223. *The Influence of Solvents and of Other Factors on the Rotation of Optically Active Compounds. Part XXXIII.* The Behaviour of β-Octyl Alcohol and of β-Octyl Acetate.*

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IN previous papers of this series it has been suggested, from the experimental evidence adduced, that the variation in rotation of a considerable number of active compounds may be regarded from a single point of view, on the supposition that different solvents at varying concentrations reveal what may be regarded as different parts of a general temperature–rotation curve; and that the only datum in regard to optically active compounds, of a really fixed character, is the point at which any two temperature–rotation or concentration curves intersect. It remains a moot question whether such temperature–rotation curves can intersect at more than one temperature, and at more than one rotation, or not.

To extend this kind of examination to substances of a slightly different character, we have recently examined β-octyl alcohol and β-octyl acetate, chiefly because these substances are fairly easily obtained, and because the work of Pickard and Kenyon suggested directions in which investigation might be prosecuted. These authors (J., 1914, **105**, 837, 844) showed that the rotation of *d*-β-octyl acetate can be made to vary through a moderate range of rotation by solution in benzene, carbon disulphide, and pyridine. They examined a large number of esters of β-octyl alcohol in various solvents, but only at laboratory temperature. We have now investigated a number of solutions over as wide a range of temperature as possible, and for six colours of light, to ascertain whether the general behaviour of these compounds corresponded to that observed in the tartrates, malates, lactates, etc. The experimental results are given at the end of the paper, and the corresponding graphs are shown in the diagrams, where, in some cases, to avoid too much confusion, all six curves are not reproduced.

To compare our material with that of Pickard and Kenyon, we first examined the rotation, over a range of temperature, of *d*-β-octyl alcohol itself, and on the whole our results [Fig. 1 (*a*)] agree very closely. The rotation, for all the colours of light examined, gradually diminishes as the temperature rises, and in such a way as, apparently, to tend towards a minimum value, or to intersect.

The solvents used by Pickard and Kenyon, and by Rule (J., 1933, 376) do not much alter the rotation of the alcohol. To them we added only one not previously examined, *viz.*, paraldehyde, which we found to raise the rotation slightly. With rise of temperature the rotation diminishes, much in the same way as does that of the homogeneous alcohol. Since the rotation of the alcohol itself, however, did not seem to be sufficiently variable for our purpose, we prepared β-octyl acetate, whose rotation is more variable, and examined its rotation at a number of different temperatures in the homogeneous condition, in benzene, and in carbon disulphide. Fig. 1 (*b*) shows the behaviour of the homogeneous acetate. The rotation values decrease gradually as the temperature increases, and in such a way as to be convex to the point of origin of the diagram, *i.e.*, as if they were tending to a minimum value. The curves are not unlike those for *d*-β-octyl alcohol, but the fall of rotation, with rise of temperature, is rather more rapid. Our results agree closely with those of Pickard and Kenyon whose data (*loc. cit.*, p. 861), when plotted, give graphs for *v*, *g*, and *y*, which intersect as follows : *v/g* at + 1·9° and 140°; *g/y* at + 1° and 167°; and *v/y* at + 1·5° and 145°.

In benzene solution of *p* = 49 [Fig. 1 (*c*)], the various curves for *d*-β-octyl acetate are depressed to some extent, whilst, with rise of temperature, the rotation further diminishes, all in such a way that intersection of the *T–R* curves takes place, and a region of visibly anomalous dispersion is brought into view. The curve for violet light cuts through all the others, intersection with green taking place at a rotation of 1·45° (*t* = 34°). In a *p* = 25 solution [Fig. 1 (*d*)] this behaviour is more marked. The curves are further depressed, and the region of intersection lies almost out of the diagram to the left. There is some intersection for the curves for the longer wave-lengths, and those for blue and violet lie completely

FIG. 1.   FIG. 2.

Temperature.

