

Chemistry. — *Minjak Pelandjau, the exudation from the Wood of Pentaspadon Motleyi Hook f.* By P. VAN ROMBURGH, A. G. VAN VEEN and A. J. HAAGEN SMIT. (Third communication.)

(Communicated at the meeting of September 27, 1930).

In our last paper on this subject¹⁾ we suggested that the hydrocarbon we isolated, when catalytic hydrogenation of the phenol (obtained by decarboxylation of pelandjauc acid) was carried to completion, may contain a methyl-group in the benzene nucleus. This view is supported by the following experiment.

In order to split off the hydroxyl-group of the tetrahydrophenol, it was distilled over zinc dust. In the distillate we found in small quantities, however, α -methylnaphtalene. The reduction of the hydroxylgroup has evidently been accompanied by a ringclosure and the elimination of the aliphatic side-chain.

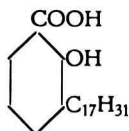
Distillation of the original phenol over zinc dust gave better results. From the distillate we could obtain, on adding an alcoholic solution of picric acid, a very good yield of picrates which proved to be a mixture of naphtalene- and methylnaphtalene picrate.

As the phenol used in this reaction was obtained by heating the liquid part of "minjak pelandjau", one cannot but acknowledge the presence of two different acids in the original exudate.

In order to ascertain the structure of either of those acids we started from pure tetrahydro-pelandjauc acid. It was hydrogenated to decahydro-acid. This was heated with zinc chloride in order to split off carbon dioxide. The crude distillate, when submitted to complete catalytic hydrogenation, yields a solid hydrocarbon m.p. 34—35°, which proved to be identical with heptadecyl-cyclohexane.

From the unsaturated hydrocarbon, obtained by heating the decahydro-phenol with zinc chloride we succeeded in preparing, by catalytic hydrogenation, a saturated hydrocarbon which could also be identified as heptadecyl-cyclohexane.

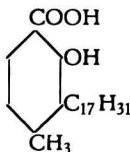
We must therefore assign to the solid acid (m.p. 25°) the structure :



¹⁾ These Proc. 23, 589 (1930).

This formula, except for the difference of the side-chain, is in accordance with the formula proposed by JONES and SMITH ¹⁾ for pentaspadonic acid.

The structure of the liquid acid must be represented as follows :



Distillation of decarboxylated tetrahydropelandjaic acid with zinc dust.

The phenol derived from pelandjaic acid was hydrogenated with platinum black, without special catalytic precautions and in a large quantity of ethyl acetate to prevent the formation of the decahydro-product or of an hydrocarbon. Slowly two molecules of hydrogen were taken up, when the hydrogenation stopped. The tetrahydrophenol melted at 58—59°.

In order to split off the hydroxyl-group 1 gram of the tetrahydrophenol was distilled over zinc dust. When fractionated, the dark yellow distillate gave the following fractions :

1. 0.2 g. boiling at $\pm 70^\circ$ (15 mm)
2. 0.25 g. „ „ $\pm 170^\circ$ (15 mm)
3. 0.2 g. „ „ $\pm 200^\circ$ (0.7 mm)

Fraction 1 produced with picric acid a yellow picrate, m.p. 139—140° after one recrystallisation from alcohol. Further crystallisations did not raise the melting point. A mixed melting point determination with picrate of α -methyl-naphtaline caused no depression. With picrate of naphtalene: mixed melting point 134°. The hydrocarbon was regenerated with potassium hydroxide solution and converted into the styphnate, m.p. 135°; no depression with the styphnate of α -methylnaphtalene.

Fraction 2 gave no picrate and contains probably the hydrocarbon split off in the reaction.

Fraction 3 contains the product free from OH-groups as was shown by the ZEREWITINOFF method.

These results led us to conclude that pelandjaic acid contains a methyl-group in the benzene nucleus.

Distillation of the original phenol with zinc dust.

In the same manner as above the original phenol was distilled over zinc dust. The naphtalenes formed in this reaction were distilled at 760 mm and gave the following fractions :

1. 0.5 g. boiling at 170—235°
2. 0.5 g. „ „ 235—240°
3. 0.3 g. „ „ 240—300°

¹⁾ Proc. Royal Soc. of Queensland 41 N°. 6, 73 (1929).

The residue was distilled at 13 mm and gave 0.5 g boiling at 200—250°.

Fraction 1 was boiled for 24 hours with nitric acid (1.2); a heavy oil separated, and from the aqueous solution a small quantity of crystals melting at 170° could be obtained. They gave with sulphuric acid and resorcinol the fluorescein reaction.

Fraction 2 was treated with potassium dichromate and sulphuric acid. No formation of iso- or terephthalic acid was observed.

Fraction 3 contains the naphthalenes and gave with picric acid a considerable quantity of picrates, which proved to be a mixture of naphthalene- and methylnaphthalene picrate. Recrystallisation from alcohol gave crystals of α -methylnaphthalene picrate. Picric acid determination: Found 61.3 Calc. for methylnaphthalene picrate 61.7.

From the alcoholic mother-liquors a picrate was isolated melting unsharp from 142—150°. After three crystallisations m.p. 145—150°, chiefly at 150°.

Picric acid determination: Found 64.9 Calc. for naphthalene picrate 64.2.

The remarkable results obtained with the zinc dust distillation made it necessary to determine which formula was to be given for the pure crystallised acid of the "minjak pelandjau".

For that purpose we used the purified tetrahydroacid which had been converted into the decahydro-acid. On heating this product carbon dioxide was evolved. Only the temperature of the decarboxylation was higher (330—350°) than in the case of the nonhydrogenated acid and the reaction was accompanied by a dehydration.

The products formed in this process boiled at 240—250° (15 mm). The oily liquid gave a strong reaction with tetranitromethane. It was, without further treatment, hydrogenated as strongly as possible with platinum oxide in acetic acid, in order to reduce the OH group of the decahydro-phenol. Quickly one molecule of hydrogen was absorbed and after inoculation with a crystal of heptadecyl-cyclohexane a crystalline product was obtained melting at 33°. A mixed melting point determination of the products showed no depression (with nonadecyl cyclohexane m.p. 36° a depression of 6° was noted).

Whereas isomerides eventually occurring, might remain in the mother-liquors, during the preparation of the pure tetrahydropelandjauic acid, we treated the decahydrophenol¹⁾ with zinc chloride in order to split off water²⁾. The unsaturated hydrocarbon formed in this reaction (b.p. 240° 15 mm) was hydrogenated with platinumoxide in acetic acid. Quickly 1 mol. of hydrogen was absorbed. The product formed in this reaction boiled at 240—241° (15 mm) and proved to be nearly pure heptadecyl cyclohexane (m.p. 32—33°, after recrystallisation 34—35°). It gave no m.p. depression with the synthetical product nor with the hydrocarbon obtained in the reaction mentioned above.

¹⁾ These Proc. 23, 591 (1930).

²⁾ These Proc. 23, 592 (1930).

On the contrary it gave depressions with closely related hydrocarbons viz. octadecyl- and nonadecyl-cyclohexane.

Therefore the crystallised acid obtained from "minjak pelandjau" must possess the structure given above.

We shall continue the study of the remaining part of the oil, in which the homologue with the methyl-group must be present. There seem to be some indications that the oil may contain some more analogous products possessing perhaps some relation to substances like thitsiol and laccol¹⁾.

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¹⁾ B. 55, 192 (1922).