

*"Camphothetic" acid: a correction.* By J. WALKER.

In a private communication, Professor Noyes kindly informed me that, by the action of dilute sulphuric acid on campholytic acid, he had obtained a solid isomeride which bore a striking resemblance to the "camphothetic" acid I described in the Transactions (1893, **63**, 504). On reinvestigating my acid, I found that it was an "isocampholytic" acid,  $C_9H_{14}O_2$ , and not "camphothetic acid,"  $C_{18}H_{30}O_4$ , as I had supposed. The analyses given of the acid and salts agree almost equally well with either formula, and I was led by an error in the molecular weight determination of the ethylic salt, and by the fact that this salt, when perfectly dry, scarcely acts on dry bromine, to attribute to the acid the saturated formula  $C_{18}H_{30}O_4$ . I find, however, that the ethylic salt immediately decolorises moist bromine in the cold, and that the acid itself when dissolved in dilute sodium carbonate solution at once decolorises a solution of potassium permanganate. A determination of the molecular weight of the ethylic salt by the depression of the freezing point of benzene gave the following results.

Weight of benzene taken = 17.6 grams.

Weight of substance.	Depression.	Mol. weight.
0.372 gram.	0.570	182
0.608 „	0.890	190

The molecular weight of ethylic isocampholytate,  $C_{11}H_{18}O_2$ , is 182. Thus the acid is doubtless unsaturated, and Professor Noyes informs me, from a direct comparison of his acid with a specimen which I sent him, that "there can be no possible doubt of the complete identity of the two." Beyond the change of formula, no other alteration has to be made at the place cited, except in the dissociation constant, in calculating which the false molecular weight was assumed. The corrected numbers are as follows.

*Isocampholytic acid*,  $C_9H_{14}O_2$ .

$$\mu_{\infty} = 351.$$

$v.$	$\mu'.$	$\mu''.$	$\mu.$	100 $m.$	100 $k.$
850	28.6	28.8	28.7	8.18	0.00086

$$K = 0.00086.$$

This constant is not far removed from the constant of the isomeric

campholytic acid,  $K = 0.00093$ , but is less certain on account of the very slight solubility of the acid. It again exhibits the abnormally small value characteristic of camphor derivatives.

Koenigs and Hoerlin (*Ber.*, 1893, **26**, 813) describe an acid,  $C_9H_{14}O_2$ , isomeric with campholytic acid, which they obtained by the action of superheated steam on sulphocamphylic acid at  $170-190^\circ$ . As this acid, from their description, exhibited a close similarity in properties to those of isocampholytic acid, it was judged advisable to compare the two substances directly. Mr. Henderson and I, accordingly, prepared a small quantity of isolaureonic acid, following the instructions of Koenigs and Hoerlin, which we can confirm in every particular. The acid obtained was crystallised first from aqueous alcohol, and afterwards from light petroleum. It then melted at precisely the same temperature as isocampholytic acid, namely,  $133^\circ$  (corr.) on an Anschütz normal thermometer. The melting point given by Koenigs and Hoerlin is  $135^\circ$ . The crystals from light petroleum had also in both cases the same crystalline habit, forming small well-defined rectangular tables. The solubility of both acids in water at  $25^\circ$  was identical, one part dissolving in 5000 parts of the solvent. A determination of the dissociation constant of isolaureonic acid gave  $K = 0.00081$ , a number almost identical with that given above for isocampholytic acid. The calcium salt is described by them as being easily soluble, and crystallising in needles with approximately 1 mol. of water of crystallisation. This is also the behaviour of the calcium salt of isocampholytic acid. There can thus be little doubt that isocampholytic acid and isolaureonic acid are identical.

As to the real ethylic camphothetate,  $C_{22}H_{38}O_4$ , it in all probability exists in the highest boiling portion of the electrolysed product; but as it seems to have no tendency to crystallise, like the isomeric ethylic allo-camphothetate, I have not yet been able to isolate it.

With the original product from the electrolysis of sodium ortho-ethylic camphorate, a comparatively large quantity of camphoric anhydride was obtained on distillation (*Trans.*, 1893, **63**, 498). With another preparation treated in a precisely similar way, not a trace of this or of any other solid substance was found. The products of electrolysis thus seem liable to considerable variation in detail.

*University College, Dundee,*  
*March, 1895.*

---