CCCCXXXII.—*Optical Activity and the Polarity of Substituent Groups. Part V.* sec.-β-*Octyl Esters of some Substituted Acetic Acids and their Behaviour towards Solvents.*

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THE examination of a number of menthyl esters of substituted acetic acids (J., 1925, **127**, 2188) has shown that the influence of the substituents on rotatory power is in approximate agreement with their general polar character. β-Octyl alcohol, in comparison with menthol, appears to yield derivatives which are more complex in their optical properties, but thanks to the work of Pickard and Kenyon it is now a readily accessible compound and has been made the subject of a number of valuable researches by these investigators. It has been concluded (see also Hunter, J., 1924, **125**, 1389) that the β-octyl esters of aliphatic carboxylic acids exhibit complex dispersion, which may become anomalous under certain conditions of temperature and in the presence of certain solvents. During the course of an examination of β-butyl acetate and β-octyl acetate, heptoate, and stearate, it was found that the optical rotatory power of each ester was affected in a similar manner by a number of solvents. Ethylene dibromide, for example, brought about an exaltation in values, as compared with those for the homogeneous esters, whereas chloroform, benzene, pyridine, and carbon disulphide led to increasingly diminished values and in most cases to a reversal of sign. Now the only atoms of marked polar character in these esters are the oxygen atoms contained in the carboxyl residue, and it is of interest to determine what specific effect, if any, on the solvent action would result from the introduction of a polar substituent into the α-position to the carboxyl group.

The following pages contain an account of the preparation and properties of the optically active β-octyl esters of methoxy-, chloro-, bromo-, and iodo-acetic acids. Rotations were measured for the compounds in the homogeneous state at temperatures between 20° and 95°, and for the four wave-lengths λ_{4358}, λ_{5461}, λ_{5780},

and λ_{5893}. Determinations were also made of the rotatory powers of these compounds in 5% solution in a number of solvents. The molecular rotations, $[M]_D$, for the homogeneous esters at 20°, 40°, 60°, 80°, and 90° are summarised in Table I. The values of $[M]_D$ in solution at 20° are given in Table II, in which the figures found by Pickard and Kenyon for β-octyl acetate are also included for the purpose of comparison.

TABLE I.

Values of $[M]_D$ *for the* d-β-*Octyl Esters* of Monosubstituted Acetic Acids in the Homogeneous State.*

t.	Methoxy-ester.	Chloro-ester.	Bromo-ester.	Iodo-ester.
20°	+16·3°	+17·9°	+28·8°	+43·7°
40	14·8	16·4	26·5	40·9 (at 37·9°)
60	13·5	15·1	24·5	37·4 (at 62°)
80	12·4	14·0	23·0	—
90	12·0	13·5	22·4	—

* To avoid confusion, the figures in Tables I and II are all quoted as for derivatives of *d*-octyl alcohol, although in some cases the experimental work was actually carried out with the *l*-isomeride. The values are read off from the smooth curves obtained from the figures given in the experimental section.

TABLE II.

Molecular Rotations, $[M]_D^{20°}$, *of* d-β-*Octyl Esters in Various* 5% *Solutions.*

Solvent.	Acetate.	Methoxy-acetate.	Chloro-acetate.	Bromo-acetate.	Iodo-acetate.
Ethylene dibromide	+16·8°	+19·2°	+21·3°	+30·3°	+41·1°
(Homogeneous ester) ...	+11·8	+16·3	+17·9	+28·8	+43·7
s-Tetrachloroethane	+10·2	+11·4	+13·4	+21·5	+35·7
Acetone	+ 9·6	+11·9	+13·2	+25·2	+45·3
Nitromethane	+ 9·0	+12·4	+14·1	+23·8	+41·9
Ethyl acetate	+ 8·9	+12·5	+14·9	+26·5	+45·1
Chloroform	+ 6·5	+11·6	+12·6	+22·7	+38·3
Acetic acid	+ 6·3	+11·6	+11·5	+25·9	+43·0
Ethyl alcohol	+ 6·1	+11·3	+12·9	+26·4	+46·8
Carbon tetrachloride.....	+ 6·0	+13·0	+16·4	+28·0	+41·4
Toluene	—	+ 0·8	—	+10·8	—
Benzene	− 1·4	− 1·0	+ 0·8	+10·1	+18·9
Phenetole	− 2·4	− 6·4	− 5·2	+ 4·9	+16·4
Chlorobenzene	− 5·3	− 7·1	− 6·7	+ 2·5	+12·1
Bromobenzene	—	− 7·0	− 8·8	+ 1·6	+ 9·1
Pyridine	− 6·5	−11·5	(−11·6)*	(−56·6)*	(−52·4)*
Iodobenzene	—	−12·7	− 9·9	− 1·0	+ 2·9
Carbon disulphide	−15·4	−14·7	−10·7	− 1·2	+ 7·1

