CCCCXXXV.—*Studies in Optical Superposition. Part VII. The Bornyl Dimethoxysuccinates.*

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In previous parts of this investigation (see J., 1924, **125**, 2579), attempts have been made to test the validity of van 't Hoff's principle of optical superposition by the only method which, as far as can be seen at present, may be expected to give the least equivocal results.*

As a further test of the validity of van 't Hoff's assumption, we have prepared the bornyl esters of *d*-, *l*-, and *meso*-dimethoxysuccinic acid with the object of comparing the mean value of the specific rotations for the former two substances with the specific rotation found for the third. If the principle holds accurately, these values should always be identical. Nevertheless it ought to be noted that even a complete agreement is not necessarily a proof of the validity of the principle. As has been shown already (J., 1915, **107**, 145), it would be possible, even in the event of complete agreement, for the so-called principle to be violated.

Bornyl l-*dimethoxysuccinate* was prepared by passing dry hydrogen chloride into a mixture of 10 g. of methyl *l*-dimethoxysuccinate (m. p. 51°; obtained by Patterson and Patterson's method, J., 1915, **107**, 142) with 60 g. of borneol for 1 hour at the ordinary temperature, partial liquefaction taking place (compare Patterson and Dickinson, J., 1901, **79**, 280), and then for 24 hours at 100°. In the operation, sublimation of the borneol causes difficulty. The product was distilled under reduced pressure after removal of excess borneol at a lower temperature. The fraction, b. p. about 265°/15 mm., consisted of 6 g. of fairly pure ester, readily soluble in organic solvents. The *ester*, after four crystallisations from 75% aqueous alcohol, had m. p. 70° and $\alpha_{g}^{14°}$ (100 mm.) constant at —2·28° (Found : C, 69·1; H, 9·4. $C_{26}H_{42}O_6$ requires C, 69·3; H, 9·3%).

Bornyl d-*dimethoxysuccinate* was prepared and purified in a similar manner. The m. p. rose from 100° to 103° after four crystallisations from aqueous alcohol and $\alpha_{g}^{16°}$ (100 mm.) became constant at + 11·4°. The ester is easily soluble in the common organic solvents (Found : C, 69·2; H, 9·3%).

Bornyl i-*dimethoxysuccinate* was prepared from *i*-dimethoxysuccinic acid (m. p. 162°), which was obtained by hydrolysis of the methyl ester. The acid (10 g.) was mixed with 60 g. of borneol and the same procedure followed as before. This ester is much less soluble than the other two in alcohol, but is readily soluble in most common organic solvents. After seven crystallisations from aqueous alcohol the m. p. was 114° and $[\alpha]_{g}^{12·5°}$ +44·79° ($c = 0·855$) (Found : C, 69·5; H, 9·4%).

These esters were examined, not in the homogeneous condition on

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* Hudson also (*J. Amer. Chem. Soc.*, 1924, **46**, 462, 979, 2591; 1925, **47**, 265, 537, 873, 2052; and other papers) has been carrying out work which involves this principle. Since it seems to us, however, that the criticism of Hudson's work which was made in Part VI (*loc. cit.*) applies in a similar manner to his later work, we shall not again refer to it here.

account of their rather high melting points, but at similar concentration in five different solvents, for three colours of light and over a range of temperature. The experimental data will be found at the end of the paper. Table I summarises the results with regard to the main point under investigation.

Table I.

Specific rotation of bornyl esters of dimethoxysuccinic acids.

Solvent.	*t.*	*c.*	I. *d*-Ester.	II. *l*-Ester.	III. *i*-Ester.	IV. Mean of I and II.	Δ IV—III.
Alcohol	0°	4·5	131·0°	−37·9°	44·7°	46·55°	1·85°
	20		126·0	−35·3	43·5	45·35	1·85
Pyridine	0	5	141·3	−55·9	37·1	42·7	5·6
	20		134·5	−52·6	36·5	40·95	4·45
Benzene	20	5	127·4	−45·5	39·2	40·95	1·75
Chloroform	0	5	128·6	−28·1	50·65	50·25	−0·4
	22		121·8	−26·45	48·0	47·7	−0·3
Ethylene dibromide	20	7	130·9	−26·2	49·2	52·35	3·15

If the hypothesis of van 't Hoff regarding optical superposition be correct, the mean of the rotations of the *d*- and *l*-forms should have the same value as that of the ester of the *i*-acid. It will be seen that this is nearly so in this series of compounds. Nevertheless the following points are to be noticed :

(1) That in each solvent for which observations are quoted for two temperatures the differences are in the same sense, which would seem to show that the differences are not due to experimental error.

