XL.—*Electrolysis of Potassium Allo-ethyllic Camphorate.*

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It has been shown by one of us (Walker, *Trans.*, 1893, **63**, 495) that when the sodium ortho-ethyllic salt of camphoric acid is subjected to electrolysis in strong aqueous solution, the chief product is the ethylic salt of an unsaturated monobasic acid $C_9H_{14}O_2$. From the behaviour of its dibromide, this campholytic acid would appear to be an $\alpha\beta$ -unsaturated acid, a fact which has a direct bearing on the position of the carboxyl groups in the camphoric acid molecule.

It appeared to us of interest to perform the electrolysis of the isomeric sodium allo-ethyllic camphorate, in which the sodium atom and the ethyl group have exchanged places, in order to obtain if possible an isomeride of campholytic acid, and to investigate the properties of its dibromide. We have in reality obtained from the corresponding potassium salt more than one isomeride, and the results of the research, so far as it is completed, are given below.

The potassium allo-ethyllic camphorate used in the electrolysis was prepared as follows. Twenty-three grams of sodium were dissolved in 350 c.c. of absolute alcohol, and to this solution of sodium ethoxide there were gradually added 182 grams of powdered camphoric anhydride, which dissolved with evolution of heat. The alcoholic solution of sodium ortho-ethyllic camphorate obtained in this way was heated with ethylic bromide in order that diethyllic camphorate might be produced. Brühl (*Ber.*, 1891, **24**, 3408) recommends heating the reacting substances for 10 hours at 130° in a sealed tube. This is a somewhat troublesome operation when large quantities of solution have to be dealt with, but as we have found that the action proceeds equally well at 100° , the following process may be adopted. 100 c.c. of the alcoholic solution are introduced into a soda-water bottle with a

quantity of ethylic bromide 10 per cent. in excess of the theoretical amount (1 mol. to 1 atom sodium). The bottle is well corked and heated in a water bath for 6 hours, the action being then practically at an end, as we found by weighing the sodium bromide which had separated from the alcoholic solution on cooling. In one case, for example, after six hours' heating, the amount of sodium bromide collected was 17 grams, the theoretical amount being 17.7 grams. After the action is complete, the bulk of the alcohol is distilled off on the water bath and water added. The aqueous solution gives a neutral reaction with litmus. The diethylic salt is separated by means of ether, which is washed first with water containing a little caustic soda, and lastly with pure water; after drying with calcium chloride and distilling off the ether, the residue is distilled under diminished pressure. The yield of diethylic camphorate of constant boiling point is rather more than equal to the amount of camphoric anhydride taken, or 73 per cent. of the theoretical.

The diethylic salt (1 mol.) is mixed with potassium hydroxide (1 mol.) dissolved in eight times its weight of absolute alcohol, and the mixture allowed to remain overnight. It is then heated for half an hour on the water bath to complete the half-saponification; the alcohol is distilled off, and the residue dissolved in two-thirds of its own weight of water, and the aqueous solution is shaken up with ether in order to remove a small quantity of unaltered diethylic camphorate. After the ethereal layer has been separated, and the aqueous layer heated to remove the ether dissolved in it, the solution of potassium allo-ethylic camphorate is ready for electrolysis.

The manner of conducting the electrolysis diverged somewhat from that previously practised. Two nickel crucibles, each of 75 c.c. capacity, were employed as cathodes, and in them the solution to be electrolysed was placed. By means of triangles made of stout insulated copper wire, wrapped round with cord, these crucibles were held in position in a shallow cylindrical metal dish, through which a stream of cold water was kept constantly flowing, the level of the outflow being only slightly beneath that of the mouths of the crucibles. Care must be taken that the crucibles are thoroughly insulated and at no part touch the metal dish. The anodes, as before, were constructed of stout platinum wire in the form of a spiral with a diameter about 1 cm. less than the diameter of the crucible. The crucibles were connected up in series with each other, and with an electrolytic resistance. The current we employed was much greater than that used by Crum Brown and Walker (*Annalen*, 1890, **261**, 112), being derived directly from a dynamo with a voltage of about 100. The electrolytic resistance consisted of a dilute solution of sodium sulphate contained in a large beaker with electrodes

