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193. *The Rotatory Dispersion of Organic Compounds. Part XXI. Cyclic Derivatives of Tartaric and Malic Acids.*

By Brynmor Jones.

Developing the suggestion implicit in the Bakerian Lecture for 1921 (Lowry and Austin, *Phil. Trans.*, 1922, *A*, **222**, 287) that the anomalous dispersion of tartaric acid may be due to rotation of the two halves of the molecule about the single link connecting them, Austin (J., 1924, **125**, 1939; 1925, **127**, 1926; *Trans. Faraday Soc.*, 1930, 415) has shown not only that such bridged derivatives as methylenetartaric acid and diacetyltartaric anhydride exhibit simple dispersion, but also that the sensitiveness of the rotatory powers to changes of solvent and concentration, characteristic of tartaric acid, also disappears. As a result it was concluded that, although simple dispersion may be simulated by certain derivatives of tartaric acid, the dispersion is really simple only when some form of bridging is present in the molecule.

The primary aim of the present investigation was to confirm this conclusion by extending the measurements in the ultra-violet as well as the visible region to cyclic derivatives of malic and tartaric acids and esters, and to determine whether or no the dispersion could be simplified by the formation of ring structures which do not exclude the possibility of rotation. The results are of particular interest, and it appears that only when the possibility of rotation is definitely excluded is the dispersion really simple. The simultaneous disappearance of the anomaly of the rotatory dispersion and the flexibility of the rotations is again observed (compare Austin, *loc. cit.*).

Tables I and II give the specific rotations between λ = 6708 and 3296 of *methyl* and *ethyl benzylidenetartrate* in ethyl acetate and methyl alcohol respectively, the dispersion equation * being the same as for methylenetartaric acid. Measured in ethyl acetate solutions of approximately the same concentration, the specific rotations of these two esters are practically identical (compare Tables I and III).

TABLE I.

Rotatory Dispersion of Methyl Benzylidenetartrate in Ethyl Acetate at 20°.

$p = 20{\cdot}36$, $d_{4^\circ}^{20^\circ} = 0{\cdot}9605$, $\alpha/\alpha_{5461} = 0{\cdot}2547/(\lambda^2 - 0{\cdot}04356)$.

		α/α_{5461}.						α/α_{5461}.			
Wave-length.	α (l=2).	Obs.	Calc.	1000 (O–C).	[α].	Wave-length.	α (l=2).	Obs.	Calc.	1000 (O–C).	[α].
Li 6708	−11·01°	0·627	0·627	±	−28·15°	Cd 5086	−20·80°	1·184	1·184	±	−53·19°
Cd 6439	12·07	0·687	0·687	±	30·85	Zn 4811	23·78	1·354	1·356	− 2	60·80
Zn 6363	12·42	0·707	0·706	+1	31·75	Zn 4722	24·87	1·416	1·419	− 3	63·59
Li 6104	13·61	0·775	0·774	+1	34·80	Li 4602	26·53	1·510	1·510	±	67·85
Na 5893	14·75	0·840	0·839	+1	37·72	Hg 4358	30·47	1·735	1·739	− 4	77·92
Cu 5782	15·39	0·876	0·876	±	39·35		α (l=1)				
Hg 5780	15·41	0·877	0·877	±	39·40	Hg 5461	4·82	—	—	—	45·01
Hg 5461	17·57	1·000	1·000	±	44·92	*Fe 4062*	*10·10*	*2·095*	*2·098*	*− 3*	*94·32*
Cu 5218	19·57	1·114	1·114	±	50·04	*Fe 3808*	*12·10*	*2·511*	*2·512*	*− 1*	*113·0*
Cu 5153	20·13	1·146	1·147	−1	51·46	*Fe 3609*	*14·10*	*2·925*	*2·936*	*−11*	*131·7*
Cu 5105	20·57	1·171	1·173	−2	52·60	*Fe 3462*	*16·10*	*3·341*	*3·337*	*+ 4*	*150·4*
						Fe 3239	*20·10*	*4·171*	*4·152*	*+19*	*187·7*

TABLE II.

Rotatory Dispersion of Ethyl Benzylidenetartrate in Methyl Alcohol at 20°.

$p = 13{\cdot}58$, $d_{4^\circ}^{20^\circ} = 0{\cdot}8322$, $\alpha/\alpha_{5461} = 0{\cdot}2547/(\lambda^2 - 0{\cdot}04356)$.

