Although negative results are seldom published, there can be little doubt that Nilson and Pettersson also obtained results entirely similar to those of Pollok but soon found the true explanation. They claimed that beryllium chloride also attacked glass, but overcame both difficulties sufficiently for vapor density determinations in one of their best researches, "Ueber ein neues mit exacter Temperature Bestimmung verbundènes Verfahren zur Festellung der Dampfdicte fleuchtiger Korper[1], which is, unfortunately, too little quoted. There can be no question that they and other investigators of the atomic weight of beryllium would have used the chloride but for the extreme difficulties of its manipulation which, unconquered, always lead to results tending in the same direction as those of Pollok.

NEW HAMPSHIRE COLLEGE,
DURHAM, N. H., Feb. 1, 1905.

A CORRECTION.

BY WILLIAM A. NOYES AND HOWARD W. DOUGHTY.[2]

Received February 1, 1905.

SOME time ago one of us[3] effected the synthesis of what were supposed to be β,β-dimethyladipic acid and α,β,β-trimethyladipic acid. Recently Blanc[4] has prepared the former acid by a method which seems not likely to involve a molecular rearrangement, but has found the properties of his acid radically different from those of ours. He has been kind enough to call our attention to the difference and to suggest that the formation of our acid may have been accompanied by a molecular rearrangement.

On examination of the literature the close agreement between the melting-point of the acid which one of us has described as β,β-dimethyladipic acid and the melting-point of β-isopropylglutaric acid,[5] and also the agreement between the melting-point of the acid which was described as α,β,β-trimethyladipic acid and that of cis-α-methyl-β-isopropylglutaric acid[6] was noticed. The β-isopropylglutaric acid might have been formed in our synthesis as follows: The chlorisocaproic ester,

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[1] *J. prakt. Chem.* (2), **33**, 1.

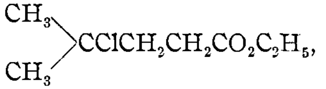
[2] The work here described was carried out with the aid of the Carnegie Institution.

[3] This Journal, **23**, 392 (1901).

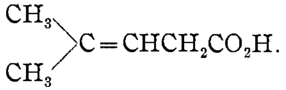
[4] *Compt. Rend.*, **139**, 800.

[5] Howles, Thorpe and Udall: *J. Chem. Soc.*, (London), **77**, 942.

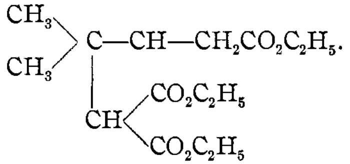
[6] *Ibid.*, **77**, 946.



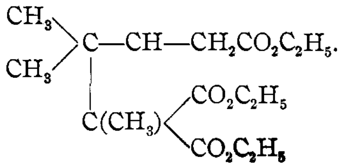
loses hydrochloric acid on boiling with the sodium malonic ester, giving pyroterebic ester,



The pyroterebic ester might then add the sodium malonic ester with the formation of the sodium derivative of the ester,



This ester on saponification and loss of carbon dioxide would give β-isopropylglutaric acid. On the other hand, if this ester were treated with sodium ethylate and methyl iodide, as was done in preparing the supposed α,β,β-trimethyladipic acid, it would give the ester,



This, on saponification and loss of carbon dioxide, would give α-methyl-β-isopropylglutaric acid.

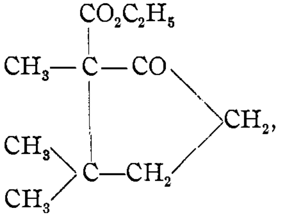
A sample of the supposed β,β-dimethyladipic acid had fortunately been saved from the previous investigation and we have now prepared from it the anhydride by treating it with acetyl chloride, as described by Howles, Thorpe and Udall.

The anhydride proved to be an oil, agreeing in this with the anhydride of β-isopropylglutaric acid, while our acid, if it were in reality dimethyladipic acid, should give no anhydride.

