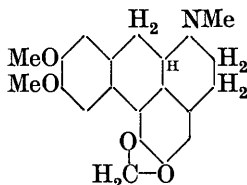


VIII.—*Resolution of dl-Dicentrine.*

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IN a previous communication (J., 1925, **127**, 2018), the synthesis of a *dl*-base, $C_{20}H_{21}O_4N$, having the constitution



suggested by Gadamer (*Arch. Pharm.*, 1911, **249**, 701) for dicentrine is described and it was pointed out that the synthetical base exhibits a series of colour reactions identical with those described by Asahina (*Arch. Pharm.*, 1909, **247**, 206) as characteristic of naturally occurring *d*-dicentrine. It has now been found that the *dl*-base may be readily resolved into its *d*- and *l*-modifications by means of tartaric acid under conditions similar to those employed by Gadamer (*loc. cit.*, p. 688) for the resolution of *dl*-glaucine. The *d*- and *l*-modifications crystallise well from ether, melt at 169° , and have $[\alpha]_D + 64.1^\circ$ and $- 63.5^\circ$, respectively.

* Partington and Carroll calculate that at the critical point hydrocyanic acid must "consist almost entirely of double molecules." On similar principles, argon at the critical point should mainly consist of A_2 . On the other hand, the possibility of association near the critical point (*i.e.*, under high pressure) must be admitted in the case of substances which are associated as liquids, and hence critical data must be used with caution in such cases.

Partington and Carroll's remaining criticisms relate principally to the author's method of calculating the results. For instance, they propose correcting for the variation with temperature of the specific heats of air; a correction which was omitted, since it makes a difference of only about 3 units in the fourth significant figure. They also suggest an alternative method (based on "calculated" critical data) for correcting for deviations from the gas laws, but later in their paper declare it to be unjustified for the reason given above. Bredig and Teichmann (*Z. Elektrochem.*, 1925, **31**, 449) observed critical data in fairly good agreement with those used by Partington and Carroll, but near the critical point a curved "rectilinear diameter" was obtained, which may indicate appreciable association under these conditions (Guye, *Arch. Sci. phys. nat.*, 1894, **31**, 38).

These constants agree closely with those assigned to dicentrine by Asahina (*loc. cit.*; m. p. 168—169°; $[\alpha]_D + 62.7^\circ$) and a direct comparison of the *d*-base with a specimen of *d*-dicentrine which Professor Gadamer kindly sent us definitely established identity.

EXPERIMENTAL.

dl-Dicentrine was prepared in the way described in our earlier communication (*loc. cit.*). Commencing with 30 g. of homoveratroylhomopiperonylamine, 7.5 g. of the dihydrochloride of 6'-aminoveratrylhydrohydrastinine were obtained and this yielded 1.3 g. of pure *dl*-dicentrine, m. p. 181° (corr.).

In an attempt to devise an alternative method for the preparation of 6'-nitroveratrylhydrohydrastinine, 6'-nitroveratrylnorhydrohydrastinine (1.5 g.), water (7 c.c.), 40% formalin (0.5 c.c.), and anhydrous formic acid (0.8 c.c.) were heated for 6 hours at 160—170° in a sealed tube. The contents of the tube were diluted with water, and the pale yellow needles collected and recrystallised from alcohol (m. p. 119°) and identified as 6-nitrohomoveratrole. The acid solution was made alkaline with sodium hydroxide, allowed to remain for 24 hours, the precipitate collected, washed with water and crystallised from petroleum (b. p. 40—60°), separating in colourless plates, m. p. 56—58° (Found: C, 68.9; H, 6.7. Calc. for $C_{11}H_{13}O_2N$, C, 69.1; H, 6.8%). The identity of this substance with hydrohydrastinine was confirmed by the preparation of the methiodide, which crystallised from methyl alcohol in colourless, rhombic prisms, m. p. 229°, and by the fact that on oxidation with iodine a solution was obtained which exhibited the characteristic hydrastinine fluorescence. The formation of 6-nitrohomoveratrole and hydrohydrastinine under the influence of formaldehyde and formic acid involves a reduction, a methylation, and a scission of the molecule of a kind similar to that observed by Hope and Robinson (J., 1911, 99, 2114) when they obtained 2·6-dinitrotoluene and cotarnine by heating anhydrocotarnine-2 : 6-dinitrotoluene with glacial acetic acid.