		α/α_{5461}.						α/α_{5461}.			
Wave-length.	α (l=4).	Obs.	Calc.	1000 (O–C).	[α].	Wave-length.	α (l=4).	Obs.	Calc.	1000 (O–C).	[α].
Li 6708	−15·35°	0·629	0·627	+2	−33·95°	Cd 5086	−28·90°	1·184	1·184	±	−63·93°
Cd 6439	16·79	0·688	0·687	+1	37·14	Zn 4811	33·04	1·354	1·356	−2	73·08
Zn 6363	17·23	0·706	0·706	±	38·11	Zn 4722	34·52	1·415	1·419	−4	76·37
Li 6104	18·92	0·775	0·774	+1	41·86	Hg 4358	42·31	1·734	1·739	−5	93·58
Na 5893	20·50	0·840	0·839	+1	45·35		α(l=1).				
Cu 5782	21·40	0·877	0·876	+1	47·33	Hg 5461	7·425	—	—	—	—
Hg 5780	21·40	0·877	0·877	±	47·33	*Fe 4085*	*15·31*	*2·062*	*2·065*	*−3*	*112·9*
Ag 5466	24·35	0·998	0·998	±	53·86	*Fe 3834*	*18·31*	*2·466*	*2·464*	*+2*	*135·0*
Hg 5461	24·40	1·000	1·000	±	53·97	*Fe 3730*	*19·81*	*2·668*	*2·666*	*+2*	*146·1*
Cu 5218	27·17	1·114	1·114	±	60·10	*Fe 3638*	*21·31*	*2·870*	*2·867*	*+3*	*157·1*
Cu 5153	27·98	1·147	1·147	±	61·90	*Fe 3558*	*22·81*	*3·072*	*3·067*	*+5*	*168·2*
Cu 5105	28·62	1·173	1·173	±	63·32	*Fe 3438*	*25·31*	*3·409*	*3·412*	*−3*	*186·7*
						Fe 3296	*29·11*	*3·920*	*3·916*	*+4*	*214·7*

TABLE III.

The Rotatory Dispersion of Ethyl Benzylidenetartrate in Ethyl Acetate at 20°.

$p = 28{\cdot}40$, $d_{4^\circ}^{20^\circ} = 0{\cdot}9700$, $\alpha/\alpha_{5461} = 0{\cdot}2573/(\lambda^2 - 0{\cdot}04086)$.

		α/α_{5461}.						α/α_{5461}.			
Wave-length.	α (l=2).	Obs.	Calc.	1000 (O–C).	[α].	Wave-length.	α (l=2).	Obs.	Calc.	1000 (O–C).	[α].
Li 6708	−16·04°	0·630	0·629	+1	−29·12°	Cu 5218	−28·30°	1·112	1·112	±	−51·37°
Cd 6439	17·55	0·690	0·689	+1	31·86	Cu 5153	29·14	1·145	1·145	±	52·90
Zn 6363	18·00	0·707	0·707	±	32·69	Cu 5105	29·82	1·172	1·171	+1	54·13
Li 6104	19·73	0·775	0·776	−1	35·82	Cd 5086	30·09	1·182	1·181	+1	54·61
Na 5893	21·38	0·840	0·840	±	38·82	Zn 4811	34·31	1·349	1·351	−2	62·30
Hg 5780	22·34	0·878	0·878	±	40·55	Cd 4800	34·54	1·357	1·357	±	62·69
Cu 5700	23·07	0·906	0·906	±	41·88	Zn 4722	35·92	1·412	1·413	−1	65·20
Ag 5466	25·42	0·999	0·998	+1	46·13	Li 4602	38·24	1·503	1·506	−3	69·41
Hg 5461	25·45	1·000	1·000	±	46·20	Hg 4358	44·04	1·731	1·727	+4	79·95

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* Although all the measurements, with the exception of those in benzene, on the benzylidene ethers can be satisfactorily represented by the above equation, it appears that the rotations observed in the visible region for the ethyl ester in ethyl acetate are best represented by an equation with slightly different constants (Table III).

TABLE IV.

Rotatory Dispersion of Methyl Benzylidenetartrate in Benzene at 20°.

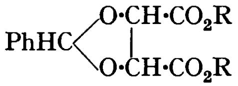
$a/a_{5461} = 0{\cdot}2627/(\lambda^2 - 0{\cdot}03547)$.

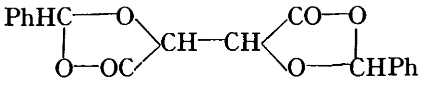
Solution I, $p = 18{\cdot}56$, $d^{20°}_{4°} = 0{\cdot}9326$. Solution II, $p = 16{\cdot}60$, $d^{20°}_{4°} = 0{\cdot}9260$.

