

Citation:

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to declare that the substance, isolated from PECKOLT's agoniadine, is identical with plumieride.

Although it is customary in such cases to retain the name given by the first discoverer, it seems to me that the name „plumieride” is preferable. It reminds of both plants from which it is obtained and by its termination it is more suited for a glucoside. I, therefore, obliterate the name „agoniadine”, which on account of its termination reminds more of an alkaloïd, from the chemical literature and in future will call *plumieride* the substance discovered by PECKOLT in 1870 in the bark of *Plumiera lancifolia*, which substance has afterwards been found by BOORSMA and also by MERCK in the bark of *Plumiera acutifolia*.

Plumieride is a methyl-ester (a methoxyl containing substance) then, it yields methyliodide with hydroiodic acid of a certain concentration. It yields, by the action of dilute alkalis or barytawater at the ordinary temperature, or by water alone at a higher temperature, an acid which I have provisionally called *plumieridic acid*¹⁾. This does not contain methoxyl but is a glucoside which on boiling with dilute acids yields a brown amorphous substance and a sugar, the osazone of which has the same melting point as that of glucose.

If plumieride is now simply a methyl-ester of plumieridic acid as nearly everything found as yet seems to bear out, the easy decomposition (saponification) by alkalis and even by water and the consequent difficulty to obtain a pure preparation by recrystallisation from water becomes apparent.

I, finally, wish to add that the solution of PECKOLT's preparation in cold water was of a very brown colour and strongly reduced FEHLING's solution; when first extracted with ethylacetate it left a good deal of a brown amorphous substance behind and it was only by repeated crystallisation from ethylacetate, which operation was attended with great loss, that it was obtained pure. The impure fractions contained glucose.

Chemistry. — “*On the crystallised constituent of the essential oil of Kaempferia Galanga L.*” By Dr. P. VAN ROMBURGH.

When the rhizomes of *Kaempferia Galanga L.*, a plant belonging to the family of the Zingiberaceae, which is cultivated on a small scale by the natives in Java for medicinal and culinary use and

¹⁾ The name plumieric acid has already been given by our deceased fellow member Prof. A. C. OUDEMANS JR. to another acid obtained from the milky juice of *Plumiera acutifolia*.

known under the name of "kentjoer" or "tjekoer", are distilled with water, the first fractions contain a small quantity of an essential oil lighter than water. Afterwards an oil heavier than water distils which deposits abundant crystals, whilst towards the end a crystalline substance is almost exclusively obtained. The distillation must be continued for a long time as this substance is but little volatile. The yield and also the relation between the solid and liquid product differ very much with different samples; most likely this depends on the age of the rhizomes, which matter I am now making the subject of practical investigation.

The crystals deposited from the oil may assume very large dimensions; they are very shining and transparent, melt at 50° and may be obtained in a beautiful form by recrystallisation from alcohol. A 20 percent alcoholic solution appeared to be optically inactive.

The elementary analysis gave numbers, which lead to the formula $C_{12}H_{14}O_3$, while the molecular weight, determined in acetone by LANDSBERGER'S method, came to 197, 206 being calculated.

On heating with alcoholic potash this substance yielded almost at once a mass of beautiful little crystals of a potassium salt; from which sulphuric acid liberates an acid crystallising in colourless needles. This acid is not easily soluble in water but easily soluble in ether and it may be very satisfactorily recrystallised from dilute methyl alcohol.

The melting point is 169° ; at that temperature it melts to an opalescent liquid which does not become transparent till 185° .

The elementary analysis gave results corresponding with the composition $C_{10}H_{10}O_3$.

The original substance differing from this by C_2H_4 must, therefore, be an ethyl-ester. To further prove this, 30 gram of the crystals were saponified with aqueous caustic potash and the resulting alcohol was distilled off. After treatment with dry potassium carbonate and rectification over anhydrous copper sulphate a liquid was obtained which boiled at 78° and showed all the properties of ethyl alcohol.

The potassium and silver salts of the acid were prepared and analysed. The potassium estimation gave 17.7 pCt. of K (theory requiring 17.6), the silver estimation gave 38.06 pCt. Ag., (theory requiring 37.9).

If a solution of the acid in ethyl alcohol is treated with hydrogen chloride, a product is obtained which melts at 50° and is identical with the original ester. The methyl ester prepared in an analogous manner melts at 90° .

The solution of the acid or its ester in chloroform absorbs two atoms of bromine forming an addition product.

