67. *Effect of Solvents on the Optical Rotation of Menthene, Bornylene, and Borneol.*

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MENTHENE, bornylene, and borneol were examined for six colours of light, namely, $\lambda = 6716{\cdot}3$, $\lambda = 6234{\cdot}3$, $\lambda = 5790{\cdot}3$ (Hg_y), $\lambda = 5460{\cdot}7$ (Hg_g), $\lambda = 4916{\cdot}4$, and $\lambda = 4358{\cdot}6$ (Hg_v) in six solvents, benzene, ethyl alcohol, pyridine, ethylene dibromide, nitrobenzene, and quinoline, at the ordinary temperature, and in addition the effect of temperature on the rotation dispersion of menthene in the homogeneous state. Comparing the values obtained by the action of the solvents on menthene with that for the homogeneous terpene hydrocarbon, it is found that all the solvents cause an increase in the rotation for all colours of light with the exception of quinoline, which gives a lowering of 13° for mercury green and a corresponding lowering for the other colours of light. Ethylene dibromide, which usually shows a marked effect in the opposite direction to quinoline, gives the greatest increase in this case also, namely, 9°, the increases with the remainder of the solvents being small. Pyridine, chloroform, and nitrobenzene have practically no effect. Increase of temperature causes the rotation of the homogeneous menthene to decrease slowly for all colours of light, the curves tending towards minima.

The values obtained were plotted on a characteristic diagram, and lay with good agreement along lines intersecting one another (practically) at the point of origin of the diagram in such a way, so far as can be judged when extrapolation has to be carried out through more than 100° of rotation, as to indicate little or no region of anomalous dispersion.

It was found that solvents have practically no effect on the rotation of bornylene, the highest rotation being observed in pyridine solution ($[\alpha]_g = +26{\cdot}45°$) and the lowest in quinoline solution ($[\alpha]_g = +25{\cdot}51°$). The points lie approximately on the same diagram as those for menthene.

The effect of solvents on *l*-borneol is more marked, the range of variation of rotation for $[\alpha]_g$ being fully 10°. Quinoline produces the greatest depression of the rotation, and pyridine the greatest elevation of the rotation, with nitrobenzene slightly below it. The effect of ethylene dibromide is one of elevation, but is small in amount. All these values for borneol also lie with good agreement on the same characteristic diagram as those for bornylene and menthene.

Thus we find that with the exception of quinoline, which produces the lowest numerical rotation in all three cases, there is considerable variation in the degree of effect of the various solvents, though the tendencies are similar in the three cases.

Since these three groups of points all lie on one characteristic diagram, the lines of which intersect at the point of origin of the diagram, it follows that the dispersion coefficients for all these compounds calculated by the ordinary method ought to be the same throughout. This is actually the case with those for menthene and borneol, while those for bornylene are slightly higher. This is seen in the following table :

	Menthene. Dispersion.		Bornylene. Dispersion.		*l*-Borneol. Dispersion.	
Solvent.	Hg_y/Hg_g.	Hg_v/Hg_g.	Hg_y/Hg_g.	Hg_v/Hg_g.	Hg_y/Hg_g.	Hg_v/Hg_g.
Benzene	—	—	0·885	1·759	0·871	1·740
Ethyl alcohol ...	0·881	1·748	—	—	0·868	1·744
Pyridine	0·870	1·741	0·891	1·769	0·865	1·764
Chloroform ...	0·872	1·740	0·879	1·784	0·869	1·755
Ethylene dibromide ...	0·875	1·748	0·870	1·780	0·865	1·747
Nitrobenzene ...	0·877	1·750	0·881	1·785	0·873	1·746
Quinoline	0·868	1·743	0·887	1·789	0·877	1·754
Homogeneous	0·873	1·750	—	—	—	—

This forms another example of a property which seems to be characteristic of many bornyl and menthyl derivatives. Kenyon and Pickard (J., 1915, **107**, 35) found that most menthyl derivatives lie on a characteristic diagram with dispersion coefficient V/G = 1·634 to 1·675, while the bornyl esters they had plotted had as coefficient V/G = 1·707 to 1·871. From this it will be seen that menthene lies, not on the same diagram as the majority of the menthyl derivatives, but on the diagram with the majority of bornyl derivatives, and bornylene. This constitutes another example of a substance transferring to the diagram of a related group, a previous one being the case of the menthyl and bornyl benzene- and naphthalene-sulphonates (Patterson and McAlpine, J., 1926, 353; 1928, 2472), all of which lie on the diagram for the majority of menthyl esters with coefficients V/G = 1·650 to 1·685.

EXPERIMENTAL.