Our first attempt to prepare the anilic acid gave a compound which decomposed with charring at 250°. This may possibly have been the dianilide or the anil, as the material was overheated at one point in the preparation. On repeating the experiment, by mixing a solution of the anhydride in benzene with aniline the aniline salt of the anilic acid was obtained. After crystallization this melts at 124°. The analyses gave 8.14 and 8.16 per cent. of nitrogen; calculated for $C_{20}H_{26}O_3N_2$, 8.20 per cent. The anilic acid melted at 121°, as given by Howles, Thorpe and Udall.[1]

There is no doubt, therefore, that the acids which one of us formerly described as dimethyl- and trimethyladipic acids were in reality β-isopropylglutaric acid and α-methyl-β-isopropylglutaric acid. The acid which Blanc has described as β,β-dimethyladipic acid[1] is, doubtless, what he supposes it to be, while the pure α,β,β-trimethyladipic acid is still unknown.

It may be added that, after the work published four years ago had been completed, a year or more was spent in the endeavor to secure a synthesis of a derivative of camphor from the acid, which was then supposed to be the trimethyladipic acid. The synthesis is tedious, but about 5 grams of the pure acid were finally obtained. This was converted into the ethyl ester and an attempt was made to condense this to a derivative of trimethylcyclopentanone,



by heating it with sodium wire and toluene. This was unsuccessful, as was also an attempt to condense the ethyl ester of the supposed dimethyladipic acid in a similar manner. The cause of the failure is now apparent, but as no positive results were obtained, an account of that work has never been published.

At the time the possibility that the supposed dimethyladipic acid might be, in reality, isopropylglutaric acid was more than once considered, but the suspicion was always dismissed because of the successful synthesis of trimethylcyclopentanone[2] which

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[1] *Loc. cit.*

[2] *Am. Chem. J.*, **23**, 128; *Ber. d. chem. Ges.*, **33**, 54 (1900). In a paper published in 1903 (*Proc. Chem. Soc.* (London) **19**, 61; *Chem. News*, **87**, 140), W. H. Perkin and J. F. Thorpe stated in describing their synthesis of the α- and β-campholytic acids that their synthesis was the first of a compound containing the trimethylcyclopentane ring which is characteristic of camphor. I at once wrote to Professor Perkin reminding him of the synthesis which I had described more than three years before. He acknowledged my

had been effected with an acid prepared in a similar manner. It might seem, on a superficial examination, that the facts now given throw a doubt on the validity of that synthesis. On examining the account of the work it will be seen, however, that in that synthesis bromisocaproic ester was used instead of the chlorisocaproic ester employed in the later work; further, that the trimethyladipic acid used was not purified, but was mixed with lime and distilled in its crude form. In the subsequent purification of the ketone and its oxime the products derived from the methylisopropylglutaric acid, which was doubtless present, were separated and the pure oxime of trimethylcyclopentanone was obtained. The comparison of the oxime with that obtained from camphor, and especially the fact that mixtures of the two had the same melting-point as either alone, placed the fact of their identity beyond question.

It seems probable, too, that the dimethylcyancarboxethylcyclopentanone[1] and the dimethyldicarboxethylcyclopentanone,[2] described by one of us, have the structure which has been assigned to them. It is difficult otherwise to account for the products formed by their saponification.

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PHOSPHORIC ACID DETERMINATIONS BY THE METHOD OF IGNITION WITH MAGNESIUM NITRATE AND BY THAT OF DIGESTION WITH ACIDS.

BY B. L. HARTWELL, A. W. BOSWORTH AND J. W. KELLOGG.

Received January 4, 1905.

THE method described by A. Neumann[3] provides for the destruction of the organic matter by digesting the material in a Kjeldahl flask with a mixture of equal volumes of concentrated

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claim to priority and promised to correct the statement in his full paper, which was to appear later. When the full account of his work was published (*J. Chem. Soc.* (London) **85**, 128 (1904)) the erroneous statement referred to was omitted but no correction of the earlier statement was made. After further correspondence Professor Perkin has agreed that I shall publish the correction myself. W. A. NOYES.

[1] *Am. Chem. J.*, **22**, 260.

[2] This Journal, **23**, 326.

[3] *Archiv. of Anat. u. Physiol. Abth.*, 159 (1900); *Ztschr. physiol. Chem.*, **37**, 115 (1902-1903); *Ibid*, **43**, 32 (1904). See also E. Poher : *An. d. l. science Agronomique*, 2d ser. **8**, T. **2**, 441 (1902-1903).