240. *Studies in Solvent Action. Part XI. Influence of Solvent, Concentration, and Temperature upon the Rotatory Powers of* l-*Menthyl* o-*Substituted Benzoic Esters.*

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The solvent effects described in the foregoing paper have also been investigated for various *l*-menthyl esters of *o*-substituted benzoic acids, in which the substituent groups are NO_2, CO_2H, OH, (H), Cl, and OMe. These compounds form a series in which the rotatory powers fall steadily in that order, the unsubstituted benzoate (H) occupying an intermediate position.

Polar Influence of Solvent.—In both aromatic and aliphatic solvents the rotatory powers of the more highly active *o*-nitro-ester * and hydrogen phthalate fall as the polarity of the medium increases. The *o*-chlorobenzoic ester also exhibits a polar influence in the same sense, except for several marked exceptions which are discussed below. For the remaining three esters, the relationship between $[M]$ and μ is not clearly defined. The optical displacements in the case of *l*-menthyl salicylate, however, appear to be in the

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* The influence of a limited number of aromatic solvents on the rotatory power of the *o*-nitrobenzoic ester has already been discussed by McLean (J., 1934, 352).

opposite direction to the above, since the highest rotations are found in benzonitrile and the lowest in the non-polar solvents benzene and toluene. As will be seen later, this

Rotatory Powers $[M]_{5461}$ *for* l-*Menthyl* o-*Substituted Benzoates in Solution*
(c = 4, l = 2, t = 20°).

			o-Substituent.					
Solvent.	$n_D^{20°}$.	$\mu \times 10^{18}$.	NO_2.	CO_2H.	OH.	Unsubs.	Cl.	OMe.
		I.	*Aromatic solvents.*					
$C_6H_3(CH_3)_3$	1·496	0	−660°	−431°	−335°	−302°	−253°	−198°
$C_6H_5{\cdot}CH_3$	1·495	0·4	671	407	327	284	248	199
C_6H_6	1·501	0	703	402	323	280	247	212
$C_6H_5{\cdot}OMe$	1·516	1·25	606	348	328	282	240	200
C_6H_5I	1·618	1·50	600	357	352	309	254	229
C_6H_5Br	1·560	1·50	577	346	346	293	242	216
C_6H_5Cl	1·525	1·52	570	344	343	289	242	212
$C_6H_5{\cdot}NH_2$	1·586	1·60	680	275	334	309	262	258
o-$C_6H_4Cl_2$	1·549	2·24	498	314	335	282	232	201
$C_6H_5{\cdot}CHO$	1·545	2·75	501	306	343	294	240	218
$C_6H_5{\cdot}CN$	1·528	3·85	468	296	353	302	234	217
$C_6H_5{\cdot}NO_2$	1·550	3·89	436	291	339	279	231	205
		II.	*Aliphatic solvents.*					
C_6H_{14}	1·375	0	585	419 †	299	261	239	164
C_6H_{12} *	1·427	0	593	393	294	246	235	151
CCl_4	1·461	0	607	386	292	243	223	168
CS_2	1·628	0	625	372	337	293	232	203
$CHCl_3$	1·446	1·10	586	345	315	264	227	171
$CH_3{\cdot}CO_2H$	1·372	1·70	550	334	320	293	237	208
CH_2Cl_2	1·424	1·61	553	353	310	270	228	171
$CH_3{\cdot}OH$	1·328	1·64	557	334	300	281	234	199
CH_3I	1·530	1·66	584	380	287	250	226	159
$CH_3{\cdot}CHO$	1·332	2·71	531	323	309	276	230	171
$CH_3{\cdot}CN$	1·344	3·05	495	300	308	273	217	167
$CH_3{\cdot}NO_2$	1·381	3·78	475	301 ‡	311	264	215	154

* *cyclo*Hexane. † $c = 0{\cdot}5$. ‡ $c = 2$.

view is supported by the variations found for the rotatory power of the salicylate with increasing concentration in benzene solution. No conclusions can be drawn from the irregular values recorded for the methoxy-ester and the unsubstituted benzoate.