of platinum foil. This solution was allowed to boil when the current passed, and the resistance could be easily regulated by varying the depth of immersion of the electrodes, the distance between them, or the concentration of the solution. As great a current was allowed to pass as was consistent with the contents of the crucibles being kept below 40° by means of the cooling apparatus. Each charge was electrolysed for 45 minutes, after which the contents of the crucibles were removed and allowed to settle in a tall separating cylinder, a fresh charge being then introduced. When all the original solution of the potassium ethylic salt had been treated in this way, the layer of ethereal liquid, which had floated to the surface, was drawn off and the solution again submitted to electrolysis for 30 minutes. A considerable additional quantity of ethereal product was thus obtained, but practically no result was obtained on a third electrolysis. The spent solution was finally extracted with ether, the whole of the ethereal portions united, dried with calcium chloride, and freed from ethylic ether on the water bath. By working with a powerful current in the above manner, the rate of the electrolysis is greatly increased, so that several hundred grams of the ethereal product can be obtained in the course of two or three days. As in the case of the sodium ortho-ethylic salt, a certain irregularity of the yield under precisely similar conditions was experienced, but slight alterations of concentration, &c., were again sufficient to secure the desired result. The vapours evolved on electrolysis have a powerful and persistent odour, but are by no means so unpleasant as those formed with the ortho-ethylic salt.

From the spent aqueous solution, a large quantity of hydrogen allo-ethylic camphorate may be recovered by acidification and extraction with ether, and this may be converted into a pure solution of potassium ethylic salt of the proper concentration, and again electrolysed. Taking this recovered portion into consideration, the actual yield on electrolysis is very satisfactory, amounting almost to 80 per cent. of that theoretically possible. Thus 600 grams of camphoric acid yielded 522 grams of camphoric anhydride, which afforded 547 grams of diethylic camphorate. After half-saponification, 30 grams of this ethereal salt were recovered unchanged, so that the aqueous solution contained 530 grams of potassium ethylic salt. On completion of the electrolysis, 128 grams of hydrogen ethylic camphorate were recovered, corresponding to 145 grams of potassium ethylic salt, so that 385 grams had been electrolytically decomposed. This quantity would yield 265 grams of ethereal product of the ordinary type, and 210 grams were actually obtained. The amount of decomposition by oxidation is thus very small.

The course of the electrolysis was normal, the chief ethereal pro-

ducts, on investigation, proving to be isomeric unsaturated ethylic salts of the formula $C_{11}H_{18}O_2$, and a saturated diethylic salt of the formula $C_{22}H_{38}O_4$, formed according to the equations

and

In accordance with the nomenclature suggested for the ortho-compounds, these substances may be termed ethereal salts of allo-campholytic acids and of allo-camphothetic acid respectively.

In order to isolate the ethereal salts, the whole product of electrolysis was distilled under a pressure of 15 mm., and the portion boiling below 140° was then refractionated at the ordinary atmospheric pressure.

Allo-ethylic Campholytate.

By far the greater portion (67 grams) of the liquid of lower boiling point passed over between 195° and 210° , and on repeated refractionation 45 grams of a colourless oil was obtained boiling constantly at 204° . This oil, on analysis, proved to have the composition $C_{11}H_{18}O_2$.

0.1565 gave 0.4153 CO_2 and 0.1410 H_2O . $C = 72.36$; $H = 10.01$.

$C_{11}H_{18}O_2$ requires $C = 72.52$; $H = 9.89$ per cent.

The sp. gr. of this ethereal salt is 0.951 at $16^\circ/4^\circ$. It is optically active, and at 19° has the specific rotation $[\alpha]_D = +39.1$, the corresponding value for the isomeric ethylic campholytate being $[\alpha]_D = +5.04$.

It readily decolorises a solution of bromine in carbon bisulphide in the cold, and when brominated in the dark under the conditions recommended by Wislicenus (*Annalen*, 1892, **272**, 13) yields a dibromide.

Dibromide of Diethylic Allo-campholytate, $C_{11}H_{18}O_2Br_2$.

This is a pale yellow liquid which gives off hydrogen bromide at the ordinary temperature and cannot be distilled, either by itself or with steam, without undergoing decomposition. For this reason, the quantity of bromine found on analysis is always less than that required by theory.

0.296 gave 0.312 gram $AgBr$. $Br = 44.6$.

$C_{11}H_{18}O_2Br_2$ requires $Br = 46.8$ per cent.

The oil has the density 1.496 at $20^\circ/4^\circ$, and is miscible with the ordinary organic solvents.

Allo-campholytic acid.

