

Chemistry. — *Anacardic acid.* By A. J. HAAGEN SMIT. (Communicated by Prof. P. VAN ROMBURGH).

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In a communication on Minjak Pelandjau, the exudation from the wood of *Pentaspadon Motleyi* ¹⁾, attention was drawn to anacardic acid, which occurs in the fruit of *Anacardium occidentale*, and the suggestion was made that it may be related to pelandjauc acid.

By courtesy of Dr. LAM, the director of the Buitenzorg herbarium, Prof. VAN ROMBURGH received about 5 KGr. of that fruit from Java, which were put at my disposal for a study of the question on the structure of anacardic acid.

STÄDELER ²⁾ and RUHEMANN, SKINNER ³⁾ noted in the pericarp of the fruit of *Anacardium occidentale*, as well as in those of *Anacardium orientale* the presence of an acid. Analysis of the acid and its salts pointed to the formula $C_{22}H_{32}O_3$ containing one carboxyl and one hydroxyl group.

Eighty fruits weighing 500 gr. had the edible kernel taken out and the skins (320 gr.) ground and extracted with ether. After evaporation of the ether, the residue was a yellow viscous liquid which turned red-brown with aqueous potassium hydroxide on exposure to the air; rapid coloration also took place if a little laccase was added, which is probably the reason why this oily substance is commonly described as red brown. A warm alcoholic solution of the residue was treated with freshly prepared lead hydroxide in order to convert the acid in its leadsalt. After having been cooled, the lead salt was filtered off and decomposed with sulfuric acid. In this way 40 gr. of crude anacardic acid was prepared. After repeating this procedure a slightly yellow coloured product was obtained, which on inoculation with pelandjauc acid, crystallised. This fact pointed to a relationship between these acids, but a small depression of the mixing melting point was noted. A difference in the position of the double linkages in the side chain could easily produce such a difference; it was therefore important to try to obtain the better crystallised tetrahydro-derivatives.

¹⁾ These Proc. **32**, 693 (1929); **33**, 589, 690 (1930).

²⁾ A. **63**, 137 (1847).

³⁾ B. **20**, 1861 (1887).

Tetrahydro-anacardic acid.

Anacardic acid was hydrogenated in ethylacetate solution with platinum-black as catalyst, two molecules of hydrogen were absorbed. The tetrahydro-product was recrystallised from diluted methylalcohol and from petroleum ether in which it is sparingly soluble in the cold. After several crystallisations the melting point remained at 92° and showed a depression of 7° with tetrahydro-pelandjauc acid, m. p. 98° .

Analysis: Found 75.98 % C. and 10.63 % H.

$C_{22}H_{36}O_3$ requires 75.79 % C. and 10.42 % H.

This tetrahydro-product gave a violet coloration with $FeCl_3$ in alcoholic solution just like tetrahydro-pelandjauc acid, from which we conclude in this case also the presence of a hydroxyl and a carboxyl group in ortho-position.

Decarboxylation of anacardic acid.

Just like pelandjauc acid this substance loses carbon dioxide by heating at 220° . After heating during one hour the decarboxylation was complete and the remaining product was distilled at 0.4 mm. Boiling point 205° . The methyl ether of this phenolic product was prepared by shaking it with dimethyl sulfate and sodium hydroxide solution. It boiled at 202° (0.5 mm.). The determination of the methoxyl group gave negative results, proving that this ether is also remarkably resistant to the action of hydriodic acid.

$d_4^{15} = 0.9240$ $n_D^{15} = 1.5076$ Found: $M_D = 101.3$.

$C_{22}H_{38}O$ requires $M_D = 100.9$.

Hydrogenation of the methyl ether of the phenol.

1.5 grs were hydrogenated in 30 grs of ethyl acetate with platinum black. In twenty minutes the reduction stopped, the aromatic double linkages resisting further hydrogenation. This tetrahydro-product melted at 30° .

Analyse: Found: 82.64 % C and 12.35 % H.

$C_{22}H_{38}O$ requires 82.94 % C and 12.05 % H.

Methyl tetrahydro anacardic methyl ester.

By shaking the acid with dimethyl sulphate and sodium hydroxyde solution the ether-ester was prepared. Boiling point $220-222^{\circ}$ (0.5 mm.),

Analysis: Found: 76.59 % C and 9.72 % H.

