X.—*Infracampholenic Acid, an Isomeride of Campholytic and* iso*Lauronolic Acids.*

By Martin Onslow Forster.

Eighteen months ago I described the unsaturated nitrile, $C_9H_{13}N$, produced on eliminating hydrogen bromide and carbon monoxide from the anhydride of bromonitrocamphane (Trans., 1899, **75**, 1141).   At that time it seemed highly probable that the nitrile, and the amide

obtained from it on hydrolysis, were derivatives of Walker's campholytic acid, because the amide, although distinct from *iso*lauronolamide, was converted into that substance by dilute mineral acids.

The investigation of the acid derived from the amide is still incomplete, but the recent appearance of a posthumous paper by Tiemann, in association with Kerschbaum and Tigges, on the two campholytic acids (*Ber.*, 1900, **33**, 2935), closely following a communication on the same subject by G. Blanc (*Bull. Soc. Chim.*, 1900, [iii], **23**, 695), obliges me to describe briefly the progress which has been made in the examination of the substance.

The nitrile has to be heated with alcoholic potash continuously for several weeks before ammonia ceases to be evolved ; there is then obtained the potassium salt of a liquid acid, $C_9H_{14}O_2$, which closely resembles Walker's campholytic acid, forming a viscous oil which boils at 145° and 239° under pressures of 24 mm. and 758 mm. respectively. Moreover, the substance is optically inactive, and treatment with dilute mineral acids transforms it into *iso*lauronolic acid, differing in no respect from the acid obtained by the action of aluminium chloride on camphoric anhydride. Here, however, the resemblance to campholytic acid ceases. According to Walker (Trans., 1893, **63**, 498), that substance absorbs a molecular proportion of bromine, yielding the dibromide $C_9H_{14}O_2Br_2$, which melts and blackens at 106—107°. When, however, the new acid is treated with bromine under the conditions specified by Walker, two molecular proportions of the halogen are engaged, hydrogen bromide is eliminated, and the solid product consists of a tribromocarboxylic acid, $C_9H_{13}O_2Br_3$, which melts to a colourless liquid, and evolves gas, at 182°. Moreover, the dibromide of the new acid, which can be obtained when bromine is slowly added in quantity scarcely sufficient to convert all the substance into the compound $C_9H_{14}O_2Br_2$, is quite distinct from the isomeric dibromide of campholytic acid, because it melts at 125° without blackening. Furthermore, whilst campholytic acid is converted by hydrobromic acid into the hydrobromide, $C_9H_{15}OBr$, several attempts, under varying conditions, to obtain a corresponding derivative from the new acid have resulted in the production of *iso*lauronolic acid.

It has now been shown that the new substance is the lower homologue of α-campholenic acid, and I propose therefore to call it infracampholenic acid, the prefix " infra " representing in this sense the converse of " homo."

Some months after the discovery of tribromodihydroinfracampholenic acid, and the consequent recognition of the fact that infracampholenic and campholytic acids are distinct, the paper by G. Blanc (*loc. cit.*) was published without any previous intimation that he proposed to
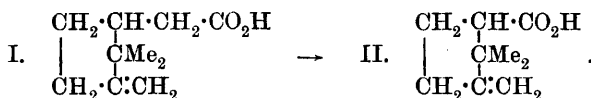
investigate the nitrile with which I was working. On reducing that substance with sodium in absolute alcohol, Blanc obtained the amine which α-campholenamide yields when oxidised with sodium hypobromite, namely, α-aminocampholene, first described by Blaise and Blanc (*Bull. Soc. Chim.*, 1899, [iii], **21**, 976); assuming that the nitrile is indeed the nitrile of campholytic acid, this result appeared to confirm the view that campholytic acid is the lower homologue of α-campholenic acid, and Blanc would have expressed its constitution by the formula

$$\begin{array}{l} CH_2 \cdot CH \cdot CO_2H \\ \quad | \quad CMe_2 \\ CH_2 \cdot C \vdots CH_2 \end{array} \quad ,$$
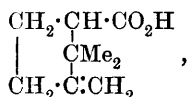
but for the appearance of Walker's latest paper on the subject (Trans., 1900, **77**, 374). In consequence of this publication, Blanc agreed that campholytic acid is a stereoisomeride of *iso*lauronolic acid,

