

XXIX.—*Researches on the Amyl Series.* By HENRY MEDLOCK, Esq.

Since the chemical nature of fousel oil, and its interesting relation to various other bodies, was first pointed out by the investigations of Dumas\* and Cahours,† this compound has been the subject of a great number of researches. Balard,‡ Krutzsch,§ H. Kopp,|| Kolbe,¶ Riecker,\*\* and various other chemists, have been successively engaged in its study; and it is to their labours that we are indebted for the knowledge of a considerable number of the derivatives of this important alcohol. Still, this series exhibits by no means the completeness which the corresponding methyl, and particularly the ethyl series, presents to us.

It was with the intention of filling up some of the existing blanks, that Dr. Hofmann invited me to undertake the examination of several of the derivatives of fousel oil.

It was my wish to have brought this investigation before the Society in a more complete form, but seeing in a recent number of the "Journal de Pharmacie"†† that M. O. Henry has announced an investigation in a similar direction, I hasten, in order to avoid collision, to publish those results which I have as yet obtained.

The original source of fousel oil, from which Dumas and Cahours were supplied with material for their investigations, was the alcoholic fermentation of potatoes; and hence the name potato oil, which has been given to this compound.

All the subsequent investigators appear to have worked on a similar product, with the exception of Balard, from whose paper we learn that the same substance exists in the inferior brandies prepared from wine. If, after the alcoholic liquors have passed over, the distillation of the cuticle of the grapes is continued for some time, an oily product is obtained, which, according to Balard's experiments, chiefly consists of œnanthic ether and fousel oil.

\* Ann. de Chim. et de Phys., Juillet, 1834.

† Idem, 3 sér. t. XII. p. 294

‡ Liebig's Annalen, Bd. LV. p. 166.

\*\* Jahrbuch der Pharmacie, Bd. XIV. p. 1.

† Idem, T. LXXV. p. 193.

§ Erdmann's Journal, Bd. XXXI. p. 1.

¶ Idem, Bd. LXV. 288.

†† October, 1848.

The substance which served for the preparation of my compounds, was procured from Mr. Bowerbank, who separates it in considerable quantity during the latter stages of the distillation of common corn spirit. I mention this fact because former investigations of fousel oil derived from this source (*Getreide-fousel oil*), have not exhibited the presence of amilic alcohol. Neither Mulder\* nor Kolbe,† who examined this kind of fousel oil, mention anything about the presence of this compound; it appears that these chemists have operated upon altogether a different product. The oily liquid occurring along with œnanthic acid, œnanthic ether (Mulder), and margaric acid (Kolbe), which they describe under the name of corn oil, exhibits in its composition (Mulder) no resemblance to the fousel oil of the potato fermentation; it is probable that they examined only the very last products of the distillation, collected after the amilic alcohol had passed over.

From the experiments which I am going to describe, it is evident that the fousel oil obtained in the distillation of spirit from barley is perfectly identical with potato oil. As obtained from the distillery, the oil still contains alcohol and water, but no other impurities. On rectification, it begins to boil at  $85^{\circ}$  ( $185^{\circ}$  F.); after about one-third has passed over, the ebullition becomes constant at  $132^{\circ}$  ( $269.6^{\circ}$  F.), the boiling point of pure hydrated oxide of amyl; at this temperature the whole of the remaining liquid distils. It was evident that the product did not contain any oil of a higher boiling point.

It remained, however, to ascertain the composition of the distillate which had been collected below  $132^{\circ}$  ( $269.6^{\circ}$  F.) Chemists are acquainted with a variety of cases in which, of late, butyric and metacetic acids have been observed as products of fermentative processes very similar to the acetic fermentation; these processes are, however, up to the present moment, by no means so well understood in their different stages as we understand the conversion of sugar into alcohol, or that of alcohol into acetic acid.

The remarkable parallelism which formic, acetic, metacetic, butyric, and valerianic acids present in all directions, render it, to a certain extent probable, that wherever we meet with these acids as products of fermentation, their formation is preceded by that of alcohols similar to pyroxilic spirit, alcohol, and fousel oil.

It appeared by no means improbable, that the first product of the distillation might contain the alcohol of metacetic or of butyric acid. In order to answer this question, to which my attention was

\* Liebig's *Annalen*, Bd. xxiv. p. 248.

