# XCII.—*Optical Activity and the Polarity of Substituent Groups. Part XVII.* l-*Menthyl Hydrogen Naphthalate, its Alkali Salts, and Methyl Ester.*

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DI-ESTERS derived from naphthalic acid are described in the literature as being somewhat unstable, and no example of an acid ester of this type is recorded in Beilstein's " Organische Chemie." It has been found, however, that l-*menthyl hydrogen naphthalate* and its alkali salts are readily prepared in a comparatively pure state, and that although the free substance slowly reverts to naphthalic anhydride and menthol it is quite stable in the form of the *methyl* ester. The optical activity of these derivatives has been examined for comparison with that of other menthyl peri-substituted naphthoic esters and the corresponding ortho-substituted benzoates.

As may be seen from the figures tabulated below, the influence of the carbomethoxy-substituent raises the rotatory power of the perinaphthoate, as well as of the ortho-benzoate, when the rotations are measured for the esters in alcoholic solution. On the other hand, the free acid ester in alcohol has a lower rotation than the unsubstituted compound, and in this respect differs from *l*-menthyl and the β-octyl hydrogen phthalates, which have high rotations. A remarkable fall in rotatory power occurs when the carboxyl group in menthyl hydrogen naphthalate is modified by salt formation. The *lithium*, *sodium*, and *potassium* salts all gave positive rotations under the conditions of experiment, the values not differing greatly from one another and being in the order $K < Na < Li \ll H$.* This change on ionisation is in the same sense as that previously observed for *l*-menthyl hydrogen phthalate and *l*-menthyl hydrogen malonate (J., 1929, 401; 1930, 1887), but is of much greater magnitude, in agreement with the enhanced influence of other substituents in the peri- as compared with the ortho-position.

*Rotations of* l-*menthyl* 8-*substituted* 1-*naphthoates* (in $CH_3{\cdot}OH$ ; $c = 4$).

| Substit. ............ | $CO_2Me$ | (H) | $CO_2H$ | $CO_2Li$ | $CO_2Na$ | $CO_2K$ |
|---|---|---|---|---|---|---|
| $[M]_{5461}^{20^\circ}$ ............... | − 383° | (− 302°) | − 218° | + 0·67° | + 4·25° | + 11·9° |

If these observed rotations are combined with those recorded elsewhere, the substituent effects in the peri-position may be expressed by

$$NO_2 > CO_2Me > H > CO_2H > Cl > OMe > COO',$$

where all compounds are examined under similar conditions in alcoholic solution. Among *l*-menthyl *o*-substituted benzoates the changes are given by

$$NO_2 > CO_2H > CO_2Me > H > COO' > Cl > OMe.$$

The two series differ in a displacement of the carboxyl group and of its ionised form.

When the rotatory powers are tested by plotting $1/\alpha$ against $\lambda^2$, the di-ester gives a straight line graph over a range 4358—6708 Å.U. when examined in benzene. The di-ester in nitromethane and the acid ester in benzene or acetonitrile solution exhibit slightly complex dispersion, whereas the salts, which have very low molecular rotations, have definitely complex dispersion.

A feature of unusual interest is the variation in the rotatory power of the esters with change of solvent. This is described in detail in another paper (in the press).

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* It is proposed to discuss the specific influence of the metals in a later communication in connexion with the corresponding salts of β-octyl hydrogen phthalate.

## EXPERIMENTAL.

l-*Menthyl Hydrogen Naphthalate.*—Metallic sodium (0·94 g.) was dissolved in a hot solution of menthol (25—30 g.) in toluene (50 c.c.), and the product added to a hot solution of naphthalic anhydride (8 g.) in toluene (1000 c.c.). The mixture was heated under reflux on a steam-bath for 2 hours; the reddish colour changed to green and a pale yellow precipitate of sodium menthyl naphthalate was then deposited. After being cooled, the liquid was extracted twice with a considerable volume of water, and the aqueous extract washed with alcohol-free ether. (Ordinary ether dissolves the sodium salt to an appreciable extent.) On acidification of the aqueous liquid, crude menthyl hydrogen naphthalate was thrown out of solution and was then taken up in ether, from which it can be recovered in a crystalline condition. The use of potassium menthoxide in this preparation gave a syrupy product which eventually hardened to a glass.

