

XXVI.—*Researches on Pelargonic Acid.*

BY M. AUGUSTE CAHOURS.

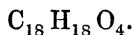
(LETTER TO DR. A. W. HOFMANN.)

The action of nitric acid on the essential oil of rue gives rise to several homologous acids. The first term of this series, to which I have given the name *Rutic acid*, only differs from the oil itself by containing two equivalents of oxygen more: the latter stands, therefore, to the former in the relation of an aldehyde. The action of nitric acid, however, is not confined to a simple oxidation of the essential oil; according to the duration of the action, $(C_2 H_2)$, $2 (C_2 H_2)$, $3 (C_2 H_2)$, are successively oxidized,—pelargonic, caprylic, and cœnanthylic acids, and probably other more simple terms of the same series being formed. It is evident that, in employing commercial acid, and allowing it to act for some time on the oil, several of these products are finally obtained, the one predominating over the others according to the duration of the reaction.

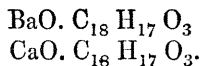
Pelargonic acid being the one least known of this group, and being also obtained the most plentifully from oil of rue, I turned my attention to it in preference; its study has furnished me with the following results:

Pure pelargonic acid is colourless, assuming an amber tint after a time. It boils steadily at 260° , and distils without undergoing alteration or change of colour, if the precaution be taken to perform

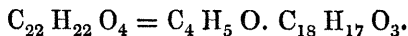
the distillation in an atmosphere of carbonic acid. The analysis of several specimens has furnished me with numbers leading to the formula,



This acid forms soluble and crystallizable salts with potassa, soda and ammonia. With baryta and strontia it yields salts slightly soluble in water and soluble in boiling alcohol, from which solution they separate on cooling in the form of crystalline scales of nacreous appearance. The analysis of these salts led to the formulæ,



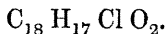
If a current of hydrochloric acid gas be passed into an alcoholic solution of pelargonic acid, an amber-coloured oil soon separates and floats on the surface; this oil, treated with a solution of carbonate of soda, washed with pure water, dried over chloride of calcium, and distilled, is obtained as a colourless liquid, the density of which is 0.86; its boiling-point is between 216° and 218° . The analysis of this product led to the formula,



On ebullition with a concentrated solution of caustic potassa, alcohol and pelargonic acid are reproduced.

Pentachloride of phosphorus acts very violently on pelargonic acid, hydrochloric acid gas being abundantly evolved; if the experiment be performed in a distilling apparatus, a colourless limpid distillate is obtained, which contains a large quantity of oxychloride of phosphorus; on re-distilling this product and rejecting the portion which passes over before the temperature becomes stationary, a limpid liquid is obtained as the latter portion of the distillate, which is heavier than water and boils at 220° . This liquid which gives off dense fumes when exposed to the air, and has a very powerful odour, evolves much heat when brought in contact with alcohol, pelargonic ether being formed.

The analysis of this product led to the formula,



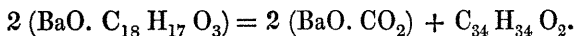
It is, therefore, the *Chloride of Pelargyl*.

Pelargonate of baryta is decomposed by dry distillation, a residue of carbonate of baryta being obtained, a brownish oil collecting in the receiver, which solidifies on cooling. This substance, when pressed between bibulous paper, yields a solid product easily soluble in ether. The ethereal solution, submitted to spontaneous

evaporation, deposits large crystalline plates, assuming a nacreous appearance on desiccation. This product, submitted to analysis, yielded numbers coinciding with the formula,



This substance is, therefore, *Pelargone*, isomeric with margaric aldehyde. Its formation is explained by the following equation :



Pelargone is violently attacked by fuming nitric acid, a nitrogenous acid being formed, which is doubtless a homologue of that obtained by the similar treatment of butyrene.

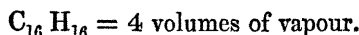
If we assume that the action of an excess of alkaline base, at a high temperature, on the acids of the acetic series, give rise to phenomena similar to those observed with benzoic acid or acetic acid itself, we should expect to obtain, by the distillation of pelargonic acid with an excess of potash-lime, either the valyl of Kolbe, or a compound isomeric with it; this presumption is not however, confirmed by experiment.

On submitting a mixture of pelargonic acid with from four to five times its weight of potash-lime to a temperature nearly approaching a dull red-heat, a large quantity of gas is disengaged, some volatile products are condensed and a residue of partially carbonated alkali is obtained. On passing the gas into bromine, a portion is absorbed, and the rest passes through unaltered. The portion absorbed by the bromine forms with this substance a very dense liquid, which, when treated with a very weak solution of potassa in order to remove the excess of bromine, yields an amber-coloured heavy liquid, consisting of three different substances; the one boils at 130° , and crystallizes when the vessel containing it is immersed into powdered ice, this is *Dibromo-mylene* $\text{C}_4 \text{H}_4 \text{Br}_2$; the second boils at 143° to 144° , and is the *Dibromo-propylene* $\text{C}_6 \text{H}_6 \text{Br}_2$; the third, which boils at 160° , is *Dibromo-butylene* $\text{C}_8 \text{H}_8 \text{Br}_2$. The first and particularly the latter of these substances, are present in very small quantity compared to the propylene-compound.

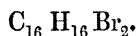
The liquid product of this reaction is of a complex nature, the larger portion boils between 105° and 110° ; the latter portion distils at 136° .

Several analyses made with different specimens of the liquid, which boiled between 106° and 110° , have given me, as a mean, 84.9 of carbon and 14.8 of hydrogen, that is to say, more hydrogen and less carbon than in olefant gas; the idea naturally suggested itself that this liquid might be a mixture of valyl and of a hydrocarbon of the series

$C_n H_n$, having a very proximate boiling-point; some experiments, however, soon convinced me of the absence of valyl, this liquid being violently attacked by some reagents that have no action on valyl. The vapour-density of this substance was found to be 3.98, which leads to the formula,



This substance, therefore, would appear to be a hydrocarbon, homologous to olefiant gas, mixed with a small quantity of foreign matter. When treated with bromine it evolves heat, yielding a liquid having an aromatic odour. The analysis of this liquid yielded numbers leading to the formula,



The gas which is not acted on by bromine consists of hydrogen and another gas containing carbon, which is probably marsh-gas. The deportment of pelargonic acid accordingly differs in this instance essentially from that of its homologue, acetic acid; the carbon-hydrogen $C_{16} H_{18}$, which should be produced in this reaction, appears to be possessed of but little stability, splitting up, as it does, into hydrogen and marsh-gas.

It is probable that all the acids of the acetic series furnish analogous results. I have convinced myself that this is the case at least with caprylic and cœnanthylic acids.* I am just now studying ethalic and margaric acids with the same view.