Twenty-two grams of the ethylic salt were boiled for three hours with 12 grams of potassium hydroxide in alcoholic solution. The alcohol and unaltered ethylic salt were distilled off with steam, and the residual aqueous solution acidified with hydrochloric acid. An oily acid separated, which was extracted with ether; the ethereal solution was then washed with water in order to remove hydrochloric acid, the ether evaporated, and the residue distilled with steam. Oily drops came over slowly, and a small quantity of tarry matter remained in the distilling flask. The aqueous distillate was neutralised with sodium carbonate, evaporated to a small bulk, acidified, and extracted with ether. On drying the ethereal solution with calcium chloride and distilling off the ether, 7 grams of an almost colourless oil were obtained, which was then fractionated under the ordinary pressure. It began to boil at 210° , but most of it came over at $233\text{--}235^{\circ}$. This is the boiling point of Fittig and Woringer's campholactone (*Annalen*, 1885, **227**, 10), which is isomeric with campholytic acid, but as the oil we obtained was readily soluble in sodium carbonate solution, very sparingly soluble in water, and did not crystallise after long exposure to the temperature of a good freezing mixture, it was evident that we were here dealing with a different substance.

Analysis of the oil yielded the following results.

0.2010 gave 0.5160 CO_2 and 0.1650 H_2O . $\text{C} = 70.01$; $\text{H} = 9.11$.

$\text{C}_9\text{H}_{14}\text{O}_2$ requires $\text{C} = 70.13$; $\text{H} = 9.09$ per cent.

The substance is, therefore, an isomeride of campholytic acid.

It is miscible with the ordinary organic solvents, and has the density 0.993 at $18^{\circ}/4^{\circ}$. It is optically active, the specific rotation being $[\alpha]_D = +57.4$ at 12° , whilst the value for the isomeric campholytic acid is $[\alpha]_D = -5.0$.

The calcium salt was prepared by neutralising the acid by calcium carbonate; it is moderately soluble in water, the cold concentrated solution becoming turbid on warming. On evaporating a dilute solution on the water bath, a crystalline scum is formed; these crystals were collected, and the water in them determined. The remaining solution was then evaporated to dryness at the ordinary temperature in an exhausted desiccator, and the amount of water determined in the crystalline residue.

I. 0.2412 lost 0.0232 at 120° and gave 0.0876 CaSO_4 .

II. 0.0976 „ 0.0089 „ „ 0.0340 „

	Calculated for $\text{Ca}(\text{C}_9\text{H}_{13}\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$.	Found.	
		I.	II.
γ_a	10.47	10.65	10.3
H_2O	9.42	9.61	9.1

The calcium salt thus contains 2 mols. of water, whether crystallised at 100° or at the ordinary temperature.

A strong solution of the sodium salt gives precipitates with silver nitrate, lead nitrate, copper sulphate, and zinc nitrate. The silver salt does not blacken readily on boiling, but does so rapidly on exposure to sunlight. The zinc salt is moderately soluble in cold water, the saturated solution becoming turbid on heating. It is very soluble in ether.

When allo-campholytic acid is treated with sulphuric acid (1 vol. H_2SO_4 sp. gr. 1.84 : 1 vol. H_2O), as described by Fittig (*Annalen*, 1894, **283**, 51), it is to a great extent carbonised, and little can be extracted from the product of the action. If, however, the mixture, instead of being boiled, was heated on the water bath for ten minutes, it became merely red; after cooling and dilution it was extracted with ether, and the ethereal layer shaken up several times with a dilute solution of sodium carbonate. After drying with calcium chloride, the ether was evaporated and an oily residue obtained, which, on standing, deposited well-formed crystals; these crystals possessed a strong odour of camphor, and melted at 50° . The substance was moderately soluble in cold water, the solution becoming turbid on gently warming, and again clear as the boiling point was approached: the phenomena were reversed on cooling. This behaviour left no doubt that the substance was the campholactone described by Fittig and Woring (*Annalen*, 1885, **227**, 10). The lactone which they obtained can be prepared from the isomeric lauronic acid $\text{C}_9\text{H}_{14}\text{O}_2$ by treatment with sulphuric acid, so it was of importance to determine if allo-campholytic acid was identical with lauronic acid. The description they give was found scarcely sufficient for purposes of identification, so a quantity of lauronic acid was prepared in the manner described by Aschan (*Ber.*, 1894, **27**, 3504), in order that a direct comparison might be made. This comparison sufficed to establish the non-identity of the two substances. In the first place, the specific rotation of lauronic acid is $[\alpha]_D = +17$, that of allo-campholytic acid being $+57$. The calcium salt of lauronic acid crystallises, according to Fittig and Woring, and also according to Aschan, with $3\text{H}_2\text{O}$, whilst the salt of our acid crystallises with $2\text{H}_2\text{O}$. Lauronic acid on treatment with bromine is converted into a bromolactone, $\text{C}_9\text{H}_{13}\text{BrO}_2$, m. p. 187° , whilst allo-campholytic acid under the same conditions gives, for the most part, a liquid dibromide.