* These figures represent combination with solvent.

Influence of Substitution.

It will be seen from the figures in Table I that the molecular rotations are comparatively low in magnitude, although higher than

that for the unsubstituted ester. In each case the values fall rapidly as the temperature rises, a property which is also common to octyl alcohol and octyl acetate (Pickard and Kenyon, J., 1911, **99**, 45; 1914, **105**, 835).

For the purpose of determining the relative effects of different substituents, the values of $[M]_D^{20°}$ may be compared with those recorded by Pickard and Kenyon for β-octyl acetate, propionate and butyrate.

Substituent.	H.	Me.	OMe.	Et.	Cl.	Br.	I.
$[M]_D^{20°}$	+11·8°	13·0°	16·3°	17·9°	17·9°	28·8°	43·7°

Here the relative influence of the three halogen atoms is the reverse of that found for the corresponding menthyl esters (Hilditch, J., 1912, **101**, 202) and for the menthyl esters of ortho-substituted benzoic acids (Cohen, J., 1914, **105**, 1892), in which cases the effect of the halogen increases with decreasing atomic weight. A change in the above sense has, however, been recorded for the nuclear-substituted methyl dibenzoyltartrates (Frankland, Carter, and Adams, J., 1912, **101**, 2470), where the relative influence is also given by H<Me<Cl<Br<I.

Except for the reverse order of the halogens among themselves, the effect of substituents on the rotatory power of β-octyl acetate, *viz.*, H<Me<OMe<Et<Cl<Br<I, is in approximate agreement with their general polar character, H<(Me,Et)<OMe<I<Br<Cl, as deduced from their influence on the molecular inductive capacity of benzene or an aliphatic hydrocarbon (J., 1924, **125**, 2159). A somewhat similar group arrangement holds for the rotatory powers of the corresponding menthyl esters of substituted acetic acids, where H<(Et,Me)<OMe<I<Br<Cl (J., 1925, **127**, 2189); for the dissociation constants of substituted acetic acids, (Et,Me)< H<OMe<I<Br<Cl; and for a number of cases of chemical reactivity (J., 1924, **125**, 2159).

In this connexion, it does not appear to have been previously pointed out that the initial disturbances observed by Pickard and Kenyon in the rotatory powers of certain homologous series of aliphatic esters, which may take the form of a depression at the C_3 acid followed by an exaltation at the C_5 acid, are paralleled by a similar disturbance in the dissociation constants of the acids. It is, in fact, becoming increasingly evident that the alteration in rotatory power due to a change in the molecular structure of an active compound often goes hand in hand with the effect of this change on other properties such as acidity, inductive capacity and chemical reactivity. An example of the last type has already been observed in the relationship existing between the influence of

substituents on further substitution in the benzene nucleus and on the rotatory power of the menthyl and β-octyl esters of *o*-substituted benzoic acids (Rule, J., 1924, **125**, 1121; Rule and Numbers, this vol., p. 2166). In many cases, however, these resemblances are masked by other effects, such as those due to dispersion. Another group effect of a hitherto undiscovered type is described later under "influence of solvents."

Dispersion.

When the values of $1/\alpha$ for the above substituted acetic esters are plotted against λ^2, it is found that the points do not lie on straight lines, the divergence being greater at the higher temperatures of experiment than at the lower. The substituted esters therefore resemble the parent compound in showing complex dispersion. This is specially marked for the esters in carbon disulphide solution, and when the rotations are plotted in the form of a characteristic diagram the points representing the values in this solvent fall outside the lines accommodating the remaining points. A small region of anomalous dispersion exists where the molecular rotations of the *d*-octyl esters approximate to $+3°$.

