OBITUARY NOTICE.

PETER GEORGE CARTER.

1902—1948.

PETER GEORGE CARTER, whose death occurred on September 20th, 1948, was born on February 19th, 1902, in Sydney, N.S.W., and attended the Darlinghurst Junior Technical School and later the Sydney Test High School. He obtained a B.Sc. degree in the University of Sydney in March 1923 and for a year acted as demonstrator in the Organic Chemistry Department. He began research work at this time on phellandrenes from eucalyptus oils, in association with the late Mr. H. G. Smith. In June he was awarded a Science Research Scholarship by the Royal Commission for the Exhibition of 1851, and proceeded to the University of St. Andrews to carry our research with Professor John Read. He was awarded the Ph.D. degree at St. Andrews for his researches on phellandrenes and related compounds; the work was published in a series of papers in the Journal of the Chemical Society during 1924—1929.

After returning for a short spell to Sydney as a lecturer in Organic Chemistry he came back to Great Britain to join Scottish Dyes Ltd. at Grangemouth in October 1929. In 1933 he married Margaret Bainbridge, who had graduated as M.A. at St. Andrews in 1931.

He remained in Grangemouth for some five years before moving in 1934 to the Research Laboratories of I.C.I., Dyestuffs Division, in Manchester, where, except during 1936—1938 when he was seconded for some research work on pyrene derivatives with Sir Ian Heilbron, he worked until his death. His researches over this later period of his life were largely concerned with the chemistry of polycyclic aromatic compounds; he coupled a mastery in this field with a strong mathematical flair and became interested in the quantum mechanical approach to the problem of chemical structure and reactivity. A paper in the Faraday Society on "An Empirical Equation for the Resonance Energy of Polycyclic Hydrocarbons" was in the press at the time of his death.

He was a quiet, reserved man, a lover of music and an enthusiastic gardener. His health, which had been poor for many years, failed to daunt his keen and somewhat dry sense of humour which made him popular among his colleagues and earned him many firm friends.

W. A. COWDREY.

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648. *The Chemical Constitution of Wattle (Mimosa) Tannin. Part I.*

By ALISTAIR M. STEPHEN.

The bark of *Acacia mollissima* yields an extract, soluble in water and in acetone, which concontains tannins and non-tannins in the ratio 10 : 1. The extract is polyphenolic in character and of molecular weight >2000. Oxidative degradation products include resorcinol, gallic acid, and styphnic acid from tannin, and veratric and *O*-trimethylgallic acids from methylated tannin. No evidence for the presence of phloroglucinol units in the structure was obtained. Calculated on a C_{15} basis, the average composition of the material corresponds to a formula $C_{15}H_{14}O_{6\cdot5}$. Of the oxygen atoms 4·25—4·5 are present in hydroxyl groups, and as other functional groups are absent the remaining oxygen is presumably present in ether linkages. Bromine replaces 4—5 hydrogen atoms per C_{15} residue.

DESPITE the extensive use of mimosa or wattle tannin in industry, little information relating to its chemical constitution has been published, and it and its analogues constitute perhaps the least-studied of all naturally-occurring high polymers. Russell (*Chem. Reviews*, 1935, **17**, 159) has classified it as a typical phlobaphen-producing tannin and has reported the formation from it of phloroglucinol and protocatechuic acid on fusion with alkalis. The constitutions of the tannins of this class are still unknown and, although Freudenberg (*Annalen*, 1934, **510**, 193; 1935, **518**, 37) and Russell *et al.* (*J.*, 1934, 218, 1069, 1506, 1940) have postulated for them structures based on the union of C_{15} units of the catechin type, such structures must be regarded as unproven.

The preliminary study of wattle tannin now recorded was carried out before 1946, and has since been interrupted. The initiation of work in this field by others has made it desirable to place the results obtained on record.

Raw material for investigation was prepared both directly from wattle bark and from commercial wattle extract by a modification of a method described by Russell (*loc. cit.*). There was little difference between material from the two sources, which contained, according to the official method of tannin analysis, 80% of "tannins," 10% of "non-tannins," and 10% of moisture. The molecular weight of dialysed material was of the order of 2000. The material was not homogeneous, and the partly acetylated tannin could be fractionated into products which, after complete acetylation, differed in molecular weight and acetyl content. Despite this, the tannin was used for degradative work, since it seemed highly probable that the lack of homogeneity was in large measure caused by similar, but not necessarily identical, units of structure being polymerised to different degrees.

Few degradation products could be obtained from the tannin. Fusion with alkali gave only low yields of resorcinol and gallic acid. The presence of resorcinol nuclei was also indicated by the isolation of styphnic acid (along with oxalic acid) as a product of oxidation with nitric acid. No evidence could be obtained for the presence of phloroglucinol residues, as indicated by Russell (*loc. cit.*). With potassium permanganate the methylated tannin afforded a mixture (15% yield) of veratric and *O*-trimethylgallic acids in nearly equal proportions. Hydrogen peroxide, lead tetra-acetate, bromine, hydrochloric acid, and other reagents gave no other degradation products, and the general conclusion must be drawn that in mimosa tannin the major proportion of the structure is condensed together in such a way as to preclude the formation of simple aromatic fission products in good yields.