† *Idem*, Bd. xli. p. 35.

particularly directed by Dr. Hofmann, I re-distilled the earlier distillates with particular care, removing the water by means of chloride of calcium, fractioning at intervals of five degrees, and separating the alcohol and fousel oil which came over in the beginning and at the end of the distillation. The result of repeated distillations of this kind, was the complete separation of this product into common alcohol and fousel oil, there being no other compound present.

I now proceed to the description of the compounds which I have prepared.

#### ACTION OF PHOSGENE GAS ON HYDRATED OXIDE OF AMYL.

*Carbonate of oxide of amyl.*—Chloro-carbonic ether obtained by Dumas\* in the reaction of chloro-carbonic acid (phosgene gas) on absolute alcohol, and urethane (carbamate of ethyl), produced by the subsequent treatment of the new ether with ammonia, are not yet represented in the amyl series. To the preparation of these my attention was first directed.

Fousel oil absorbs phosgene gas with great avidity, heat being evolved during the process; one gramme of fousel oil absorbed about one liter of gas.

When perfectly saturated, hydrochloric acid was abundantly evolved, the liquid assuming a rich amber colour and separating into two strata, the lower one consisting of a very small quantity of accidental water, strongly charged with hydrochloric acid.

The new compound floating on the surface was now mixed with nearly an equal volume of distilled water, which, after having been in contact with it for a quarter of an hour, was removed by means of a pipette. The water, although strongly impregnated with hydrochloric acid, had by no means removed the last traces of the gas; the compound was therefore left for some time in contact with protoxide of lead, and finally dried by means of chloride of calcium. On submitting the liquid to distillation, with the view of determining its boiling point, it became at once evident that it could not be heated without suffering decomposition; it blackened immediately, torrents of hydrochloric and carbonic acids being evolved, and the boiling point rapidly rising from  $150^{\circ}$  ( $302^{\circ}$  F.) to  $224^{\circ}$  ( $435.2^{\circ}$  F.), where it became perfectly stationary. To obtain the key to this peculiar decomposition, it was necessary to study the oily product which distilled during the evolution of carbonic and hydrochloric acids. This product, after another rectification, became a perfectly clear and transparent liquid, of an agreeable odour, very

\* Ann. de Chim et de Phys. t. LIV. p. 225.

different from the original odour of fousel oil that had been treated with phosgene gas; it had a specific gravity of 0.9144 at 15.5° (60° F.), and its constant boiling point at 224° (435.2° F.), indicated a definite compound.

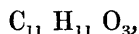
By combustion with protoxide of copper, the following results were obtained.

I.	0.2480	gram.	of substance gave
	0.5925	„	of carbonic acid and
	0.2458	„	of water.
II.	0.2158	„	of substance gave
	0.5165	„	of carbonic acid and
	0.2110	„	of water.

Per centage composition :

	I.	II.
Carbon . . . .	65.15	65.23
Hydrogen . . . .	11.01	10.87

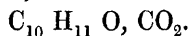
The simplest atomic expression for these numbers is the formula :



as may be seen from the following comparison of the theoretical values with the experimental results :

	Theory.	Mean of the experiments.
11 equivs. of carbon . .	66	65.15
11 „ of hydrogen . .	11	10.89
3 „ of oxygen . .	24	23.77
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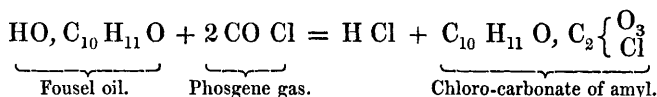
The new compound, then, is carbonate of oxide of amyl :\*



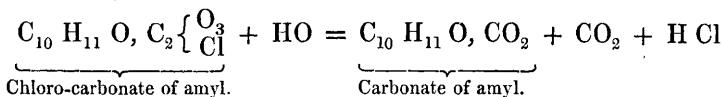
If the analysis had left a doubt regarding its nature, this would