Wave-length.	I $a(l = 2)$.	a/a_{5461}. Obs.	a/a_{5461}. Calc.	a/a_{5461}. 1000 (O–C).	$[a]$.	II $a(l = 2)$.	a/a_{5461}. Obs.	a/a_{5461}. 1000 (O–C).	$[a]$.
Li 6708	−8·90°	0·635	0·634	+1	−25·72°	−7·88°	0·634	±	−25·63°
Cd 6439	9·73	0·694	0·693	+1	28·10	8·60	0·691	−2	27·98
Zn 6363	9·98	0·712	0·712	±	28·83	8·85	0·711	−1	28·78
Li 6104	10·91	0·779	0·779	±	31·52	9·70	0·780	+1	31·56
Na 5893	11·80	0·842	0·843	−1	34·09	10·48	0·842	−1	34·09
Hg 5780	12·32	0·880	0·880	±	35·60	10·94	0·880	±	35·60
Cu 5700	12·69	0·906	0·907	−1	36·66	11·29	0·908	+1	36·72
Ag 5466	13·96	0·997	0·997	±	40·33	—	—	—	—
Hg 5461	14·01	1·000	1·000	±	40·46	12·44	1·000	±	40·46
Cu 5218	15·51	1·108	1·110	−2	44·80	13·80	1·110	±	44·90
Ag 5209	—	—	1·114	—	—	13·83	1·112	−2	45·00
Cu 5153	15·97	1·140	1·141	−1	46·14	14·20	1·142	+1	46·20
Cd 5086	16·50	1·178	1·177	+1	47·67	14·60	1·174	−3	47·50
Zn 4811	18·76	1·339	1·341	−2	54·19	16·67	1·340	−1	54·22
Cd 4800	18·88	1·348	1·348	±	54·55	16·75	1·347	−1	54·47
Zn 4722	—	—	1·401	—	—	17·42	1·400	−1	56·66
Li 4602	20·86	1·489	1·490	−1	60·27	18·53	1·489	−1	60·28
Hg 4358	23·84	1·702	1·702	±	68·86	21·17	1·702	±	68·86

As with tartaric acid, ring formation is accompanied by the development of simple dispersion and high rotatory powers relatively insensitive to changes of solvent and concentration. Although the changes observed in the rotatory powers are somewhat greater than those found with methylenetartaric acid, they do not affect in any way the simple character of the dispersion and are of a totally different order from those observed with tartaric acid and its methyl and ethyl esters (compare experimental section). There can be little doubt of the correctness of formula (I) for the alkyl benzylidenetartrates, and the simple character of their rotatory dispersion establishes for the esters the correctness of the view that the bridging of the hydroxyl groups eliminates the optical anomalies.

Condensation of tartaric acid with benzaldehyde gave a dextrorotatory dibenzylidenetartrate of exceptionally high rotatory power. Although a pure specimen was not obtained, the dispersion was approximately simple. Of two specimens prepared independently, one gave rotation values which agreed with a one-term Drude equation more satisfactorily than the other. Such behaviour suggests that a pure specimen would show simple dispersion, although this cannot be regarded as established. As with dimethylenetartrate (compare Austin, *loc. cit.*), two formulæ are possible, a five- or a six-membered ring structure, but in the light of the present evidence (III) is preferable to (II) since its greater rigidity eliminates the rotation which is still possible in (II).


(I.)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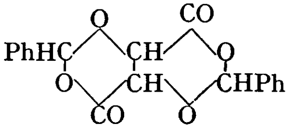

(III.)

The effect of such a bridging on the rotatory power and dispersion of tartaric acid and its esters having been established, malic acid was investigated. Condensation of the carboxyl groups with the formation of an anhydride ring is readily effected when the hydroxyl group is acetylated at the same time. *Acetylmalic anhydride* is strongly lævorotatory, and Tables V and VI show that solutions in acetone and acetic anhydride exhibit simple dispersion. In the presence of a small amount of water the anhydride ring opens to form acetylmalic acid and mutarotation is observed.

TABLE V.

Rotatory Dispersion of Acetylmalic Anhydride in Acetone at 20°.

$\alpha/\alpha_{5461} = 0{\cdot}2204/(\lambda^2 - 0{\cdot}07758)$.

Solution I, $p = 31{\cdot}87$, $d^{20°}_{4°} = 0{\cdot}9345$. Solution II, 18·83 g. in 100 c.c.