$$\begin{array}{l} CH_2 \cdot C \cdot CO_2H \\ \quad | \quad CMe \\ CH_2 \cdot CMe_2 \end{array} \quad ,$$
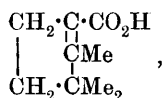
and adopting Bouveault's formula for α-campholenic acid, I, represented the constitution of infracampholenic acid by the expression II :

$$\text{I.} \quad \begin{array}{l} CH_2 \cdot CH \cdot CH_2 \cdot CO_2H \\ \quad | \quad CMe_2 \\ CH_2 \cdot C \vdots CH_2 \end{array} \quad \longrightarrow \quad \text{II.} \quad \begin{array}{l} CH_2 \cdot CH \cdot CO_2H \\ \quad | \quad CMe_2 \\ CH_2 \cdot C \vdots CH_2 \end{array} \quad .$$
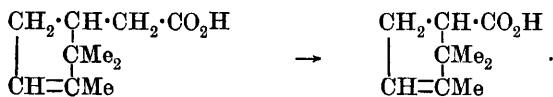
Working with Noyes' active campholytic acid, that is to say, with the acid obtained by the action of nitrous acid on dihydroaminocampholytic acid, Tiemann (*loc. cit.*) arrived at αα-dimethyltricarballylic acid by oxidation with dilute nitric acid, and therefore represents the constitution of campholytic acid by the formula III :

$$\text{III.} \quad \begin{array}{l} CH_2 \cdot CH \cdot CO_2H \\ \quad | \quad CMe_2 \\ CH \vdots CMe \end{array} \quad .$$
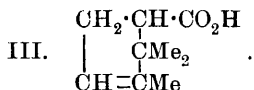
This view is now endorsed by Blanc (*Compt. rend.*, 1900, **131**, 803), who has oxidised inactive campholytic acid, derived on this occasion from *iso*lauronolic acid by Walker's process, obtaining also αα-dimethyltricarballylic acid.

In giving expression to this change of view, Blanc does not refer to the result of his experiment with the nitrile of infracampholenic acid, which showed that this acid is the lower homologue of α-campholenic acid ; the formula III, which, in agreement with Tiemann, he ascribes to campholytic acid, represents the latter substance as the lower

homologue of a-campholenic acid, the constitution of which is best expressed by Tiemann's formula,

$$CH_2 \cdot CH \cdot CH_2 \cdot CO_2H \qquad\qquad CH_2 \cdot CH \cdot CO_2H$$
$$| \quad CMe_2 \qquad \rightarrow \qquad | \quad CMe_2 \quad .$$
$$CH{=}CMe \qquad\qquad\qquad CH{=}CMe$$

In view of the fact, established in this paper, that campholytic and infracampholenic acids are distinct, one of three things follows: Tiemann's formula for a-campholenic acid is incorrect, Blanc's reduction of infracampholenonitrile to a-aminocampholene is misleading, or the expression III does not truly represent the structure of campholytic acid.

Now Tiemann's formula for a-campholenic acid is based on the production of *iso*ketocamphoric acid, $COMe \cdot CMe_2 \cdot CH(CH_2 \cdot CO_2H)_2$, on oxidation, and appears therefore to be well founded. There is likewise no reason to mistake the conclusion to be drawn from Blanc's experiment showing that a-campholenic acid is the homo-derivative of infracampholenic acid. There remains, therefore, the third possibility, namely, the invalidity of the formula for campholytic acid advocated by Tiemann and by Blanc.
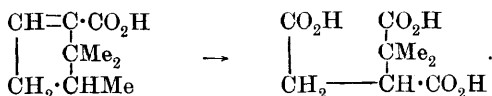
While discussing the constitution of that substance, the last-named investigators do not allude to the alternative formula,