\* The production of the carbonate of oxide of amyl, by means of phosgene gas, as described by Mr. Medlock, seemed to point out an easy method of obtaining the carbonates of the ethers in general. Chemists know the remarkable, but still somewhat mysterious process, by means of which the carbonate of ethyl was first obtained by Dr. Ettling, viz., by the action of potassium on oxalic ether (Liebig's Annalen, v. XIX. p. 17). The corresponding methyl compound has never been prepared. In order to see whether chloro-carbonate of methyl and of ethyl undergo a similar decomposition, I induced Mr. Charles Bloxam to study the action of water on these compounds. From these experiments it is evident this chloro-carbonate of ethyl is likewise acted upon by water, but too slowly to give a satisfactory method of preparing the carbonate. After four or five distillations with water, only a very small quantity of the chloro-carbonate is decomposed. The presence of bases destroys the compound altogether. It remains to be tried whether a different result might not be obtained by the action of water at a higher temperature under pressure.—DR. A. W. HOFMANN.

have been dispelled by its behaviour with the alkalis. When treated with an alcoholic solution of potash, the suffocating odour of fousel oil became at once perceptible, while the liquid solidified into a crystalline mass of carbonate of potash. The formation of carbonate of oxide of amyl admits of an easy explanation. The action of phosgene gas on fousel oil is perfectly analogous to that which it exerts on alcohol, hydrochloric acid and chlorocarbonate of amyl being formed.



The chloro-carbonate of amyl, however, is a compound of very unstable character; when brought into contact with water, it is decomposed into hydrochloric acid, carbonic acid, and carbonate of oxide of amyl.



The conversion of the chloro-carbonate into carbonate had evidently taken place chiefly during the washing of the compound with water. In a second operation, therefore, the washing was altogether omitted; nevertheless, on distilling the compound after removal of the hydrochloric acid by protoxide of lead, the same phenomena as before were observed. It was quite obvious that the accidental moisture,\* which cannot be well avoided, and the water formed in the conversion of protoxide of lead into proto-chloride, must have been sufficient to effect the decomposition. It is nevertheless probable, if not certain, that the chloro-carbonate exists, and may be obtained by a very careful exclusion of every trace of moisture. The powerful odour of fousel oil saturated with phosgene gas, having nothing in common with the suffocating odour of the latter, but closely resembling that of chloro-carbonic ether, appears in favour of this opinion, which is rendered still more probable by the behaviour of this crude product

\* Both the chlorine and carbonic oxide employed for the preparation of phosgene gas had been carefully dried by sulphuric acid; the bottles, with ground-glass stoppers, in which the gases were allowed to combine, were perfectly dry; the fousel oil, likewise, was absolutely anhydrous; nevertheless the oil, when nearly saturated with gas, separated always into two strata, of which the lower one was an aqueous solution of hydrochloric acid. It is evident that on pouring the fousel oil from one bottle of phosgene gas into another, a certain amount of moisture was attracted from the atmosphere, a quantity which must have been considerable, if we reflect that this operation had to be repeated from twenty-five to thirty times.

with ammonia. It is well known that the action of ammonia on chloro-carbonate of ethyl gives rise to the formation of the substance which Dumas, the discoverer, called urethane, and which we are now in the habit of considering as the ether of carbamic acid. If the crude product of the action of phosgene gas on fousel oil is treated with an alcoholic solution of ammonia, a white precipitate is formed, which consists of two substances, chloride of ammonium and a fatty crystalline organic compound, very similar in appearance to spermaceti. By washing with water, the former was dissolved, and the latter remained in a state of purity. Unfortunately, although working with considerable quantities, I did not obtain enough of this compound for combustion; but its comportment, as well as analogy, allows the conclusion, that it was the urethane of the amyl series, produced by the action of ammonia on the small quantity of undecomposed chloro-carbonate of amyl which the mixture might have still contained at that period. There is one objection which could be made to this supposition, viz., that we know from some experiments, which have been lately published by M. Cahours,\* that carbonate of ethyl, when treated with ammonia, yields likewise urethane. In our case, however, the carbonate could not have caused the formation of this compound. I have vainly tried to obtain it by digesting for weeks pure carbonate of amyl, with an aqueous as well as an alcoholic solution of ammonia, both of which have no action upon it whatever. The existence, however, of a chloro-carbonate of amyl is by no means established by the foregoing experiments. I intend to return to this question as soon as the weather will allow a rapid preparation of phosgene gas.

*Sulphocyanide of Amyl.*—The interest naturally attached to the sulphocyanides of methyl and ethyl, has of late been considerably increased by their conversion into hyposulphomethylic and hyposulphethylic acids by Dr. Muspratt.