$C_{24}H_{36}O_3$ requires 77.23 % C and 9.75 % H.

Methoxyl determination: Found: OCH_3 16.0 %.

$C_{21}H_{30}COOCH_3OCH_3$ requires: OCH_3 16.67 %.

Hydrogenation of this ether-ester with platinum-black in ethyl acetate

produced the tetrahydro-derivative which crystallised from alcohol m.p. 38° .

Analysis: Found: 76.57 % C and 10.84 % H.

$C_{24}H_{40}O_3$ requires: 76.59 % C and 10.72 % H.

Methoxyl determination: Found: OCH_3 16.59 %.

$C_{21}H_{34}COOCH_3OCH_3$ requires: 16.49 % OCH_3 .

Oxidation of the tetrahydro ether ester.

1 gram oxidised with CrO_3 in acetic acid yielded a crystalline acid, which precipitated when diluted with water. It proved to be insoluble in aqueous sodium hydroxide. After filtration of the sodium salt, this was transferred into the acid with sulfuric acid. After crystallisation from alcohol and from petroleum ether the melting point was raised to 59° . The substance gave no depression with palmitic acid, on the other hand melting point depressions were obtained with stearic acid and myristic acid.

From this result we conclude that a normal chain of 16 carbon atoms is present, in which no hydrogen is replaced by the carboxyl or hydroxyl group.

Hydrogenation of the phenol $C_{21}H_{31}OH$.

The decarboxylation product of anacardic acid was hydrogenated with platinum oxide in acetic acid solution. After taking up 5 mols of hydrogen the reduction came to an end. After evaporating the solution a substance m.p. 31° could be obtained. This proved to be the dekahydro product.

Hydroxyl determination: Found: OH 5.74 %.

$C_{21}H_{41}OH$ requires 5.48 %.

Dehydration of the phenol.

To obtain the hydrocarbon free from hydroxyl the dekahydro product was heated for three hours with three times its weight of $ZnCl_2$ at 220° . After washing with ether and water the ether layer was evaporated and the residue distilled. Boiling point $180-185^{\circ}$ (0.5 mm.). This product gave a yellow coloration with tetranitromethane, which demonstrated the presence of a double bond. It was submitted to complete hydrogenation with platinum oxide in acetic acid. One molecule of hydrogen was absorbed.

The remaining hydrocarbon distilled at 178° (0.7 mm.) m.p. 25° and proved to be identical with the synthetical pentadecyl-cyclohexane prepared from myristic acid and benzyl bromide by converting the acid in tetradecyl bromide and combining this by a FITTIG's reaction with benzyl bromide. Boiling point 178° (0.7 mm.) m.p. 25° .

The anacardic hydrocarbon gave no melting point depression with the pentadecyl-cyclohexane. Both substances gave depressions with the pelandjauc hydrocarbon and with synthetic heptadecyl- and octadecyl-cyclohexane.

Analysis: Found: 85.89 % and 14.45 % H.

$C_{21}H_{42}$ requires 85.70 % C. and 14.30 % H.

$$n_D^{20} = 1.4612 \quad d_4^{19.5} = 0.8323 \quad \text{Found: } M_D = 97.0$$

$$C_{21}H_{42} \text{ requires } 97.0$$

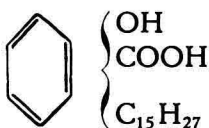
Hydrocarbon from pelandjaic acid. Boiling point 194°C (0.4 mm.).

$$n_D^{24} = 1.4596 \quad n_D^{37.5} = 1.4542 \quad \text{Found } M_D: 106.1$$

$$C_{23}H_{46} \text{ requires } 106.2.$$

$$d_4^{18} = 0.8332 \quad d_4^{37.5} = 0.8821.$$

In anacardic acid we have a lower homologue of pelandjaic acid with a difference of two CH_2 groups. The following formula is to be assigned to anacardic acid:



The further study of this acid is to be continued and there are indications, that the remaining oil, named cardol, may contain some more analogous products possessing some relation to substances like urushiol¹⁾, the two carbon atoms lower homologue of thitsiol and laccol²⁾.

¹⁾ B. 46, 4080 (1913).

²⁾ B. 55, 172 (1922).