ON VALERIANIC ACID,
AND A
NEW SUBSTANCE PRODUCED FROM CASEINE,
AND ON
VINOUS FERMENTATION.

By BARON LIEBIG,
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Mix thoroughly pressed cheese, prepared from fresh or curdled milk, and freed as much as possible from adherent particles of butter, with an equal weight of hydrate of potass (or highly concentrated hot solution of potass); melt the mixture by the application of heat, and keep it in this state of fluidity until hydrogen gas begins to be evolved, and also ammonia; dissolve the mass now in hot water, super-saturate the solution slightly with acetic acid, filter, and allow the filtrate to cool, when a mass of very fine needles will separate. This mass is very difficultly soluble in cold water, and absolutely insoluble in alcohol and ether; by repeated solution in water slightly mixed with carbonate of potass, and subsequent reprecipitation with acetic acid, the substance of which this mass consists is obtained in crystalline needles of a pure white colour and silky lustre.

The composition of this substance is expressed by the formula $C_{16}H_{19}O_5$; the analyses, however, from which this formula results, require confirmation. This substance, although readily soluble in alkalies, combines with acids; the mother liquor from which it is crystallized yields subsequently, upon further evaporation, a copious amount of LEUCINE.

If the melted mass is super-saturated with tartaric acid instead of acetic acid, and the fluid is subsequently subjected to distillation, a distillate of an acid re-action is obtained; upon saturating this with water of barytes, evaporating the mixture to dryness, and distilling the dry barytes salt in conjunction with phosphoric acid, a colourless, oily acid, and an aqueous acid fluid, possessing the odour, and all the properties of valerianic acid, are produced. Leucine, when fused with hydrated potass, yields ammonia and hydrogen gas, and the residue contains valerianate of potass. The formation of valerianic acid, upon melting caseine with potass, seems, accordingly, to be preceded by that of leucine. Except one equivalent of hydrogen, the formula of leucine expresses the composition of an ether, which consists of one atom of cyanic acid, one atom of oxide of amyle, and two atoms of water. The transmission of the vapour of hydrated cyanic acid through anhydrous fousel oil, causes the formation of a solid crystalline substance, soluble in water and ether; this substance crystallizes readily from aqueous and ethereal solutions, and bears in its external appearance the very closest resemblance to leucine; its solubility in ether, however, distinguishes it from the latter substance.

Long protracted melting of the mixture of caseine with hydrated potass causes the formation of a copious amount of butyric acid by the side of valerianic acid. The salt of silver prepared with the oily valerianic acid produced from caseine, left, upon combustion, 51.62 of silver; this removes all doubt regarding the identity of this oily acid with the common valerianic acid. The crude distillate contained, besides valerianic acid, a volatile substance exhaling the odour of human excrements; this substance reduced nitrate of silver to the metallic state, but it contained no formic acid; the alkaline solution yielded a copious crystallization of oxalate of potass, previously to the super-saturation with tartaric acid.

M. Mulder states, that while acting with potass upon albumine, he obtained two greasy, syrupy substances, which he denominates protide, and erythroprotide. I did not observe the formation of any such substances by the action of potass upon caseine, nor do I believe that either M. Mulder himself or any other chemist will ever produce them again of the same composition which he assigns to them. These substances are simply a mixture of intermediate products, the composition of which alters according to the different state of the temperature, the duration of the action of the alkali upon the albumine or caseine, the concentration of the alkaline solution, &c.

ON VINOUS FERMENTATION.

At page 45 of Vol. xxxvi., No. 1, of Erdmann and Marchand's *Journal of Practical Chemistry*, there occur the following remarks on Subfermentation of Wine, by Dr. Schubert, of Würzburg:—

"Babo communicated to the assembly of German vine and fruit growers at Treves, (1843,) that since 1841 he had applied the subfermentation method to red wines, with excellent success; and that he thought the same method might be applied, with equal success, to white wines.

"I resolved to test Babo's conclusion by experiment; for although in practical matters of this description experiments on a large scale are unquestionably preferable to minute chemical ones, yet the omission of comparative experiments is a defect which cannot but impair the force of Babo's conclusions.

"I left a portion of white grape-must of 1844, to ferment in an open and shallow glass,* at a temperature little exceeding 46 degrees, (in the month of November;) an equal portion of the same must was left to ferment in a narrow-necked flask; but in all other respects in the same manner, and under the same circumstances, as the first portion.