The preparation of sulphocyanide of amyl is perfectly analogous to that of the corresponding ethyl and methyl compounds.

Two parts of sulphamylate of lime, intimately mixed with one part of finely-powdered sulphocyanide of potassium, were introduced into a retort capable of holding twice the amount of the mixture; on the application of heat, some water and fousel oil distilled over, possessing a very peculiar odour; on increasing the temperature, a considerable quantity of a reddish-yellow oil passed over, having the same remark-

\* Compt. rend. T. **xxi.** p. 629.

able odour. This oil is the sulphocyanide of amyl.\* The crude product was washed with distilled water, and subsequently digested with chloride of calcium, in order to remove the last trace of moisture, which it retains with great pertinacity. The anhydrous oil possesses the property of dissolving chloride of calcium in considerable quantity, from which it has to be separated by distillation.

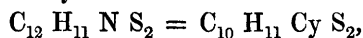
The anhydrous compound, when submitted to distillation, commenced boiling at 150° (302° F.), the thermometer continuing to rise to 195° (383° F.), at which point it became almost stationary, by far the greater part of the product distilling over at about this temperature. The latter portion, when re-distilled, boiled at the constant temperature of 197° (386·6° F.). The following analyses were made of the product collected at this temperature.

- I. 0.2816 grm. of sulphocyanide, burned in a tube containing oxide of copper, oxide of lead, and copper turnings, gave :  
 0.5748 grm. carbonic acid, and  
 0.2280 „ water.
- II. 0.2894 „ of sulphocyanide gave :  
 0.5914 „ carbonic acid, and  
 0.2320 „ water.
- III. 0.3195 „ of sulphocyanide, burned with soda-lime, gave :  
 0.5525 „ of the double salt of platinum and ammonium.

Per centage composition :

	I.	II.	III.
Carbon . . .	55.66	55.73	—
Hydrogen . .	8.99	8.90	—
Nitrogen . .	—	—	10.84

These numbers closely coincide with the formula :



as may be seen by the following table :

	Theory.		Mean of experiments.
12 eqs. of Carbon . . . . .	72	55.81	55.69
11 „ „ Hydrogen . . . . .	11	8.52	8.95
1 „ „ Nitrogen . . . . .	14	10.85	10.84
2 „ „ Sulphur . . . . .	32	24.82	—
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1 eq. of sulphocyanide of amyl . . . . .	129	100.00	

\* To avoid violent intumescence, the sulphamylate of lime and sulphocyanide of potassium should be dried as perfectly as possible.

This compound, when perfectly pure, has an oily appearance, and a slightly yellow colour, which becomes darker by keeping. It is miscible with alcohol and ether in all proportions, but separates again on the addition of water, in which it is nearly insoluble. Its boiling point is exactly  $197^{\circ}$  ( $386.6^{\circ}$  F.), which nearly corresponds with the temperature calculated from the boiling point of sulphocyanide of ethyl, as observed by Cahours.\*

$$146^{\circ} + 3 \times 19 = 203^{\circ}.$$

At  $15.5^{\circ}$  ( $60^{\circ}$  F.), the specific gravity of the sulphocyanide of amyl is 9381.1.†

#### ACTION OF NITRIC ACID ON SULPHOCYANIDE OF AMYL.

*Hyposulphamylic acid.*—Nearly equal parts of sulphocyanide of amyl and moderately strong nitric acid were introduced into a small retort, and distilled at a gentle temperature after the very violent action had ceased. In order to complete the re-action, nitric acid must be occasionally added, and the distillate returned to the retort, until the whole of the sulphocyanide has disappeared. In this process, carbonic acid, nitrogen, binoxide of nitrogen, and nitrous acid, are abundantly evolved; sulphuric acid likewise is formed by the oxidation of a portion of the sulphur; the quantity, however, of this acid greatly varies with the strength of the nitric acid employed; if moderately dilute, scarcely a trace of it is produced, but on the contrary, if fuming acid be employed, a dense precipitate of sulphate of baryta is obtained by the addition of chloride of barium; as soon as the action had entirely ceased, the liquid was evaporated on a water-bath until the nitric acid was expelled; a reddish oily fluid remained, possessing a pungent alliaceous odour and a hot acrid taste. It was then treated with water, in which it readily dissolved, filtered, and again evaporated. The liquid was thus freed from the last traces of nitric acid, and rendered almost colourless. In order to obtain the acid in a state of perfect purity, I prepared the lead-salt by saturating an aqueous solution with the carbonate of that metal. After treating the solution with hydrosulphuric acid, filtering, and careful evaporation on a water-bath, until the last traces of hydrosulphuric acid were expelled, the pure acid remained as a colourless oily liquid, which, when exposed in vacuo over sulphuric

\* Ann. de Chim. et de Phys. 3 sér. T. XVIII. p. 257.