Temperature.
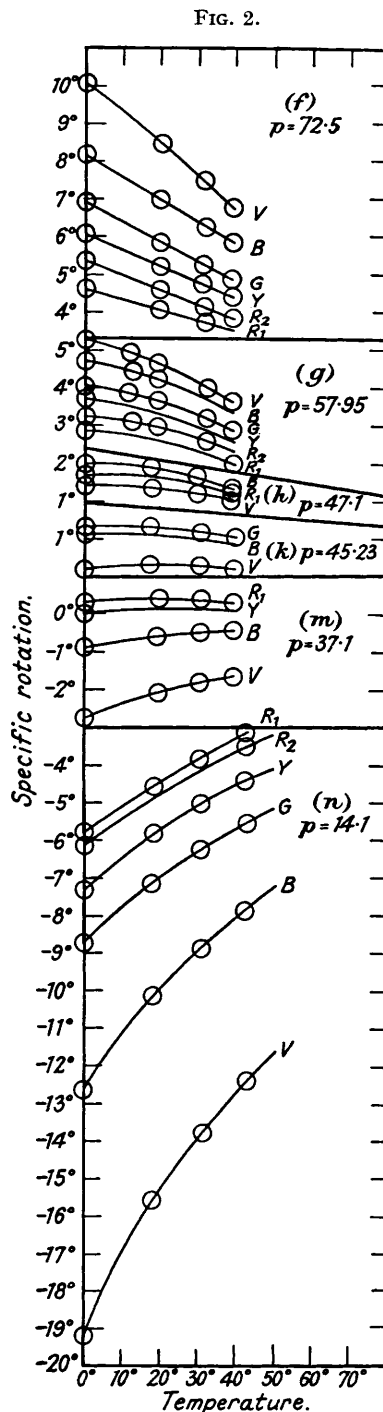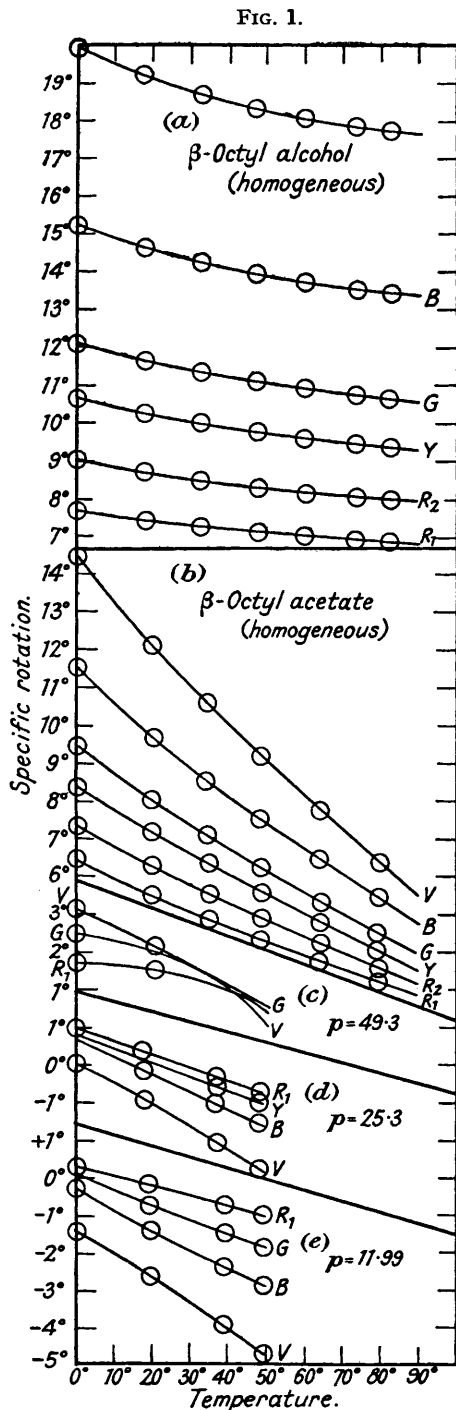
below the others.   In a $p = 12$ solution [Fig. 1 (e)] this process has obviously proceeded further ; the sequence of the curves is the opposite to that of the homogeneous ester, and they do not intersect at all within the range of the diagram.   Hence, it would seem that benzene tends to move the T–R curves of the homogeneous ester towards the left of the

diagram, and thus make apparent, at ordinary temperatures, the region of anomalous dispersion, which, in the homogeneous ester, exists at a temperature of about 140—170°