Aschan obtained from lauronolic acid a solid amide, melting at 72° : allo-campholytic acid, on treatment with phosphorus pentachloride and ammonia, yields a liquid amide.

Allo-campholytic acid is thus distinct from lauronolic acid, but would seem to be identical with the acid obtained by Noyes from the chloride of amino-lauronolic acid by the action of sodium nitrite. The calcium salt of this acid (*Amer. Chem. J.*, 1894, **16**, 508) crystallises with $2\text{H}_2\text{O}$, and the zinc salt is soluble in ether. In a private communication, Prof. Noyes also states that his acid yields campholactone on treatment with dilute sulphuric acid (1 : 1), and that its amide is liquid so far as he has observed. In these points it therefore shows a strong resemblance to allo-campholytic acid.

Dibromide of Allo-campholytic acid.—Five grams of allo-campholytic acid in 20 c.c. of carbon bisulphide were gradually added to 7 grams of dry bromine dissolved in 20 c.c. of carbon bisulphide. The mixture was allowed to remain over-night, and the carbon bisulphide removed on the following morning by a stream of dry air. The residue was mostly liquid, but contained a small quantity of a crystalline substance. The liquid was washed away from the crystals by a little light petroleum, and the residual solid recrystallised from warm benzene. The crystalline substance then melted at 184° , blackening at the same time, and was probably the bromolactone described by Aschan (*loc. cit.*), which melts at 187° . The small quantity, however, precluded an accurate analysis.

The liquid obtained after evaporation of the light petroleum gave the following numbers by the Carius method.

0.4399 gave 0.5284 AgBr. Br = 51.1.

0.4134 „ 0.4912 AgBr. Br = 50.8.

$\text{C}_9\text{H}_{14}\text{Br}_2\text{O}_2$ requires Br = 50.9 per cent.

The liquid was thus a dibromide formed by the direct addition of bromine to the unsaturated acid. The action of alkalis on this dibromide will be described in a subsequent paper.

Solid Acids.—From the ethylic salt which was recovered on saponification of the ethereal product boiling at 204° , a new acid was obtained on prolonged treatment with very concentrated alcoholic potash. The potassium salt separated from the alcoholic solution, and, on acidification with hydrochloric acid, yielded a solid acid, which was volatile with steam; on recrystallisation from benzene and light petroleum, it melted at 158° . It is an unsaturated acid isomeric with allo-campholytic acid.

Another acid, melting at 146° , was obtained along with a liquid acid from the ethereal product boiling at 220 – 230° . These substances, together with the fractions boiling between 110° and 240° ,

under 15 mm. pressure, are being investigated, and will form the subject of a future communication.

Diethylic Allo-camphothetate.

The tarry residue left on distilling the ethereal product of electrolysis up to 240° , under 15 mm. pressure, became partially solid on long standing. It was spread in a thin layer on porous plates which, after several weeks, absorbed the bulk of the tar, a crystalline substance being left. This was scraped off and spread on a fresh porous surface; it soon became pale brown, and was then recrystallised repeatedly from light petroleum. When the solvent was allowed to evaporate very slowly, the substance separated in the form of large rhombic tables; it melts at $67-68^{\circ}$, and is insoluble in water, but soluble in all ordinary organic solvents. The following results were obtained on analysis.

- I. 0.0851 gave 0.2260 CO_2 and 0.0813 H_2O . C = 72.42; H = 10.61.
 II. 0.1026 ,, 0.2712 ,, ,, 0.0987 H_2O . C = 72.09; H = 10.67.
 $\text{C}_{22}\text{H}_{38}\text{O}_4$ requires C = 72.13; H = 10.38 per cent.
 $\text{C}_{11}\text{H}_{18}\text{O}_2$,, C = 72.52; H = 9.89 per cent.

These numbers agree better with the formula $\text{C}_{22}\text{H}_{38}\text{O}_4$ than with $\text{C}_{11}\text{H}_{18}\text{O}_2$, but in order to ascertain definitely if the ether were a synthetic product, it was necessary to make a determination of the molecular weight of the substance. Beckmann's boiling-point method was used with ether as solvent, since it was of importance to recover the substance, the quantity at our disposal being very small.

Ether taken = 18.3 grams.

	Weight of substance.	Elevation of b. p.	Mol. weight.
I	0.296	0.103	331
II	0.226	0.072	362

Molecular weight of $\text{C}_{22}\text{H}_{38}\text{O}_4$ = 366.