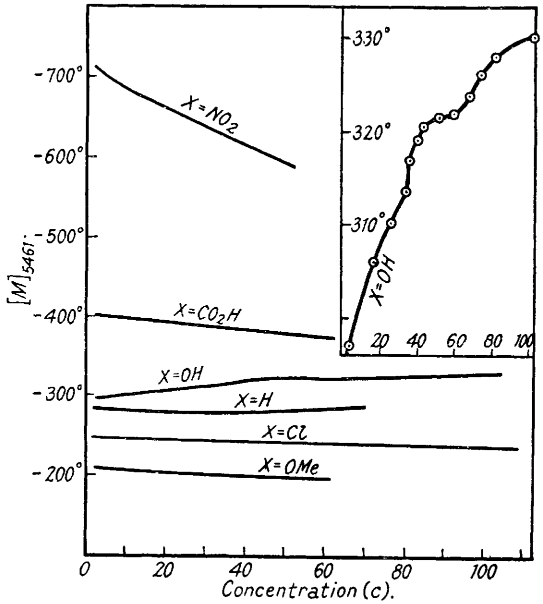
The considerable differences observed with solvents of zero polarity may be referred in part to differences in the state of association of the esters in such solutions; *e.g.*, *l*-menthyl hydrogen phthalate (*M*, 304) is found by the Menzies–Wright ebullioscopic method to be more strongly associated in carbon disulphide solution (*M*, 555 for $c = 1{\cdot}16$) than in benzene (*M*, 392 for $c = 1{\cdot}2$), in agreement with its lower rotatory power in the former medium.

Influence of Refractive Index of Solvent.—The values in the foregoing tables, however, provide evidence of another factor affecting the rotatory power of the solutions. It has been deduced theoretically by Boys (*Proc. Roy. Soc.*, 1934, *A*, **144**, 690) that the rotatory power of an optically active solute of simple *non-polar* structure should vary directly with the refractive index of the medium, $\alpha \propto (n^2 + 2)(n^2 + 5)$. This relationship has also been demonstrated qualitatively for *d*-pinane by Rule and Chambers (*Nature*, 1934, **133**, 910). Attempts have previously been made by Gans, Born, and others to establish this dependence upon refractivity for optically active solutes in general, but, as has been shown in this series of investigations, the predominant factor for solutes of polar character is the state of association in which the compound exists in the solution. Even with polar solutes, however, the influence of the refractive index of the medium may become evident in exceptional cases. Among solvents listed in the foregoing tables, the aliphatic compounds have refractive indices $n_D^{20°}$ varying from 1·328 to 1·530, carbon disulphide possessing the very high value 1·628; for aromatic solvents the values range from 1·495 to 1·618. On the whole, the benzenoid solvents have considerably higher refractive indices than the aliphatic ones, and in agreement with the above relationship the solutions in aromatic media exhibit, in general, the higher rotatory powers.

Further confirmation of this influence in the present instance may be sought in the variations observed with solvents possessing strongly divergent values of refractive index. Outstanding examples in the aromatic group are iodobenzene (1·618) and aniline (1·586); in the aliphatic group carbon disulphide (1·628) is exceptional. Reference to the foregoing tables shows that with few exceptions the rotatory powers of solutions in these three solvents are abnormally high in comparison with the dipole moments of the solvents. The rotation of *l*-menthyl hydrogen phthalate in aniline, however, is low owing to the incidence of salt formation between solute and solvent (cf. Rule, *Trans. Faraday Soc.*, 1930, **26**, 328).

Since the rotatory powers of *d*-octyl *o*-methoxybenzoate in solution have been shown to be closely related to the polarity of the solvent (Rule, Smith, and Harrower, J., 1933, 378), it is of interest to inquire whether the absence of such a relationship in the corresponding menthyl ester can be traced to differences in the molecular structures of the esters. The observed optical influences are assumed to be dependent upon dipole association between polar groups contained in the solute and solvent molecules, and in this connexion it is evident that the presence of the two bulky cyclic systems of the menthyl ester offers a considerably greater degree of steric hindrance to a coupling of the dipoles than does the more open structure of the octyl derivative. This hypothesis is further supported by the normal polar influence of solvents previously established for *l*-menthyl acetate (Rule and Ritchie, J., 1932, 2335), which resembles octyl methoxybenzoate in possessing one ring structure united to an open-chain residue.

Fig. 1.

