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Synthetic Tannins

Georg Grasser

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AUTHOR'S PREFACE

Whilst the synthesis of the natural tannins has been successfully outlined by Emil Fischer, it has been left to the Chemical Industry, notably the Badische Anilin und Soda-fabrik in Ludwigshafen-on-the-Rhine, to discover the means of making possible the production of the synthetic tannins.

The scientific results of Fischer's researches are to-day common knowledge, and these, together with questions arising therefrom, will only be lightly touched upon in the book herewith presented. Even an attempt at enumerating the present synthetic tannins has so far not been published, and I have therefore availed myself of the opportunity of making a brief summary of them. My work at the B.A.S.F. deepened my insight in this new field; ample opportunity of applying these synthetic products in practice was given me when, as a result of the war, I was appointed technical consultant to the Austrian Hide and Leather Commission, and in this capacity was called upon to act as general adviser to the trade. The ultimate object of my scientific researches was then to investigate the chemistry of this particular field, and this has led me to present a picture, complete as far as it goes, of this branch of chemical technology.

The intention of the present volume is to communicate to the reader what has so far been scientifically evolved and practically applied in this field. First of all, however, it may illustrate the extreme importance and the universal applicability of the synthetic tannins in the making of leather. The modern leather industry cannot, to-day, be without these important products, but also in those tanneries, where the synthetic tannins have not so far been regarded as indispensable, their use is strongly recommended. Just as in the case of the coal-tar dyes, the synthetic tannins will make us independent of foreign supplies, and thus keep within our own borders the vast sum of money required in former days for the purchase of foreign tanning materials. May this book prove the means of

providing an incentive for a still wider application of the synthetic tannins.

GRASSER.

GRAZ, *August* 1920.

TRANSLATOR'S PREFACE

Doctor Grasser hardly needs an introduction to the leather trade of this country in its scientific aspect, but if one be sought for, none could serve the purpose better than a translation of the book herewith presented to the British-speaking public.

Viewed with curiosity from their start, the synthetic tannins needed—like many other important discoveries—an extreme emergency for the purpose of showing their value. The Great War provided the opportunity of which chemical industry was to avail itself, and to-day we do not only see synthetic tannins placed upon the market as a veritable triumph of chemical technology and a creditable triumph of manufacturing chemistry; we also see their immensely practical qualities established as a fact, and, as the author aptly remarks, no modern tanner can to-day dissociate himself from the use of synthetic tannins for the production of leather in the true sense of this word. There is no branch of leather-making where synthetic tannins cannot help and improve processes already established.

The immense number of substances patented by German manufacturing chemists for the purpose of producing synthetic tanning materials is almost staggering. In view of this fact it is doubly pleasing to see that British chemists have found new ways, and are able to produce equally good and more varied synthetic tannins than has hitherto been deemed possible. The originator of these products and his acolytes must at least share the credit with those who, in spite of the limitations necessarily set by the former, have been able to find new and better ways.

In his book Dr. Grasser gives a short review of the necessary forerunner of any work upon synthetic tannins: the investigations and syntheses of the natural tannins. It is certainly to be hoped that we may soon see such works as those of Fischer's and Freudenberg's, recently published, translated into English. For the guidance of the reader it may be noted that a short account of the works of these

authors may be found in the *Journal of the Society of Leather Trades' Chemists*, vol. v. (May issue); in addition to this some of the matter contained in the chapter on synthesis of tanning matters appeared in the January 1921 issue of the *Journal of the American Leather Chemists' Association*.

In addition to these two sections, the last part of this book deals with the practical applications of synthetic tannins, and it is hoped that the tanner will find much valuable information in these pages. The main outlines of the synthesis of tanning matters should prove of great value to the chemist engaged in this branch of chemical technology.

The translator takes great pleasure in the acknowledging the valuable assistance rendered him by Mr. Robin Bruce Croad, A.R.T.C., F.I.C., and by Mr. Arthur Harvey.

F. G. A. ENNA

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INTRODUCTION

CLASSIFICATION OF SYNTHETIC TANNINS

In laying down a definition of "Synthetic Tannins," it is first of all necessary to clearly define the conception of "tannin." Primarily, tannins may be considered those substances of vegetable origin which may be found, as water-soluble bodies, in many plants, exhibiting certain chemical behaviour, possessing astringent properties and being capable of converting animal hide into leather. This latter property of the tannins, that of converting the easily decomposable protein of animal hide into a permanently conserved substance and imparting to this well-defined and technically valuable properties, has become the criterion of the practical consideration of a tannin. It appears that different substances certainly show the chemical reactions peculiar to the tannins, and to a certain extent also exhibit astringent character without, however, possessing the important property peculiar to the tannins of converting hide into leather. Such substances, in our present-day terminology, are termed pseudo-tannins (*e.g.*, the "tannin" contained in coffee-beans). Decomposition products of the natural tannins, to which belong, for instance, gallic acid and the dihydroxybenzenes, exhibit the well-known reactions of the tannins (coloration with iron salts), but they cannot be regarded as tannins from either a technical or a physiological standpoint.