Analytical results for the tannin and for its acetylated and methylated derivatives support the view that ether linkages play an important rôle in the molecular structure, since only a portion of the oxygen content of such derivatives can be accounted for by the acetyl and methoxyl contents, and other oxygen-containing functional groups cannot be detected.

It is clear that the structure of this material is comparable in complexity with that of lignin. Experiments are now in progress to explore the effects of hydrogenation and of ether-splitting reagents on the tannin and its derivatives.

EXPERIMENTAL.

(Some of the analyses were performed by Mr. H. Lowitt.)

Preparation of Raw Material.—(*a*) *From wattle bark.* Sliced, dried bark was leached with cold water by the counter-current method for a few days, and the tanning liquor obtained as a reddish-brown syrup. After filtration, salt was added to saturate the liquor, and the precipitated tannin was air-dried and extracted with acetone. The bulk of the solvent was then distilled off, the viscous solution was desiccated, and the resulting flakes of pale-brown solid were ground and dried at 80° in an evacuated flask. The acetone extraction was repeated on this substance, and the powdered tannin dried as before. On heating the material at 125°, the water content was lowered by a further 6·7%, but the tannin present (estimated by the official method) dropped rapidly from the original value (88% on the dry basis).

Samples of bark from *Acacia mollissima* grown in a variety of South African climates varied considerably in the total quantity of tannin and its distribution through the bark. As tanning extracts prepared from wattle bark are difficult to standardise for colour and tanning properties owing to many variables, it was desirable to find out what chemical differences could be detected in the samples. Carbon and hydrogen values in material dried at 100° *in vacuo* over "Anhydrone" lay within the range: C, 57·4—62·8; H, 4·7—5·0%. Purification of a typical specimen by electrodialysis in 5% aqueous solution did not affect the composition (Found: C, 60·0; H, 5·1%; *M*, 1800, ebullioscopically in water).

(*b*) *From wattle extract.* Commercial wattle extract (60% tannins, 20% non-tannins, 20% moisture) was a more convenient laboratory source. This was extracted twice with acetone and dried in the usual way; the acetone-soluble portion resembled that obtained from bark, and the insoluble portion contained non-tannins and tannins in the ratio 3 : 1.

Tannin Acetates.—Dried tannin (about 6% moisture) was boiled with an excess of acetic anhydride and pyridine (1 : 4) for 20—40 minutes, and a pale flesh-coloured powder recovered by pouring the mixture into ice-cold dilute sulphuric acid. A better method was to reflux tannin (2 g.) with acetic anhydride (15 c.c.) and anhydrous sodium acetate (0·5—1 g.) for 40 minutes, cool the mixture, cautiously add glacial acetic acid and dilute sulphuric acid, and pour the mixture into ice-water; the procedure was then repeated on the dried product. This material was purified by precipitation in very dilute sulphuric acid from its solution in acetic acid. Analysis was by the trans-esterification method of Matchett and Levine (*Ind. Eng. Chem. Anal.*, 1941, **13**, 98) as any process involving hydrolysis with alkali leads to the production of acids from the tannin portion of the molecule (see Stephen, "The Properties and Practical Application of Wattle Tannin," Part 2, pp. 34—40, Leather Industries Research Institute, Grahamstown, South Africa) (Found, on tannin acetate from electrodialysed tannin: OAc, 41·0. On derivatives from 5 tannin samples: OAc, 39·6, 40·1, 40·1, 38·6, 41·0%).

The effect of leaching a single bark sample with water at different temperatures is shown in the following table of acetyl contents and molecular weights (f.-p. depression of dioxan) of the acetates from the isolated tannins:

Temp. of leaching	6—8°	35°	55°	70—80°
Acetates: OAc, %	35·1	36·5	39·1	37·2
M	1670	1950	3000	3200

Heat probably causes polymerisation of the tannin, and the molecular weights quoted do not necessarily bear a direct relation to the molecular size of the tannin in the unextracted bark.

Fractionation of Tannin Acetates.—Tannin from wattle extract was used in these experiments. Preliminary trials on partly and fully acetylated tannin indicated that the material most conveniently fractionated by precipitation in acetic acid of various dilutions was not fully esterified but was sufficiently acetylated to prevent loss through its solubility in water. A bulk preparation was therefore made from tannin (1 mol.) and acetic anhydride (0·6 mol., working on the basis that 40% OAc is the maximum obtainable), the product containing 24·2% OAc. This material was dissolved in warm glacial acetic acid, and a first fraction precipitated by adding one volume of 6N-acetic acid and one volume of water. The cooled mixture was filtered and the filtrate collected in an excess of distilled water. Each of the solids was isolated, dried, and divided into two portions by a similar procedure. By a fractional precipitation involving between 25 and 30 fractions, four fractions were finally recovered, totalling 70% of the weight of starting material. A portion of each was fully acetylated, giving results as below :

	OAc, %.	OAc, % after acetylation.	% Increase.
A (least soluble) (4·7 g.)	23·0	34·5	11·5
B (7·5 g.)	24·5	37·0	12·5
C (15·5 g.)	24·5	39·0	14·5
D (most soluble) (3·6 g.)	22·5	40·5	18·0

It is evident that the starting material is non-homogeneous, the difference between products A and D corresponding to >1 acetyl group in a C_{15} unit. On the basis $(C_{15}H_{13}O_6)_n$ for wattle tannin, A contains 3·4 and D 4·6 acetyl groups. The solubility differences between A, B, C, and D before complete acetylation are due to the numbers of free hydroxyl groups increasing while the acetyl contents of the fractions remain the same.

