

Citation:

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Chemistry. — “*On the essential oil from the leaves of *Alpinia malaccensis* Rose*”. By Dr. P. VAN ROMBURGH.

In a communication¹⁾ on the occurrence of methyl cinnamate in the rhizomes of *Alpinia malaccensis*, I incidentally mentioned that the leaves of this plant yield an essential oil, which is likewise rich in this substance. Since then, I have prepared this oil in larger quantity and investigated the same jointly with Dr. TROMP DE HAAS, Assistant to the Agric. Chem. Laboratory of the Government Botanical Gardens at Buitenzorg.

From 700 Kilos. of fresh leaves, with the stalks attached, 1100 c. m. of oil were obtained. The yield is, therefore, 0.16 percent. The sp. gr. at 26° was 1.02. Rotation + 6.5°. When treated with aqueous soda 25 percent of the oil are not attacked, forming a liquid compound, the bulk of which boils from 160°—170°. This liquid may be isolated in a still more simple manner by treating the essential oil with steam; it then readily distils over whilst the methyl cinnamate, of which the oil consists to the extent of 75 percent, remains behind in a practically pure condition, and forms beautiful crystals on cooling.

By fractional distillation, the liquid portion yields a liquid, boiling from 158°—160°, having a sp. gr. of 0.857 at 26.5°. In a 200 m.m. tube it showed a rotation of 43° 20' to the right. The analysis and the vapour density agreed with that of a substance of the composition C₁₀ H₁₆.

This hydrocarbon clearly belongs to the pinene group; with nitrosyl chloride it yields a compound which²⁾, by the action of piperidine, gives pinene nitropiperidine melting at 118° — 119°.

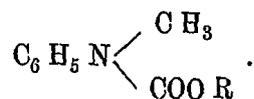
Chemistry. — “*On the action of nitric acid on the esters of methyl-phenylaminoformic acid.*” By Dr. P. VAN ROMBURGH.

Some years ago, I have shown that by the action of nitric acid on the esters of phenyl-aminoformic acid, under definite circumstances, two or three NO₂-groups simply enter the benzene nucleus without any substitution of NO₂ for the amino-hydrogen, or liberation of the formic acid-residue taking place.

¹⁾ Report of ordinary meeting Kon Akad v. Wetensch 23 April 1898.

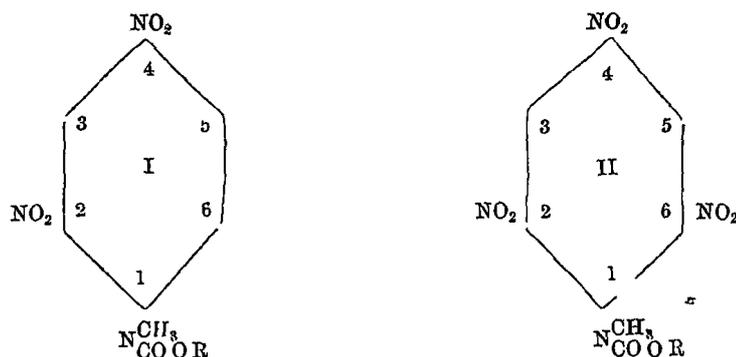
²⁾ This nitrosylchloride compound does not, however, melt at 103° but at 108°. I also found that melting point for an analogous compound from the terpene from the leaves of *Myristica fragrans*.

In continuation of that research, I have now studied the action of nitric acid on the methyl derivatives of the esters :



The possibility should exist here that, besides nitration of the nucleus, the formic acid-residue might be replaced by NO_2 with the formation of trinitrophenylmethylnitramine which is very stable towards nitric acid, or the methyl group might be replaced by hydrogen or, what is least likely, by NO_2 .

The result of the research was, however, quite different from what was expected. The methyl group as well as the formic acid-residue remain intact and the reaction is limited to the introduction of NO_2 -groups into the benzene nucleus. Whilst, however, when dealing with phenylaminoformic esters, it is an easy matter to introduce *three* nitrogroups into the nucleus, this is not successful with the methyl compound and only *di*-nitroderivatives are obtained of the formula I:



Trinitroderivatives of the formula II may however, be prepared by an indirect way, so that one is led to suppose that there exists a so called sterical obstacle to the introduction of the third NO_2 -group in the place 6.

The methyl ester of methylphenylcarbamic acid was prepared by the action of methylaniline on the methyl ester of chloro-formic acid in the presence of water and obtained in the form of a nicely crystallising compound melting at 44° . The boiling point is situated at 243° . When its solution in sulphuric acid is added to very concentrated nitric acid a substance is obtained, which crystallises in beautiful glossy transparent crystals melting at 98° . This is the di-nitroderivative.

The ethyl ester of methylphenylcarbamic acid has already been prepared by GEBHARDT¹⁾ by the action of methylaniline on the ethyl ester of chloro-formic acid in ethereal solution. I also succeeded very well with the preparation in the presence of water. I found the boiling point 5° higher than that of the methyl ester.

By the action of nitric acid a product is obtained melting at 112° which is the dinitro-compound²⁾.

Heating in sealed tubes with fuming hydrochloric acid at 150° breaks up both dinitrocompounds with formation of carbon dioxide, alkyl chloride and dinitromethylaniline $C_6H_3(NO_2)_2NHCH_3$, melting at 178°, which for the purpose of identification was treated with fuming nitric acid, which formed trinitrophenylmethylnitramine melting at 127°.

When both dinitroderivatives are boiled with fuming nitric acid they do not appear to become altered. Up to the present I have not succeeded in introducing a third nitrogroup.

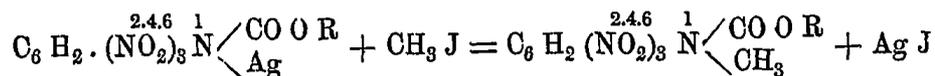
As it did not seem without importance to ascertain whether the desired trinitrocompounds might not be prepared by another method. I have made the following experiments.

An aqueous solution of the potassium compound of the methyl ester of trinitrophenylcarbamic acid was treated with silver nitrate, which forms the sparingly soluble silver salt. This is then treated with methyl iodide in the presence of methyl alcohol. Silver iodide is formed, and from the methyl alcohol may be isolated a yellow compound, which after being recrystallised a few times, melts at 112—113° and is the desired trinitrocompound.

In an analogous manner, I prepared the ethyl ester, which melts at 65°.

That indeed the methyl group in these compounds is linked to the nitrogen of the aminogroup could be demonstrated by boiling them with a solution of potash which caused a liberation of *methylamine* which could be proved beyond doubt by the reaction with bromodinitrobenzene, which formed dinitromethylaniline melting at 178° and yielding, by treatment with nitric acid, trinitrophenylmethyl-nitramine melting at 127°.

The reaction with methyl iodide has, therefore, proceeded normally



¹⁾ B. B. 17, S. 3042.

²⁾ It is peculiar that this nitrated ethyl ester has a higher melting point than the corresponding methyl ester.