"The deoxidizing action which the vegetable albumen exercises upon the other constituents of the wine, when the access of air is limited, was most strikingly apparent from the simple comparison of the colour of the two samples. The ruddy-brown colour of the must in the narrow-necked vessel had turned to an exceedingly pale yellow, whilst the must in the shallow basin exhibited the colour of beer, and did not bear the remotest resemblance to wine; moreover, the fluid in the shallow glass had deposited 1.10 per cent. of yeast; while that in the narrow-necked flask had deposited only 1.05 per cent. After the termination of the process, I filtered the wine fermented in the open and shallow glass; and upon tasting it, I found it so absolutely insipid and deficient in alcoholic flavour, that I thought distillation altogether useless. This insipidity surprised me the less, as I found that the fluid in the shallow and open vessel had lost 30 per cent. of its volume by evaporation; whilst that in the narrow-necked flask had lost only two per cent., although the fermentation in the former lasted only eighteen days, whilst the process in the latter occupied fifty days.

"In the month of December, I made a similar experiment with must prepared from black grapes. Although the product was in this instance superior to that obtained from the white grape must, yet the red wine produced by subfermentation became turbid in the month of May, and is now becoming acid.

"A wine-grower who lives in the vicinity of this town told me, that he made a similar experiment many years ago, and that the result was so decidedly bad as to deter him from making a second attempt.

"In my first experiment, moreover, the wine fermented in the open vessel, so far from having excreted the whole of its nitrogenous matter, deposited afterwards in a close vessel a considerable quantity of this matter in the course of a few weeks.

"It would be very desirable in future, that the results of experiments made on a large scale should be tested by comparative experiments on a small scale."

To these remarks of Dr. Schubert, I must add the following article, which appeared in the *Bavarian Messenger*, of Munich, of the 30th of November:—"Actual experiments soon proved that Liebig too often allows his skill and ingenuity in syllogizing to overstep all decent boundaries, and that he permits his chemical imagination to soar too boldly beyond the confines of chemical experience. Thus, he asserted, for instance, 'Beer is no aliment;' and this assertion was at once disproved by science, and refuted by the every-day experience of life in our own country. After this appeared another theoretical thesis of his, regarding the preparation of the second and more noble of our national drinks, wine—a thesis tending to level at one blow the practice of a millenium, and, withal, of such exceeding ingenuity and probability, that it seemed almost irrefutable. A valiant champion, however, arose and beat Liebig also out of this field, with the irresistible weapon of experience. The fact that the *objectum litis* is a home-grown and home-made product of our own country, and more still, the circumstance of the conqueror being a Bavarian citizen, induce us to mention this subject in our paper. The following are the circumstances of the case:—Liebig asserted that wine, if left to ferment in the same manner as beerwort is in Bavaria—viz., in wide and open vessels, and at a temperature not exceeding from 46.4 to 50°, instead of being fermented in the old manner—viz., at a higher temperature, and removed from the access of air,—will acquire in the shortest possible space of time the same maturity and quality which

* The depth of the fluid bore the proportion of 5 : 7 to the diameter of the surface.

it takes now several years to attain. Mr. Oppmann, Royal Cellar-master at Würzburg, has tested Liebig's theory by the most conclusive experiments, supervised and attested by the most competent authorities in this branch of industry. Mr. Oppmann treated portions of the same must respectively, according to the prescriptions of the old, and of Liebig's new method, and the result of his experiments has proved that Liebig's hypothesis is totally untenable, and that the old method is vastly superior to the new method proposed by this chemist; nay, the wine produced, according to Liebig's instructions, could not bear even the remotest comparison in strength, sugar, and flavour, with that prepared according to the old method. In communicating this to our readers, we cannot help expressing our pleasure and satisfaction at seeing a chemical fable, which, upon the *jurare in verba magistri* principle, was for a moment believed through the whole of Germany, refuted by one of our own countrymen in a manner so able and competent, and so far exceeding the scientific requirements of his station, as Mr. Oppmann has done, more particularly in the last number of Dingler's *Polytechnic Journal*."