† Sulphocyanide of amyl, although in an impure state, has been likewise obtained by M. O. Henry, who analysed a product boiling between  $195^{\circ}$  ( $383^{\circ}$  F.) and  $211.1^{\circ}$  ( $412^{\circ}$  F.), which yielded, on combustion, one per cent of carbon above the theoretical proportion.—*Journal de Pharmacie*, Oct. 1848.



acid, gradually became a granular crystalline mass, attracting moisture, and liquefying immediately on exposure to the air.

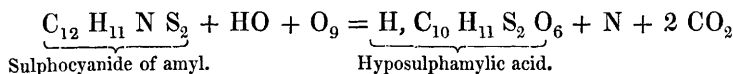
Hyposulphamylic acid, for this is the compound in question, cannot be heated without suffering decomposition; it evolves a very disagreeable odour, a charred mass remaining behind.

The formula for hyposulphamylic acid, as resulting from the analysis of its salts, is :

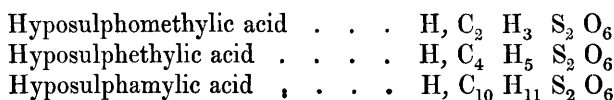


It accounts easily for the formation of this compound, the sulpho-cyanogen being decomposed under the influence of nitric acid the sulphur is oxidized and the cyanogen evolved in the form of nitrogen and carbonic acid.

The following equation represents this decomposition :



Hyposulphamylic acid corresponds to hyposulphethylic and hyposulphomethylic acids lately obtained by Dr. Muspratt\* by analogous reactions, the latter having been previously obtained by Dr. Kolbe† as a product of the metamorphosis of chloro-carbo-hyposulphuric acid, when under the influence of galvanic electricity.



I have examined the compounds of hyposulphamylic acid with barytes, with protoxide of copper and protoxide of lead.

*Hyposulphamylate of Barytes.*—This salt is obtained by saturating an aqueous solution of the acid with carbonate of barytes; when perfectly neutralized, the filtered liquid is slowly evaporated on a water-bath, and allowed to crystallize. This salt is extremely soluble, both in water and alcohol, and can be obtained in well-formed crystals only by allowing the aqueous solution to evaporate spontaneously, when brilliant pearly scales are deposited.

I. 0.4880 grm. of the salt, dried at 100° (212° F.), gave :

0.4915 „ carbonic acid = 27.46 per cent. of carbon,

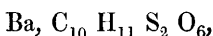
0.2295 „ water = 5.22 „ of hydrogen.

II. 0.3015 „ of the salt gave 0.1594 sulphate of barytes = .1170 grm. barium.

\* Quarterly Journal of the Chemical Society, vol. i. p. 45.

† Memoirs of the Chemical Society, vol. II. p. 360.

These numbers lead to the formula :



as may be seen from the following table :

	Theory.	Experiment.
10 eqs. of Carbon . . . . .	60	27.46
11 „ „ Hydrogen . . . . .	11	5.22
2 „ „ Sulphur . . . . .	32	14.56
6 „ „ Oxygen . . . . .	48	21.88
1 „ „ Barium . . . . .	68.64	31.11
1 eq. of Hyposulphamylate of Barytes	219.64	100.00

I have determined the amount of water lost at 100° (212° F.); it is much less than one equivalent, showing that the salt is anhydrous.\*

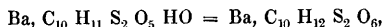
*Hyposulphamylate of Copper.*—It is difficult to obtain this salt in well-defined crystals; the best method, however, of preparing it, is to saturate an aqueous solution of the acid with carbonate of copper, to evaporate the filtered solution on a water-bath, to dryness, and to treat the residue with absolute alcohol. The filtered solution deposits minute crystalline plates, when allowed to evaporate spontaneously in narrow tubes.

