

Citation:

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Chemistry. — “*The unsaturated alcohol of the essential oil of freshly fermented tea-leaves.*” By Prof. P. VAN ROMBURGH.

(Communicated at the meeting of May 31, 1919).

In 1895 in collaboration with my assistant at that time, Mr. C. E. J. LOHMANN, I investigated the ethereal oil from freshly fermented tea¹⁾, a small quantity of which we were successful in preparing with the cooperation of several tea-planters. The yield of this ethereal oil is extremely small, fifteen kilograms of the fresh leaves giving only one c.c.

We were able at that time to detect the presence in the oil of an unsaturated alcohol (b.p. 153°—155°) of the composition $C_6H_{12}O$, evidently a hexylene alcohol. From this by oxidation an acid could be obtained, smelling like rancid butter, the calcium salt of which gave on analysis a result which indicated the presence of butyric acid. Lack of material prevented us from determining whether the acid formed was the normal or the iso-butyric acid. Later, shortly before my departure from Java, I had the opportunity of obtaining a larger quantity of the ethereal tea-oil (about 120 c.c.), which enabled me to resume the research and to investigate more in detail whether by the oxidation of the unsaturated alcohol one or other of the butyric acids is really formed. A knowledge of the nature of the acid is of course of primary importance for the elucidation of the structure of this acid.

After treatment with alkali in order to saponify the methyl salicylate²⁾ (the presence of which we had demonstrated in 1896) and other esters³⁾ possibly present, the crude oil was fractionated several times. The largest fractions boiled between 154° and 156° and between 156° and 158°. These were mixed and distilled in vacuo; the principal fraction boiled at 75°—80° at 28—30 mm. pressure.

The sp. gr. at 15° was 0.8465; n_D^{20} 1.43756.

Elementary analysis gave 71.17% C. and 12.74% H. The formula $C_6H_{12}O$ requires 71.91% C. and 12.10% H.

1) Verslag omtrent den staat van 's Lands Plantentuin te Buitenzorg for the year 1895, p. 119.

2) The same for the year 1896, p. 168.

3) The salicylic acid isolated was not odourless. The smell resembled that of phenyl acetic acid.

The liquid was now treated with anhydrous sodium sulphate and again distilled in vacuo. Further analysis of the product gave, however, no better results. (71.08 % C. and 12.59 % H).

The unsaturated tea-alcohol forms with avidity an addition compound with bromine, as was previously shown. The quantity of bromine added, however, was smaller than is to be expected from a substance of the formula $C_6H_{12}O$, being only 87 % of that amount.

Two fresh determinations gave the following results:

I. 1.017 grm. of the alcohol in chloroform solution cooled in ice-water add 1.363 grm. bromine.

II. 0.529 grm. add 0.707 grm.

From these result it appears that only 83.2 % and 83.5 %, respectively of the calculated quantity of bromine is added.

As I suspected that the unsaturated alcohol perhaps contained a hexyl alcohol as impurity, I attempted to purify a larger quantity of the bromine addition compound ¹⁾ from this by heating in vacuo at 100°. A subsequent treatment with zinc dust should give the hexylene alcohol in a pure state. Since, however, the bromine addition product gave hydrobromic acid, I was unable to carry out this intention.

Treatment of the unsaturated alcohol with phenylisocyanate gave no crystallised product. On the other hand α -naphthylisocyanate gave an α -naphthylurethane (m. p. 76°), the melting point of which could be raised to 80° after repeated recrystallisation from petroleum ether.

On treatment with phthalic anhydride, the tea alcohol gave a liquid acid ester of which the silver salt melted at 140°.

Oxidation of the tea alcohol with potassium permanganate in neutral as well as in alkaline sodium carbonate solution, proceeds very smoothly. About 3 c.c. of acid were obtained from 11.5 grm. on treatment with 50 grm. potassium permanganate in 4 % solution. This acid, as before, had a smell resembling that of butyric acid. On distillation of the acid, however, the principal fraction, besides a small first fraction in which formic acid could be detected, was a liquid boiling between 125° and 145°, while the residue in the flask consisted of a liquid of higher boiling point with a smell of perspiration. The principal fraction, on redistillation, gave a liquid of boiling point 140°—145°; which on being boiled with water and calcium carbonate was transformed into a calcium salt which was found on analysis to contain 21.2 % Ca. This result in conjunction with the boiling point of the acid obtained, show that the latter

¹⁾ This does not solidify in liquid ammonia

consists of propionic acid, the calcium salt of which contains 21.5 % Ca. On heating the ammonium salt an amide with a melting point of 78° was obtained which, on mixing with propion-amide, produced no depression of the melting point.

The hexylene alcohol obtained from tea-oil might therefore be hexene-3-ol-6 of the formula $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH} : \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2\text{OH}$. A hexylene alcohol has been obtained by H. WALBAUM ¹⁾ from Japanese peppermint oil to which after investigation he attributes the structure of a β - γ -hexenol. This alcohol is presumably the same as that extracted from tea oil.

On oxidation with potassium permanganate the β - γ -hexenol gives propionic acid as principal product. With chromic acid a hexylene acid is obtained. The α -naphthylurethane prepared from the alcohol melts at 80°, while the melting point of the silver salt of the acid phthalic acid ester melts at 126°. On treatment with bromine only 70 % of the quantity required by theory is absorbed.

It is true that the melting points of WALBAUM's silver salt and my own do not agree, but the other properties of the tea-alcohol justify the assumption that the latter to a great extent consists of β - γ -hexenol. I am, however, for the moment unable to explain why, on oxidation with potassium permanganate, an acid was obtained previously, the calcium salt of which contained only 18.6 % of calcium. The acid on that occasion was *not* distilled, as the quantity available was too small, and may have contained, for example, hexylic acid, by which the calcium content of the propionic acid formed would be lowered. Finally it may be possible that the heating of the crude oil with alkali in order to remove the methyl salicylate, has caused a shifting of the double bond.

This research, as well as the investigation of the other constituents of the tea-oil, is being continued ²⁾.

Postscript.

Since the above paper was communicated, the firm Messrs. SCHIMMEL and Co. of Leipsic sent me at my request a small quantity of the unsaturated alcohol prepared from Japanese peppermint oil, for which I desire herewith to express my thanks. The α -naph-

¹⁾ Journ. f. prakt. Chemie, **96**, 254 (1917).

²⁾ The ethereal oil of tea was some time ago the subject of an investigation by Dr. DEUSS (Mededeelingen van het Proefstation voor Thee, XLII, 21, 1917). This research merely confirmed our own observation that the oil contained an unsaturated alcohol together with methyl salicylate.

thylurethane obtained from this (m. p. 80°) when mixed with that prepared from the tea-oil caused no alteration of the melting point.

The acid phthalic acid ester prepared from it, gave a silver salt-melting at 128° . By recrystallisation from alcohol the melting point could be raised to 134° (not sharp). With the silver salt prepared from the tea-alcohol it gave a mixture melting at 138° .

The assumption is thus justified that the unsaturated alcohol prepared *by me from the tea-oil is identical with the β - γ -hexenol, that is, with hexene-3-ol-6.

Utrecht.

Org. Chem. Laboratory of the University.