$$CH{=}C \cdot CO_2H$$
$$\text{IV.} \quad | \quad CMe_2 \quad ,$$
$$CH_2 \cdot CHMe$$
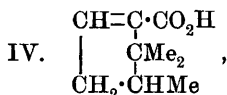
from which, by oxidation, aa-dimethyltricarballylic acid might be obtained. Perhaps the drawback which presented itself to them was the conversion of the complex $\cdot CMe_2 \cdot CHMe \cdot$ into the grouping $\cdot CMe_2 \cdot CH(CO_2H) \cdot$, a change which is certainly unusual. In view of the present difficulty, however, this formula deserves consideration because the structure of infracampholenic acid would then be represented by the expression III.

The following arguments may be brought forward in support of this suggestion.

1. The formula IV, with the qualification already mentioned, accounts for the production of aa-dimethyltricarballylic acid,

$$CH{=}C \cdot CO_2H \qquad\qquad CO_2H \quad CO_2H$$
$$| \quad CMe_2 \qquad \rightarrow \qquad | \quad CMe_2 \quad .$$
$$CH_2 \cdot CHMe \qquad\qquad CH_2{-}{-}CH \cdot CO_2H$$

2. It represents campholytic acid as an $a\beta$-unsaturated acid, in accordance with the results of Walker's experiments.

3. It reconciles the facts that infracampholenic acid is distinct from

campholytic acid, and is nevertheless a lower homologue of α-campholenic acid.

4. The representation of infracampholenic acid by the formula III explains the production of a tribromo-derivative by direct action of bromine, the α-carbon atom being hydrogenised, and therefore susceptible to the action of bromine.

5. The formula IV is more consistent with the behaviour of campholytic acid towards bromine than the representation which is given by Tiemann and by Blanc, because dihydro*iso*lauronolic acid,
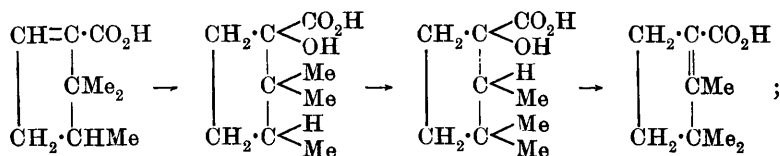
$$\begin{array}{l} CH_2 \cdot CH \cdot CO_2H \\ \quad\ \ | \quad CHMe \\ CH_2 \cdot CMe_2 \end{array} \quad ,$$
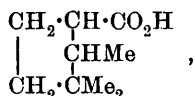
can be brominated in the α-position (Perkin, Trans., 1898, **73**, 838), and tetramethylenecarboxylic acid,

$$\begin{array}{l} CH_2 \cdot CH \cdot CO_2H \\ CH_2 \cdot CH_2 \end{array} \quad ,$$
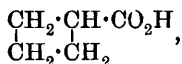
readily undergoes the same change (Perkin and Sinclair, Trans., 1892, **61**, 42) ; if therefore, campholytic acid has the structure III, it might be expected to behave like infracampholenic acid, and give a tribromoderivative instead of a dibromide.

6. On the lines of Lapworth's proposal, according to which the production of *iso*lauronolic acid from camphoric acid involves the migration of a methyl group (Trans., 1900, **77**, 1057), the conversion of campholytic acid into *iso*lauronolic acid can be explained as follows :

$$\begin{array}{llll} CH{=}C \cdot CO_2H & CH_2 \cdot C{<}^{CO_2H}_{OH} & CH_2 \cdot C{<}^{CO_2H}_{OH} & CH_2 \cdot C \cdot CO_2H \\ \quad | & \quad\ |\ \ C{<}^{Me}_{Me} & \quad\ |\ \ C{<}^{H}_{Me} & \quad\ \| \\ \quad CMe_2 \rightarrow & & \rightarrow & \quad CMe \rightarrow \\ CH_2 \cdot CHMe & CH_2 \cdot C{<}^{H}_{Me} & CH_2 \cdot C{<}^{Me}_{Me} & CH_2 \cdot CMe_2 \end{array} \quad ;$$

this scheme is no less plausible than that adopted by Blanc (*Compt. rend.*, 1900, **131**, 805 ; Abstr., 1901, **80**, i, 11) for the same purpose.