		α/α_{5461}.					α/α_{5461}.		
Wave-length.	I $\alpha(l = 4)$.	Obs.	Calc.	1000 (O–C).	[α].	II $\alpha(l = 2)$.	Obs.	1000 (O–C).	[α].
Li 6708	−21·80°	0·590	0·592	−2	−18·30°	−7·09°	0·592	±	−18·82°
Cd 6439	24·15	0·654	0·654	±	20·27	7·82	0·653	−1	20·76
Zn 6363	24·82	0·672	0·674	−2	20·84	8·07	0·674	±	21·43
Li 6104	27·58	0·747	0·747	±	23·16	8·95	0·747	±	23·77
Na 5893	30·18	0·817	0·817	±	25·33	9·79	0·817	±	26·00
Hg 5780	31·69	0·858	0·859	−1	26·60	10·29	0·859	±	27·31
Ag 5466	36·87	0·998	0·996	+2	30·95	—	—	—	
Hg 5461	36·95	1·000	1·000	±	31·02	11·98	1·000	±	31·82
Cu 5218	41·90	1·134	1·132	+2	35·17	13·59	1·134	+2	36·08
Cu 5153	—	—	1·172	—	—	14·04	1·172	±	37·28
Cu 5105	44·53	1·205	1·204	+1	37·39	14·43	1·205	+1	38·32
Cd 5086	—	—	1·218	—	—	14·62	1·220	+2	38·83
Zn 4811	53·00	1·434	1·434	±	44·49	17·23	1·438	+4	45·74
Cd 4800	—	—	1·443	—	—	17·29	1·443	±	45·89
Li 4602	60·76	1·644	1·643	+1	51·00	19·68	1·643	±	52·26
Hg 4358	72·51	1·963	1·963	±	60·87	23·50	1·962	−1	62·40

TABLE VI.

Rotatory Dispersion of Acetylmalic Anhydride in Acetic Anhydride at 20°.

13·33 Grams of the anhydride in 100 c.c. of solution.

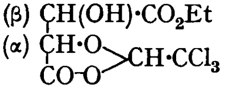
$\alpha/\alpha_{5461} = 0{\cdot}2209/(\lambda^2 - 0{\cdot}07718)$.

			α/α_{5461}.					
Wave-length.	I α.	II α.	I obs.	II obs.	Mean, obs.	Calc.	1000 (O–C).	Mean, [α].
Li 6708	−5·48°	−5·45°	0·593	0·592	0·593	0·593	±	−20·51°
Cd 6439	6·06	6·03	0·655	0·654	0·655	0·655	±	22·68
Zn 6363	6·24	6·20	0·675	0·673	0·674	0·674	±	23·34
Li 6104	6·93	6·89	0·749	0·747	0·748	0·748	±	25·92
Na 5893	7·57	—	0·818	—	0·818	0·818	±	28·39
Na 5780	7·95	7·92	0·860	0·859	0·860	0·860	±	29·77
Cu 5700	—	8·21	—	0·891	0·891	0·891	±	30·79
Ag 5466	—	9·21	—	0·999	0·999	0·997	+2	34·54
Hg 5461	9·25	9·22	1·000	1·000	1·000	1·000	±	34·63
Cu 5218	10·48	10·45	1·133	1·133	1·133	1·132	+1	39·25
Ag 5209	—	10·51	—	1·140	1·140	1·138	+2	39·42
Cu 5105	—	11·10	—	1·203	1·203	1·204	−1	41·63
Zn 4811	13·26	13·21	1·433	1·433	1·433	1·432	+1	49·64
Zn 4722	14·01	13·97	1·515	1·516	1·516	1·515	+1	52·48
Li 4602	15·18	15·13	1·642	1·641	1·642	1·641	+1	56·84
Hg 4358	18·10	18·05	1·958	1·958	1·958	1·960	−2	67·80

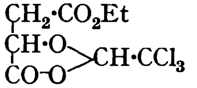
Columns I and II contain completely independent measurements of the same solution.

In view of the agreement of all these results with the idea that anomalous rotatory dispersion is associated with the possibility of mutual rotation of the two halves of the molecule, it seemed desirable to extend the measurements to cyclic derivatives in which the possibility of rotation is not excluded, since the formation of ring structures irrespective of the conception of rotation may play a decisive part in changing the character of the dispersion.

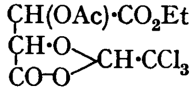
Two such compounds are (IV) and (V), first prepared by Patterson and McMillan (J., 1912, **101**, 795) by the action of chloral on ethyl tartrate and ethyl malate.



(IV.)



(V.)



(VI.)

The ethyl tartrate–chloral product, ethyl β′β′β′-trichloro-α′-hydroxyethyl α-anhydrotartrate, is dextrorotatory in ethyl alcohol and the specific rotations of a 12·41% and a 21·25% solution are practically identical, while the dispersion in the visible region appears to be simple. This observed simplicity must, however, be regarded with some suspicion, since the dispersion ratio, $\alpha_{4358}/\alpha_{5461}$ = 1·613, although above the theoretical minimum 1·57 for a simple dispersion, is a little lower than the lowest value (1·630) usually found with compounds of simple dispersion. Moreover, acetylation gave an acetyl derivative having a dispersion ratio of 1·531. Such a value, well below the theoretical minimum, shows that the dispersion cannot possibly be simple. Since the results of analysis agree satisfactorily with a compound of structure (VI), this definite departure from simplicity suggests that, although simple dispersion may be simulated by compounds having a ring structure of the type shown, the dispersion is not really simple.

The dispersion results are summarised in Tables VII, VIII, and IX.

TABLE VII.