Carbon disulphide appears to exert a different and more powerful influence, which, on account of the low boiling point of the solvent, could only be examined through a short range of temperature. The T–R curves for a $p = 72·5$ solution [Fig. 2 (*f*)] of *d*-β-octyl acetate are somewhat depressed as compared with the homogeneous ester, but they are practically straight lines, whereas those for the homogeneous ester are convex to the point of origin of the diagram. In a solution of $p = 57·9$ [Fig. 2 (*g*)] the values are again lowered, and the curvature has become concave to the point of origin of the diagram. In the $p = 47$ solution [Fig. 2 (*h*)], with further depression of rotation, the dispersion has become visibly anomalous, the sequence of colours at 0° being v, r_1, r_2, y, g, b, and at 40° v, r_1, r_2, y, b, g. The curve for blue cuts that for green at a temperature of about 28° and a rotation of about $+ 1·7°$. It is evident that the curves are all close to a maximum value, which, as the dilution increases, and the rotation falls, moves from the left of the diagram towards the right.

The rotation diminishes so rapidly with dilution, in carbon disulphide, that there is again quite a distinct difference in a $p = 45$ solution [Fig. 2 (*k*)], the violet curve being more depressed, and a maximum value more distinct. In the $p = 37$ solution [Fig. 2 (*m*)], with further depression of the rotation the maximum has passed to the right, so that the

Fig. 3.

curves for violet and blue rise, with increase of temperature, and this is much more marked for the $p = 14$ solution [Fig. 2 (*n*)].

Although a little puzzling at first sight, it seems probable from these results that, whilst benzene and carbon disulphide both depress the rotation of *d*-β-octyl acetate, the former moves the T–R curve to the left and brings into view a region of anomalous dispersion lying towards the right, whereas the latter has exactly the opposite effect.

On comparing the curves in Figs. 1 (*d*) (where, we may take it, there is definite intersection) and 2 (*m*), it is clear that the latter set could not pass into the former by a single intersection, since this would bring the resulting curves out in the wrong order. If, however, there were two intersections, the results actually found might be expected.

This will be seen also from Fig. 3 (α), which indicates what we consider to be the nature of the general temperature–rotation curves for *d*-β-octyl acetate, if the substance could be examined over a sufficient range, particularly in the low-temperature direction. The influence of benzene tends to move the whole curve towards the left, and thus bring into view the anomalous region at A, whereas carbon disulphide tends to move the whole curve to the right and bring into view the region of anomalous dispersion at B. Regions corresponding roughly to the sets of curves in Figs. 1 and 2 are marked on the diagram, and it will be seen that only by *two* intersections—at A and B—could the proper sequence be arrived at, in passing from the curves of Fig. 2 (*m*) to those of Fig. 1 (*e*).

Unfortunately, it is difficult to investigate this second region of anomalous dispersion, partly owing to the low boiling point of carbon disulphide, and partly because the inter-

section of the different curves takes place at a rotation value very near zero, which makes measurement rather difficult. It seems possible, however, that the characteristic diagram given by Pickard and Kenyon (J., 1914, **105**, 847) may really be made up of two separate characteristic diagrams, relating severally to the region of intersection to the right and to the left of the diagram. Such a possibility has already been discussed by one of us with Buchanan (J., 1928, 3006), and referred to, or implied in, other papers with Todd (J., 1929, 2885, Fig. 3), with Loudon (J., 1932, 1728, Fig. 2), and with McCreath (J., 1933, 763, Fig. 4A; 1934, 100).