The crude acid ester was most profitably purified by solution in alcohol and titration with alcoholic sodium ethoxide, using an external indicator. The greater part of the naphthalic acid present was thus precipitated as the disodium salt, which was filtered off. The neutral filtrate was then evaporated to dryness in a vacuum at room temperature, and the sodium menthyl naphthalate (11 g.) recrystallised three times from methyl alcohol. Subsequent treatment with acid and extraction with ether gave an ethereal solution of the acid ester, which on slow evaporation of the solvent deposited well-shaped rhombic crystals of l-*menthyl hydrogen naphthalate*. Final purification was effected by crystallisation in the cold from ether–hexane until the rotatory power underwent no further change (Found: C, 74·3; H, 7·6. $C_{22}H_{26}O_4$ requires C, 74·6; H, 7·3%).

Even at room temperature the ester decomposes slowly, a faint odour of menthol becoming perceptible in 7—8 days. In a preheated bath it melts at 141° (decomp.) without complete liquefaction, and the product then solidifies to melt again in the neighbourhood of 271°, the m. p. of naphthalic anhydride.

The *sodium* salt (Found: Na, 6·07. $C_{22}H_{25}O_4Na$ requires Na, 6·11%) also decomposes slowly at room temperature. It is very sparingly soluble in water. On evaporation in a desiccator, a solution in a mixture of methyl and ethyl alcohols deposited feathery clusters of crystals. The salt so obtained contained a minute proportion of insoluble anhydride, which interfered with polarimetric readings. The rotatory power was therefore determined from solutions prepared from the parent compound by adding the calculated amount of sodium methoxide in methyl alcohol.

*Potassium* l-*menthyl naphthalate* (Found : K, 10·2. $C_{22}H_{25}O_4K$ requires K, 10·0%) was prepared directly from the anhydride. It crystallises from acetone in rhombic crystals and is less stable than the sodium salt.

The *lithium* salt (Found : Li, 1·8. $C_{22}H_{25}O_4Li$ requires Li, 1·9%) was obtained by titrating the acid with a concentrated methyl-alcoholic solution of lithium hydroxide, and purified from methyl alcohol. Like the other salts, it acquires a smell of menthol after 2—3 days' standing.

l-*Menthyl methyl naphthalate* was readily prepared from the silver salt, which is apparently quite stable at the ordinary temperature, by shaking it for 2—3 days with excess of methyl iodide. The methyl ester was isolated in well-formed rhombic crystals (Found : C, 75·1; H, 7·87. $C_{23}H_{28}O_4$ requires C, 75·0; H, 7·61%). It is very soluble in ether, moderately soluble in benzene, and dissolves only very sparingly in cold methyl alcohol. It was therefore recrystallised from a mixture of methyl alcohol and ether, the solvents being partially removed in a vacuum. After three crystallisations it was optically pure and melted at 96·5—97° (slight decomp.). The di-ester is quite stable at moderate temperatures.

### *Rotatory Powers.*

l-*Menthyl methyl naphthalate.*

| Solvent. | *l.* | *t.* | *c.* | $[\alpha]_{6708}$. | $[\alpha]_{5893}$. | $[\alpha]_{5461}$. | $[\alpha]_{4358}$. |
|---|---|---|---|---|---|---|---|
| Benzene | 2 | 18° | 4·004 | − 89·4° | − 120·1° | − 147·7° | − 268·2° |
| Nitromethane | 2 | 18 | 3·996 | − 35·3 | − 48·3 | − 59·4 | − 133·8 |
| | | | l-*Menthyl hydrogen naphthalate.* | | | | |
| Benzene | 2 | 20 | 4·014 | + 117·1 | + 165·9 | + 203·3 | + 397·9 |
| Acetonitrile | 2 | 20 | 4·008 | − 35·2 | − 47·4 | − 55·8 | − 82·3 |

(The acid ester is practically insoluble in nitromethane.)

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