(2) That the differences are not the same in the various solvents used seems also to favour the view that our results are not due to any constant error such as impurity of one or more of the esters used, but are really due to invalidity of the principle.

(3) The effect of change of temperature upon these differences seems to us to be significant. Table II shows the data for these three esters dissolved in chloroform and in alcohol, values in the latter case being taken from smoothed temperature–rotation curves.

Table II.

Variation of Δ with change of temperature.

In chloroform	*t*°	0	22	44·8	
	Δ	−0·40	−0·28	+0·36	
In alcohol	*t*°	0	20	40	60
	Δ	1·8	1·6	1·2	0·3

In chloroform, the difference which at first was negative became less so as the temperature increased and changed into a positive value at higher temperatures. The difference in the case of alcohol diminished gradually as the temperature rose. It thus appears that in chloroform one could realise a condition of affairs in which the difference would be zero and van 't Hoff's principle would hold completely in these particular circumstances. Although this temperature is not actually reached in alcohol, it also might be realised. The fact that the differences observed in experiments such as ours is dependent upon the temperature in this way seems to us to indicate that van 't Hoff's supposition cannot be regarded as a general principle, especially since, although in some cases such as those presently recorded the agreement of the experimental data with the requirements of the principle is close, in other cases, *e.g.*, the secondary octyl esters of the tartaric acids (J., 1924, **125**, 1476) and their menthylamine salts (*ibid.*, 1915, **107**, 142), the difference is very considerable.

[*Note added*, 11*th October*, 1926.] Some time after this paper had been sent in for publication Professor A. McKenzie directed our attention to the fact that commercial borneol was liable to contain *l*-*iso*borneol, and this we found in the sample we had used. Its rotation had been determined for various colours of light, but the fact that this was too low had been overlooked. Therefore, as a crucial test of the purity of the esters at this late stage, we decided to recover the borneol by hydrolysis from the specimens we still had left, but as we had only a small quantity of each (about 0·4 g.), we mixed together * approximately that amount of each ester and hydrolysed the mixture with alcoholic potash. After neutralisation, the borneol was extracted with ether, the solution dried with potassium carbonate, and the ether distilled off. The addition of a few drops of alcohol and water brought about the separation of the borneol. This was filtered off and dried. The melting point of the substance thus obtained, without recrystallisation, was 205° (uncorr.) and 208·7° (corr.). Its rotation was examined in alcoholic solution at 19·5° in a 100 mm. tube ($c = 12{\cdot}268$).

λ	5892 D.	5792 Hg_y.	5461 Hg_g.	4358 Hg_v.
α	+4·62°	4·75°	5·475°	9·34°
$[\alpha]$	37·7°	38·7°	44·6°	76·1°

Haller (*Ann. Chim. Phys.*, 1892, **27**, 394) gives for alcohol ($c = 15{\cdot}4$, $t = 10$—$15°$), $[\alpha]_D = +37{\cdot}33°$. Pickard and Littlebury (J., 1907, **91**, 1978) give + 37·08° and + 37·03° for solutions in alcohol of about the same concentration.

It appears, therefore, that the borneol recovered from these

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* The total quantity of borneol recovered was just over 0·6 g. Had each ester been hydrolysed separately, the quantity of borneol obtained from each would, we were afraid, have been too small for accurate polarimetric measurement.

esters was quite pure and this seems to be very sound evidence that the esters themselves were pure.