After the foregoing experiments were completed, we happened also to try ethyl cinnamate as a solvent, and found it to be of distinct and novel interest, and to corroborate and amplify our conclusions. It had, in the first place, an even greater depressing effect than
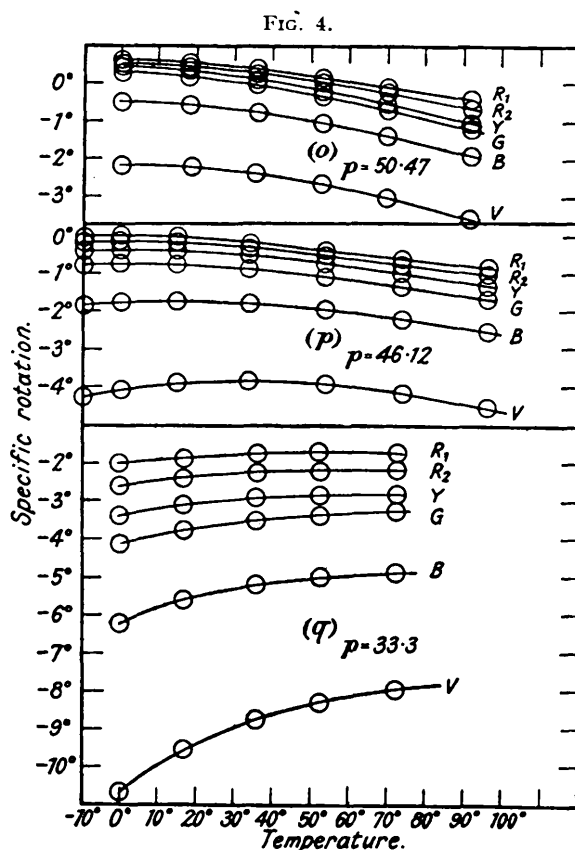
FIG. 4.

carbon disulphide. The T–R curves for a $p = 33\cdot3$ solution are shown in Fig. 4 (q). For all colours the rotations are considerably depressed, and although, with rise of temperature, they increase again, it seems highly improbable that they would intersect at any ordinary temperature, since it is clear that even below 100° they have in all cases practically reached their maximum values.

The T–R curves for a solution of $p = 50\cdot47$ are shown in Fig. 4 (o), from which it is evident that in this more concentrated solution the maximum rotation occurs at a lower temperature, lower by about 100°. These T–R curves also do not appear to intersect.* Neither of these two sets of curves exhibits an actual maximum value, but in a solution of $p = 46\cdot12$ [Fig. 4 (p)] this maximum is realised, and is found to move towards a lower temperature in passing from violet to red. It is clear that there is no intersection of these

* In a solution of $p = 66\cdot02$, which was examined later intersection is very definite, the curves for v and b cutting right across those for the other colours.

curves. It is of some special interest that the curve for r_1 in this figure just cuts the zero axis twice, a behaviour which, as far as we are aware, has not previously been observed. A similar behaviour would doubtless be observed for the g, y, r_2, and r_1 curves of Fig. 4 (*o*) were it convenient to carry the cooling to a sufficiently low temperature. The experiments just described suggest an extension of our ideas regarding the general character of the *T–R* curves in this case. Those for benzene and carbon disulphide led us to the suggestion of the general *T–R* curves shown in Fig. 3 (α). The later ones with ethyl cinnamate suggest that depressing solvents of this character may alter the curves in such a way that, as the rotation value is lowered and the maximum moved towards the right, the more arched violet curve is, as it were, thrust downwards through the red curve, the progressive stages being as shown in Fig. 3 (β) and (γ)*. The experimental curves shown in Fig. 4 would then correspond to the general curves of Figs. 3 (β) and (γ). Only at higher concentrations would intersection begin to take place, and then the maximum would have moved so much to the left that it would be difficult or impossible to make the experimental observations.

It may be mentioned that dispersion curves, corresponding to the *T–R* curves of Fig. 4 (*p*), would alter slightly in shape, with rise of temperature, until a maximum in the temperature–rotation curves was passed, when they would gradually return at higher temperatures to something closely approaching their shape at zero, some of the curves, however, cutting one another. This behaviour seems quite different from that exhibited by such substances as the tartrates examined by Winther (*Z. physikal. Chem.*, 1902, **41**, 117, 338, 360, etc.) and from the kind of behaviour discussed by Lowry (J., 1915, **107**, 1200), but they would be analogous to the dispersion curves corresponding to the regions *k* and *m* of the inset diagram in Fig. 2 of Patterson and Todd (J., 1929, 2885).

In view of the markedly different behaviour of benzene and carbon disulphide as solvents, we thought it worth while to calculate the apparent molecular solution volume of β-octyl acetate in each of them, since the apparent *M.S.V.* of ethyl tartrate in different solvents sometimes shows a variation corresponding to change in rotation (J., 1901, **79**, 214, 484; 1902, **81**, 1131).

Apparent molecular solution volumes (M.S.V.) (*in c.c.*) *of* β-*octyl acetate at* 20°.

(*M.V. of homogeneous ester at* 20° = 199·4 c.c.)

