Chemistry.— *On polymerides of methylchavicol.* By J. M. V. D. ZANDEN.
(Communicated by Prof. P. VAN ROMBURGH).

(Communicated at the meeting of September 25, 1937.)

After heating methylchavicol, $CH_3O-\langle\ \rangle-CH_2-CH:CH_2$, for 48 hours at 250° in sealed tubes, VAN ROMBURGH obtained, by distilling off, a residue from which a solid deposited. The oil was removed from the crystalline mass by suction. After repeated recrystallisation the main product melted, not very sharply, at 98°, another at 166°, while also traces of a substance melting above 200° were obtained.

The elementary analysis and the determination of the molecular weight showed the probability of the products 98° and 166° being dimerides of methylchavicol. The product 98° is unsaturated; it formed a dibromide, melting at 87° [1]).

Further investigation showed, that extension of the length of heating somewhat increased the yield of crystalline mass.

The syrup, from which the crystals were filtered by suction, was fractionated. The fraction 283–313° (15 mm) deposited a handsome amount of solid matter.

At 350° the residual mass was cracked; the distillate contained inter alia p.methoxycresylether $CH_3O-\langle\ \rangle-CH_3$.

Oxidation of the product 98° with permanganate in acetone yielded anisic acid $CH_3O-\langle\ \rangle-CO_2H$ and an acid melting at 113°, having, according to the elementary analysis and the titration, the formula $C_{12}H_{16}O_3$. The literature does not mention an acid of these properties.

Further oxidation of the acid 113° with the Kiliani-mixture yielded an acid melting at 138° [2]). The elementary analysis and the determination of the equivalent value agree with the formula $C_{12}H_{14}O_4$.

The stock of methylchavicol for this investigation, obtained from an essential oil, distilled in Java, was exhausted before the purpose to acquire insight into the process of the polymerisation was accomplished. A new quantity was prepared by the procedure indicated in the German patent $Kl.12_0Nr.154654$ [3]).

Bromination of anisole gave p. bromoanisole in a yield of 88 %; the magnesium compound reacts with allylbromide giving methylchavicol (75–80 per cent of the theoretical amount).

$$CH_3O-\langle\ \rangle MgBr + BrH_2C-CH:CH_2 \rightarrow CH_3O-\langle\ \rangle-CH_2.CH:CH_2$$

[1]) Verslag Koninklijke Akad. v. Wetenschappen, Amsterdam, **17**, 16 (1909).
[2]) VAN ROMBURGH en VAN DER ZANDEN, Verslag Koninklijke Akad. v. Wetenschappen, Amsterdam, **25**, 1303/4 (1917).
[3]) Chem. Zentr. 1904, II, 1354.

This time we heated the methylchavicol for 200 hours at 250° for the polymerisation. After this, over 60 % distilled at the boiling point of methylchavicol; then the distillation temperature was raised to 200° (3 mm). The fractions up to 300° solidify partially. The residue, abt. $1/12$ of the starting material, is at room temperature a hard asphaltic like mass.

The solid part of the fractions 200–300° (3 mm) was filtered off and then freed from adherent oil by washing with petroleum benzine. It melts at abt. 90°. The fraction 210–220° (2 mm) gives th best yield. Extraction and recrystallisation from petroleum benzine, alcohol and acetone furnished as chief product a substance melting rather sharply at 93°; fractions melting at 95–98° were also obtained. The yield of product 167° was small. We also separated a fraction, melting point 46–47°. The micro elementary analysis, the determinations of the methoxyl content and the molecular weight in camphor all point to this substance being a dimeride of methylchavicol, whereas the same determinations for another product, melting point 135°, obtained in the same reaction, indicate a trimeride.

The investigations on the constitution of the main product 93° have given the same results as in 1917. The oxidation with permanganate in acetone produced anisic acid and an acid $C_{12}H_{16}O_3$, melting point now 114–114.5°; further oxidation of this acid with KILIANI-mixture, yielded an acid $C_{12}H_{14}O_2$, melting at 140–140.5°.