Rotatory Dispersion of the Ethyl Tartrate–Chloral Condensation Product in Ethyl Alcohol at 20°.

p = 21·25, $d^{20°}_{4°}$ = 0·8856, α/α_{5461} = 0·2860/(λ^2 − 0·01230).

		α/α_{5461}.						α/α_{5461}.			
Wave-length.	α (*l*=2).	Obs.	Calc.	1000 (O–C).	[α].	Wave-length.	α (*l*=2).	Obs.	Calc.	1000 (O–C).	[α].
Li 6708	+11·06°	0·654	0·653	+1	+29·39°	Cu 5218	+18·57°	1·099	1·100	−1	+49·34°
Cd 6439	12·00	0·710	0·711	−1	31·80	Cu 5153	19·11	1·130	1·129	+1	50·76
Zn 6363	12·33	0·729	0·729	±	32·76	Cd 5086	19·58	1·159	1·161	−2	52·02
Li 6104	13·39	0·793	0·794	−1	35·58	Zn 4811	22·08	1·307	1·306	+1	58·65
Na 5893	14·43	0·854	0·854	±	38·34	Cd 4800	22·14	1·310	1·311	−1	58·83
Hg 5780	15·02	0·889	0·889	±	39·91	Cd 4678	23·38	1·383	1·385	−2	62·13
Cu 5700	15·46	0·915	0·915	±	41·08	Li 4602	24·21	1·433	1·434	−1	64·33
Ag 5466	16·84	0·996	0·998	−2	44·75	Hg 4358	27·20	1·610	1·610	±	72·28
Hg 5461	16·90	1·000	1·000	±	44·91						

TABLE VIII.

Rotatory Dispersion of the Ethyl Tartrate–Chloral Condensation Product in Ethyl Alcohol at 20°.

p = 12·41, $d^{20°}_{4°}$ = 0·8460, α/α_{5461} = 0·2845/(λ^2 − 0·01366).

		α/α_{5461}.						α/α_{5461}.			
Wave-length.	α (*l*=2).	Obs.	Calc.	1000 (O–C).	[α].	Wave-length.	α (*l*=2).	Obs.	Calc.	1000 (O–C).	[α].
Li 6708	+6·115°	0·652	0·652	±	+29·12°	Ag 5209	+10·36°	1·105	1·105	±	+49·34°
Cd 6439	6·64	0·708	0·710	−2	31·63	Cu 5153	10·56	1·126	1·130	−4	50·30
Zn 6363	6·83	0·728	0·728	±	32·52	Cu 5105	10·83	1·155	1·152	+3	51·58
Li 6104	7·43	0·792	0·793	−1	35·38	Cd 5086	10·90	1·162	1·161	+1	51·91
Na 5893	8·00	0·853	0·853	±	38·12	Zn 4811	12·26	1·307	1·307	±	58·40
Hg 5780	8·32	0·887	0·888	−1	39·64	Cd 4800	12·31	1·312	1·313	−1	58·63
Cu 5700	8·55	0·912	0·914	−2	40·75	Li 4602	13·49	1·438	1·436	+2	64·26
Hg 5461	9·38	1·000	1·000	±	44·68	Hg 4358	15·13	1·613	1·615	−2	72·06
Cu 5218	10·31	1·099	1·100	−1	49·10						

TABLE IX.

Rotatory Dispersion of the Acetyl Derivative of the Ethyl Tartrate–Chloral Condensation Product in Ethyl Alcohol at 20°.

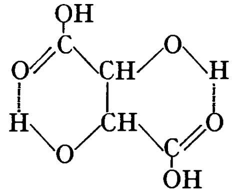
p = 9·06, $d^{20°}_{4°}$ = 0·8282.

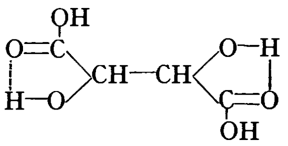
Wave-length.	α(*l* = 4).	Obs.	[α].	Wave-length.	α(*l* = 4).	Obs.	[α].
Li 6708	+5·465°	0·666	+18·21°	Cu 5218	+8·960°	1·092	+29·85°
Cd 6439	5·975	0·728	19·91	Cu 5153	9·170	1·118	30·55
Zn 6363	6·110	0·745	20·36	Zn 4811	10·520	1·282	35·05
Li 6104	6·582	0·802	21·95	Cd 4800	10·565	1·288	35·22
Na 5893	7·090	0·864	23·62	Zn 4722	10·940	1·333	36·46
Hg 5780	7·345	0·895	24·47	Cd 4678	11·045	1·346	36·81
Cu 5700	7·515	0·916	25·04	Li 4602	11·340	1·382	37·79
Hg 5461	8·205	1·000	27·35	Hg 4358	12·560	1·531	41·85

Each value of α is the mean of two independent sets of measurements.

DISCUSSION.