In benzene.				In carbon disulphide.				Ethyl cinnamate.			
p.	*M.S.V.*	*p.*	*M.S.V.*	*p.*	*M.S.V.*	*p.*	*M.S.V.*	*p.*	*M.S.V.*	*p.*	*M.S.V.*
49·3	200·3	12	201·5	72·5	201·9	37·1	209·7	50·5	198·4	33·3	197·8
25·3	200·4	0	202·3	58	203·6	14·1	214·7	47·9	198·4	19·1	196·3
				47·1	205·6	0	219·0	45·3	198·0	0	193·0
				45·2	207·5						

It appears, in fact, that although, in benzene, the apparent *M.S.V.* of β-octyl acetate only increases slightly, from 199·4 c.c. to approximately 202·3 c.c. at infinite dilution, in carbon disulphide, on the other hand, it increases much more rapidly, being already 214·7 c.c. at $p = 14$, and at infinite dilution it would presumably be about 219 c.c. There is thus a very considerable difference in this respect between benzene and carbon disulphide as solvents. It must, however, be remembered that the formula used in calculating these values attributes the whole change in volume to the β-octyl acetate, and this, almost certainly, is not the case. But even then the difference is worthy of note. Unfortunately, however, the behaviour of ethyl cinnamate in this respect does not agree with that of carbon disulphide. Instead of the increase of volume which, from analogy, was to be expected, there is a decrease, to approximately 193 c.c. at infinite dilution.

<div align="center">EXPERIMENTAL.</div>

The colours of light used were as follows :

	$r_1.$	$r_2.$	$y.$	$g.$	$b.$	$v.$
λ, A.	6716	6234	5790	5461	4916	4358

* One of us and McCreath (J., 1933, 764, note) predicted, in connection with certain of the *T–R* curves for the tartrates, the possibility of this behaviour.

In our experiments the d-form was used in the case of the homogeneous alcohol, for the alcohol in paraldehyde, and for homogeneous octyl acetate. For octyl acetate in benzene and carbon disulphide, however, the l-form (prepared from l-octyl alcohol) was used. In ethyl cinnamate both forms were used. The experimental data quoted are those actually observed, but where the l-compound was used, the values have been inverted *in the graphs* to make the results comparable with those for the d-alcohol and the corresponding acetate.

Homogeneous d-β-octyl alcohol.

t.	d.	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
0°	0·8341	7·695°	9·08°	10·66°	12·12°	15·24°	19·96°
17·8	0·8216	7·45	8·72	10·27	11·63	14·61	19·22
32·5	0·8107	7·29	8·50	9·98	11·34	14·28	18·70
47·3	0·7997	7·15	8·21	9·75	11·11	13·946	18·36
60·3	0·7902	7·07	8·19	9·66	10·91	13·73	18·09
73·6	0·7803	6·92	8·09	9·47	10·77	13·58	17·84
82·5	0·7739	6·88	8·04	9·40	10·70	13·45	17·76

d-β-Octyl alcohol in paraldehyde (p = 9·9584).

0	0·9960	8·85	10·42	12·04	14·08	17·64	22·79
18·6	0·9751	8·794	10·00	11·80	13·75	17·26	22·49
35·3	0·9562	8·41	9·79	11·35	13·28	16·73	22·03
47·5	0·9418	8·42	9·27	11·25	13·02	16·41	21·80
64·7	0·9235	8·18	9·17	11·00	12·65	16·03	21·10
78·3	0·9073	8·20	9·22	10·87	12·28	15·72	20·70
95	0·8866	7·97	9·10	10·57	12·27	15·07	20·24

Homogeneous d-β-octyl acetate.

0	0·8800	6·51	7·40	8·40	9·49	11·61	14·45
20·4	0·86224	5·48	6·25	7·24	8·04	9·62	12·15
34·8	0·8500	4·81	5·44	6·35	7·06	8·60	10·60
48·6	0·8383	4·34	4·88	5·59	6·23	7·51	9·20
64·1	0·8244	3·74	4·22	4·79	5·31	6·39	7·80
79·6	0·8115	3·19	3·59	4·03	4·53	5·41	6·38

l-β-Octyl acetate in benzene (p = 49·2744).