Isolation and Purification.—Menthene. Menthene was obtained by the method of Tschugaev from menthyl methyl xanthate, and after purification by distillation with metallic sodium showed b. p. 167—167·5°, $d_{4^\circ}^{20^\circ}$ 0·8130, and $[\alpha]_{5460}^{20^\circ}$ + 137·5°, $[\alpha]_{5790}^{20^\circ}$ + 119·75° (Tschugaev gives $d_{4^\circ}^{20^\circ}$ 0·8132 and $[\alpha]_D$ + 114·77°).

Bornylene. Bornylene, prepared by the same method as menthene, was purified by treatment with hydrogen peroxide (compare Henderson and Caw, J., 1912, **101**, 1416) and showed m. p. 113°, $[\alpha]_{5461}^{17^\circ}$ 26·76°, $[\alpha]_{5790}^{17^\circ}$ 23·70° in benzene (c = 5%), Brühl's constants being $[\alpha]_D$ = 23·94° in benzene (c = 8·23).

Borneol. Commercial *l*-borneol was converted into bornyl methyl xanthate, and the ester purified by crystallisation and hydrolysed with alcoholic potassium hydroxide. The borneol was then steam-distilled, and recrystallised from light petroleum; it then showed m. p. 208°, and $[\alpha]_{5461}^{17^\circ}$ 43·63° in benzene (c = 5%).

Menthene.

(*a*) In solvents. T = 22°.

Solvent.	Conc.	$[a]_{r_1}$.	$[a]_{r_2}$.	$[a]_y$.	$[a]_g$.	$[a]_b$.	$[a]_v$.
Ethyl alcohol ...	5	+91·28°	+105·9°	+125·6°	+142·5°	+181·2°	+249·0°
Pyridine	5	87·30	102·1	119·9	138·9	176·9	241·9
Chloroform ...	5	87·90	103·1	121·9	139·7	178·3	243·1
Ethylene dibromide ...	5	93·75	109·7	129·2	147·6	188·9	258·0
Nitrobenzene ...	5	88·78	103·5	122·2	139·3	177·8	244·0
Quinoline	5	81·00	93·4	109·7	126·5	161·5	220·5

(*b*) In the homogeneous state.

Temp.	Density.	$[a]_{r_1}$.	$[a]_{r_2}$.	$[a]_y$.	$[a]_g$.	$[a]_b$.	$[a]_v$.
10·1°	0·8194	+86·81°	+102·1°	+120·4°	+138·0°	+177·6°	+241·5°
26·9	0·8064	85·84	101·1	119·5	137·2	176·1	239·7
43·5	0·7936	85·04	100·6	118·6	136·3	175·0	237·9
58·3	0·7821	84·63	99·75	117·7	135·2	174·4	236·0
69·1	0·7734	84·18	99·30	117·3	134·3	173·2	235·1
91·0	0·7547	83·32	98·23	116·2	133·3	171·6	232·9

d-*Bornylene.*

In solvents. $T = 24°$.

Solvent.	Conc.	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_{y}$.	$[\alpha]_{g}$.	$[\alpha]_{b}$.	$[\alpha]_{v}$.
Ethyl alcohol...	5·01	+15·11°	+19·39°	+22·76°	+25·75°	+31·23°	+45·43°
Benzene	5·20	16·75	19·39	23·70	26·78	34·69	47·10
Pyridine	5·18	16·79	20·08	23·56	26·49	34·17	47·47
Chloroform ...	5·01	15·37	19·26	23·16	26·34	34·13	47·41
Ethylene dibromide ...	5·01	16·55	19·54	22·93	26·33	34·29	46·99
Nitrobenzene ...	5·00	16·59	19·59	23·09	25·79	34·00	46·07
Quinoline	5·08	15·23	18·89	22·82	25·52	33·87	45·72

l-*Borneol.*

In solvents. $T = 22·5°$.

Solvent.	Conc.	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_{y}$.	$[\alpha]_{g}$.	$[\alpha]_{b}$.	$[\alpha]_{v}$.
Benzene	5	−27·55°	−32·15°	−38·20°	−43·85°	−55·35°	−76·35°
Ethyl alcohol...	5	25·40	30·00	34·20	39·40	49·80	67·90
Pyridine	5	29·90	33·80	40·40	46·70	60·90	80·60
Chloroform ...	5	25·45	29·95	34·95	40·20	51·85	70·55
Ethylene dibromide ...	5	27·82	32·40	37·50	43·90	55·30	76·70
Nitrobenzene ...	5	31·20	36·00	40·80	46·00	60·00	80·30
Quinoline	5	24·60	28·00	32·10	36·60	47·00	64·20

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