Although most investigators have adopted the view first put forward in 1858 by Arndsten, that the anomalous rotatory dispersion of tartaric acid is due to the presence of two optically active forms of opposite rotatory power and unequal dispersion, and have attempted to account for the anomalies by some form of isomerism, the nature of this isomerism even at present receives less general assent than its existence. In an attempt to make this hypothesis more definite Lowry and Austin have speculated on the origin of such forms, and have tentatively suggested that the composite character of the dispersion may be due to the formation of internal co-ordination compounds of the type shown below; such compounds depending for their existence on an interaction between the carboxylic oxygen and the hydroxylic hydrogen.





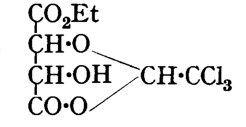
While such co-ordination compounds might be formed in the case of tartaric acid and its esters, this type of co-ordination must be impossible in such derivatives as methoxysuccinic acid and diacetyltartaric esters where the hydroxylic hydrogen has been replaced by alkyl or acyl groups respectively. This is evident from the study of ortho-substituted phenols of the type $X\cdot C_6H_4\cdot OH$ (where X is NO_2, CHO, or CO_2Me), where solubility and parachor data show that the co-ordination of the phenols vanishes in the methyl ethers (Sidgwick and Callow, J., 1924, **125**, 527; Sidgwick and Bayliss, J., 1930, 2027). Thus, although this interpretation accounted for most of the observations on tartaric acid and is a distinct advance on the view of Astbury (*Proc. Roy. Soc.*, 1923, *A*, **102**, 506), it cannot provide a general theory for the anomalous rotatory dispersion in the tartaric acid series, since it fails to harmonise with the observed anomalous dispersion of diacetyltartaric esters (Austin, J., 1928, 1825). Bancroft's recent attempt to formulate the two isomerides postulated in Arndsten's hypothesis is open to similar criticism (Bancroft and Davis, *J. Physical Chem.*, 1930, 899).

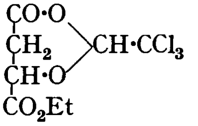
More recently Austin has supported the idea that the anomalous character of the dispersion may be due to the possibility of rotation about the single link joining the asymmetric carbon atoms and has established the simple character of the dispersion of certain cyclic derivatives. Whether the development of ring systems irrespective of their position in the molecule is capable of producing simple dispersion remained unknown.

From the above results it appears now that, while the formation of ring systems plays a decisive part in removing the gross anomalies of the parent acids and their esters and in the development of high rotatory powers, the dispersion is never really simple except in those ring structures in which freedom of rotation is prevented, either by bridging the two hydroxyl groups as in ethyl benzylidenetartrate or the two carboxyl groups as in diacetyltartaric and acetylmalic anhydride.

This interpretation would have rested on a surer foundation, however, if it were definitely known that formulæ (IV) and (V) represent the true structure of the chloral condensation products. Unfortunately, others are possible, namely (VII) and (VIII), and at present there is no definite proof that the compounds studied have the 5- and not the 6-membered ring structure.

(VII.)





(VIII.)

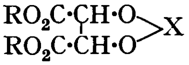
The presence in the molecule of a 6-membered ring of the above type would exclude the possibility of rotation as efficiently as the 5-membered ring in ethyl benzylidenetartrate, and consequently, if the origin of the anomalous dispersion is to be sought in terms of rotation, the dispersion of such compounds should be simple. While there is no direct evidence which would discriminate between the two alternate structures, indirect evidence is provided by the predominance of 5-membered rings in (1) the condensation of glycerol with benzaldehyde (Irvine, Macdonald, and Soutar, J., 1915, **107**, 337; Hibbert and coworkers, *J. Amer. Chem. Soc.*, 1928, **50**, 2235, 2242), (2) the formation of sugar carbonates and the acetone sugars (Haworth, "Constitution of Sugars," Ed. Arnold & Co., 1929), and (3) the formation and hydrolysis of lactones (Haworth, *op. cit.*). The evidence from the study of lactones is noteworthy, since, owing to the presence of carboxyl groups, they resemble more closely the tartrates examined in the present investigation. On the other hand, the opposing tendency, *i.e.*, the formation of 6-membered rings, is manifest in the sugars themselves.

Reviewing the whole of the evidence summarised above, it appears reasonable to conclude in the absence of more direct evidence that in the condensations of ethyl tartrate and ethyl malate with chloral, the 5-membered ring structure is the more likely, and that the compounds studied in the present investigation have the structures (IV) and (VI).