Against the propositions made in this paper will be urged the fact that aminodihydrocampholytic acid,

$$\begin{array}{l} CH_2 \cdot CH \cdot CO_2H \\ \quad\ \ | \quad CMe_2 \\ CH_2 \cdot CMe \cdot NH_2 \end{array} \quad ,$$
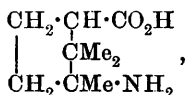
under the influence of nitrous acid, is more likely to yield a substance having the formula III than the alternative compound, IV. This is, *primâ facie*, true, but it must be borne in mind that the substituents

in this complex display great mobility, which is shared by the hydrogen atoms.

In the hope of settling definitely the constitution of infracampholenic acid, a study of its products of oxidation is being made, and I expect to gain evidence of its structure also by examining the alcohol obtained from aminoinfracampholene, $C_8H_{13}\cdot NH_2$, by the action of nitrous acid; the base itself is described in this paper, being readily furnished by infracampholenamide when treated with sodium hypobromite.

Before proceeding to the experimental details, I think it is desirable to draw attention to the nomenclature for campholytic and *iso*lauronolic acids adopted by Tiemann's collaborators in the paper first mentioned (*Ber.*, 1900, **33**, 2935). They distinguish these substances, which are perfectly well recognised under the original names, as a- and β-campholytic acids respectively. This distinction seems to be somewhat unfortunate. In the first place, the substance which they propose to call a-campholytic acid, is derived from β-camphoramic acid, whilst a-camphoramic acid yields, not β-campholytic acid, but lauronolic acid. Secondly, it is claimed that the use of these letters illustrates the relationship of the acids to a- and β-campholenic acids; no evidence is adduced in the paper, however, to show that such a relation holds good, and although Blanc's investigations suggest that β-campholenic acid is the homoderivative of *iso*lauronolic acid, the same author has shown that a-campholenic acid is not connected with campholytic acid in a similar manner. In these circumstances, confusion will be avoided by adherence to the original names for campholytic and *iso*lauronolic acids.

EXPERIMENTAL.

Infracampholenic Acid, $C_9H_{14}O_2$.

The readiness with which the amide, $C_8H_{13}\cdot CO\cdot NH_2$, is converted into *iso*lauronolamide under the influence of dilute hydrochloric acid renders this agent useless for the purpose of hydrolysis. Attempts have been made under varied conditions to transform the amide into the acid by means of nitrous acid, but on each occasion the unchanged substance was recovered. The only alternative was to use alcoholic potash, and although the action is extremely slow, and involves heating the liquid during several weeks, this method was ultimately adopted.

Twenty grams of the purified amide were dissolved in 100 c.c. of alcohol, and heated with 25 grams ($3\frac{1}{2}$ mols.) of potassium hydroxide dissolved in the minimum quantity of water, until no further evolution of ammonia took place. Hydrolysis was complete after 200 hours. The liquid was then evaporated on the water-bath, and the viscous residue washed two or three times with ether, dissolved in water, and

just acidified with cold, dilute, hydrochloric acid, which precipitated a pale brown, viscous oil. This was dissolved at once in ether, washed with water, redissolved in sodium carbonate, and then extracted with ether in order to remove any non-carboxylic impurities. The solution of the sodium salt was exactly neutralised with dilute sulphuric acid, and on removing the precipitated oil with ether, drying the extract with fused sodium sulphate, and afterwards evaporating the solvent on a water-bath, 19 grams of the acid were obtained. The product, which was pale brown and very viscous, was then distilled under reduced pressure ; various specimens boiled at 145°, 170°, 180°, and 239° under pressures of 24 mm., 60 mm., 105 mm., and 758 mm. respectively, yielding a colourless, or very pale yellow, viscous oil, having a faint, somewhat disagreeable odour.

$$0\cdot2000 \text{ gave } 0\cdot5122 \text{ } CO_2 \text{ and } 0\cdot1630 \text{ } H_2O. \quad C = 69\cdot85 \text{ ; } H = 9\cdot05.$$
$$C_9H_{14}O_2 \text{ requires } C = 70\cdot13 \text{ ; } H = 9\cdot09 \text{ per cent.}$$

A 20 per cent. solution in ether is optically inactive, and a 10 per cent. solution of the amide in absolute alcohol is also devoid of activity. The acid has a sp. gr. $1\cdot0146$ at 16°, and a refractive index μ^{Na} $1\cdot4660$ at 19°.