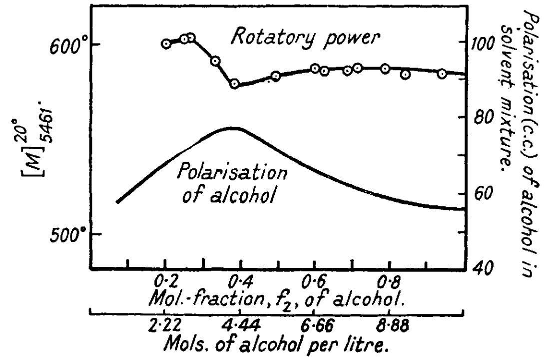


Rotatory powers of l-*menthyl* o-*substituted benzoates* ($X{\cdot}C_6H_4{\cdot}CO_2C_{10}H_{19}$). *Benzene was used as solvent except for the salicylic ester* (OH), *for which* n-*hexane was employed. The diagram for the salicylate is reproduced on a larger scale in the inset.*

Concentration Changes.—In earlier papers of this series, it has been shown that a rise in the degree of solute–solvent association, brought about by dissolving the optically active compound in a solvent of higher polarity, displaces the rotation in the same direction as a rise in the degree of solute–solute association resulting from an increase in the concentration of the compound dissolved in a non-polar medium. Similarly, the changes in rotatory power undergone by the above esters with increasing concentration in benzene solution confirm the conclusions already drawn from the data in the above tables; for instance, the rotations of the nitro-, carboxy-, and chloro-derivatives fall as the concentration rises (Fig. 1). In accordance with theory, the fall is greatest for the nitro-ester, which contains the most strongly polar *o*-substituent and will therefore most readily undergo association.

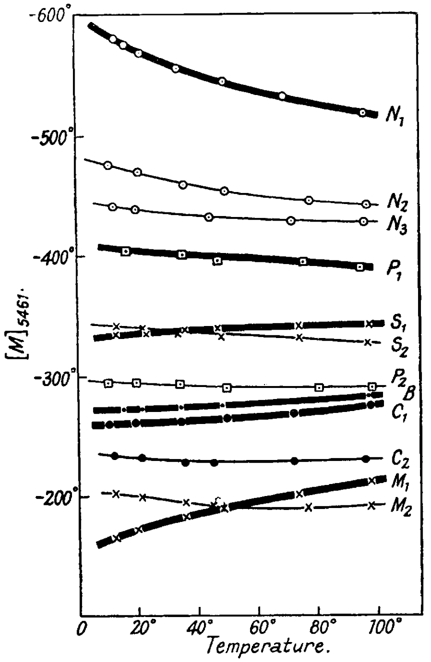
l-Menthyl salicylate appears from the above data to be subject to a solvent effect of the opposite type, the lowest rotatory powers being found in non-polar solvents. This conclusion is supported by the upward trend of the curve for the hydroxy-ester in Fig. 1, indicating a rise in rotation with increasing concentration, and consequent increasing degree of association. In view of the unusual character of salicylic compounds, with their ability to undergo internal association to form a chelate ring, the molecular weight of the ester (*M*, 276) was examined by the cryoscopic method (Menzies–Wright apparatus) with *cyclo*hexane as solvent. The calculated values are given below, and represent a steady increase in the degree of association between adjacent molecules with rise in concentration.

FIG. 2.



l-*Menthyl* o-*nitrobenzoate in mixtures of* n-*butyl alcohol and* n-*hexane. The rotatory powers plotted above are those deduced for the alcoholic component of the solution alone. The same inflexion in the curve is also evident from an inspection of the rotations observed for the mixtures, although it is then smaller in magnitude* (*see p.* 1048).

FIG. 3.



Temperature–rotation curves for l-*menthyl esters in solution.* o-*Nitrobenzoate in decalin* (N_1), *benzonitrile* (N_2), *and nitrobenzene* (N_3); *hydrogen phthalate in decalin* (P_1) *and nitrobenzene* (P_2); *salicylate in decalin* (S_1) *and nitrobenzene* (S_2); *benzoate in decalin* (B); o-*chlorobenzoate in decalin* (C_1) *and nitrobenzene* (C_2); o-*methoxybenzoate in decalin* (M_1) *and nitrobenzene* (M_2).

Wt. of ester, g.	*c.*	Δ*t.*	*M.*	Wt. of ester, g.	*c.*	Δ*t.*	*M.*
0·1629	1·08	1·071°	264	0·4848	3·23	3·056°	275
0·2249	1·49	1·455	269	0·5764	3·84	3·559	282

A further peculiarity of the diagram for the salicylate in *n*-hexane (Fig. 1) is that the central portion (*c* = *ca.* 35—65) is represented by a maximum superimposed upon the main curve. This feature is illustrated more clearly by the inset graph drawn on a larger scale. Maxima of this kind have previously been observed for tartaric esters by Patterson and co-workers (J., 1902, **81**, 1099; cf. also Rule, Barnett, and Cunningham, J., 1933, 1217) and for *d*-octyl alcohol (Rule, Smith, and Harrower, *loc. cit.*). Such effects would appear to be a characteristic of hydroxylic compounds and may be related to the maxima commonly found in the curves showing the change of polarisation of an alcohol on continued dilution with a non-polar solvent (Debye, " Dipol Moment ").