The acid does not show either aldehydic, alcoholic or phenolic properties. Heated with hydriodic acid it yields alkyl iodide. A quantitative estimation according to ZEISEL gave an amount of silver iodide corresponding with 16.85 pCt. of methoxyl, theory requiring 17.4 pCt.

On oxidation with potassium permanganate in neutral solution, the ester gives off an agreeable odour resembling hawthorn, while an acid is also produced which proved to be identical with anisic acid. The oxidation of the acid in an alkaline solution proceeds more quickly; the odour of anisic aldehyde is also noticed here and a good yield of anisic acid is obtained. From this it follows that in regard to the side-chain the group OCH_3 is situated in the para-position and in connection with the additive power the formula is therefore, most probably $1.4 \text{ C}_6 \text{ H}_4 \begin{matrix} \text{OCH}_3 \\ \text{CH} = \text{CH} - \text{COOH} \end{matrix}$, consequently that of p. methoxycinnamic acid.

The properties do indeed correspond with those recorded of this acid ¹⁾. The only thing which is not mentioned is the peculiar behaviour on melting, so that I thought it necessary to prepare the synthetical acid for comparison purposes.

According to KNOEVENAGEL ²⁾ it is obtained by condensation of anisic aldehyde with malonic acid under the influence of alcoholic ammonia. The acid prepared by this method also melted at 169° to an opalescent liquid which did not get clear till 185° .

VORLÄNDER ³⁾ obtained the ethyl ester of p. methoxycinnamic acid by condensation of anisic aldehyde with ethyl acetate. This I also prepared and found it to be identical with the product obtained from "Kentjoer", whilst the acid obtained from it by saponification again showed the properties mentioned above.

I dare not, as yet, decide what may be the cause of this peculiar behaviour. Perhaps a polymeric body is formed, or else the acid exists in two liquid isomeric modifications ⁴⁾. By heating above the melting point, the acid is gradually decomposed with evolution of carbon dioxide, but if the decomposition already exercised some

¹⁾ In Beilstein's Handbuch it is erroneously stated that p. methoxycinnamic acid crystallises in yellow needles.

²⁾ Berl. Ber. 31 S. 2606.

³⁾ Ann. der Chemie. 294, S. 295.

⁴⁾ Compare: RUDOLF SCHENCK, Untersuchungen über die krystallinischen Flüssigkeiten. Zeitschr. f. phys. Chemie XXV, S. 337, XXVII S. 167.

influence during the determination of the melting point, this would be found lower on repeating the experiment, but this is, however, not the case.

By treating the alcoholic solution of the acid obtained from kentjoer with sodium amalgam p. methoxyphenylpropionic acid is formed, which melts at 102° and has already been described by WILL¹⁾. The methyl ester of methyl naringenic acid²⁾ prepared by the same chemist, which is identical with the methyl ester of p. methoxycinnamic acid, melts at 90° just like the methyl ester obtained by myself, whilst its bromine-addition product showed the melting point of the methyl ester of dibromomethylparacumaric acid.

There cannot, therefore, be any further doubt that the crystallized substance which forms the chief constituent of the essential oil from *Kaempferia Galanga L.*, is the ethyl ester of p. methoxycinnamic acid, a substance which had not yet been met with in nature and which now goes to increase the comparatively small number of known ethyl esters from the vegetable kingdom.

From the liquid portion of the oil I could separate in addition to the above mentioned ester a small quantity of a terpene boiling at 160°—170° and a bluishgreen liquid boiling at 150° in vacuo (probably a sesquiterpene). There is also present an acid of a lower melting point which I am still investigating.

Pathology. — “*On the durability of the agglutinative substances of the bloodserum.*” By Dr. J. E. G. VAN EMDEN. (Communicated by Prof. Th. H. MAC GILLAVRY.)

WIDAL and SICARD³⁾ and also ACHARD and BENSAUDE⁴⁾ have communicated that the bloodserum of patients suffering from febris typhoidea and that of animals, that had been rendered immune against the bacille of EBERTH, keeps its agglutinative power undiminished for many months; the agglutinines are so resistant that they do not perish even in mouldy and putrefying serum.

On the contrary I found that serum after some six weeks indeed

¹⁾ Berl. Ber. XX S. 2530.

²⁾ Berl. Ber. XX S. 301.

³⁾ Annales de l'Institut. Pasteur XI p. 353.

⁴⁾ BENSAUDE: Le Phénomène de l'Agglutination des Microbes. (Paris 1897).