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$NH_4NO_3 - (NH_4)_2SO_4 - H_2O$ [1])

Besides the two anhydrous salts NH_4NO_3 and $(NH_4)_2SO_4$ there occur also at 0°, 30° and 70° the two anhydrous double salts

$$2NH_4NO_3 . (NH_4)_2SO_4$$

and $3NH_4NO_3 . (NH_4)_2SO_4$

as solid phases.

So far as they have been investigated up to the present, the ammonium salts behave quite differently from the potassium salts and in their behaviour show more resemblance with the lithium and sodium salts.

These investigations are being continued at other temperatures and also with nitrates and sulphates of other metals.

Chemistry. — *"On Dipterocarpol"*. (Preliminary communication) By Prof. L. VAN ITALLIE. (Communicated by Prof. A. P. N. FRANCHIMONT).

(Communicated in the meeting of February 24, 1912).

In the investigation of the balsam of Dipterocarpus Haseltii and D. trinervis (Minjak Lagam) a substance was obtained in well-defined crystals.

When the balsam is mixed with petroleum ether, the solution decanted and the remainder extracted with petroleum ether until nothing more dissolves therein 34 % of the balsam is left behind in the form of small white crummy pieces, mixed with small particles of wood. On boiling with alcohol and filtering, a liquid is obtained from which on cooling, colourless crystals are deposited to the extent of 19 % of the original balsam.

The crystals have a melting point of 128° which by repeated crystallisation from alcohol, may be raised to 134°—135°, but then remains constant. On warming with alcoholic potash and subsequent crystallisation from alcohol the melting point also remains constant

The substance obtained gives the colour reactions characteristic for phytosterols, with acetic anhydride and sulphuric acid, with chloroform and sulphuric acid etc. As it differs, however, in more than one respect, from the known phytosterols, it will be designated provisionally by the name of Dipterocarpol.

[1]) F. A. H. SCHREINEMAKERS and P. H. J. HOENEN. l.c. Determination of the isotherm at 30°. A. J. C. DE WAAL. Dissertation, Leiden 1910; determination of the isotherms at 0° and 70°.

Dipterocarpol forms colourless biaxial crystals showing double refraction and straight extinction. They are readily soluble in chloroform, ether, and acetic ether, but with difficulty in cold alcohol.

At 130° they lose no water of crystallisation.

In the elementary analysis the following results were obtained:

	combustion with copper oxide:		combustion with lead chromate:	
C =	80.78	80.68	80.69	80.53
H =	11.43	11.41	11.45	11.35

Average: C 80.67 H 11.41.

In the determination of the molecular weight, according to the method of the lowering of the freezing point, was found M = 433.

The formula $C_{27} H_{46} O_2$ requires C. 80.59, H. 11.44 and a molecular weight of 402. The values found are, therefore, sufficiently in agreement therewith.

Dipterocarpol is dextrorotatory; α_D (determined in chloroform) + 64.6°.

In the ordinary way of acetylation by boiling with acetic anhydride and sodium acetate, in which the time of boiling was much varied, no crystallisable acetyl derivative could be obtained; also none with acetic anhydride and sulphuric acid or zinc chloride. As phytosterols are generally so readily acetylised, dipterocarpol therefore forms an exception.

When dipterocarpol is heated with sodium acetate and acetic anhydride for 3 hours at 160°, the contents of the tube when cold solidify to a crystalline mass from which, after washing with water may be obtained by recrystallisation from alcohol, colourless crystals showing double refraction and straight extinction and melting at 69°—70°.

These crystals form the anhydride of dipterocarpol.

In the elementary analysis was found:

	I	II	The formula $C_{27} H_{44} O$ requires:
C	84.74	84.20	84.37
H	11.82	11.36	11.47

Dipterocarpol anhydride is also formed together with diphenylurea by heating dipterocarpol for a short time with phenylisocyanate.

When dipterocarpol is dissolved in benzene and shaken for 6 or 7 hours with Kiliani's chromic acid mixture, it is converted into a ketone (dipterocarpone) which can be obtained from alcohol in well-developed crystals.

Dipterocarpone forms pillar-shaped, pointed rhombic crystals melting at 183°—184°. They contain no water of crystallisation and

give, on application of the well-known phytosterol reactions, less intense colorations than dipterocarpol and its anhydride. The latter, in particular is characterised by very strong colour reactions.

In the elementary analysis was found:

	I	II	The formula $C_{27} H_{44} O_3$ requires:
C	77.85	77.45	77.88
H	10.43	10.58	10.66

The molecular weight was found to be: 409, the calculated molecular weight 416.

When dipterocarpone was dissolved in benzene and again shaken for 6 hours with the chromic acid mixture it could be recovered unchanged from the benzene solution. The melting point was found to be 182°—183° and the C-content and H-content 77.69 and 10.30, respectively.

Dipterocarpone is dextrorotatory; α^D (in chloroform) $= + 71.03°$.

From the dipterocarpone was made an oxime by means of hydroxylamine hydrochloride and potassium hydroxide. This oxide is only very little soluble in alcohol and is best recrystallised from glacial acetic acid. It then separates in microscopic small crystals which melt at 249°—250° with decomposition.

The nitrogen content was found to be 3.5 %. The formula: $C_{27} H_{44} (NOH)$ requires 3.48 %.

When dipterocarpole is dissolved in glacial acetic acid and oxidised with chromic acid we again obtain dipterocarpone m.p. 183°—184°. A solution of dipterocarpol in acetone is not acted upon by potassium permanganate.

The action of bromine did not lead to the formation of a crystallised product. Only amorphous, resinous substances were obtained, with evolution of hydrogen bromide.

On treating a solution of dipterocarpol in carbon tetrachloride with Wijs's iodine monochloride solution a little more than 3 atoms of halogen was absorbed. The halogen not only acted additive, but also caused substitution. On adding water to the iodised liquid, fumes of halogen-hydrogen were noticed.

In the reduction of dipterocarpol with sodium in boiling amyl alcohol, no crystallised dihydro-product was obtained, but only an amorphous resinous mass.

As the result of this preliminary investigation it may be stated that dipterocarpol is a phytosterol of the formula $C_{27} H_{46} O_2$ from which one molecule of $H_2 O$ can be readily eliminated.

Leiden, February 1912.