Although the disappearance of the optical anomalies can be accounted for in terms of rotation, Wolf (*Trans. Faraday Soc.*, 1930, 317; *Physikal. Z.*, 1930, **31**, 227; "The Structure of Molecules," Blackie, 1932), from a preliminary study of the dipole moments of ethyl tartrate, considers that rotation of the two halves of the molecule is not *free* but that there are several (probably 3) positions of minimum potential energy in which the molecule may become stationary and that at moderately low temperatures an equilibrium is set up between various rotational isomerides. Such an hypothesis would still be in accordance with the view here advanced, as the ring formation which leads to simple dispersion would then stabilise the molecules in one form.

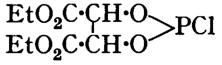
The effect on the dispersion of another centre of asymmetry, however, must not be overlooked, for, apart from the possible formation of more than one type of ring structure, condensation of chloral with ethyl tartrate results in the carbon atom originally belonging to the aldehyde group of the chloral molecule becoming asymmetric. Whether the production of another such centre of asymmetry is sufficient to account for the complexity of the dispersion remains unknown, but it is interesting in this connection to recall that the simple rotatory dispersion of sucrose is not destroyed by the presence of nine asymmetric atoms in the molecule.

Apart from the change in the character of the dispersion, cyclic derivatives of tartaric and malic acids are of particular interest on account of the marked exaltation in the rotatory power that accompanies ring formation, and of the reversal of sign that takes place in the former when the two halves of the molecule are bridged as in formula (X). Thus in addition to the strongly lævorotatory methyl and ethyl benzylidenetartrates and methylenetartaric acid there are other examples in the literature of compounds of similar structure which are lævorotatory, *e.g.*, methyl and ethyl thionyltartrate.



$$\begin{matrix}RO_2C\cdot CH\cdot O\\ RO_2C\cdot CH\cdot O\end{matrix}\!\!>X$$

(X. R = H or Alkyl; X = CH_2, CHPh, or SO)



$$\begin{matrix}EtO_2C\cdot CH\cdot O\\ EtO_2C\cdot CH\cdot O\end{matrix}\!\!>PCl$$

(XI.) $[\alpha]_D = -120°$ (*ca.*).

By warming ethyl tartrate with thionyl chloride, Schiller (*Ber.*, 1909, **42**, 2017) obtained a product which gave $[\alpha]_D$ − 56·7°: the corresponding methyl ester gave $[\alpha]_D$ − 61°. McKenzie and Barrow (J., 1911, **99**, 1920), however, found that when the reaction was carried out at room temperature a much higher rotatory power was observed, $[\alpha]_D^{19\cdot5°}$ − 184·6° in ethyl alcohol, and $[\alpha]_D$ − 189° for the ethyl ester. In spite of the discrepancy in the actual values of the rotatory powers there can be little doubt that the alkyl thionyltartrates are strongly lævorotatory.

Further evidence is provided by the isolation by Clough (*Trans. Faraday Soc.*, 1914, 136) of a compound (XI) obtained by the action of phosphorus trichloride on ethyl tartrate.

On hydrolysis it gives hydrogen chloride, phosphorous acid, alcohol, and tartaric acid. Potassium ethyl borotartrate is also lævorotatory, $[\alpha]_{5461}^{20^\circ}$ — 24·63° in methyl alcohol.

In view of the fact that all the above compounds are lævorotatory irrespective of the nature of the fifth atom forming the ring, it appears that whenever the hydroxyl groups are bridged in this manner with the formation of a 5-membered ring there is a reversal of the sign of rotation, lævorotation resulting.

EXPERIMENTAL.

Each rotation value recorded in the tables is the mean of at least ten readings of the analyser scale : with the more difficult blue lines, the usual number was sixteen. Whenever possible, doubtful readings were redetermined.

Measurements of the specific rotations first confined to the visible were later extended to the ultra-violet region whenever the amount of substance permitted such extension. In each case fresh solutions had to be made, and although the concentrations of the solutions used for the visible and the photographic readings were not identical they were sufficiently alike not to vitiate in any way the deductions made. Considerable difficulty was experienced in some cases in getting satisfactory readings at the shorter wave-lengths although several of the exposures were an hour in length, and a few even longer. Nevertheless, most of the measurements recorded have been carried out over a sufficiently large range of wave-lengths to give a true indication of the dispersion.

Ethyl Benzylidenetartrate.—To a warm mixture (70—80°) of 21 g. of ethyl tartrate and 10·5 c.c. of freshly distilled benzaldehyde were added during 30 minutes 14 g. of phosphoric oxide (compare van Ekenstein and Blanksma, *Rec. trav. chim.*, 1906, **25**, 162). After 15 minutes, the whole was cooled and poured into 100 c.c. of water; the dark brown oil obtained, after solidifying and crystallising (thrice) from alcohol, gave white crystals, m. p. 48·5—49·5° (Found : C, 61·25; H, 6·2. $C_{15}H_{18}O_6$ requires C, 61·45; H, 6·2%). The rotatory dispersion in ethyl acetate and methyl alcohol was simple. Both solutions were strongly lævorotatory, and although the concentration of the ethyl acetate (p = 28·40) was approximately twice that of the alcoholic solution (p = 13·58) the difference in specific rotation was less than 20%.