Influence of Solvents.

The figures in Table II reveal a number of interesting regularities in the variation of rotatory power with change of solvent and in the effect of substituents contained in the solvent molecule.

Variation of Rotatory Power with Change of Solvent.—The first point to be observed is that the rotatory powers of all five esters are affected in a very similar manner by solvent action. In every case, a maximum depression is produced in carbon disulphide solution, which in general reverses the sign of rotation, and with the exception of the iodo-compound each ester gives an increased value in ethylene dibromide. All the aromatic solvents, including pyridine, resemble carbon disulphide in diminishing the rotatory powers. Owing to the low values of the observed rotations, it is possible that a few of the minor displacements in the columns are due to experimental errors, but the differences displayed by the iodo-ester are more definite, and are chiefly connected with the relatively higher values given by the oxygen-containing solvents ethyl alcohol, acetone, ethyl acetate, and acetic acid. It is significant that the substituent having the most pronounced effect on the rotatory power of the parent ester should also bring about the most specific changes in the behaviour of the substituted esters towards solvents. Pyridine, as might be expected, combines readily with the halogen derivatives. When it is mixed with the bromo-

or iodo-ester, heat is developed and the rotation rises rapidly to a limiting value.

A second point of interest is that the order of the rotatory powers of the five esters in any given solvent is the same as that for the esters in the homogeneous state. The only exceptions to this statement are small displacements of the values for the acetate in pyridine, chlorobenzene, and phenetole, and for the chloro-ester in bromobenzene.

These regularities appear to show that solvents influence the rotatory power chiefly through the medium of the carboxyl group, and that any specific solvent effect due to the presence of the substituents in question is a minor one. This is in agreement with the comparatively weak polar character of the substituents and their greater distance from the asymmetric complex.

Effect of Substituents in the Solvent Molecule.—On comparing the changes produced in the rotatory powers of the esters by solution in benzene or one of its substituted derivatives, it will be seen that toluene produces the least and iodobenzene the greatest alteration in value. The relative depressions due to the entry of different substituents into the benzene molecule are given by Me<H<OEt<Cl<Br<I, and this sequence holds for all five esters. In view of the fact that no connexion has yet been established between the nature of a solvent and its influence on the optical rotation of a dissolved substance, it is a point of unusual interest that this series so closely resembles that representing the effect of the substituents when introduced into the molecule of β-octyl acetate, *viz.*, H<Me<OMe<Cl<Br<I. In both cases, the order of the halogens among themselves is the reverse of that which might have been expected from their relative polarity, but whereas substitution in the asymmetric molecule increases the positive rotation of the *d*-ester, substitution in the solvent benzene molecule diminishes the positive rotation. It is probable that efforts to determine the relationship between rotatory power and solvent influence would be attended by a greater measure of success if more use were made of solvent series such as the above, in which the character of the molecule as a whole does not undergo any violent change from member to member.

Experimental.

The general method of procedure employed in the preparation and examination of the esters has been described in earlier communications (J., 1925, **127**, 2188; this vol., p. 2116). The first three compounds mentioned below were prepared from the corresponding acid chlorides, the iodo-ester being obtained from the chloro-ester by treatment with ethereal magnesium iodide (Bodroux and Taboury,

Bull. Soc. chim., 1907, **1**, 909). All the esters are colourless, odourless liquids.

β-*Octyl methoxyacetate*, b. p. 120°/15 mm. (Found : C, 65·2; H, 11·1. $C_{11}H_{22}O_3$ requires C, 65·3; H, 11·0%).

β-*Octyl chloroacetate*, b. p. 119—120°/15 mm. (Found : Cl, 17·6. $C_{10}H_{19}O_2Cl$ requires Cl, 17·2%).

β-*Octyl bromoacetate*, b. p. 121°/15 mm. (Found : Br, 31·7. $C_{10}H_{19}O_2Br$ requires Br, 31·8%).

β-*Octyl iodoacetate*, b. p. 146—147°/17 mm. (Found : I, 42·6. $C_{10}H_{19}O_2I$ requires I, 42·6%).

Densities and Rotatory Powers of the Esters in the Homogeneous State.

