

**Chemistry.** — *2-Decenal-1. The principal constituent of the essential oil of Ahasma Walang Val.* By P. VAN ROMBURGH.

(Communicated at the meeting of November 30, 1929).

By courtesy of Ir. H. L. WELTER, Director of the Division of Industry, Government Department of Agriculture and Commerce, Buitenzorg, I received on my last visit to Java some samples of the essential oil from the leaves, the petioles and the rhizomes of *Ahasma Walang Val*. The odour of these oils resembles very much that of the *walang sangit* (*Leptocorisa varicornis*) a bug living on young riceplants in Java.

According to DE JONG<sup>1)</sup> and to WELTER<sup>2)</sup> these oils consist mainly of aldehydes.

From the three samples, I could isolate by repeated careful fractional distillation in vacuo a principal fraction forming a colourless liquid with boiling point of 104° (13 mm.).

At ordinary atmospheric pressure it boils at 229—231°.

Analysis: Found: C 77.78, H 11.80.  $C_{10}H_{18}O$  requires C 77.92 H 11.69  
 $d_{15}^{19} = 0.846$ ,  $n_D^{19} = 1.4538$ .

MR<sub>D</sub> found 49.27; calc. for  $C_{10}H_{18}O$  47.87.

This substance shows typical aldehydic reactions. Heated with an ammoniacal solution of silver oxide it deposits a silver mirror.

With semicarbazide in alcoholic solution it yields a semicarbazone which after crystallisation from alcohol formed colourless glistening plates, m.p. 162°.

Analysis: Found: N 19.77, 19.86.  $C_{11}H_{20}N_3O$  requires N 20.0.

Though according to the results of the work described in this communication the aldehyde is unsaturated it does not give a colouration with tetranitromethane.

#### *Oxydation of the aldehyde with potassium permanganate.*

To 11 g. of the aldehyde suspended in a potassium carbonate solution was slowly added at room temperature 4 % potassium permanganate solution till a permanent pink colour persisted. 50 g. of permanganate were needed.

<sup>1)</sup> Jaarboek v. h. Departement van Landbouw, Nijverheid en Handel in Ned.-Indie 1911 p. 46.

<sup>2)</sup> Ibid. 1921 p. 76.

The solution was then filtered from manganese dioxide and the filtrate acidified with sulfuric acid. An oily liquid separated which was extracted with ether. The extract was dried with anhydrous sodium sulfate. After removal of the ether from the extract the residual liquid was fractionated. The main fraction, having a faint unpleasant odour reminiscent of fatty acids, boiled at  $234^{\circ}$  and crystallised on cooling in ice. The melting point was  $13.5^{\circ}$ .

The analysis of the silver salt gave figures in good agreement with the formula of octoid acid  $C_8H_{16}O_2$ .

Analysis : Found : Ag 42.98 .  $C_8H_{15}O_2$  Ag requires 43.03 Ag.

By heating with aniline the acid was converted into its amide m. p.  $50^{\circ}$ . The compound was identical with the amide from caprylic acid and showed no depression of melting point in admixture.

#### *Hydrogenation* <sup>1)</sup> *of the unsaturated aldehyde.*

5.3 g. of the aldehyde dissolved in neutral ethyl acetate were hydrogenated catalytically in the presence of 0.1 g. of platinum black.

At room temperature only a little hydrogen was absorbed ; on warming and on activating the catalyst with air addition of 2 mol of hydrogen (1500 cc.) was complete in the course of some days.

After evaporation of the ethyl acetate the reduction product was fractionated.

The main fraction consisted of a colourless liquid which almost distilled at  $228-231^{\circ}$  and was identified as decanol.

With  $\alpha$ -naphthylisocyanate it produced an  $\alpha$ -naphthylurethane, which crystallised from petroleum ether (b. p.  $40-60^{\circ}$ ) in white needles m. p.  $70^{\circ}$ .

The compound was identical in all respects with the naphthylurethane which I prepared from pure decanol.

By heating with 2-3-4-6-tetranitro—1-methylnitraminobenzene the decanol gave yellow crystals of 2-4-6-trinitro—3-oxydecyl—1-nitraminobenzene m. p.  $76^{\circ}$ .

Both products did not give a m. p. depression when mixed with the corresponding derivatives prepared from pure decanol.

With platinum oxide the hydrogenation gave the following results. In a first experiment 11 g. of the aldehyde (four times distilled in an  $CO_2$ -atmosphere) at 12 mm. in ethyl acetate with 0.1 g. Pt  $O_2$  were shaken with hydrogen. At room temperature 500 cc. of hydrogen were absorbed per 12 hours with constant velocity till 1590 cc. — corresponding with 1 mol  $H_2$  per mol of the aldehyde — had been taken up. Prolonged treatment with hydrogen caused no further absorption. After removal of the solvent I obtained by fractional distillation in vacuo, besides a liquid

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<sup>1)</sup> I desire to express my thanks to Mr. A. G. VAN VEEN D.Sc. for help in the catalytic reduction of the aldehyde.

portion, as main product a crystalline substance which proved to be decoic acid m. p.  $30.5^{\circ}$ .

MW (by titration) found : 172.4.

MW  $C_{10}H_{20}O_2$  172.

In a second experiment 8 g. of the aldehyde in ethyl acetate solution with 0.1 g. of platinum oxide absorbed at room temperature 1150 cc. of hydrogen. Then air was admitted into the flask but further shaking and the application of heat were ineffective in causing further hydrogenation.

On distillation at 13 mm., after removal of the solvent, I collected a liquid portion with a boiling point ranging from  $100-105^{\circ}$ , then the temperature mounted quickly and decoic acid passed over.

36 g. in 4 portions were treated in the same manner.

The liquid distillate was fractionated and a constant boiling fraction obtained (b. p.  $99^{\circ}$  at 15 mm.) having the characteristics of a saturated aldehyde. It was identified as decanal by its semicarbazone, melting at  $99-100^{\circ}$  and by oxydation to decoic acid.

#### *Oxydation of the unsaturated aldehyde.*

A steady current of oxygen was passed through the aldehyde till the absorption had practically ceased.

The reaction mixture was shaken with a solution of sodium carbonate and extracted with ether to remove neutral products present.

The alkaline portion was acidified with sulfuric acid and the acid removed by ether extraction.

After removal of solvent the acid was subjected to fractional distillation at 15 mm., which gave as main fraction a colourless liquid b. p.<sup>15</sup>  $165^{\circ}$ . On cooling in the icechest the liquid solidified. M. p.  $8^{\circ}$ .

MW (by titration) 169.8      MW  $C_{10}H_{18}O_2 = 170$ .

The silver salt was prepared and analysed

Analysis : Found : 38.89 Ag.       $C_{10}H_{17}O_2$  Ag requires 38.96.

The study of the properties of this unsaturated acid is being continued.