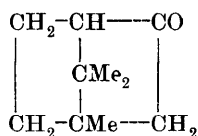


CLXXXVIII.—d- and dl-*Epicamphor*.

By REGINALD FURNESS and WILLIAM HENRY PERKIN, jun.

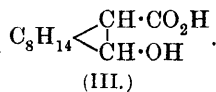
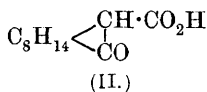
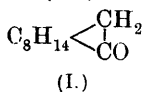
IN the previous communication (Bredt and Perkin, T., 1913, **103**, 2182) it was shown that *l*-epicamphor,



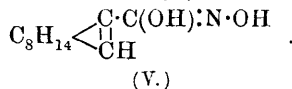
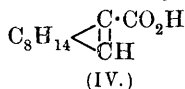
may be prepared from *d*-camphor by several different processes, and of these one of the most convenient is the following:

d-Camphor (I) is converted into camphorcarboxylic acid (II), and

this, on electrolytic reduction, yields the isomeric borneolcarboxylic acids (III):

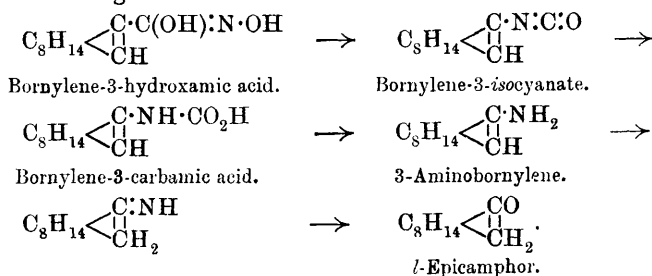


These acids readily lose water when treated with acetyl chloride with the formation of bornylene-3-carboxylic acid (IV) from the ester of which, by the action of hydroxylamine in the presence of sodium methoxide, bornylene-3-hydroxamic acid (V) is obtained:



This hydroxamic acid readily undergoes intramolecular change when it is heated or subjected to the action of toluene-*p*-sulphonyl chloride, and the product, on distillation with hydrochloric acid in a current of steam, yields *l*-epicamphor (m. p. 182°; $\alpha_D - 58.21^\circ$).

This process is probably correctly represented by the following series of changes:



It will be seen that the conversion of *d*-camphor (m. p. 177—178°; +39.1°) into *l*-epicamphor ($\alpha_D - 58.21^\circ$) has been accompanied by a reversal of the sign of rotation. In continuing this investigation it was thought that it would be interesting to prepare *d*-epicamphor, and this has been rendered possible by the generosity of Prof. W. J. Pope, who kindly placed at our disposal a quantity of optically pure *l*-camphor sufficient for this purpose. This was first converted, by the action of sodamide and carbon dioxide (compare T., 1913, **103**, 2214), into *l*-camphorcarboxylic acid, which does not appear to have been previously described.

The acid obtained in this way crystallised well from water or from a mixture of benzene and light petroleum, melted at 125—127°, and 0.8598, dissolved in ethyl acetate and made up to 20 c.c., gave $\alpha_D - 57.4^\circ$.

This acid was reduced electrolytically by the process described by Brecht and his co-workers (*Annalen*, 1906, **348**, 200; 1909, **366**,

1) to a mixture of *l*-borneolcarboxylic acids, from which, by the action of acetyl chloride and subsequent distillation, *l*-bornylene-3-carboxylic acid was obtained. This acid, like the corresponding *d*-acid, was found somewhat difficult to purify; it was recrystallised several times from dilute acetic acid and from acetone, and then melted at 110—112°, and had, in ethyl acetate, $\alpha_D - 144^\circ$, whereas the *d*-acid melts at 112° and has $\alpha_D + 149.5^\circ$. The ester of this acid was next converted into *l*-bornylene-3-hydroxamic acid (m. p. 135—136°), and then into *d*-epicamphor by the process already described in detail in the case of the preparation of *l*-epicamphor (T., 1913, **103**, 2206). After purification by means of the semicarbazone,* *d*-epicamphor melted at 182°, and had, in benzene solution, $\alpha_D + 58.4^\circ$; the semicarbazone melted at 237—238°, and *d*-epicamphoroxime had m. p. 103° and $\alpha_D - 98.9^\circ$ in benzene solution, and these properties, except for the reversal of the sign, are practically identical with those of *l*-epicamphor.

dl-Epicamphor was prepared by mixing the methyl-alcoholic solutions of equal quantities of *d*- and *l*-epicamphor and precipitating by the addition of water, but larger quantities were made from *dl*-bornylene-3-carboxylic acid. This acid was obtained by mixing *d*-bornylene-3-carboxylic acid with an equal amount of the corresponding *l*-acid, and crystallising the product from dilute acetic acid; it melted at the same temperature as the active modifications, namely, at 110—112°, and was converted into *dl*-epicamphor through the hydroxamic acid in the usual manner. *dl*-Epicamphor separates from light petroleum (b. p. 50—60°, in which it is very readily soluble), especially when the highly concentrated solution is left for some days in the ice-chest, as a paste of definite crystals, and melts at 180° (uncorr.), that is to say, at practically the same temperature as the corresponding active modifications.

The oxime separated from dilute alcohol in needles, and melted at 98—100°, and *bromo*-*dl*-epicamphor, prepared by the direct action of bromine (compare *loc. cit.*, p. 2209), after recrystallisation from light petroleum, from which it separated in nodular masses, melted at 135°.

In all these cases the melting points practically coincide with those of the active epicamphors and their derivatives, and in this

* In preparing epicamphor from the hydroxamic acid, instead of proceeding with the purification as described in the previous communication (*loc. cit.*, p. 2207), a much more advantageous method is to convert the crude epicamphor, after distillation in steam, into the semicarbazone by boiling with an equal weight of semicarbazide hydrochloride and of sodium acetate in 70 per cent. alcoholic solution for two hours.

After remaining overnight in the ice-chest, the crystalline mass is collected and washed with ice-cold alcohol until colourless; it is then mixed with hydrochloric acid and distilled in a current of steam, when pure epicamphor passes over.

respect epicamphor behaves like camphor, since the active and inactive modifications of camphor all melt at practically the same temperature, namely, at about 178° . Few only of the derivatives of *dl*-camphor have been described, but the oxime melts at the same temperature (118°) as the active camphoroximes, and other derivatives will doubtless be found to behave in a similar manner.

We wish to express our thanks to Messrs. R. R. Baxter and R. G. Fargher for undertaking the preparation of considerable quantities of the active epicamphors required for this investigation. We also wish to state that part of the expense of this investigation was covered by a grant from the Research Fund of the Royal Society.

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