I think that the interests of the wine-growers demand that I should offer a few remarks upon these strictures of Dr. Schubert, and of the *Bavarian Messenger*. No one will attempt to deny the very great improvements which have taken place in our own time in the fabrication of wine; very fine wines are produced now in parts which formerly sent only inferior sorts to the market; and extraordinary progress has been made in the choice of the various sorts of grapes respectively adapted for the particular climate of different places; and great improvements have been made also with regard to the cultivation of the vine, and the gathering and selection of the grapes; but with these improvements the vintner has hitherto rested perfectly satisfied. The must gained at so great an expenditure of capital and labour is simply poured into a tub, barrel, or pipe, and abandoned to fate, just as our ancestors did from time immemorial. Whilst all the other conditions upon which the production of a good wine depends are most carefully weighed and considered, the chemical process, by which the product thus improved by cultivation is actually transformed into wine, has been left in its originally imperfect state, although every one admits that the mode and manner of fermentation exercises the greatest influence upon the strength and quality of wine in general. I have called the attention of wine-growers to this defect, and have pointed out to them that the process of fermentation pursued at present is capable of great amelioration. I have endeavoured to induce the producer of wine to apply the sub-fermentation method, which yields such excellent results in the production of beer, to the fabrication of wine. In deciding a question of such vast importance, and which tends to produce a very material increase in the wealth and capital of many countries, it is a matter of perfect indifference whether certain experiments attempted by Mr. Cellar-master Oppmann, or Dr. Schubert, of Würzburg, have proved successful or not; the only point we have to look to is, whether the principle of the sub-fermentation method is correctly comprehended and determined. When this has been done, and when the wine-growers have taken lessons of the beer-brewer, and have clearly and correctly ascertained all the conditions required to produce beer of a superior quality, by the sub-fermentation method—then, but not till then, successful experiments can be expected to be made with wine-must. We must ascertain, first, in how far these conditions, access of air, temperature, size of the vessels, &c., are applicable to wine-must, and what modifications they will require, before we can proceed to form a safe and correct method of sub-fermentation as applied to must. Experiments made so slovenly and with such total want of knowledge as those of Mr. Oppmann and Dr. Schubert, ought not to discourage the more intelligent class of vintners; they ought to persevere in their endeavours to improve the process of fermentation.

Is it not quite absurd in Dr. Schubert to state that the wine which he left to ferment in an open vessel lost thirty per cent. (near one-third of its volume) by evaporation? As if the principle of the sub-fermentation method comprehended evaporation among its essential conditions! Had Dr. Schubert left the very best and oldest wine to evaporate in the air to the extent of one-third of its volume, surely the residue would have been no longer wine, but a stale and nauseous fluid. Leaving altogether out of the question here whether an aqueous and alcoholic fluid, of the strength of our ordinary wines, could possibly lose thirty per cent. of its volume by eighteen days' evaporation in the air, at a temperature of 46.4, unless a pair of bellows be put to work to aid the pro-

cess, I beg to ask Dr. Schubert why he did not use the very simple precaution of covering his fermenting vessel* with a piece of paper, which, whilst fully permitting the free exchange of the air and carbonic acid, would have prevented the profuse evaporation? Dr. Schubert's experiments prove one thing at all events—viz., that must, fermented at 46.4, does not turn acid, notwithstanding the very worst treatment. Had Dr. Schubert's must turned acid, how gladly would this gentleman have availed himself of this additional charge against the sub-fermentation method! *But his must did not turn acid.* Now this is a point of the very highest importance, and calculated to inspire vintners desirous of trying the application of the principle of this method with confidence, since the acidification of the must is the only event that could be apprehended in the case of very weak wines. I should like to know what results and conclusions Dr. Schubert would have arrived at had he tried his comparative experiment on the respective merits of the sub and super-fermentation methods with a quart of beer-wort, taken from one of the Würzburg breweries. I entertain hardly any doubt but that the results of his experiments, if made in the same manner as those which he made with the must, would have led him to pronounce the centenarian practice of the Bavarian brewers a downright absurdity, since, instead of beer, he would have obtained a stale residue, of disagreeable taste, and exceedingly deficient in alcohol.

About nine years ago, many hundred casks of beer, brewed after the Bavarian method at Giessen, and in many other places of the Grand Duchy of Hesse, turned acid, because our brewers were at that time not thoroughly versed in every detail of that method. However, none of them thought for a moment to impugn the Bavarian method, and to ascribe his failure, and consequent loss of money, to defects inherent in the principles of that method.

The writer in the *Bavarian Messenger* labours under a very great mistake if he supposes that it requires judgment, intelligence, and sagacity, to make experiments which *fail*; such *failures* as that of Mr. Oppmann prove the very reverse. It is rather strange that the said writer should consider it a matter of most triumphal congratulation, that Mr. Oppmann is really incapable of making experiments according to the rules of sound and scientific investigation; and Mr. Oppmann's Bavarian fellow-citizens have indeed no great cause to be particularly proud of their illustrious disprover of my *chemical fallacies*, although "competent authorities" may vouch for the perfect conclusiveness of his experiments and their results. All this is extremely pitiable, and affords a sad indication of the standing which these "competent authorities" occupy in science.