We also recovered the *d*-bornyl *l*-dimethoxysuccinate from its solutions in pyridine and ethylene bromide, which had been used in the polarimetric experiments, and separated the borneol as above. Only 0·2822 g. was obtained which had m. p. 202—203° and gave $\alpha_{5461}^{16^\circ} = + 2{\cdot}44^\circ$, whence $[\alpha]_{5461}^{16^\circ} = 43{\cdot}3^\circ$. Considering the smallness of the quantity at our disposal and that it could not be purified, this value agrees as closely as could be expected with the other.

For still further confirmation, we prepared a fresh specimen of *d*-bornyl *d*-dimethoxysuccinate from *d*-dimethoxysuccinic acid and *d*-borneol purified by boiling in benzene solution with zinc chloride (Pickard and Littlebury, *loc. cit.*), the rotation having thus been raised from $[\alpha]_{5461} = 34{\cdot}28^\circ$ to $[\alpha]_{5461} = 43{\cdot}49^\circ$ ($c = 12{\cdot}268$ in alcohol). After crystallisation from aqueous alcohol, this melted at 104° and had, in benzene solution, $\alpha_{5461}^{20^\circ}$ (154·1 mm.) $= + 9{\cdot}79^\circ$, whence $[\alpha]_{5461}^{20^\circ} = + 128{\cdot}07^\circ$, the value previously found being 127·42°.

Further, *l*-bornyl *i*-dimethoxysuccinate was prepared afresh from methyl *i*-dimethoxysuccinate and natural *l*-borneol of $\alpha_{5461} = - 43{\cdot}04^\circ$ ($c = 12{\cdot}268$ in alcohol). After one crystallisation from aqueous alcohol, the ester softened at 105° and melted at 113—114°. In benzene ($c = 5$), $\alpha_{5461}^{20^\circ}$ (154·1 mm.) $= - 2{\cdot}97^\circ$, whence $[\alpha]_{5461}^{20^\circ} = - 39{\cdot}0^\circ$, the value previously found being $- 39{\cdot}2^\circ$.

It seems clear, therefore, that the processes of purification to which our original preparations had been subjected had eliminated the influence of any *l*-*iso*borneol present in the borneol used.

EXPERIMENTAL.

The solvents were all carefully purified before use.

The wave-lengths of the light used were 5790·3, 5460·7, and 4358·3 and, to save space, are denoted throughout by the letters *y*, *g*, and *v*, respectively.

The solutions of the three esters were prepared as nearly as possible of the same strength, and were examined under similar conditions.

Bornyl *d*-dimethoxysuccinate in ethylene dibromide.

Densities det. : 2·0963/12·3°, 2·0475/37°, 2·0058/57·1°, 1·9725/74·6°, 1·9231/98·5°. $p = 3{\cdot}3518$.

t.	a_y.	a_g.	a_v.
20°	12·27°	14·07°	23·18°
45·5	11·32	12·99	21·31
73	10·59	11·94	19·17
99·7	9·74	11·07	17·37

Bornyl *d*-dimethoxysuccinate in chloroform.

Densities det. : 1·4649/13°, 1·4449/25°, 1·4110/43·4°. $p = 3{\cdot}4310$.

t.	a_y.	a_g.	a_v.
0°	8·76°	10·11°	16·66°
22	8·24	9·34	15·34
44·7	7·68	8·78	14·40

Bornyl *d*-dimethoxysuccinate in benzene.

Densities det.: 0·8947/10°, 0·8714/32°, 0·8470/58°. $p = 5·6115$.

t.	α_y.	α_g.	α_v.
20°	8·34°	9·74°	16·27°
39·2	7·93	9·21	15·22
57	7·67	8·78	14·38

Bornyl *d*-dimethoxysuccinate in pyridine.

Densities det.: 0·9908/14°, 0·9738/31·6°, 0·9553/50·3°. $p = 5·0458$.

t.	α_y.	α_g.	α_v.
0°	9·56°	11·03°	18·01°
20	9·04	10·30	16·92
44·2	8·47	9·52	15·68

Bornyl *l*-dimethoxysuccinate in chloroform.

