

Citation:

H.J. Backer, On the nitration of methylurea, in:
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The newly found molar is most likely a third genuine molar of the left lower-jaw. It is much worn out by mastication, so that at

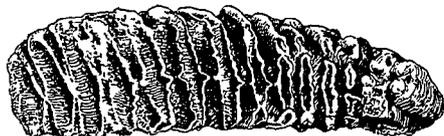


Fig. 1.

the frontal side a few lamillas have already disappeared. Extant are still $\frac{1}{2}$ 12x at $221 \times 68 \times 117$ mm. During the wearing-out mastication there are formed on each lamina first a median, tape-shaped and two lateral, ring-shaped figures, which remain a long time separated, but finally fuse into a distinctly rhombic figure, so that the mastication-figures of two succeeding lamellae touch each other in the middle. (fig. 1). The enamel is $2\frac{1}{2}$ —3 mm. thick and strongly plaited. The mentioned dimensions and characteristics are all extremely typical for *Elephas antiquus Falc.*

The molar was not much worn out and between the laminae it contained still a little ferruginous quartz-sand and some small pebbles of quartzite.

Much less typical is the remnant of mastication of another molar, belonging likewise most likely to *El. antiquus*. (fig. 2).

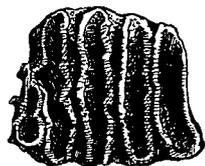


Fig. 2.

It contains still 4 laminae of 55×56 mm. and is most likely a fragment of a first genuine molar of the upper-jaw. The very strongly plaited enamel is 2— $2\frac{1}{2}$ mm. thick. The figures of mastication can hardly be called rhombic; we must however take into consideration that these figures lose their typical character in the same measure as a molar is worn out by mastication. This fossil cannot possibly belong to *El. primigenius*; on account of its narrowness the molar shows the greatest affinity with *El. atiquus*.

Chemistry. — “On the nitration of methylurea.” By Dr. H. J. BACKER. (Communicated by Prof. FRANCHIMONT).

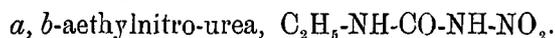
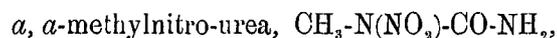
The behaviour of methylurea and of ethylurea on nitration is considered as a remarkable instance of the different influence which the methyl and ethyl group can exert on the properties of a compound.¹⁾

DEGNER and VON PECHMANN²⁾ have stated that with *methylurea* the nitration takes place at the *imino*-nitrogen atom, whereas according

¹⁾ DEGNER and VON PECHMANN, B. 30, 654 (1897). Also compare V. MEYER and JACOBSON's Lehrb. d. Org. Chemie I², 1394 (1913).

²⁾ B. 30, 652 (1897).

to THIELE and LACHMAN ¹⁾ *ethylurea* is nitrated at the *amino*-nitrogen atom. The nitration products thus should be :



It has now been found that the idea as to the nitration of methylurea is not correct.

D. and v. P. carried out the reaction by treating the sulphuric acid solution of methylurea at a low temperature with the theoretical quantity of ethyl nitrate. As products, they obtained methyl-nitramine and a methylnitro-urea melting with decomposition at 156—157°.

I have carried out the nitration in various ways, namely with the theoretical quantity of ethyl nitrate or absolute nitric acid in sulphuric acid solution, and also by introducing the nitric acid compound of methylurea into sulphuric acid. Invariably, a compound was obtained decomposing between 90 and 100° with evolution of gas and having the composition of methylnitro-urea; methylnitramine was not formed.

If this product is dissolved in cold aqueous ammonia and then mixed with dilute sulphuric acid, methylnitro-urea is precipitated, melting with decomposition against 159°.

D. and v. P. state that this compound is decomposed by ammonia at 100° and then yields methylnitramine; from this they conclude that it consists of α, α -methylnitro-urea.

It has now appeared, however, that this compound m.p. 159° is the α, β -methylnitro-urea; I have proved this structure firstly by reduction to the corresponding semicarbazide and further by studying the behaviour towards different bases.

a. Reduction. This was carried out electrochemically, because also in the non-substituted urea the electrical reduction gives far better results than the chemical one ²⁾. The operation took place in dilute sulphuric acid with a cathode of tinned copper gauze.

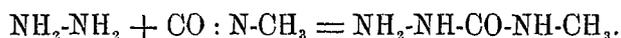
The generated product with benzaldehyde gave a semicarbazone m.p. 166°. From the latter was formed, on heating with dilute sulphuric acid, the free methylsemicarbazide m.p. 118°. This compound when decomposed by alkalis gave the non-substituted hydrazine N_2H_4 , and, hence, cannot be anything else but the hydrazineformic-methylamide $\text{NH}_2\text{-NH-CO-NH-CH}_3$. Consequently the nitrocompound was the α, β -methyl-nitro-urea $\text{NH(NO}_2\text{)-CO-NH-CH}_3$.