What we have principally to consider for the present, is to ascertain the conditions which the principle of the sub-fermentation method requires and demands; but not to make experiments at random. Everybody knows how a shoe is made by the shoemaker, and a coat by the tailor, and yet methinks that neither Dr. Schubert nor Mr. Oppmann could manage to make a pair of common slippers or an under vest.

How could these gentlemen expect successful results from their experiments, neither of them possessing the requirements indispensable to attain the end in view, at least their requirements and conditions are as yet not ascertained! What their experiments prove most strikingly is, not the fallacy or incorrectness of the principle, but simply this—that the manner in which they conducted their experiments is not correct, and that a very different way from theirs ought to be pursued. Even this is, of course, a gain for others desirous of trying the new method: nay, I verily believe, were I to give Messrs. Schubert and Oppmann a perfect and detailed method for the subfermentation of wine, (as I have not, nor could have done, since such a method does not as yet exist,) these gentlemen would fail. When a physician prescribes a mixture to a patient, and this mixture is prepared by a competent apothecary, and strictly according to the instructions of the physician, the effect produced upon the patient may be properly considered as a criterion of its efficacy: but if a patient altogether ignorant of the medical and pharmaceutical art should himself attempt to prepare the draught prescribed for him, would he be justified in impugning science, or clamouring against his physician, should the effect not answer his expectations? I have been invited by a great many vintners to their respective places, in order to make on the spot experiments which might lead to the discovery and establishment

* For which purpose he seems to have used a small glass, seven inches wide and five inches deep; such we are led to suppose, at least, from the circumstance of his making the counter-experiments with an equal volume of must in a narrow-necked flask.

of a correct sub-fermentation method, which, as I have said, does not at present exist. These gentlemen were willing to afford me every facility for conducting my experiments. I declined their offers, however, since it is not by any means my purpose to improve the wine of any individual proprietor, and moreover, because I thought I had a right to suppose that these gentlemen were themselves possessed of the knowledge and skill requisite for this purpose. But I see now that clear-headed and unprejudiced men, animated by a sincere and earnest desire, and endowed with the intellectual capacity required for such an undertaking, are very rare.

The writer of the article in the *Bavarian Messenger*,—Counsellor Buchner, of Munich,—to judge from the style, feels highly gratified that my advice and propositions should have led to nothing in the hands of M. Oppmann. He should rather have wept with sorrow at this failure, if he had the true interests of the wine-growers and drinkers at heart.

At the termination of his article in *Erdmann and Marchand's Journal*, p. 47, Dr. Schubert favours us with a new method for the production of butyric acid. He recommends for this purpose to keep boiled potatoes or starch paste in contact with meat for the space of from five to six days. This sample is quite sufficient to indicate the extent of Dr. Schubert's chemical knowledge. I cannot comprehend how the editors of so esteemed a journal as that of Erdmann and Marchand could have consented to admit such gross and palpable nonsense into their columns. This method might serve to produce putrid meat, but certainly not butyric acid!

ON EPIDEMIC SCARLATINA.

By J. J. KELSO, Esq., M.D., Lisburn, Ireland.

(Read before the Belfast Medical Society.)

IN taking leave to submit to the notice of the Society the following account of an epidemic of scarlatina which recently prevailed to a very great extent, under a rather severe and fatal form, in Lisburn and the neighbouring country, as well, I believe, as in several other towns and places in this part of Ulster, I shall content myself by simply advert to some of the more prominent or important features which characterized its history, pathology, and phenomena, together with some of its commonest sequelæ, observing, at the same time, all the brevity consistent with perspicuity. The facts or observations, many of them, which I am about to mention, are not put forward as presenting, in themselves, much that is very peculiar or novel; yet they may prove not altogether uninteresting or devoid of some degree of practical value. These observations, it is but right here to add, have reference more particularly to 200 odd cases of the disease of which memoranda of some kind have been preserved; but that many of these are defective in more or fewer particulars of interest in elucidation of its history, character, and progress as influenced by treatment, and occasionally even the manner of its termination, it were in the last degree culpable, because in opposition to truth, not candidly and explicitly to avow. For instance, did a case terminate fatally,—and I have noted eight deaths,—no *post-mortem* examination could be obtained, for the prejudices of the great body of the people of this country against such a procedure in ordinary circumstances still remain, it is well known, quite unconquerable. Again, for reasons which it is unnecessary here particularly to mention, several of the cases were seen only once, and many not more than twice; in which case, as a matter of course, the after progress of the complaint, as affected by the treatment, could not be otherwise than very generally noted, on account of the very questionable evidence founded in report, granting such report, apart from its general accuracy, to have been always furnished, which it were out of common course almost for a moment to expect. I might, were it to serve any good purpose, easily add to these, other grounds of imperfection in the stock of materials which is to form the substantial part of this paper; but with all these many and important drawbacks, partly unavoidable and incidental to private practice, and in part dependent on personal oversight or carelessness in noting the particulars of cases as they were observed, I would fain hope and believe that the available portion which remains, if properly arranged and considered, will not prove altogether valueless, or unworthy some share of your attention.