When infracampholenic acid is warmed with dilute sulphuric acid it soon solidifies, yielding *iso*lauronolic acid, which was compared with a specimen obtained from camphoric anhydride ; it melts at the same temperature, and like the acid from this source, is optically inactive.

Certain salts of infracampholenic acid are well defined. A neutral solution of the ammonium salt gives no precipitate with magnesium sulphate, calcium chloride, or barium chloride, but the *mercuric* salt forms minute white needles, sparingly soluble in cold water. The *copper* salt separates immediately as a dark green, crystalline precipitate, which dissolves readily in hot alcohol, forming a deep green solution ; this deposits nodular aggregates of minute green needles. The *lead* salt forms a white, flocculent precipitate, soluble in boiling water, from which it crystallises in small, transparent, six-sided plates. The *silver* salt is soluble in hot water, separating in colourless crystals which are affected only slowly by light.

Tribromodihydroinfracampholenic Acid, $C_9H_{13}O_2Br_3$.

In the first attempts to prepare a dibromide, the conditions prescribed by Walker (*loc. cit.*) were observed. Seven grams of bromine dissolved in 20 c.c. of dried carbon disulphide were placed in a wide-mouthed bottle through the stopper of which passed a tap-funnel and a tube containing calcium chloride ; the bottle was immersed in melting ice in a large, blackened beaker. Five grams of infracampholenic

acid dissolved in 20 c.c. of dried carbon disulphide were then added slowly through the tap-funnel, the solution of bromine being shaken continuously during the process, and the operation being carried out in a darkened room. Colourless crystals were soon deposited in the bottle, and hydrogen bromide escaped through the calcium chloride tube. After remaining 12 hours in the dark, the solution was decanted, and the crystals washed with light petroleum ; the crude material obtained in this way amounted to 4·5 grams, a further quantity being obtained from the mother liquor. The freshly precipitated substance melted at 178°. It was recrystallised from hot ethyl acetate, in which it dissolves readily, being deposited in aggregates of small, hard needles, which melt to a colourless liquid, evolving gas, at 182° ; the melting point is dependent on the rate at which the temperature rises, and has been observed as high as 187°.

0·2164 gave 0·2174 CO_2 and 0·0649 H_2O. $C = 27·40$; $H = 3·33$.
0·1725 ,, 0·2465 AgBr. $Br = 60·80$.
$C_9H_{13}O_2Br_3$ requires $C = 27·48$; $H = 3·33$; $Br = 61·07$ per cent.

The operation just described has been repeated many times, and the same result was obtained in each case. Even when the halogen solution was cooled by a freezing mixture, and the acid added as slowly as possible, in a dark room, hydrogen bromide was evolved after a very short interval, and crystals were deposited in the bottle when only a small proportion of the material had been added. Increasing the quantity of bromine does not improve the yield of the substance, which rarely exceeded 65 per cent. of the theoretical amount.

The tribromide of infracampholenic acid dissolves readily in alcohol, and the cold solution immediately develops with silver nitrate a turbidity which rapidly intensifies to a copious precipitate. It dissolves in aqueous sodium carbonate with liberation of carbon dioxide, forming a bromohydrocarbon and an unsaturated acid ; if the alkali is added in small quantities amounting in all to one molecular proportion only, nearly two-thirds of the substance remains unchanged.   The following experiment was therefore performed.