0	0·8873	−1·736	−1·941	−2·284	−2·510	−2·882	−3·148
20·8	0·8682	−1·58	−1·715	−1·934	−2·04	−2·212	−2·148
37·6	0·8528	−1·154	−1·273	−1·332	−1·392	−1·428	−1·184
50	0·8416	−0·437	−0·464	−0·467	−0·524	−0·467	−0·054

l-β-Octyl acetate in benzene (p = 25·315).

0	0·8918	−0·786	−0·842	−0·903	−0·864	−0·687	−0·083
17·5	0·8745	−0·463	−0·344	−0·344	−0·169	+0·141	+0·975
36·9	0·8562	+0·092	+0·124	+0·338	+0·531	+0·983	+1·978
48·1	0·8446	+0·392	+0·544	+0·696	+0·895	+1·526	+2·77

l-β-Octyl acetate in benzene (p = 11·9943).

0	0·8938	−0·268	−0·443	−0·408	−0·163	+0·371	+1·364
19·1	0·8759	+0·131	+0·262	+0·583	+0·797	+1·429	+2·63
38·9	0·8559	+0·731	+0·828	+1·145	+1·558	+2·254	+3·82
48·7	0·8451	+0·913	+1·06	+1·53	+1·74	+2·799	+4·698

d-β-Octyl acetate in carbon disulphide (p = 72·5).

0	0·9420	+4·7	+5·4	+6·09	+6·93	+8·21	+10·13
19·8	0·9237	4·11	4·61	5·22	5·84	7·02	8·43
31·5	0·9124	3·67	4·20	4·81	5·27	6·31	7·53
39·0	0·9050	3·57	3·89	4·43	4·92	5·85	6·80

l-β-Octyl acetate in carbon disulphide (p = 57·9564).

0	1·012	−2·88	−3·26	−3·72	−4·07	−4·74	−5·24
19·3	0·9816	−2·72	−3·06	−3·47	−3·74	−4·30	−4·74
32·3	0·9679	−2·20	−2·51	−2·85	−3·14	−3·63	−3·97
38·8	0·9609	−2·01	−2·38	−2·76	−2·93	−3·39	−3·69

t......................	12·8°	12·6°	11·8°	11·3°	12·5°	11·9°
d	0·9883	0·9885	0·9894	0·9899	0·9886	0·9893
	$[\alpha]_{r_1} =$	$[\alpha]_{r_2} =$	$[\alpha]_y =$	$[\alpha]_g =$	$[\alpha]_b =$	$[\alpha]_v =$
	$-2·774°$	$-3·128°$	$-3·50°$	$-3·806°$	$-4·396°$	$-4·91°$

d-β-*Octyl acetate in carbon disulphide* (p = 47·0747).

t.	d.	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
0°	1·0295	+1·53°	+1·73°	+1·81°	+1·95°	+2·04°	+1·44°
17·8	1·0250	1·42	1·67	1·77	1·85	1·90	1·35
29·8	1·0119	1·28	1·42	1·61	1·64	1·69	1·10
38	1·0076	1·04	1·23	1·33	1·39	1·37	1·08

l-β-*Octyl acetate in carbon disulphide* (p = 45·229).

0	1·0372	−1·287	−1·346	−1·33	−1·364	−1·138	−0·237
17·3	1·0228	−1·246	−1·259	−1·302	−1·332	−1·119	−0·376
30·4	1·0117	−0·992	−1·090	−1·104	−1·145	−1·010	−0·265
39·8	1·0038	−0·986	−1·054	−1·052	−1·071	−0·898	−0·223

l-β-*Octyl acetate in carbon disulphide* (p = 37·1).

0	1·0678	−0·372	−0·297	−0·05	+0·098	+0·906	+2·732
19·3	1·0518	−0·388	−0·359	−0·192	−0·019	+0·554	+2·073
30·6	1·0426	−0·382	−0·339	−0·188	−0·061	+0·443	+1·781
39·3	1·0355	−0·358	−0·309	−0·179	−0·036	+0·472	+1·68

l-β-*Octyl acetate in carbon disulphide* (p = 14·1451).