However, in the beginning of March last, numerous cases of scarlatina began to present themselves, and before the end of the month, the disease had increased to such an extent, both in town and country, as properly to merit the designation of epidemic. But in the following months of April and May it raged most extensively, attacking not only the poorer

classes in society, but those in more comfortable circumstances; not only the young, but the middle-aged, and, in some instances, even the comparatively old. And although many cases have occurred since, and are indeed now and then still occurring, in the commencement of the latter half of June it began evidently to abate; thus extending altogether, it will be seen, over a period of at least three months. Now, the rather unusual period of the year at which the epidemic made its appearance, challenges here a passing remark. Referring to the common periods of such visitations, Dr. Tweedie says, "Although sporadic cases are met with at all seasons, it (scarlatina) is more prevalent at the end of summer, and in the autumn, than at other periods of the year. Epidemic visitations have been most frequently observed after a warm summer, especially when the heat has been accompanied with continued rains; and when the succeeding winter has been open and mild, the disease has continued till it has been checked by frost. It generally disappears in the spring months,* &c., &c." If this statement be regarded as the correct expression of the results of experience on the point in question, then, in the instance to which I am now taking the liberty of calling your attention, we discover a very remarkable exception. Nor, as intimately related to the appearance and history of this in common with that of all other epidemic visitations, should I omit a passing allusion to the kind of weather by which it was preceded and accompanied. Now the unusual mildness of the last winter season, in this country at least,—during which, by the way, fever of the common continued type prevailed to a great extent in and about Lisburn,—must be in the recollection of you all. March, however, was generally a very severe month; the weather, though dry, being cold and blowing, accompanied almost throughout by intense frost; April was characterized by a greater degree of mildness; and May, the latter part of the month especially, was genial, if not fine, calling into renewed life and activity the different families of the insect as well as those of the vegetable world.

It may not, perhaps, be out of place here, to remind the Society that scarlatina has been regarded very differently by different writers, and a corresponding difference has, as a matter of course, obtained in their descriptions of it. Thus, by the great majority of authors, from Sydenham down to our own times, the more common outward and cognizable symptoms, peculiar as they are, of the affection, have been considered in their ever-varying occurrence, degrees of development, or intensity and virulence, as constituting the essential elements in the chain of morbid actions which go to form the disease; and, in conformity with this view, they are adopted as the basis of arrangement into the several species or varieties under which it has now so long been contemplated. Consistently with this symptomatological arrangement, the disease will be found, as is known, to include these different species, or rather varieties, which I put down as they occur in books:—1. Scarlatina simplex; 2. Scarlatina anginosa; 3. Scarlatina maligna. To which Dr. Tweedie, with equal propriety, has added, 4. Scarlatina faucium.

But, on the other hand, this description of classification, however convenient it may be in some respects, is strongly and not unreasonably objected to by some, as not springing from a consideration of the pathological conditions of certain of the internal vital organs and functions which the disease, in common with the other eruptive as well as non-eruptive fevers, necessarily involves in some degree, and which of right, they contend, should exclusively be regarded in any divisional distribution it may be thought advisable to frame, as most conducive to a proper exposition of the subject. Among the ablest advocates, perhaps, of this particular view, which, at least, it must freely be conceded, is by far the more scientific of the two, are Dr. Hamilton, sen., and Dr. Mackintosh, the latter of whom, in quoting the following passage from the former, adopts it to the very letter:—"It is altogether foreign to my purpose to engage in this controversy, and more so, as the distinction begins to lose ground as our knowledge of the disease becomes more comprehensive and accurate. The time may not be far distant when scarlatina will be received as the generic disease, the full history of which will include the more aggravated symptoms as they occur in scarlatina anginosa and in cynanche maligna, in the same manner as the history of variola comprehends the varieties of the distinct and confluent small-pox."† In consonance with this fundamental position, scarlatina, in common with the other exanthemata, has been regarded as consisting of two great varieties, which have been

* Cyclopædia of Practical Medicine, vol. iii. p. 643.

† Practice of Physic, vol. i. p. 184. Fourth Edition.