As regards their chemical constitution, the natural (true) tannins probably belong to different groups of organic compounds, and with our present-day scant knowledge of their chemistry, it is impossible to classify them. One is, however, justified in assuming that both the natural tannins and the related humic acids are ester-derivatives of hydroxybenzoic acids. [Footnote: E. Fischer, *Ber.*, 1913, 46, 3253.]

The production of synthetic tannins employs two quite distinct methods; one is to synthesise the most simple tannin, *viz.*, the tannic acid contained in galls (tannin), or to build up substances similar in

character to the tannins, from hydroxybenzoic acids. The other, entirely new way, is to produce chemical substances, which certainly have nothing in common with the constitution of the natural tannins, but which behave like true tannins in contact with animal pelt, and in addition, since they can be manufactured on a commercial scale, are of practical value.

Owing to the fact that, until recently, the constitution of tannin has remained unknown, it is easy to comprehend that the efforts to synthesise the latter substance, or compounds similar to it, have been mainly attempted on similar lines. The oldest investigation in this direction dates from H. Schiff, [Footnote: *Liebig's Ann.*, 1873, 43, 170.] who prepared substances similar to tannin by dehydrating hydroxybenzoic acids. By allowing phosphorus oxychloride to interact with phenolsulphonic acid, he obtained a well-defined substance possessing tanning properties, which he considered an esterified phenolsulphonic acid anhydride, the composition of which he determined as $\text{HO.C}_6\text{H}_4\text{SO}_2\text{O.C}_6\text{H}_4\text{HSO}_3$. It is, however, probable that this substance is not homogeneous, but consists of a mixture of higher condensation products.

Klepl [Footnote: *Jour. pr. Chem.*, 1883, 28, 208.] obtained — by simply heating *p*-hydroxybenzoic acid — a so-called di- and tridepside, but this simple method is not applicable to many other hydroxybenzoic acids, since these are decomposed by the high temperature required to induce reaction.

Amongst other attempts to produce condensation products with characteristics similar to those possessed by the tannins, those by Gerhardt [Footnote: *Liebig's Ann.*, 1853, 87, 159.] and Loewe [Footnote: *Jahresh. f. Chem.*, 1868, 559.] must be especially noted; they treated gallic acid with phosphorus oxychloride or arsenic acid, and thereby obtained amorphous compounds, exhibiting the reactions characteristic of tanning substances. E. Fischer and Freudenberg, [Footnote: *Liebig's Ann.*, 372, 45.] by treating *p*-hydroxybenzoic acid in the same way, succeeded in obtaining a didepside, and during the last years practically only these two investigators have demonstrated the syntheses of these depsides and produced high-molecular polydepsides.

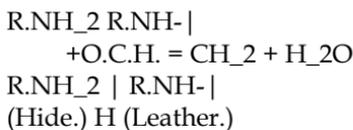
At the same time researches were instituted with the object of determining the constitution of tannin, and E. Fischer succeeded in demonstrating its probable composition as being that of a glucoside containing 5 molecules of digallic acid per 1 molecule of glucose.

This last-named class of synthetic tannins — which may be properly termed "tanning matters" in contradistinction to the true tannins — exhibit very distinct tanning character when brought in contact with animal hide, but from the point of view of chemical constitution have nothing in common with the natural tannins. Not only are they of interest to the industry from a practical point of view; they have also been examined very closely from a chemical standpoint.

It is, however, necessary to differentiate with great exactitude between the conception of *true tanning effect* and *pickling effect* when considering the action of chemical substances on pelt (i.e., animal hide, treated with lime, depilated, and the surplus flesh removed). Whereas any *true tannage* is characterised by the complete penetration of the substance and its subsequent fixation by the pelt in such a way that a thorough soaking and washing will not bring about a reconversion (of the leather) to the pelt state; *pickling*, on the other hand, is only characterised by the penetration of the substance in the pelt and fixation to such an extent that a subsequent washing of the pickled pelt will bring back the latter to a state closely approximating that of a true pelt. Simple as such a differentiation appears, there are still a number of cases occupying a position between the two referred to, and which we may term *pseudo-tannage*. An example of the latter is formaldehyde tannage; formaldehyde has for a long time been employed in histological work for the purpose of hardening animal hide, by which it is readily absorbed from solution whereby it hardens the hide without, however, swelling it. A hide which has thus been treated with formaldehyde absorbs the natural tannins with greater ease; this, on the one hand, argues the probability of formaldehyde acting as a pickling agent; on the other hand, it is also one of its characteristics that it will either in neutral acid, [Footnote: R. Combret, Ger. Pat, 112, 183.] or, still better, in alkaline [Footnote: J. Pullman, Ger. Pat, 111,408; Griffith, *Lea. Tr. Rev.*, 1908.] solution, convert pelt into leather. In a formaldehyde-tanned leather, however, no trace of tannin can be detected; and the

yield (of leather, based on the pelt employed), which, from a practical standpoint, is so important, is so very low that it is hardly possible to speak of it as a tannin in the ordinary sense of the word. Formaldehyde must, therefore, be termed a pseudo-tannin.