It was very probable that the last mentioned substance was a ketonic acid. It was therefore advisable to try to obtain an oxime, and then the BECKMANN conversion with hydrolysis of the amide might help to decide the structure of the starting acid.

Hydroxylamine combined with the acid, giving an oxime melting at 97–97.5°. This oxime being converted by concentrated sulphuric acid, the hydrolysis, followed by acidulation, gave an organic acid melting at 99–100°, the equivalent weight of which proved to be 66. This acid might be glutaric acid $HO_2C(CH_2)_3CO_2H$. The melting point determination of a mixture with this acid confirmed the conclusion.

From this fact it could be derived that the acid $C_{12}H_{14}O_4$ must be δ(p. methoxyphenyl)-δ ketovaleric acid, CH₃O–⟨ ⟩–CO(CH₂)₃CO₂H.

The interaction of glutaric acid and anisole with aluminium chloride as a catalyst yielded, in an amount of 75 %, an acid identical, as anticipated, with the oxidation product 140°.

$$CH_3O-\langle \ \rangle + O:\overset{\overset{\text{O}}{|}}{C}-(CH_2)_3-C:O \rightarrow CH_3O-\langle \ \rangle CO(CH_2)_3-CO_2H$$
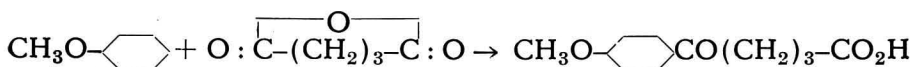
The paranitrophenylhydrazone melts at 198—200°; the 2,4-dinitrophenylhydrazone at 142.5°.

When the BECKMANN conversion was carried out with phosphorus pentachloride in ether, we acquired an exhaustive information on the course of the reaction. The first product separated, melting at 172—172.5°,

according to the analysis $C_{12}H_{13}O_3N$, is in all appearance a cyclic imide. The action of 1 equivalent KOH, followed by acidulation converted the imide to a substance $C_{12}H_{15}O_4N$, melting at 147—148°; the nitrogen ring is opened. Strong hydrochlorid acid split up the acid $C_{12}H_{15}O_4N$ (147—148°) to glutaric acid and paramethoxyaniline. Interaction of glutaric acid and paramethoxyaniline produced the imide 172—172.5°.

The oxidation of the acid $C_{12}H_{14}O_2$ (140—140.5°) by permanganate in water yielded chiefly anisic acid; as a by-product we obtained an acid, melting at 92—92.5°. The elementary analysis and the determination of the equivalent weight accorded to the formula $C_9H_8O_4$, from which can be concluded, that the acid should be paramethoxyphenylglyoxylic acid, $CH_3O-\langle\rangle-CO-CO_2H$. BOUGAULT [4] prepared this acid by oxidation of p.methoxyacetophenone, $CH_3O-\langle\rangle-CO-CH_3$. Repeating of his procedure gave a product identical (melting point of the mixture) with the oxidation product from acid 140—140.5°.

We had obtained the anisoylbutyric acid by oxidation of the acid $C_{12}H_{16}O_3$, melting point 114—114.5°. Therefore the last mentioned acid must be the δ-p. methoxyphenylvaleric acid $CH_3O-\langle\rangle-(CH_2)_4CO_2H$. We succeeded in synthetising this acid in the way described hereafter. Following a method employed by CLAISEN [5] in preparing the cinnamic ester from anisic aldehyde and ethyl acetate in presence of sodium, we prepared p. methoxycinnamic ester, $CH_3O-\langle\rangle-CH:CH-CO_2C_2H_5$. This ester was reduced by sodium and alcohol, — the sodium having been pulverized in toluene —, to p.methoxyphenylpropylalcohol, $CH_3O-\langle\rangle-(CH_2)_2CH_2OH$ (B.p. 10 mm 149°; m.p. 25—26°), the latter was converted to the bromide $CH_3O-\langle\rangle-(CH_2)_2CH_2Br$ by phosphorus tribromide.