These numbers, together with the fact that bromine is without action on the ether; suffice to show that the substance is the saturated diethylic salt which is normally obtained as a product of electrolysis. The quantity which could be extracted from the tarry residue of high boiling point amounted altogether to little more than a gram, but this is in all probability only a very small proportion of the amount actually formed, the bulk remaining in the tar.

Several attempts were made to saponify the ethereal salt, but they met with little success. The substance is practically unattacked by strong, boiling, alcoholic potash, or by a mixture of concentrated hydrochloric acid and glacial acetic acid. Fuming hydrobromic acid at $160-180^{\circ}$ attacks it, but the acid formed has not yet been isolated in sufficient quantity for a study of its properties.

Constitution of Camphoric acid.

As one of us has shown (Trans., 1893, **63**, 506), the electrolysis of sodium ortho-ethylc camphorate and the nature of the products obtained can best be explained by the assumption that camphoric

acid contains the complex $\begin{array}{c} \text{H} \\ | \\ -\text{C}\cdot\text{COOH} \text{ (ortho)} \\ | \\ -\text{C}\cdot\text{COOH} \text{ (allo)} \\ | \end{array}$. This conclusion is

accepted by Noyes, who states that his observations on the behaviour of the camphoramic acids "agree best with the supposition that camphoric acid contains this complex" (*Amer. Chem. J.*, 1894,

16, 509). Campholytic acid has thus the grouping $\begin{array}{c} -\text{C}\cdot\text{COOH} \\ || \\ -\text{C} \\ | \end{array}$,

and is an $\alpha\beta$ -acid. Allocampholytic acid may be put into the class of $\beta\gamma$ -unsaturated acids, on account of the ease with which campholactone may be obtained from it. In its electrolytic formation, the orthocarboxyl group leaves the molecule, together with a hydrogen atom from one of the neighbouring carbon atoms. This hydrogen atom cannot be attached to the allo-carbon atom, for then an $\alpha\beta$ -unsaturated acid would be produced. It must, therefore, be attached to a carbon atom in the γ -position relatively to the allo-carbon atom, that is, the molecule of camphoric acid must contain the atomic

grouping $\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ -\text{C}-\text{C}\cdot\text{COOH} \\ | \\ -\text{C}\cdot\text{COOH} \end{array}$, and allo-campholytic acid the grouping

$\begin{array}{c} -\text{C}=\text{C}-\text{H} \\ | \\ -\text{C}\cdot\text{COOH} \end{array}$. Allo-camphothetic acid would then contain the group

Since lauronic acid yields the same campholactone as allocampholytic acid, it also must be a $\beta\gamma$ -unsaturated acid, and its carboxyl group must occupy the allo-position in the camphoric acid skeleton. The nature of the isomerism of the two acids will probably become clear when further experiments have been undertaken on their reciprocal transformation. Aschan has recently shown that bromocamphoric anhydride, on treatment with alkalis, yields directly a large quantity of lauronic acid. This, as he points out, indicates that the bromine atom is in the β -position to one of the carboxyl groups, and the simultaneous formation of camphanic acid proves

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that it is in the γ -position relatively to the other. On our assumption we should have the following groupings

Now camphanic acid, on dry distillation, passes largely into launolic acid and carbonic anhydride, just as terebinic acid passes into pyroterebinic acid (compare Bredt, *Ber.*, 1893, 27, 2098).

The analogy here is much more perfect than that exhibited when Bredt's formula for camphoric acid is employed, and in the case of Ballo's formula one would expect the launolic acid derived directly from bromocamphoric anhydride to be different from that derived from camphanic acid, namely, a $\beta\gamma$ -acid in the first instance, and a $\gamma\delta$ -acid in the second.

Applying the rules previously found to hold good in electrolysis of alkaline salts of carboxylic acids, Bredt's formula would place both ortho-campholytic and allo-campholytic acids in the $\gamma\delta$ -series. Ballo's formula would make them both $\beta\gamma$ -acids. But we have found that the two acids undoubtedly belong to different series, namely, ortho-campholytic acid to the $\alpha\beta$ -series, and allo-campholytic acid to the $\beta\gamma$ -series. This fact seems to us, therefore, a strong argument against the validity of these formulæ. Two formulæ have been proposed, however, which are in harmony with the above exposition, Armstrong's formula (*Trans.*, 1879, 35, 757) and Collie's formula (*Ber.*, 1892, 25, 1116). These are

Either of these formulæ explains the results obtained on electrolysis as well as the other, and their further verification must depend on other reactions.