- I. 0.4960 grm. of the dried salt, burned with chromate of lead, gave :  
 0.5936 „ carbonic acid = 32.63 per cent. carbon,  
 0.2754 „ water = 6.16 per cent. hydrogen.  
 0.3970 „ of the dried salt gave : 0.863 grm. oxide of copper  
 = 17.33 per cent. copper.

These numbers lead to the formula :



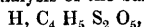
\* The acid prepared by Mr. Medlock is evidently identical with the compound which Messrs. Gerathewohl and Erdmann<sup>(1)</sup> obtained as a product of the decomposition of the mercaptan of the amyl series by means of nitric acid, although these chemists adopt a different formula for that compound. The formula which they give for the barytes salt of their acid is :



differing from Mr. Medlock's formula :



by one equivalent of hydrogen. In four hydrogen determinations, however, a deficiency was found, oscillating between 0.2 and 0.4 per cent., whilst our analyses generally give a slight excess. A similar objection can be made to the analysis of several salts of the acid, obtained by the action of nitric acid on the mercaptan of the ethyl series. It would be interesting to repeat the analysis of the barytes-salt, on which the formula



assigned to this acid, is principally founded. It is very probable that the opinion of M. Gerhardt respecting it will prove correct.—Dr. A. W. HOFMANN.

<sup>(1)</sup> Erdmann's Journal, vol. xxxiv. p. 447.

as the following comparison will show :

	Theory.	Experiment.
10 eqs. of Carbon . . . . .	60	32.63
11 „ „ Hydrogen . . . . .	11	6.16
2 „ „ Sulphur . . . . .	32	—
6 „ „ Oxygen . . . . .	48	—
1 „ „ Copper . . . . .	31.66	17.33
1 „ „ Hyposulphamylate of Copper	182.66	100.00

The salt does not contain any water of crystallization.

*Hyposulphamylate of Lead.*—This salt is prepared in the same manner as the preceding; it is extremely soluble in water, and may be obtained in beautiful satiny needles by allowing an aqueous solution to evaporate spontaneously. When heated, it is decomposed, evolving a most disagreeable odour, sulphide of lead remaining.

I. 0.5690 grm. of the salt, dried at 100° (212° F.), and burned with chromate of lead, gave :

0.4936 „ carbonic acid = 23.65 per cent. carbon,  
0.2168 „ water = 4.23 „ hydrogen.

II. 0.3340 „ of the dried substance gave :

0.1986 „ sulphate of lead = 40.63 per cent. lead.

These numbers lead to the formula :



as may be seen by the following table :

	Theory.	Experiment.
10 eqs. of Carbon . . . . .	60	23.65
11 „ „ Hydrogen . . . . .	11	4.23
2 „ „ Sulphur . . . . .	32	—
6 „ „ Oxygen . . . . .	48	—
1 „ „ Lead . . . . .	103.56	40.63
1 „ „ Hyposulphamylate of Lead . .	254.56	100.00

This salt is likewise anhydrous.

The following table includes the salts of hyposulphamylic acid, which I have analysed :

Barytes salt . . .	Ba, C <sub>10</sub> H <sub>11</sub> S <sub>2</sub> O <sub>6</sub>
Copper „ . . .	Cu, C <sub>10</sub> H <sub>11</sub> S <sub>2</sub> O <sub>6</sub>
Lead „ . . .	Pb, C <sub>10</sub> H <sub>11</sub> S <sub>2</sub> O <sub>6</sub>

I have prepared various other compounds of the amyl series, but their analyses not being yet complete, I refrain from entering into details. I may, however, mention that I have studied the action of

potassium on cyanide of amyl, and that of chloride of zinc on fousel oil. In the former process, simultaneously with a gaseous product, a beautiful organic alkaloid, corresponding to kyanethine, is formed. In the latter I have obtained the liquid hydrocarbons of M. Balard, accompanied by a gaseous carbo-hydrogen, of the same composition as olefiant gas, the production of which has not been observed before. The description of these compounds I shall shortly communicate to the society.

I cannot conclude without expressing the great obligation I am under to Professor Hofmann for his valuable aid and unremitting attention during the prosecution of my experiments.