Densities det.: 1·4585/17·8°, 1·4378/30°, 1·4120/44°. $p = 3·4315$.

t.	α_y.	α_g.	α_v.
0°	−1·86°	−2·21°	−3·30°
22	1·67	2·03	3·07
44·7	1·60	1·93	2·80

Bornyl *l*-dimethoxysuccinate in alcohol.

Densities det.: 0·8099/14·7°, 0·8006/26·7°, 0·7887/40·6°, 0·7767/53·7°. $p = 5·5874$.

t.	α_y.	α_g.	α_v.
0°	−2·19°	−2·68°	−4·16°
20	2·00	2·45	3·87
39·4	1·83	2·25	3·51
55	1·69	2·09	3·27

Bornyl *i*-dimethoxysuccinate in ethylene dibromide.

Densities det.: 2·0922/13°, 2·0503/33·7°, 2·0057/56·7°, 1·9680/75·5°, 1·9188/98·5°. $p = 3·3382$.

t.	α_y.	α_g.	α_v.
20°	4·72°	5·26°	8·95°
43·7	4·41	4·95	8·51
73	4·09	4·59	8·03
99	3·86	4·37	7·41

Bornyl *d*-dimethoxysuccinate in alcohol.

Densities det.: 0·8088/12·2°, 0·7892/36°, 0·7808/45·5°, 0·7698/58°. $p = 5·5774$.

t.	α_y.	α_g.	α_v.
0°	8·13°	9·22°	15·15°
20	7·65	8·69	14·35
38·8	7·23	8·17	13·55
54	6·86	7·77	12·91

Bornyl *l*-dimethoxysuccinate in ethylene dibromide.

Densities det.: 2·0980/11°, 2·0481/37°, 1·9982/61·5°, 1·9668/78°, 1·9241/98°. $p = 3·3511$.

t.	α_y.	α_g.	α_v.
20°	−2·49°	−2·82°	−4·31°
44·3	2·27	2·57	3·83
73·8	1·95	2·22	3·23
99·5	1·69	1·98	2·66

Bornyl *l*-dimethoxysuccinate in benzene.

Densities det.: 0·8814/24°, 0·8669/38·2°, 0·8463/57·7°. $p = 5·6116$.

t.	α_y.	α_g.	α_v.
20°	−3·08°	−3·48°	−5·64°
38·7	2·89	3·25	5·25
56·5	2·70	3·05	4·95

Bornyl *l*-dimethoxysuccinate in pyridine.

Densities det.: 0·9892/15°, 0·9724/32·5°, 0·9551/50°. $p = 5·0482$.

t.	α_y.	α_g.	α_v.
0°	−3·79°	−4·36°	−6·85°
20	3·53	4·03	6·31
45·5	3·17	3·59	5·65

Bornyl *i*-dimethoxysuccinate in chloroform.

Densities det.: 1·4590/17°, 1·4339/32°, 1·4116/44°. $p = 3·4282$.

t.	α_y.	α_g.	α_v.
0°	3·52°	3·98°	6·63°
22	3·23	3·69	6·15
44·8	3·10	3·40	5·80

Bornyl *i*-dimethoxysuccinate in benzene.

Densities det. : 0·8859/20·5°, 0·8663/39·1°, 0·8496/55°. $p = 5{\cdot}5854$.

t.	α_y.	α_g.	α_v.
20°	2·69°	2·99°	4·98°
39	2·54	2·87	4·84
56	2·46	2·79	4·72

Bornyl *i*-dimethoxysuccinate in alcohol.

Densities det. : 0·8037/17·6°, 0·7916/31·8°, 0·7800/45·5°, 0·7689/58°. $p = 5{\cdot}5830$.

t.	α_y.	α_g.	α_v.
0°	2·84°	3·15°	5·38°
20	2·70	3·00	5·08
38·5	2·55	2·89	4·82
54·2	2·41	2·80	4·61

Bornyl *i*-dimethoxysuccinate in pyridine.

Densities det. : 0·9883/15·7°, 0·9703/34·5°, 0·9522/52·3°. $p = 5{\cdot}0453$.

t.	α_y.	α_g.	α_v.
0°	2·53°	2·89°	4·76°
20	2·45	2·79	4·63
44·6	2·30	2·64	4·45

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