Resolution of dl-Dicentrine.—A 2*N*-absolute alcoholic solution of *d*-tartaric acid (0.6 c.c.) was added slowly to a solution of *dl*-dicentrine (0.5 g.) in absolute alcohol (25 c.c.) until a faint acid reaction was observed towards litmus. The clear tartrate solution was converted into the hydrogen tartrate by the gradual addition of a further quantity of *d*-tartaric acid (0.6 c.c.); an amorphous precipitate then separated which redissolved on gently warming. On vigorously scratching, *l*-dicentrine hydrogen *d*-tartrate (0.2 g.) separated from the warm solution in small crystals which, after cooling, were collected and washed with alcohol.

The filtrate and washings were evaporated to dryness, the gummy residue dissolved in water, the bases liberated by the addition of sodium hydroxide, extracted with ether, the extract dried, and the ether removed. The residue (0.37 g.) was dissolved in absolute alcohol (20 c.c.) and titrated with a 2*N*-absolute alcoholic solution of *l*-tartaric acid (0.45 c.c.) * until a faint acid reaction was obtained. The clear solution was then treated with a further quantity of *l*-tartaric acid (0.45 c.c.); an amorphous precipitate then separated which redissolved on gently warming. *d*-Dicentrine hydrogen *l*-tartrate (0.2 g.) separated, on scratching, as a crystalline powder, which was collected and washed with alcohol.

The salts in the filtrate and washings were reconverted into base and the treatment with *d*- and *l*-tartaric acid was repeated under the same conditions, when further quantities of *l*-dicentrine hydrogen *d*-tartrate (0.1 g.) and *d*-dicentrine hydrogen *l*-tartrate (0.1 g.) were obtained.

Both *l*-dicentrine hydrogen *d*-tartrate and *d*-dicentrine hydrogen *l*-tartrate are soluble in water but almost insoluble in alcohol, and both crystallise from alcohol containing a little water in colourless, nodular masses.

d-Dicentrine was obtained by dissolving the recrystallised *d*-dicentrine hydrogen *l*-tartrate in water, making slightly alkaline with sodium hydroxide, extracting with ether, drying over anhydrous sodium sulphate, and concentrating the filtered ethereal solution, when *d*-dicentrine separated in long, colourless prisms, *m. p.* 169° (*corr.*). When mixed with a specimen of the *d*-dicentrine obtained from Professor Gadamer, no alteration in *m. p.* was observed. In chloroform solution: $l = 1$, $c = 1.433$; $\alpha_D^{25} = 0.92^\circ$, whence $[\alpha]_D^{25} = +64.1^\circ$. *d*-Dicentrine is readily soluble in alcohol, ethyl acetate, and benzene, almost insoluble in petroleum, and is more soluble in ether than *dl*-dicentrine. It is readily soluble in chloroform, the solution gradually becoming yellow (compare Asahina, *loc. cit.*). The recovery of the base from the chloroform solutions used for optical measurements is a wasteful process, because when the solutions are concentrated a double compound insoluble in ether separates. This can be decomposed by the addition of a little methyl-alcoholic potassium hydroxide and the *d*-dicentrine crystallised from ether, when it is recovered as prisms (*m. p.* 169°), which, however, are always yellow.

l-Dicentrine was obtained from recrystallised *l*-dicentrine hydrogen *d*-tartrate exactly as described in the case of the *d*-base. It crystallises from ether in long, colourless prisms, *m. p.* 169°

* Our thanks are due to Sir W. J. Pope for the *l*-tartaric acid used in these experiments.

(corr.). When mixed in about equal proportions with a specimen of *d*-dicentrine, the mixture softens at 168°, but does not melt completely until about 178°. In chloroform: $l = 1$, $c = 1.700$, $\alpha_D^{17} = -1.08^\circ$, whence $[\alpha]_D^{17} = -63.5^\circ$. *l*-Dicentrine resembles the *d*-base in its behaviour towards solvents and is recovered as yellow prisms, m. p. 169°, from a chloroform solution.

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