An irregularity of the same kind has been found to occur in the rotatory power of *l*-menthyl *o*-nitrobenzoate when dissolved at a fixed concentration in various mixtures of *n*-butyl alcohol and *n*-hexane. In this case the effect is probably due to the irregular change in the polarisation of the alcohol–hexane mixture, and the rotation falls to a minimum when the mol.-fraction, f_2, of butyl alcohol is 0·38, in close agreement with the known point of maximum polarisation, which exists at $f_2 = 0{\cdot}37$ (see Fig. 2). On the other hand, in solvent mixtures of benzene with carbon tetrachloride or disulphide, the rotatory power of the dissolved nitrobenzene ester varied smoothly as the composition of the mixture changed, thus conforming to the established absence of maxima or minima in the polarisation curves for such mixtures.

Temperature Changes.—As may be seen from Fig. 3, when the six esters under discussion are examined in decalin solution (heavy curves) the main result of a rise in temperature appears to be a damping out of the influence due to the ortho-substituent; for instance, to mention only the two extreme cases, the high rotation of the nitro-ester (N_1) falls and the low rotation of the methoxy-ester (M_1) increases on passing from 20° to 100°. Menthyl benzoate in decalin (B) occupies an intermediate position and undergoes little change in rotatory power over the temperature range under consideration. One reason for a change of this type may be visualised in an increase in the average distance between the ortho-substituent and the carbomenthoxy-grouping as a result of the greater molecular vibration at high temperatures (cf. Ebert, *Leipziger Vorträge*, 1930, 50), which would tend to displace the rotatory power in each case towards that of the unsubstituted menthyl benzoate.

The influence of a rise in temperature in affecting the rotatory power by leading to a diminution in the degree of association between solvent and solute may also be traced in Fig. 3; *e.g.*, a comparison of the curves N_1, N_2, and N_3 for the nitrobenzoate dissolved in decalin, benzonitrile, and nitrobenzene, respectively, shows that at lower temperatures the rotatory power is strongly depressed by the highly polar solvents benzonitrile and nitrobenzene. As the temperature rises, however, the degree of solvation of the optically active molecules diminishes, and the depressions due to the polar solvents become less pronounced. Hence, at higher temperatures the curves for these two solvents converge towards that of the non-polar medium decalin (cf. Rule, Smith, and Harrower, *loc. cit.*). A similar effect may be noted with the curves P_1 and P_2, representing the hydrogen phthalate in decalin and in nitrobenzene respectively. For the remaining esters no definite polar influence of the solvent was observable in the data given in the tables, and consequently no temperature effect of the above type is visible in Fig. 3.

In addition to the temperature changes related to modifications in the state of association and the spatial arrangement of the optically active molecules, however, we must assume further effects arising from variations in the refractive index of the solvent employed: the alicyclic compound decalin has a lower refractive index ($n_D^{20°}$ 1·476) than the aromatic compounds nitrobenzene and benzonitrile, which probably results in all the curves for decalin in Fig. 3 being displaced to positions of lower rotation than would be the case had this factor been absent.

EXPERIMENTAL.

l-Menthyl *o*-methoxybenzoate was most readily prepared from *o*-iodobenzoic acid, which was converted into methoxybenzoic acid (91% yield) by treatment with an alcoholic solution of sodium methoxide in the presence of copper-bronze (Rule and Barnett, J., 1932, 2729), and thence by way of the acid chloride into the ester. In the penultimate stage, phosphorus pentachloride was used in place of thionyl chloride, as the latter led to chlorination of the benzene nucleus. *l*-Menthyl salicylate ($\alpha_{5461}^{20^\circ} = -125{\cdot}7^\circ$, $l = 1$) was obtained as described by Rule and McGillivray (J., 1929, 405), and the remaining esters by standard methods.