In order to further confirm this conclusion the methylsemicarbazide

¹⁾ A. 288, 285 (1895).

²⁾ R. 31, 25 (1912).

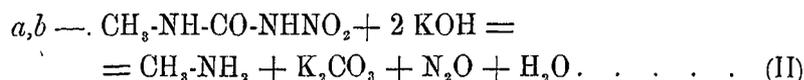
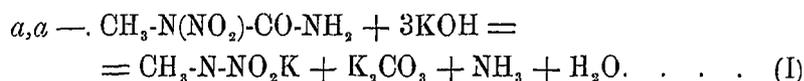
was also prepared synthetically from methylisocyanate and hydrazine:



The product m.p. 118° proved to be identical with the methylsemicarbazide obtained by reduction. The above-mentioned condensation product with benzaldehyde (m.p. 166°) and the semicarbazones formed with other aldehydes were also identical.

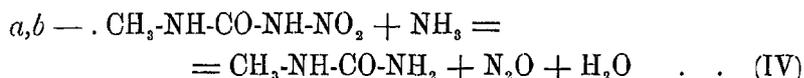
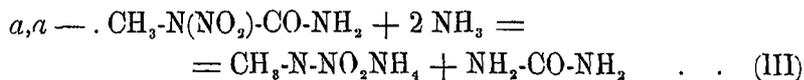
b. Decomposition by bases. The reaction with bases affords a suitable means of deciding whether we are dealing with a primary nitramine or with an alkylnitramide. A primary nitramide Ac-NH-NO_2 will, on hydrolysis, yield nitramide NH_2NO_2 , from which is formed on subsequent decomposition nitrous oxide N_2O , but an alkylnitramide $\text{Ac-N(NO}_2\text{)R}$ gives the monoalkylnitramine RNHNO_2 .

Hence, the reaction of the *a,a*- and the *a,b*-methylnitro-urea will be expressed by the following equations:



The methylnitro-urea m.p. 159° on heating with bases gives one mol. of nitrous oxide; in addition methylamine is formed but no methylnitramine. These observations all agree with equation II, but they all are opposed to equation I.

The reaction of primary nitramides and alkylnitramides with ammonia differs somewhat from that with alkalis, but is still quite as useful for distinguishing the two classes. The decomposition of the two isomers by ammonia is represented by the following equations:



The compound m.p. 159° gives on decomposition by ammonia methylurea (identified in the form of its nitroso-derivative) and no methylnitramine is formed. This tallies with equation IV, but not with equation III.

The reactions with alkalis and ammonia therefore prove that the methylnitro-urea m.p. 159° is, indeed, the *a,b*-compound.

Further, I have investigated the crude nitration product before it was treated with ammonia.

This product which melts very unsharply (at about 90°—100°)

with evolution of gas, has the empirical composition of methylnitro-urea and yet on purifying with ammonia, we obtain only about half the weight of *a,b*-methylnitro-urea. Hence the presumption that the admixture consists of the isomere, *a,a*-methylnitro-urea.

As a matter of fact, on treating this crude product with alkalis or ammonia, methylnitramine is formed which I was able to show by the melting point and other properties. On decomposing with baryta water a quantity of methylnitramine was obtained, pointing to the presence of 40% *a,a*-methylnitro-urea.

The quantity of nitrous oxide formed on heating with potassium hydroxide indicated 55% of *a,b*-compound in the mixture.

Summary of the results.

1. On nitrating methylurea in sulphuric acid solution a mixture is formed of the two isomeric mononitro-derivatives.

2. On treating this mixture with cold ammonia solution, the *a,a*-methylnitro-urea is decomposed, whilst the *a,b*-compound is converted into its ammonium salt and is obtained in a pure condition by addition of an acid.

The structure of this *a,b*-methylnitro-urea is proved:

a. by reduction: hydrazino-formic-methylamide $\text{NH}_2\text{-NH-CO-NH-CH}_3$ is formed, the composition of which is proved analytically (formation of hydrazine on heating with alkalis) and synthetically (preparation from N_2H_4 and CONCH_3).

b. by the decomposition with alkalis and ammonia, which agrees in all respects with the formula of the *a,b*-compound and is opposed to the formula of the *a,a*-compound.

3. The mixture of the isomers found in one of the nitration experiments contained about 55% of the *a,b*-methylnitro-urea and, as appears from the decomposition with bases, fully 40% of the *a,a*-compound.

4. The essential difference in the behaviour of methylurea and ethylurea towards nitration agents, as accepted up to the present, is herewith annulled.

The experimental details and the new compounds obtained in this study will be described elsewhere.