

## 77. Phosphoric Acid Compounds of Menthols and Other Alcohols.

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IN the course of work upon the industrial production of pure *dl*-menthol from the mixtures of isomerides obtained in the catalytic hydrogenation of menthones, menthenones, thymol, etc., it was noticed that menthol forms a compound,  $3C_{10}H_{20}O, H_3PO_4$ , with orthophosphoric acid. Further investigation led to the isolation of crystalline derivatives of this type from other stereoisomeric menthols. They are prepared by mixing the menthol at the ordinary temperature with orthophosphoric acid ( $d$  1.75) and recrystallising the resulting solid product from light petroleum or other organic solvent. The derivatives exhibit distinctive physical characteristics, and are fairly stable at the ordinary temperature, although they possess definite menthol vapour pressures. They show sharp melting points, and fusion occurs without decomposition; above the melting point, however, they decompose into their constituents, and the decomposition may be accompanied by partial dehydration of the liberated menthol. The following melting points have been observed for the phosphoric acid compounds of menthols: *l*-menthol,  $74^\circ$ ; *dl*-menthol,  $74^\circ$ ; *d*-neomenthol,  $86^\circ$ ; *dl*-neomenthol,  $86^\circ$ ; *dl*-isomenthol,  $46^\circ$ ; *d*-neoisomenthol,  $60^\circ$ . Owing to its ready solubility, the derivative of *dl*-isomenthol is difficult to purify, and hence the recorded melting point may be unduly low.

On account of their differing solubilities and their ready crystallisation from suitable organic solvents, these derivatives have proved very useful in separating mixtures of stereoisomeric menthols. This method of purification is, in fact, in industrial use for purifying synthetic *dl*-menthol; moreover, it has greatly facilitated the isolation of such stereoisomerides as *dl*-neomenthol and *dl*-isomenthol. Recently, the method has been

applied successfully in this laboratory in isolating *d-neoisomenthol*, which has thereby become available for the first time in a pure condition. Details of the properties and relationships of this menthol are summarised by Read and Grubb (preceding paper), with whom the present authors have been in collaboration. That paper also describes the method of preparing *d-neoisomenthol* as carried out in this laboratory.

The reaction with phosphoric acid, first observed with menthol, is given by nearly all the terpene and hydroaromatic alcohols investigated and also by certain aliphatic alcohols, *e.g.*,  $\alpha$ -terpineol, borneol, *isoborneol*, fenchyl alcohol, *cyclohexanol*; *tert.*-butyl alcohol in particular gives a beautifully crystalline derivative, m. p. 52°. Some of these have three molecules of the alcohol, others only one such molecule, in combination with each molecule of phosphoric acid.

Some account of the properties and methods of preparation of these new derivatives can be found in the British Patents specifications Nos. 374,893 and 392,571 (see also preceding paper).

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