*Effect of concentration on rotatory power.**

(All rotations negative; $t = 20^\circ$, $l = 1$.)

l-Menthyl phthalate in benzene:

c	3·038	6·044	13·98	14·18	20·09	26·26	43·0
$[M]_{5461}$	400°	399°	397°	396°	392°	389°	382°

l-Menthyl benzoate in benzene:

c	3·064	10·00	15·11	25·01	38·58	45·07
$[M]_{5461}$	283°	282°	281·7°	281·9°	282·2°	282·3°

l-Menthyl chlorobenzoate in benzene:

c	4·00	10·16	23·14	42·20	62·93	77·01
$[M]_{5461}$	247°	246·9°	246·7°	244·1°	242°	240°

l-Menthyl *o*-methoxybenzoate in benzene:

c	4·00	9·99	16·02	25·98
$[M]_{5461}$	211°	209°	206°	205°

l-Menthyl salicylate in *n*-hexane:

c	4·01	9·02	16·84	27·31	34·27	36·09	42·11
$[M]_{5461}$	297°	300°	306°	310°	313·3°	316·7°	319·1°
c	45·49	52·26	60·13	69·29	75·23	82·88	
$[M]_{5461}$	320·3°	321·3°	321·7°	323·6°	325·9°	327·7°	

* The data observed for the *o*-nitrobenzoate with change of concentration in benzene and nitrobenzene solutions agreed with those recorded by McLean (*loc. cit.*) and are not repeated here.

l-*Menthyl* o-*nitrobenzoate* (c = 5, t = 20°) *in mixtures of solvents.*

Benzene (1) and carbon disulphide (2): *

f_2	1·000	0·910	0·602	0·318	0·233	0·152	0·117	0·000
†$[M_{1,2}]_{5461}$	625°	631°	655°	674°	683°	690°	694°	703°
$[M_2]_{5461}$	625°	622°	618°	616°	613°	600°	600°	—

Benzene (1) and carbon tetrachloride (2):

f_2	1·000	0·955	0·863	0·631	0·385	0·282	0·150	0·000
$[M_{1,2}]_{5461}$	607°	610°	617°	639°	663°	672°	686°	703°
$[M_2]_{5461}$	607°	606°	604°	599°	587°	582°	573°	—

n-Hexane (1) and *n*-butyl alcohol (2):

f_2	1·000	0·936	0·843	0·787	0·717	0·699	0·625	0·601
$[M_{1,2}]_{5461}$	584°	584°	584°	583°	583°	584°	583°	584°
$[M_2]_{5461}$	584°	584°	584°	586°	587°	585°	586°	586°
f_2	0·491	0·381	0·328	0·266	0·262	0·203	0·000	
$[M_{1,2}]_{5461}$	583°	581°	584°	586°	585°	584°	579°	
$[M_2]_{5461}$	584°	579°	591°	604°	601°	599°	—	

* The mol.-fraction of component 2 in the solvent mixture is given as f_2.

† $[M_{1,2}]$ denotes the observed molecular rotation in the mixed solvents: $[M_2]$ is the rotation deduced as a first approximation from $[M_{1,2}]$ for the solution in the component of higher dielectric constant alone and calculated by deducting the rotation contributed by the benzene or hexane component (Rule and McLean, J., 1931, 682).

Effect of temperature on rotatory power (l = 1).

Solvent.	$d_{4^\circ}^{t^\circ}$.	Temp.	α_{5461}.	$[M]_{5461}^{t^\circ}$.	Solvent.	$d_{4^\circ}^{t^\circ}$.	Temp.	α_{5461}.	$[M]_{5461}^{t^\circ}$.
				l-Menthyl *o*-nitrobenzoate.					
$C_6H_5{\cdot}NO_2$	1·207	12·5°	5·82°	441°	Decalin	0·898	13·0°	7·64°	581°
,,	1·200	20·0	5·75	439	,,	0·896	16·0	7·55	576
,,	1·177	44·5	5·55	432	,,	0·891	21·8	7·44	570
,,	1·175	46·5	5·54	431	,,	0·885	34·0	7·20	556
,,	1·151	71·8	5·38	428	,,	0·871	49·0	6·96	546
,,	1·128	95·8	5·28	429	,,	0·856	69·2	6·69	533
					,,	0·836	96·0	6·35	519
C_6H_5Br	1·492	13·2	7·81	591	$C_6H_5{\cdot}CN$	1·017	11·0	6·27	476
,,	1·483	20·0	7·60	579	,,	1·005	21·0	6·13	471
,,	1·447	48·0	7·05	550	,,	0·994	36·0	5·92	459
,,	1·423	66·0	6·80	540	,,	0·983	49·8	5·79	454
,,	1·381	98·5	6·35	519	,,	0·960	78·0	5·55	446
					,,	0·944	96·8	5·39	441