Twenty grams of the finely powdered tribromide were suspended in water, and treated with a cold solution of 21 grams (4 mols.) of anhydrous sodium carbonate. The substance dissolved almost immediately without liberating carbon dioxide, as this was absorbed by the excess of alkali. The turbid solution, after 24 hours, had deposited a heavy, colourless oil, which was removed by means of ether, washed twice with water, and freed from ether on the water-bath ; on passing a current of steam through the residue, a bromohydrocarbon was obtained having an agreeable odour.
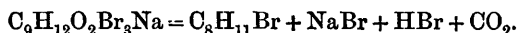
0·1908 gave 0·1781 AgBr.   Br = 39·71.
0·1818   ,,   0·1702 AgBr.   Br = 39·83.
$C_8H_{11}Br$ requires Br = 42·78 per cent.

It is probable that this substance does not represent the initial product arising from the tribromide by the elimination of carbon dioxide and hydrogen bromide according to the equation :

$$C_9H_{12}O_2Br_3Na = C_8H_{11}Br + NaBr + HBr + CO_2.$$

Most likely the hydrocarbon dibromide, $C_8H_{12}Br_2$, is first produced, and undergoes resolution into the bromo-derivative, $C_8H_{11}Br$, and hydrogen bromide during the process of isolation, because the substance extracted by ether is colourless, becoming pale yellow when distilled in steam ; the aqueous residue in the distilling flask contains a considerable amount of hydrobromic acid, and holds some dark brown, non-volatile, tarry matter in suspension.

It will be interesting to ascertain the nature of the acid produced along with the hydrocarbon, and steps are being taken in this direction, but unfortunately the substance is resinous, and the only information concerning it which has been gained so far is the fact that it is unsaturated and contains bromine.

Dibromodihydroinfracampholenic acid, $C_9H_{14}O_2Br_2$.

Four grams of infracampholenic acid were dissolved in 100 c.c. of dry chloroform, and to the solution, immersed in a good freezing mixture, rather less than 4 grams of bromine, dissolved in 50 c.c. of cold chloroform, were slowly added.   Owing to the readiness with which one atom of hydrogen in infracampholenic acid is replaced by bromine, great care was taken to keep the solution in a state of agitation, and the solution of bromine was admitted drop by drop ; liberation of hydrogen bromide was thus reduced to a minimum, and only towards the end of the operation did the gas make its appearance.   Without removing the vessel from the freezing mixture, a current of dry air was aspirated through the pale yellow liquid during one hour, after which interval the solution was allowed to acquire the temperature of the atmosphere.   When the chloroform had completely evaporated, a white, butter-like mass remained ; this was drained on porous earthenware, and washed several times with cold petroleum.   The snow-white, micro-crystalline powder obtained in this way melts at 117° to a colourless liquid evolving gas ; it dissolves very readily in alcohol and in cold ethyl acetate, but is rather sparingly soluble in boiling petroleum, which deposits it in minute rectangular plates ; these melt and evolve gas at 125°.

0·2152 gave 0·2653 CO_2 and 0·0853 H_2O. C = 33·62 ; H = 4·40.
0·1599 ,, 0·1940 AgBr. Br = 51·62.
 $C_9H_{14}O_2Br_2$ requires C = 34·14 ; H = 4·46 ; Br = 50·95 per cent.

The dibromide dissolves immediately in aqueous sodium carbonate, and the turbid solution deposits a bromohydrocarbon on standing.

The Amide of Infracampholenic Acid.

When the extraordinary indifference of infracampholenamide towards alkaline hydrolytic agents was first observed, an attempt was made to study the oxidation products of the acid by oxidising the amide and hydrolysing the product.

Oxidation of Infracampholenamide.—Ten grams of the amide were dissolved in 5000 c.c. of boiling water and rapidly cooled, the temperature of the solution being finally reduced to about 0° by immersion in melting ice. Three hundred c.c. of a 2 per cent. solution of potassium permanganate were added in small quantities, the colour of the solution being immediately destroyed. The liquid was then treated with 15 grams of potassium carbonate, boiled, filtered, and evaporated to small bulk, when a dark yellow oil separated, and solidified on cooling. After being drained on porous earthenware, washed with a small quantity of cold water, and again drained, the colourless pro duct weighed 8·5 grams.

