·45	±0	3071	110·42	110·15	+0·27
4480	45·45	45·40	+0·05	2957	120·41	120·70	−0·29
4280	50·45	50·30	+0·15				

(B) *In alcohol.* $t = 20°$. $l = 1$ dm. $c = 16·624$. $[\alpha]_\lambda^{20°} = 6·0154a_\lambda$. $a_\lambda = 8·98392/(\lambda^2 - 0·02333) - 0·48395/(\lambda^2 - 0·04919)$.

λ.	$a_{obs.}$.	$a_{calc.}$.	Diff.	λ.	$a_{obs.}$.	$a_{calc.}$.	Diff.
6708	+19·83°	+19·85°	−0·02°	3842	67·44°	67·37°	+0·07°
6137	23·95	23·95	±0	3670	74·94	75·02	−0·08
5893	26·11	26·11	±0	3529	82·44	82·35	+0·09
5805	26·94	26·96	−0·02	3364	92·44	92·44	±0
5515	30·09	30·09	±0	3227	102·43	102·37	+0·06
5225	33·82	33·82	±0	3108	112·42	112·41	+0·01
4887	39·15	39·14	+0·01	2957	127·40	127·49	−0·09
4681	43·07	43·04	+0·03	2832	142·36	142·36	±0
4480	47·44	47·46	−0·02	2760	152·36	152·07	+0·29
4382	49·94	49·87	+0·07	2723	157·35	157·40	−0·05
4282	52·44	52·53	−0·09	2690	162·34	162·34	±0
4043	59·94	59·88	+0·06	2631	172·34	171·60	+0·74

(C) *In chloroform.* $t = 20°$. $l = 1$ dm. $c = 16·403$. $[\alpha]_\lambda^{20°} = 6·0965a_\lambda$. $a_\lambda = 7·860/(\lambda^2 - 0·021) - 0·01946/(\lambda^2 - 0·065)$.

λ.	$a_{obs.}$.	$a_{calc.}$.	Diff.	λ.	$a_{obs.}$.	$a_{calc.}$.	Diff.
6708	+18·19°	+18·27°	−0·08°	3883	60·44°	60·34°	+0·10°
6495	19·47	19·55	−0·08	3754	65·44	65·29	+0·15
6137	22·02	22·04	−0·02	3638	70·44	70·30	+0·14
5893	24·01	24·02	−0·01	3533	75·44	75·38	+0·06
5805	24·80	24·80	±0	3399	82·94	82·76	+0·18
5616	26·62	26·62	±0	3280	90·43	90·32	+0·11
5515	27·66	27·68	−0·02	3178	97·92	97·71	+0·21
5225	31·07	31·10	−0·03	3084	105·41	105·41	±0
4887	35·99	35·97	+0·02	2975	115·41	115·60	−0·19
4746	38·44	38·36	+0·08	2882	125·39	125·57	−0·18
4534	42·44	42·45	−0·01	* 2763 ⎱	140·37	⎰ 140·31	+0·06
4356	46·44	46·42	+0·02	* 2761 ⎰		⎱ 140·59	−0·22
4202	50·46	50·36	+0·08	2690	150·36	150·39	−0·03
4031	55·44	55·35	+0·09				

* Alternative readings, either of which may be correct.

In each of these three solvents the rotatory dispersion of tetramethyl α-methylglucopyranoside was complex, but the anomalies predicted by the equation lay outside the range of the experimental observations.

(D) *Homogeneous.* $t = 20°$. $l = 0·5$ dm. $d_4^{20°} = 1·108$. $[a]_\lambda^{20°} = 1·805a\lambda$. $a\lambda = 28·827/(\lambda^2 - 0·0205)$.

λ.	$a_{obs.}$	$a_{calc.}$	Diff.	λ.	$a_{obs.}$	$a_{calc.}$	Diff.
6708	+66·97°	+67·12°	−0·15°	4871	132·46°	132·57°	−0·11°
6292	76·66	76·74	−0·08	4722	142·46	142·37	+0·09
6104	81·84	81·87	−0·03	4578	152·46	152·46	±0
5893	88·23	88·22	+0·01	4332	172·46	172·44	+0·02
5805	91·11	91·09	+0·02	3952	212·46	212·46	±0
5515	101·70	101·63	+0·07	3610	262·46	262·49	−0·03
5225	114·34	114·16	+0·18	3358	312·46	312·45	+0·01
4887	132·26	132·04	+0·22	3316	322·46	322·24	+0·22
4882	132·27	132·33	−0·06				

The rotatory dispersion was simple throughout the range λ 6708—3316.