Rotations were determined in a 1-dcm. tube, except those for the methoxy-ester and others marked with an asterisk, which were measured in a 0·5-dcm. tube.

Observed Densities and Rotations.

Octyl methoxyacetate.

$D_4^{t°}$	0·9721 at 20·5°; 0·9568 at 40·7°; 0·9435 at 57·6°; 0·9253 at 80·9°.
α_{5893}	3·90° at 20·9°; 3·51° at 38·5°; 3·20° at 60·5°; 2·70° at 93·7°.
α_{5780}	4·08° at 20·5°; 3·65° at 38·7°; 3·33° at 60·4°; 2·81° at 93·2°.
α_{5461}	4·60° at 20·7°; 4·12° at 38·6°; 3·73° at 60·9°; 3·20° at 93·7°.
α_{4358}	7·33° at 20·6°; 6·52° at 38·5°; 5·88° at 60·3°; 4·84° at 93·5°.

Octyl chloroacetate.

$D_4^{t°}$	0·9900 at 20·3°; 0·9747 at 39·4°; 0·9603 at 58·4°; 0·9413 at 81·1°.
α_{5893}	8·64° at 18·7°; 7·82° at 38·2°; 7·06° at 59·5°; 6·13° at 89·9°.
α_{5780}	9·04° at 19·0°; 8·24° at 38·3°; 7·21° at 59·6°; 6·47° at 90·0°.
α_{5461}	10·14° at 18·6°; 9·19° at 38·3°; 8·10° at 59·7°; 7·24° at 89·7°.
α_{4358}	16·09° at 18·8°; 14·78° at 38·7°; 12·94° at 59·7°; 11·51° at 90·3°.

Octyl bromoacetate.

$D_4^{t°}$	1·1731 at 22·6°; 1·1549 at 40·8°; 1·1360 at 59·6°; 1·1127 at 83·8°.
α_{5893}	13·34° at 22·0°; 12·40° at 37·8°; *5·67° at 53·4°; *5·20° at 75·6°.
α_{5780}	13·89° at 22·5°; 13·02° at 37·5°; *6·03° at 53·4°; *5·49° at 75·4°.
α_{5461}	15·71° at 22·5°; 14·67° at 37·7°; *6·75° at 53·4°; *6·24° at 75·7°.
α_{4358}	26·58° at 22·0°; 24·72° at 37·7°; *11·29° at 53·5°; *10·24° at 75·4°.

Octyl iodoacetate.

$D_4^{t°}$	1·3013 at 21·2°; 1·2812 at 41·9°; 1·2587 at 64·3°.
α_{5893}	19·08° at 20·0°; 17·63° at 37·9°; 15·79° at 62°.
α_{5780}	19·89° at 20·0°; 18·32° at 37·9°; 16·36° at 63°.
α_{5461}	22·72° at 19·8°; 20·89° at 37·8°; 18·58° at 63°.
α_{4358}	39·49° at 19·7°; 36·10° at 38·2°; 31·80° at 63°.

Rotatory Powers of the Esters in Solution (approx. 5%) at 20°.

The solvents employed were the purest products obtainable and were in all cases submitted to further purification. The acetone

used was "from the bisulphite compound." Alcohol was dehydrated over calcium. Owing to the yellow colour of the iodobenzene it was not possible to obtain measurements of α_{4358} in this solvent. The values for the halogen esters in pyridine represent compound formation, the rotations for the bromo- and iodo-esters rising continuously from the time of the first observation.

Rotatory Power of l-β-*Octyl Methoxyacetate in Solvents.*

$l = 2$, except for solvents marked, where $l = 1$. w = weight in g. of ester in 25 c.c., or * in 10 c.c.