Under these conditions, the amide is oxidised to a dihydroxy-derivative. The substance dissolves very readily in water, forming a solution which is neutral to litmus. Alcohol also dissolves it freely, and ethyl acetate is the most convenient solvent from which to crystallise it, depositing the derivative in prisms containing $1H_2O$. A specimen dried in the desiccator was analysed, with the following result :

0·1775 gave 0·3492 CO_2 and 0·1534 H_2O. C = 53·65 ; H = 9·60.
 $C_9H_{17}O_3N,H_2O$ requires C = 52·68 ; H = 9·27 per cent.

In the hydrated condition the substance has no definite melting point, but liquefies at about 110°, when water is liberated. If the crystals deposited by ethyl acetate are powdered finely and dried at 90° until no further loss of water takes place, the substance melts at 170°, without evolving gas.

0·1816 gave 0·3861 CO_2 and 0·1500 H_2O. C = 57·99 ; H = 9·17.
0·2073 ,, 0·4415 CO_2 ,, 0·1694 H_2O. C = 58·08 ; H = 9·08.
0·2218 ,, 14·2 c.c. of nitrogen at 16·5° and 779 mm. N = 7·63.
 $C_9H_{17}O_3N$ requires C = 57·75 ; H = 9·09 ; N = 7·48 per cent.

The oxidised amide is hydrolysed by alcoholic potash much more

readily than infracampholenamide, but the acid obtained in this way takes the form of a resin.

Hydrobromide of Infracampholenamide, $C_9H_{16}ONBr$.—The amide of infracampholenic acid was dissolved in 48 per cent. hydrobromic acid, and allowed to remain in the desiccator. After some days, clusters of flat, transparent, rhomboidal plates separated. Cold alcohol dissolves the substance very readily, and it is also soluble in cold water, forming an acid solution; when potassium permanganate is added to this liquid, the colour is destroyed and bromine set free. The hydrobromide is insoluble in petroleum, and very sparingly soluble in cold ethyl acetate, but it dissolves readily in the boiling liquid, which deposits it in transparent plates melting at 144°, with vigorous disengagement of gas.

0·2165 gave 0·1603 AgBr.   Br = 31·50.
$$C_9H_{16}ONBr \text{ requires } Br = 34·18 \text{ per cent.}$$
$$C_9H_{16}ONBr,H_2O \quad ,, \qquad Br = 31·74 \quad ,,$$

An attempt to prepare the hydrobromide by dissolving the amide in more concentrated acid (sp. gr. 1·83) resulted in the production of *iso*lauronolamide. The clear solution in the acid deposited lustrous, colourless crystals melting indefinitely between 70° and 80°, and yielding *iso*lauronolamide and hydrobromic acid on treatment with water, which first converts the crystals into an oil; *iso*lauronolamide itself yields similar crystals under the influence of the concentrated acid, the product consisting most likely of an unstable salt.

Dibromide of Infracampholenamide, $C_9H_{15}ONBr_2$.—Ten grams of the amide were dissolved in dried chloroform, cooled in a freezing mixture, and treated with 10 grams of bromine (1 mol.) in the same solvent, the halogen being added in small quantities at a time; the bromine was immediately decolorised, and no hydrogen bromide was liberated. On evaporating the chloroform, colourless crystals were deposited, and the product was filtered from a small quantity of oil, washed with chloroform, and recrystallised from boiling ethyl acetate, which deposited it in white needles melting at 114°.

0·2148 gave 0·2435 AgBr.   Br = 48·33.
0·2660 ,,   0·3017 AgBr.   Br = 48·26.
0·3321 ,,   13·1 c.c. of nitrogen at 20° and 762 mm.   N = 4·47.
$$C_9H_{15}ONBr_2 \text{ requires } Br = 51·12; N = 4·60 \text{ per cent.}$$
$$C_9H_{15}ONBr_2,H_2O \quad ,, \qquad Br = 48·34; N = 4·23 \quad ,,$$

The dibromide is insoluble in petroleum, but dissolves readily in alcohol, and is very freely soluble in water, forming a neutral solution from which it crystallises in white prisms; the aqueous liquid precipitates silver bromide from the nitrate, but does not liberate iodine

from potassium iodide, even when acidified with dilute sulphuric acid. It is indifferent towards a neutral solution of potassium permanganate, but in presence of dilute sulphuric acid bromine is liberated, and the permanganate decolorised.