Methyl Benzylidenetartrate.—10 G. of methyl tartrate gave 8 g. of the crude *benzylidene* derivative, m. p. 74° after three crystallisations from methyl alcohol (Found : C, 58·7; H, 5·3. $C_{13}H_{14}O_6$ requires C, 58·6; H, 5·3%). The dispersion was simple in ethyl acetate and benzene, the specific rotations changing by 10% on passing from an ethyl acetate (p = 20·36) to a benzene solution (p = 16·60). The fall from 1·735 to 1·702 in the dispersion ratio, observed on changing the solvent (Tables I and IV) from ethyl acetate to benzene, cannot be due to the presence of impurity in the ester, since the specific rotations over the whole range of wave-lengths used and the dispersion ratio remained unaltered after further crystallisation. Table IV, then, in addition to confirming the change in the dispersion ratio, indicates the reproducibility of the measurements.

Dibenzylidene Tartrate.—The method of van Ekenstein and Blanksma (*loc. cit.*) was followed, but difficulty was experienced in getting a specimen sufficiently pure for dispersion measurements. The best specimen obtained, m. p. 143°, gave $[\alpha]_{5461}^{20^\circ}$ + 164·7° and $[\alpha]_{5893}^{20^\circ}$ + 138° (c = 4·33 in ethyl acetate). Van Ekenstein and Blanksma give m. p. 145°, and $[\alpha]_D$ + 128° in methyl alcohol. There is reason to believe that the dispersion would be simple, but since the specimen prepared could not be completely purified, figures for the dispersion are not submitted.

Acetylmalic Anhydride—Malic acid was acetylated by means of acetic anhydride and a drop of concentrated sulphuric acid. Since the *anhydride* was very soluble in acetic acid and anhydride, these were removed by distillation under reduced pressure. Crystallisation from carefully purified benzene not sufficing to purify it (compare J., 1925, **127**, 1926), very pure specimens were obtained by allowing hot solutions in A.R. acetic anhydride to cool in a desiccator. Owing to the deliquescent nature of the anhydride the acetic anhydride is best removed by desiccation over solid potassium hydroxide, or by washing with dry purified ether; m. p. 58° (Found : C, 45·3; H, 3·9. $C_6H_6O_5$ requires C, 45·5; H, 3·8%). Table V summarises the rotations observed with a solution in carefully purified acetone. Although no mutarotation was observed during the course of the measurements, the specific rotations had changed over a period of 24 hours, the dispersion ratio falling from 1·963 to 1·926. On repeating the measurements with a specimen of the anhydride that had been crystallised from acetic anhydride almost immediately before use, in acetone dried over phosphoric oxide and fractionated, the dispersion was identical with the previous one. In acetone the specific rotations for all wave-lengths were practically independent of concentration. To ensure that the rotatory power was being measured in a solvent free from traces of water, a solution in acetic anhydride was examined (Table VI). As anticipated, no mutarotation was observed over a period of several hours, but this change of solvent raised the specific rotations about 7% without producing an appreciable change in the dispersion. Since the observed rotations were small, two completely independent sets of readings were taken, thus increasing their accuracy.

Ethyl β'β'β'-Trichloro-α'-hydroxyethyl α-Anhydrotartrate (IV).—50 G. of ethyl tartrate and 100 g. of chloral were refluxed at 125—130° for 30 hours (compare Patterson and McMillan, *loc. cit.*). Distillation at ordinary pressure, followed by distillation at reduced pressure, removed most of the excess chloral and unchanged ester. No attempt was made to distil the condensation product, since it showed signs of decomposition even at 4 mm. pressure. The dark brown viscous oil, after cooling, was poured into water, roughly dried, and dissolved in light petroleum. On aspirating a current of air over the surface, small white crystals contaminated with a colourless oil were obtained. These after 5 crystallisations from light petroleum melted at 72·5°—a value 4·5° higher than that recorded by Patterson and McMillan (Found : C, 31·3; H, 3·05. Calc. for $C_8H_9O_6Cl_3$: C, 31·2; H, 2·95%).

The acetyl derivative, obtained by means of acetic anhydride, had m. p. 74° after crystallisation from light petroleum and alcohol (Found : C, 34·5; H, 3·35. Calc. for $C_{10}H_{11}O_7Cl_3$: C, 34·35; H, 3·17%). The specific rotations were considerably lower than those of the parent substance, and the dispersion was no longer simple.

The author thanks Professor T. M. Lowry, F.R.S., for much helpful advice and criticism, and the Chemical Society for a grant. The work was done during the tenure of a Fellowship of the University of Wales.

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[*Received, May* 1*st*, 1933.]