Solvent.	w.	α_{5893}.	α_{5461}.	α_{4358}.	$[M]_{5461}$.	$[M]_{4358}$.
$C_2H_4Br_2$	1·2242	−0·93°	−1·06°	−1·80°	−21·9°	−37·0°
Ester (homog.)	—	−7·86	−9·26	−14·70	−19·25	−30·56
CCl_4	1·2267	−0·63	−0·72	−1·15	−14·8	−23·7
$CH_3{\cdot}CO_2Et$	1·1931	−0·59	−0·71	−1·15	−15·0	−24·4
$CH_3{\cdot}NO_2$	1·2055	−0·59	−0·70	−1·12	−14·7	−23·5
$(CH_3)_2CO$	1·2503	−0·59	−0·67	−1·11	−13·5	−22·4
$CH_3{\cdot}CO_2H$	1·1961	−0·55	−0·63	−0·97	−13·3	−20·5
$CHCl_3$	1·2015	−0·55	−0·62	−0·97	−13·0	−20·4
s-$C_2H_2Cl_4$	1·2872	−0·58	−0·64	−1·04	−12·6	−20·4
C_2H_6O	1·2285	−0·55	−0·64	−1·04	−13·2	−21·4
C_7H_8	1·3013	−0·04	—	—	—	—
C_6H_6	1·2710	+0·05	+0·07	+0·24	+1·4	+4·8
$C_6H_5{\cdot}OEt$	1·1883	+0·30	+0·34	+0·72	+7·2	+15·3
C_6H_5Cl	0·5141*	+0·18	+0·23	+0·44	+9·0	+17·3
C_6H_5Br	0·5198*	+0·18	+0·23	+0·44	+8·9	+17·1
C_5H_5N	1·2290	+0·56	+0·68	+1·16	+14·0	+23·9
C_6H_5I	0·4945*	+0·31	+0·37	—	+15·1	—
CS_2	1·2058	+0·70	+0·79	+1·80	+16·6	+37·7

Rotatory Power of l-β-*Octyl Chloroacetate in Solvents.*

$l = 2$, except for solvents marked, where $l = 1$. w = weight in g. of ester in 25 c.c., or * in 10 c.c.

Solvent.	w.	α_{5893}.	α_{5461}.	α_{4358}.	$[M]_{5461}$.	$[M]_{4358}$.
$C_2H_4Br_2$	1·2710	−1·05°	−1·20°	−2·06°	−24·4°	−41·9°
Ester (homog.)	—	−8·58	−10·06	−16·03	−20·99	−33·45
CCl_4	1·2133	−0·77	−0·91	−1·48	−19·4	−31·5
$CH_3{\cdot}CO_2Et$ ...	1·2322	−0·71	−0·90	−1·43	−18·9	−30·0
$CH_3{\cdot}NO_2$	1·2635	−0·69	−0·80	−1·25	−16·3	−25·6
s-$C_2H_2Cl_4$	1·2284	−0·64	−0·74	−1·27	−15·6	−26·7
$(CH_3)_2CO$	1·2688	−0·65	−0·80	−1·23	−16·3	−25·0
C_2H_6O	1·2806	−0·64	−0·78	−1·21	−15·7	−24·4
$CHCl_3$	1·2252	−0·60	−0·72	−1·10	−15·2	−23·2
$CH_3{\cdot}CO_2H$	1·2078	−0·54	−0·66	−1·06	−14·1	−22·7
C_6H_6	1·2592	−0·04	−0·05	−0·09	−1·0	−1·8
$C_6H_5{\cdot}OEt$	1·1941	+0·24	+0·32	+0·60	+6·9	+13·0
C_6H_5Cl	0·4950*	+0·16	+0·23	+0·41	+9·6	+17·1
C_6H_5Br	0·4924*	+0·21	+0·22	+0·42	+9·2	+17·6
C_6H_5I	0·4988*	+0·24	+0·29	—	+12·0	—
CS_2	1·2677	+0·51	+0·66	+1·52	+13·9	+32·0
C_5H_5N	1·2677	(+0·57)	—	—	—	—

Rotatory Power of l-β-*Octyl Bromoacetate in Solvents.*

$l = 2$, except for solvents marked, where $l = 1$. w = weight in g. of ester in 25 c.c., or * in 10 c.c.