Aminoinfracampholene, $C_8H_{13} \cdot NH_2$.

Ten grams of purified infracampholenamide were finely powdered and suspended in 25 c.c. of water; 10 grams of bromine were then dissolved in 100 c.c. of water containing 10 grams of caustic soda, and added to the amide. On gently warming the liquid, a basic odour became perceptible in a few minutes, and an oil rose to the surface. After about an hour, during which period the liquid was agitated, and at intervals gently heated, the base was extracted with ether, washed several times with water, and after removing the ether on a water-bath, distilled in an atmosphere of steam. The colourless oil obtained in this manner was collected by ether, dried with solid potash, and freed from ether on the water-bath. The yield amounted to 4 grams, and might possibly be augmented by manipulating smaller quantities of the amide at one time, because an experiment in which 25 grams of material were employed yielded only 9 grams of base.

Aminoinfracampholene is a colourless, limpid oil having a pungent, somewhat pleasant odour, and boils at 158—160° under 754 mm. pressure; it has a sp. gr. 0·8770 at 14°, and refractive index μ_{N_a} 1·4748 at 19°. The base absorbs carbon dioxide readily from the air, forming a crystalline carbonate.

The *hydrochloride* is readily soluble in cold water, and crystallises in lustrous leaflets melting at 213°.

The *platinichloride* separates immediately in pale red crystals on adding aqueous platinic chloride to a solution of the hydrochloride in water. It dissolves very freely in hot alcohol, and crystallises in beautiful, lustrous, pale red leaflets.

0·1528 gave 0·0450 Pt.   Pt = 29·45.

$(C_8H_{15}N)_2, H_2PtCl_6$ requires Pt = 29·48 per cent.

The salt darkens at about 200°, and melts to a charred mass at 238—240°.

The *picrate* crystallises in clusters of sulphur-yellow needles on adding to the base a hot solution of picric acid in alcohol.

0·2452 gave 33·8 c.c. of nitrogen at 18° and 752 mm.   N = 15·75.

$C_8H_{15}N, C_6H_3O_7N_3$ requires N = 15·82 per cent.

It melts at 213° to a deep brown liquid which soon begins to evolve gas.

The *benzoyl* derivative is very readily soluble in ethyl acetate

and in alcohol, crystallising from the latter in rosettes of long, slender prisms melting at 105° ; it is sparingly soluble in boiling petroleum, from which it separates in lustrous, silky needles which melt also at 105°.

0·1672 gave 0·4631 CO_2 and 0·1225 H_2O. $C = 75·54$; $H = 8·14$.
$C_{15}H_{19}ON$ requires $C = 75·31$; $H = 7·95$ per cent.

The *carbamide* derivative is not precipitated immediately on mixing moderately concentrated solutions of the hydrochloride and potassium cyanate, but soon crystallises when the liquid is heated on the water-bath ; it forms lustrous, white needles melting at 182°.

0·1658 gave 24·5 c.c. of nitrogen at 17·5° and 756 mm. $N = 17·01$.
$C_9H_{16}ON_2$ requires $N = 16·66$ per cent.

The *phenylcarbamide* derivative separates in aggregates of flat, lustrous needles on adding a solution of phenylcarbimide in a mixture of ether with petroleum to a solution of the base (1 mol.) in ether.

0·1831 gave 0·4920 CO_2 and 0·1357 H_2O. $C = 73·28$; $H = 8·23$.
$C_{15}H_{20}ON_2$ requires $C = 73·77$; $H = 8·19$ per cent.

The substance crystallises from alcohol in very long, flat, transparent needles and melts at 180°.

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