Solvent.	$d_{4^\circ}^{t^\circ}$.	Temp.	α_{5461}.	$[M]_{5461}^{t^\circ}$.	Solvent.	$d_{4^\circ}^{t^\circ}$.	Temp.	α_{5461}.	$[M]_{5461}^{t^\circ}$.
l-Menthyl hydrogen phthalate.									
$C_6H_5{\cdot}NO_2$	1·209	10·5°	3·91°	295°	Decalin	0·899	10·8°	5·32°	402°
,,	1·200	20·0	3·89	296	,,	0·895	17·0	5·33	404
,,	1·186	34·5	3·82	294	,,	0·882	35·5	5·22	402
,,	1·171	50·0	3·72	290	,,	0·873	47·5	5·10	397
,,	1·142	81·0	3·62	289	,,	0·853	76·0	4·97	396
,,	1·125	98·5	3·58	290	,,	0·839	94·5	4·82	390
l-Menthyl salicylate.									
$C_6H_5{\cdot}NO_2$	1·203	13·2	4·98	341	Decalin	0·896	13·4	4·92	337
,,	1·195	22·0	4·91	339	,,	0·890	22·3	4·88	337
,,	1·184	34·0	4·82	336	,,	0·879	36·0	4·85	338
,,	1·170	48·2	4·72	333	,,	0·871	47·0	4·82	339
,,	1·145	74·5	4·61	332	,,	0·851	74·0	4·76	343
,,	1·123	97·0	4·45	327	,,	0·834	97·0	4·68	344
l-Menthyl benzoate.									
$C_6H_5{\cdot}NO_2$	1·201	14·5	4·38	283	Decalin	0·893	15·2	4·19	272
,,	1·194	21·6	4·32	281	,,	0·888	21·5	4·17	272
,,	1·181	35·5	4·25	280	,,	0·879	34·5	4·15	274
,,	1·170	47·2	4·17	277	,,	0·869	48·2	4·12	275
,,	1·145	73·0	4·07	276	,,	0·855	67·0	4·09	277
,,	1·122	97·7	3·96	274	,,	0·834	96·8	4·08	284
l-Menthyl *o*-chlorobenzoate.									
$C_6H_5{\cdot}NO_2$	1·206	12·5	3·19	233	Decalin	0·900	10·5	3·57	260
,,	1·198	21·2	3·15	232	,,	0·893	19·5	3·55	260
,,	1·186	36·0	3·06	227	,,	0·882	35·0	3·52	262
,,	1·174	46·2	3·02	227	,,	0·870	50·0	3·50	264
,,	1·149	72·0	2·99	229	,,	0·854	72·0	3·50	268
,,	1·126	96·0	2·91	228	,,	0·835	98·0	3·52	276
l-Menthyl *o*-methoxybenzoate.									
$C_6H_5{\cdot}NO_2$	1·204	12·0	2·81	202	Decalin	0·896	12·5	2·29	165
,,	1·196	21·0	2·74	199	,,	0·891	20·0	2·38	172
,,	1·182	36·0	2·65	194	,,	0·879	35·5	2·51	184
,,	1·173	45·0	2·59	191	,,	0·869	48·5	2·52	187
,,	1·149	77·0	2·51	189	,,	0·851	74·0	2·64	200
,,	1·123	98·0	2·48	192	,,	0·853	98·5	2·72	211

SUMMARY.

The influence has been examined of solvent, concentration, and temperature upon the rotatory powers of *l*-menthyl benzoate and the *o*-nitro-, *o*-carboxy-, *o*-hydroxy-, *o*-chloro-, and *o*-methoxy-benzoates in solution.

With the more polar nitro-ester and hydrogen phthalate, the rotations fall as the polarity of the solvent increases, or as the concentration of these esters in a non-polar solvent rises. In each case the temperature–rotation curves for the ester in polar and in non-polar solvents converge as the temperature rises. These changes are explained on the theory of dipoles by assuming varying degrees of solute–solute or solute–solvent association, in accordance with the experimental conditions.

For the four remaining esters the observed changes are less definite or entirely irregular. In general, solvents of exceptionally high refractive index tend to yield solutions of abnormally high rotatory power with each of the six esters examined, thus showing the existence of a minor effect due to the refractive properties of the solvent.

In *n*-hexane solution the rotatory powers of *l*-menthyl salicylate exhibit an exaltation between the concentrations $c = 35$ and $c = 65$.

The authors thank the Moray Fund for a grant, and the Carnegie Trust for the award of a Teaching Fellowship (to H. G. R.).

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[*Received, June 5th*, 1935.]