Solvent.	w.	α_{5893}.	α_{5461}.	α_{4358}.	$[M]_{5461}$.	$[M]_{4358}$.
$C_2H_4Br_2$	1·2109	− 1·17°	− 1·32°	− 2·32°	−34·2°	−60·1°
Ester (homog.)	—	−13·46	−15·97	−26·85	−34·10	−57·37
CCl_4	1·2654	− 1·13	− 1·37	− 2·33	−34·0	−57·8
$CH_3{\cdot}CO_2Et$ ...	1·2657	− 1·07	− 1·29	− 2·20	−32·0	−54·6
C_6H_6O	1·2584	− 1·06	− 1·28	− 2·17	−31·9	−54·1
$CH_3{\cdot}CO_2H$	1·2618	− 1·04	− 1·22	− 2·10	−30·3	−52·2
$(CH_3)_2CO$	1·1302	− 0·91	− 1·12	− 1·82	−31·1	−50·5
$CH_3{\cdot}NO_2$	1·2537	− 0·95	− 1·16	− 1·99	−29·0	−49·8
$CHCl_3$	1·2159	− 0·88	− 1·02	− 1·69	−26·3	−43·6
s-$C_2H_2Cl_4$	1·3139	− 0·90	− 1·07	− 1·76	−25·6	−42·0
C_7H_8	0·5238*	− 0·22	—	—	—	—
C_6H_6	1·2478	− 0·40	− 0·46	− 0·78	−11·6	−19·6
$C_6H_5{\cdot}OEt$	1·3415	− 0·21	− 0·28	− 0·39	− 6·5	− 9·1
C_6H_5Cl	0·4970*	− 0·05	− 0·06	− 0·09	− 3·0	− 4·5
C_6H_5Br	0·4607*	− 0·03	− 0·04	− 0·06	− 2·2	− 3·3
C_6H_5I	0·5130*	+ 0·02	+ 0·05	—	+ 2·4	—
CS_2	1·2924	+ 0·05	+ 0·07	+ 0·39	+ 1·7	+ 9·5
C_5H_5N	1·2641	(+ 2·28)	—	—	—	—

Rotatory Power of d-β-*Octyl Iodoacetate in Solvents.*

$l = 2$, except for solvents marked, where $l = 1$. w = weight in g. of ester in 20 c.c., or * in 10 c.c., or † in 25 c.c.

Solvent.	w.	α_{5893}.	α_{5461}.	α_{4358}.	$[M]_{5461}$.	$[M]_{4358}$.
C_2H_6O	1·0310	+ 1·62°	+ 1·97°	+ 3·36°	+57·0°	+97·1°
$(CH_3)_2CO$	1·0066	+ 1·53	+ 1·82	+ 3·17	+53·9	+93·8
$CH_3{\cdot}CO_2Et$ ...	1·0184	+ 1·54	+ 1·84	+ 3·21	+53·9	+94·9
Ester (homog.)	—	+19·08	+22·72	+39·49	+51·98	+90·33
$CH_3{\cdot}CO_2H$	0·4846*	+ 0·70	+ 0·84	+ 1·48	+51·6	+91·0
$CH_3{\cdot}NO_2$	0·5050*	+ 0·71	+ 0·87	+ 1·53	+51·4	+90·3
CCl_4	1·0232	+ 1·42	+ 1·70	+ 3·00	+49·5	+87·4
$C_2H_4Br_2$	0·9941	+ 1·37	+ 1·64	+ 2·79	+49·2	+83·7
$CHCl_3$	1·0279	+ 1·32	+ 1·55	+ 2·64	+45·0	+76·5
s-$C_2H_2Cl_4$.....	0·5425*	+ 0·65	+ 0·76	+ 1·35	+41·8	+74·2
C_6H_6	1·2837†	+ 0·65	+ 0·78	+ 1·35	+22·7	+39·2
$C_6H_5{\cdot}OEt$	0·9964	+ 0·55	+ 0·65	+ 1·10	+19·4	+32·9
C_6H_5Cl	0·4917*	+ 0·20	+ 0·23	+ 0·44	+13·9	+26·7
C_6H_5Br	0·4896*	+ 0·15	+ 0·17	—	+10 3	—
CS_2	0·9690	+ 0·23	+ 0·26	+ 0·26	+ 8·0	+ 8·0
C_6H_5I	0·5168*	+ 0·05	+ 0·07	—	+ 4·0	—
C_5H_5N	1·1197	(− 1·97)	—	—	—	—

In conclusion the authors desire to thank the Earl of Moray Fund for a grant which has covered most of the expenses incurred in this investigation.

UNIVERSITY OF EDINBURGH. [*Received. October 20th*, 1926.]