The interaction of this bromide and sodium malonic ester gave us $CH_3O-\langle\rangle-(CH_2)_3-CH(CO_2C_2H_5)_2$. The ester was saponified and the resulting diacid lost CO_2 by heating at 130° and yielded the same acid 114—114.5° as obtained before in oxidising the dimeride, m.p. 93°.

This polymeride consequently gives in the first oxidation δ-p. methoxyphenylvaleric acid $CH_3O-\langle\rangle-(CH_2)_4CO_2H$ and anisic acid $CH_3O-\langle\rangle-CO_2H$. It is unsaturated and proved to have the formula $C_{20}H_{24}O_2$. This polymeride is therefore 1,6-di-p.methoxyphenylhexene-1,

$$CH_3O-\langle\rangle-(CH_2)_4-CH:CH-\langle\rangle-OCH_3.$$
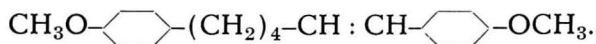
It was hydrogenated with palladium as a catalyst. The saturated product melting at 71.5—72° has the formula $C_{20}H_{26}O_2$, it must be 1,6-di-p. methoxyphenylhexane. We prepared this substance by the method

[4]) Ann. [7] **25**, 541 (1902).
[5]) Ber. **23**, 977 (1890).

of WÜRTZ, starting from p.methoxyphenylpropyl bromide. It proved to be identical with the saturated product, mentioned before.

The structure of the polymeride 93° has now been proved; the investigation of the other polymerides being continued. We are at present engaged in preparing polymerides of analogical substances so as to obtain fresh points of view on polymerisation.

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Botany. — *Die chemischen Vorgänge im Sauromatum-Kolben.* III. Mitteilung. Von A. W. H. VAN HERK. (Communicated by Prof. J. C. SCHOUTE.)

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Die Versuche, über die in der zweiten Mitteilung [1]) berichtet worden ist, haben gezeigt, dass der Faktorenkomplex, welcher die plötzlich auftretende Atmungssteigerung im Appendix von *Sauromatum guttatum* hervorruft, sich nicht in diesem Organ selbst befindet, sondern in den männlichen Blüten.

Es ist nun naheliegend sich vorzustellen, dass die Korrelation, welche nach diesem Befunde zwischen beiden Teilen des Blütenkolbens besteht, auf einer stofflichen Beeinflussung zurückzuführen ist. Die Grundidee wäre dann die folgende:

Der erwachsene Appendix enthält grosse Mengen Verbrennungssubstanzen, die mit geringer Geschwindigkeit von den Oxydationsfermenten verbrannt werden. Das Atmungssystem kann seine ganze Aktivität nicht entfalten, da ihm eine oder mehrere Substanzen, — Aktivatoren —, fehlen. In einem bestimmten Entwicklungsstadium werden diese Aktivatoren von den männlichen Blüten gebildet. Sie wandern von dieser Zone der Infloreszenz nach dem Anhängsel. Hier ergänzen sie das Oxydationssystem: nach einer Latenzzeit steigern sie die Atmungsintensität der Zellen der peripheren Gewebeschicht stark.

Diese Vermutung wird in der vorliegenden Arbeit experimentell bestätigt.

Die Isolierung der wirksamen Substanz.

Einige Stunden vor der Blüte schneidet man die Zone der Infloreszenz ab, welche die männlichen Blüten trägt. Man entfernt das weisse Markgewebe. Das Material (mindestens 10 Pflanzen) wird mit Kohlensäureschnee sofort zum Erfrieren gebracht und mit gereinigtem Quarzsand fein zerrieben. Die zerkleinerten Pflanzenteile werden mit ± 25 ccm Wasser bei 0° während einer Viertelstunde unter stetigem Umschütteln extra-

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[1]) Proc. Royal Acad. Amsterdam, **40**, 607 (1937).