The tanning effect of formaldehyde is, according to Thuau, [Footnote: *Collegium*, 1909, 363, 211.] increased by those salts which bring about colloidal polymerisation of the formaldehyde, the resultant compounds being absorbed by the hide fibre. Fahrion considers this to be a true tannage, and is supported by Nierenstein [Footnote: *Ibid.*, 1905, 157, 159].—



A peculiar combination between true tannage and pickling is to be found in the tawing process (tannage with potash, alum, and salt), whereby, firstly, the salt and the acid character of the alum produce a pickling effect, and secondly, the alum at the same time is hydrolysed, and its dissociation components partly adsorbed by the hide, thereby effecting true tannage. This double effect is still more pronounced in the synthetic tannins which contain colloidal bodies of pronounced tanning intensity on the one hand, inorganic and organic salts on the other, which then act as described above. Their real mode of action can only be explained with the aid of experimental data. The following chapters will deal with the different behaviour of the various groups of synthetic tannins.

PART I SECTION I

THE SYNTHESIS OF VEGETABLE TANNINS

1. TANNIN

The first investigations of gall-tannin date from the year 1770, at which time, however, no exact differentiation between tannin and gallic acid was made. The first step in this direction was made when Scheele, [Footnote: Grell's *Chem. Ann.*, 1787, 3, I.] in 1787, discovered gallic acid in fermented gall extract, and in the same year Kunzemuller [Footnote: *Ibid.*, 1787, 3, 413.] separated gallic acid (or pyrogallol) as a crystalline body from oak galls. Dize [Footnote: *Jour. Chim. et Phys.*, 1791, 399.] continued the investigations, which were brought to a conclusion with Deyeux' work [Footnote: *Ann. Chim.*, 1793, 17, I.]; both recognised that the substance isolated was not a single substance, but was a mixture of gallic acid, a green colouring matter, a rosin (tannin?), and extraneous matter. Proust [Footnote: *Ibid.*, 1799, 25, 225.] was the first to differentiate the crystalline gallic acid from the amorphous, astringent substance, which latter he named "Tannin."

Amongst the numerous subsequent investigations of tannin must be especially noted the one by Berzelius [Footnote: *Pogg, Ann.*, 1827, 10, 257.], who purified the potash salt and decomposed this with sulphuric acid. Pelouze [Footnote: *Liebig's Ann.*, 1843, 47, 358.], later on, observed the formation of the crystalline gallic acid from tannin, when the latter is boiled with sulphuric acid; this had already been observed by J. Liebig. [Footnote: *Ibid.*, 1843, 39, 100.] Both had noticed the absence of nitrogen. In addition to the methods of preparation of tannin then in vogue neutral solvents were mainly employed by subsequent investigators; Pelouze [Footnote: *Jour. Prakt. Chem.*, 1834, 2, 301, and 328.] treated powdered galls with ether containing alcohol and water, and considered the upper layer to be a solution of gallic acid and impurities, the bottom layer to contain the pure tannin.

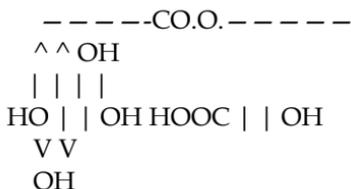
The EMPIRICAL FORMULA of tannin has also been the subject of much speculation by the different investigators, the difficulty here being that of obtaining a pure specimen of the substance free from sugars, and which could be submitted to elementary analysis. Whereas these early purified substances were thought to correspond to the formula of digallic acid (galloylgallic acid), C₁₄H₁₀O₉, Fischer and Freudenberg [Footnote: *Ber.*, 1912, 915 and 2709.] were able to show, with approximate certainty, that the constitution of tannin is that of a pentadigalloyl glucose.

Early attempts at *hydrolysing tannin* gave varying results, some investigators claiming the presence, and others the absence of sugars. Here, again, E. Fischer and Freudenberg [Footnote: *Ibid.*] were able to conclusively prove that on hydrolysing tannin with dilute acids, 7.9 per cent. glucose is dissociated, and that hence glucose forms part of the tannin molecule. Fischer and Freudenberg also determined the optical activity of pure tannin in water: [Greek: α]_D was found to lie between +58° and +70°.

