

Citation:

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Chemistry. — “*The essential oil of Litsea odorifera Val. (Trawas oil)*”. By Prof. VAN ROMBURGH. (Preliminary communication.

(Communicated in the meeting of September 30, 1911).

Some years ago I received from Dr. BOORSMA of Buitenzorg a small bottle of an essential oil obtained by distilling with water trawas leaves which are sold at the “pasar” (market) at Buitenzorg as a medicine. The quantity of oil was only sufficient for a preliminary investigation. Having been since in Java myself, I was able to purchase the whole of the leaves from some trawas trees, whilst Dr. DE JONG was kind enough to prepare for me the essential oil in the agricultural chemical laboratory at Buitenzorg. Meanwhile Dr. VALETON had taken in hand the determination of the tree which belongs to the family of the Laurineae and given it the name of *Litsea odorifera* Val. I am much obliged to these gentlemen for their trouble.

The trawas oil has a pale yellow colour and a disagreeable odour. The Sp. Gr.₁₅ of the different specimens of the crude oil varied from 0,836 to 0,846 whilst the rotation in a 20 cm. tube amounted to from $-10'$ up to $-7'$. Under the ordinary pressure the bulk of the oil passed over at 233° , under 10 mm. pressure most of it distilled between 120° and 125° .

The oil does not give aldehyde reactions. If it is shaken with a solution of sodium hydrogen sulphite, a solid compound is formed, which after washing with ether and decomposition with sulphuric acid yielded a liquid which showed but a faint left-handed rotation. An aqueous solution of potassium permanganate is decolourised by the crude oil; if so much of the oxidiser is added that the violet colour no longer disappears and the mixture is then distilled in a current of steam, an oily liquid passes over with the water vapours, which gives with sodium hydrogen sulphite a crystallised compound.

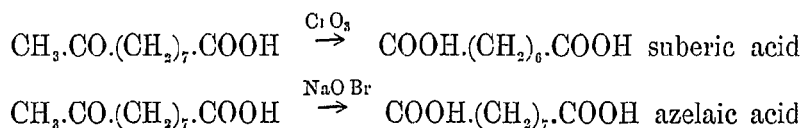
With semicarbazide and a little acetic acid the crude oil gives a crystallised semicarbazone; a portion of it, however, does not combine with the reagent but gives a crystallised phenylurethane with phenylisocyanate.

An elementary analysis of the fraction boiling at 233° gave results which showed that it might be a mixture of compounds of the composition $C_{11}H_{20}O$, $C_{11}H_{22}O$ and $C_{11}H_{24}O$.

In order to separate the ketones from the alcohols a large quantity of the oil was treated with semicarbazide and acetic acid. The semicarbazone formed melted at 114° . The melting point increased a little on recrystallisation, but could not be got higher than 116° .

On treatment with dilute sulphuric acid the ketones were again liberated from the carbazone. A liquid was obtained which appeared to be optically inactive. Potassium permanganate still had a strong action, therefore so much was added that the permanganate colour no longer disappeared. If now a current of steam was passed through the liquid, a colourless oily liquid distilled over with the water vapours (m. p. 12° , Sp. Gr.₁₇ 0.829, b. p.₇₆₀ 234°) which, on treatment with semicarbazide, gave a compound melting at 124° .

The elementary analysis led to the formula $C_{11}H_{22}O$, the properties mentioned quite agree with those of methyl-11. nonylketone (2-undecanone) the main constituent of the essential oil of *Ruta graveolens*. From the oxidised liquid could be isolated an acid which melts at 49° and has according to the analysis, the composition $C_{10}H_{18}O_2$. This proved to be 2-ketodecanic acid $CH_3.CO.(CH_2)_7.COOH$, which on oxidation with chromic and sulphuric acids yielded suberic acid, whereas on treatment with sodium hypobromite azelaic acid and carbon tetrabromide were formed.



From the results obtained it follows that to the unsaturated ketone must be attributed the formula: $CH_2 = CH - (CH_2)_7 - CO.CH_3$. It is, therefore, nonylene-(1)-methylketone or undecene (1) one (10).

As no separation of the semicarbazones from the ketones could be effected by recrystallisation, another course was taken to isolate the unsaturated ketone and it was endeavoured to convert it first into a bromine addition product. Methylnonylketone however, is attacked readily, with evolution of hydrogen bromide, when acted on by a solution of bromine in chloroform or carbon tetrachloride. On the other hand a methyl-alcoholic solution of bromine¹⁾ acts very slowly on this saturated ketone. A solution of bromine in methyl alcohol is, therefore, allowed to run into the mixture until the liquid just assumes a yellow colour. The alcohol is distilled off and the residue washed with sodium carbonate solution to remove traces of hydrogen bromide. On now heating in vacuo at 160° , the saturated compounds pass over, leaving the bromine addition product behind. At 204°_{16} the greater portion of this distils as a colourless liquid which, however, becomes dark on keeping.

¹⁾ According to LOBRY DE BRUYN (B. 26, 272 [1893]) bromine acts very slowly on methyl alcohol; for this reason a methyl-alcoholic solution of bromine is much to be preferred to an ethyl-alcoholic one.

On boiling the dibromide with zinc dust and alcohol the bromine is eliminated and the unsaturated ketone can then be readily separated by distillation in a current of steam. After purification via the semicarbazone it is obtained as a colourless liquid which melts at -7° ¹⁾ and boils at 235° SG_{11,5} 0,848. MR = 52,47 (calculated for C₁₀H₂₀O = 52,51).

The alcohols from the trawas oil obtained in the treatment with semicarbazide may be isolated in a similar manner. In this case a solution of bromine in carbon tetrachloride may be used.

The saturated alcohol proved to be methyl-n.-nonylcarbinol. It has a left handed rotation²⁾ $\alpha = -5^{\circ}.40'$ ($l = 1$ dM.). On oxidation with chromic acid in sulphuric acid solution methyl-n.-nonylketone is formed which was identified by the semicarbazone melting at 124° .

The unsaturated alcohol also has a left handed rotation ($\alpha = -5^{\circ} 10'$ $l = 1$ dM.). The boiling point was situated at 233° ; Sp.Gr₁₀ = 0,835. On oxidation with chromic and sulphuric acids a ketone was obtained the semicarbazone of which melted at 113° whereas by oxidation with potassium permanganate 2-ketodecanic acid was formed. This alcohol therefore, consists of undecene (1) ol (10).

The results of this research will be communicated more fully elsewhere.

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Botany. — "*Investigation of the transmission of light stimuli in the seedlings of Avena*". By P. C. VAN DER WOLK. (Communicated by Prof. F. A. F. C. WENT.)

(Communicated in the meeting of September 30, 1911).

§ 1.

The investigations, which are recorded in this preliminary communication were carried on in the Botanical Laboratory at Utrecht, in a phototropic room which, in order to eliminate the harmful constituents of the air, is isolated from the laboratory building and forms part of the group of hothouses in the Botanic Garden. Accordingly these experiments have in general been carried out at higher

¹⁾ This melting point must be given with some reservation as the unsaturated ketone may possibly contain traces of the saturated compound formed during the action of the zinc dust. These cannot affect to any extent the other properties.

²⁾ Power and LÉES (Soc. 81, 1593 [1902]) found in Algerian essential oil of Rue an active methyl. n. nonylcarbinol $\alpha = -1^{\circ}18'$ ($l = 0.25$ dm.).