0	1·1945	+5·74	+5·97	+7·42	+8·71	+12·68	+19·32
18·0	1·1692	+4·52	+4·92	+5·77	+7·14	+10·15	+15·55
30·6	1·1515	+3·84	+4·34	+5·01	+6·33	+ 8·84	+13·72
42·7	1·1355	+3·11	+3·495	+4·43	+5·518	+ 7·87	+12·41

l-β-*Octyl acetate in ethyl cinnamate* (p = 66·021).

0	0·9369	−2·72	−3·03	−3·34	−3·75	−4·03	−4·23
18·8	0·9208	−2·34	−2·63	−2·92	−3·12	−3·39	−3·53
34·8	0·9069	−2·11	−2·21	−2·33	−2·56	−2·796	−2·67
50·7	0·8934	−1·59	−1·87	−1·90	−2·07	−2·01	−1·85
72·4	0·8750	−1·19	−1·28	−1·36	−1·39	−1·25	−0·82
93·3	0·8578	−0·78	−0·82	−0·80	−0·77	−0·54	+0·15

l-β-*Octyl acetate in ethyl cinnamate* (p = 50·47).

0	0·9657	−0·62	−0·59	−0·50	−0·37	+0·44	+2·16
17·8	0·9503	−0·52	−0·47	−0·42	−0·17	+0·59	+2·17
35·5	0·93524	−0·25	−0·24	−0·035	+0·085	+0·75	+2·26
52·4	0·9210	−0·12	−0·06	+0·13	+0·37	+1·03	+2·59
69·3	0·90599	+0·05	+0·18	+0·505	+0·65	+1·30	+2·96
91·2	0·8864	+0·35	+0·61	+1·03	+1·07	+1·878	+3·42

d-β-*Octyl acetate in ethyl cinnamate* (p = 46·12).

−10	0·9830	−0·005	−0·14	−0·39	−0·78	−1·80	−4·31
0	0·9740	+0·014	−0·14	−0·42	−0·73	−1·75	−4·06
+14·8	0·9613	−0·034	−0·19	−0·43	−0·76	−1·69	−3·93
33·8	0·9450	−0·20	−0·33	−0·55	−0·89	−1·74	−3·77
53·9	0·9274	−0·33	−0·48	−0·79	−1·11	−1·95	−3·95
73·8	0·9099	−0·54	−0·72	−0·97	−1·34	−2·21	−4·16
96·0	0·8900	−0·79	−0·98	−1·26	−1·65	−2·53	−4·48

l-β-*Octyl acetate in ethyl cinnamate* (p = 33·2876).

0	0·9998	+1·98	+2·56	+3·37	+4·07	+6·18	+10·66
16·6	0·98435	1·87	2·33	3·04	3·73	5·60	9·49
35·7	0·9682	1·80	2·19	2·88	3·46	5·18	8·73
52·1	0·9537	1·69	2·17	2·81	3·37	4·99	8·235
72·2	0·9361	1·68	2·13	2·79	3·23	4·87	7·97

l-β-*Octyl acetate in ethyl cinnamate* (p = 19·08).

0	1·0280	+4·27	+5·70	+7·07	+8·39	+11·62	+19·34
18	1·0121	3·96	5·22	6·59	7·75	11·08	17·44
37	0·99559	3·79	4·83	5·93	6·98	9·92	15·60
53·2	0·98147	3·71	4·43	5·50	6·46	9·14	14·38
72·1	0·96455	3·44	4·24	5·18	6·06	8·41	13·14
91·7	0·94738	3·39	4·05	4·95	5·80	7·99	12·34

SUMMARY.

An examination of the rotation of β-octyl acetate in benzene, in carbon disulphide, and in ethyl cinnamate leads to the conclusions that the *T–R* curves, could they be examined over a sufficient range of temperature, would usually show two regions of visibly anomalous dispersion; and that solution in benzene, whilst lowering the maximum rotation, tends to

displace the family of $T–R$ curves towards the left, bringing the high-temperature region of anomalous rotation dispersion into view; whereas carbon disulphide and ethyl cinnamate, although also depressing the rotation, appear to displace the $T–R$ curves to the right, but in such a way that, with increasing dilution, these regions of intersection disappear, leaving the graphs for the various colours of light entirely free of each other.

Although carbon disulphide and ethyl cinnamate have very similar effects on β-octyl acetate as regards rotation, they have opposite effects on its apparent molecular solution volume.