Graham found [Footnote: *Phil. Transact.*, 1861, 183.] that the *tannin molecule* is of considerable size, since its diffusion velocity is 200 times less than that of common salt. Paternò [Footnote: *Zeits. phys. Chem.*, 1890, iv. 457.] was the first to determine the molecular weight of tannin, employing Raoult's method; he found that tannin in aqueous solution behaves like a colloid and that hence Raoult's method is not applicable. When, on the other hand, he dissolved tannin in acetic acid, results concordant with the formula of C₁₄H₁₀O₉, corresponding to a molecular weight of 322, were obtained. Sabanajew [Footnote: *Ibid.*, 1890, v. 192.] later determined the molecular weight of tannin in aqueous solution as 1104, in acetic acid solution as 1113-1322, Krafft [Footnote: *Ber.*, 1899, 32, 1613.] as 1587-1626 in aqueous solution. Walden [Footnote: *Ibid.*, 1898, 3167.] determined the molecular weight of tannin-schuchardt as 1350-1560, tannin-merck as 753-763, digallic acid as 307-316 (calculated 322). Feist [Footnote: *Chem. Ztg.*, 1908, 918.] determined the molecular weight of tannin as 615 and one of his own preparation as 746, Turkish tannin as 521 and Chinese tannin as 899. In this connection it should be noted that the calculated molecular weight of pentagalloyl glucose, which in E. Fischer's opinion forms a substantial part

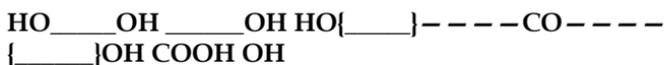
of the tannin molecule, is 940, but Fischer also thinks that this compound possesses a much higher molecular weight.

STRUCTURE OF TANNIN—The oldest structural formula of tannin is Schiff's digallic acid formula:—[Footnote 1: *Ber.*, 1871, 4, 231.]

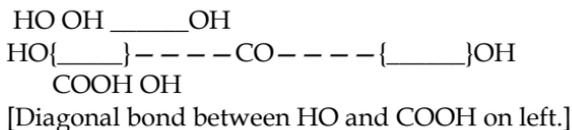


A drawback to the acceptance of this formula is the absence of an asymmetrical C-atom; the formula, therefore, does not explain the optical activity exhibited by tannin. Schiff attempted to overcome this difficulty by adopting a diagonal structural formula, but even when adopting Clauss' diagonal formula for benzene the optical activity of a number of other compounds depends upon the existence of the asymmetrical C-atom. Biginelli [Footnote 2: *Gazz chim. Ital.*, 1909, 39, 268.] also opposed the digallic acid formula, and supported his view by referring to the arsenic compounds obtained by him on heating arsenic acid and gallic acid, instead of obtaining digallic acid. Walden, [Footnote 3: *Ber.*, 1898, 31, 3168.] on the other hand, found, on analysing the digallic acid thus prepared, only slight traces of arsenic and, by the elementary analysis, obtained figures closely corresponding to those of digallic acid.

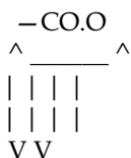
Bottinger [Footnote 4: *Ibid.*, 1884, 17, 1476.] prepared the so-called [Greek: b]-digallic acid by heating ethyl gallate with pyroracemic acid and sulphuric acid and proposed the so-called ketone-tannin formula:—



Schiff completed this formula by a diagonal, so as to explain the optical activity observed—



The ketone formula was corroborated by Nierenstein, [Footnote: *Ber.* 1905, 38, 3641.] who distilled tannin with zinc dust and obtained diphenylmethane (smell of benzene) and a crystalline product, M.P. 70°-71° C. (M.P. of diphenyl = 71° C.). König and Kostan-ecki [Footnote: *Ibid.*, 1906, 39, 4027.] sought to find the constitution of the tannins in the leuco-compounds of the oxyketones, to which catechin belongs. Nierenstein (see above), however, emphasises that the high molecular weight and the optical activity speak against the digallic acid formula, but in favour of this are the following points: (1) the decomposition of tannin with the formation of gallic acid; (2) the decomposition of methylotannin with the formation of di- and trimethyl esters of gallic acid; and (3) the production of diphenylmethane on distillation with zinc dust. The latter reaction especially illustrates the analogous formation of fluorene from compounds of the type—



Nierenstein gave the name "Tannophor" to the mother-substance of tannin, phenylbenzoate, C₆H₅-COO-C₆H₅.

Dekker [Footnote: "De Looistoffen," vol. ii, p. 30 (1908).] was, however, unable to detect diphenylmethane on distilling with zinc dust, and did, therefore, not accept Nierenstein's views. In proposing the formula—