The solubility of tannin acetates in dilute acetic acid is also influenced by the molecular weight. Tannin from a single bark source was fully acetylated and divided by fractional precipitation (4 steps) into 3 portions (Found : OAc, 38·7, 38·4, 39·4%). Molecular-weight measurements cryoscopically in dioxan were inaccurate on account of traces of moisture in the acetates, but the molecular weight of the insoluble fraction was higher (4500) than that (1500—2500) of the other two, which were indistinguishable.

Methylated Tannins.—Methylation of tannin was most conveniently achieved thus. To a solution of dry wattle tannin (60 g.) in methanol was added methyl sulphate (51 c.c.), and nitrogen was led through the reaction flask. Potassium hydroxide (30 g.) in a minimum of aqueous methanol was then admitted from a dropping-funnel, with continuous shaking. Similar quantities of methyl sulphate and alkali were added twice during 2½—3 hours. The cold, slightly acid mixture was then poured into very dilute sulphuric acid at 0—5°, and the finely-divided flesh-coloured precipitate was filtered off and washed with water. The dried substance was then re-methylated as before and purified by precipitation in water from methanol solution (Found, in material dried at 100° *in vacuo* : OMe, 33·6, 34·3%). A portion re-methylated with warm methyl sulphate and strong potassium hydroxide showed a slightly higher methoxyl content (35·8, 35·2%) but this value was not increased by treatment with hot methyl sulphate–alcoholic potassium hydroxide. The maximum acetylation possible corresponds to a methoxyl content of 36·5%. It is possible to raise the methoxyl content of methylated tannin to this value by treating the substance (3 g. ; 34% of OMe) with silver oxide (12 g.) and methyl iodide (12 c.c.) in methanol; extraction of the derivative with hot acetone–methanol, concentration of the solution, and precipitation in very dilute acid affords a practically white powder (Found, in material dried at 100° *in vacuo* : OMe, 36·5%). Electrodialysed tannin, methylated similarly, contained 36·2% of OMe. Attempts to use diazomethane proved unsatisfactory.

Acetylation of methylated tannin gave a product acetylated to some degree, as the following figures illustrate :

Substance acetylated ; OMe, %.	Product. OMe, %.	Product. OAc, %.	Method.
Methylated tannin ; 31·0	—	7·6	Ac_2O–pyridine
,, 33·2	—	4·0	Ac_2O–NaOAc
,, 34·0	30·1	5·4	,,
,, 34·5	32·5	3·0	,,
,, 36·5	34·3	4·0	,,

In each case the methoxyl content is lowered slightly more than would be expected if the acetylating agent merely affected free hydroxyl groups, the reaction causing 2—3% of demethylation. The compound containing OMe 34·3% and OAc 4·0% is the most completely substituted yet obtained.

Interpretation of Analytical Data.—In view of the non-homogeneity of tannin and its derivatives it is not to be expected that analytical results would afford empirical formulæ containing integral numbers of hydrogen and oxygen atoms in each postulated C_{15} unit. The approximate formula $(C_{15}H_{14}O_{6\cdot5})_n$ is the nearest approach for electrodialysed tannin (Found : C, 60·0 ; H, 5·1. $C_{15}H_{14}O_{6\cdot5}$ requires C, 60·4 ; H, 4·7%) ; on this basis a purified preparation of tannin acetate (once acetylated with a large excess of reagents) contained four acetate groups [Found : C, 59·1 ; H, 4·7 ; OAc, 36·0. Calc. for $C_{15}H_{10}(OAc)_4O_{2\cdot5}$: C, 59·2 ; H, 4·7 ; OAc, 37·0%], and a sample of methylated tannin, not methylated to completion with methyl sulphate, approx. 3·5 methoxyl groups (Found : C, 63·3 ; H, 5·6 ; OMe, 32·0. Calc. for $C_{15}H_{10\cdot5}(OMe)_{3\cdot5}O_3$: C, 63·9 ; H, 6·1 ; OMe, 31·3%).

Oxidation of Tannin and its Derivatives.—The instability of tannin to extremes of pH, causing condensation in presence of mineral acids and uncontrollable oxidation in alkaline solution, makes it an unsuitable starting-point for oxidative degradations. Methylated tannin (OMe, 33%), oxidised in suspension with 5% aqueous permanganate during 3 hours, first in the cold and then on the water-bath, gave 30% of bright-red material insoluble in ether, together with tar and a small yield of ether-soluble acids, m. p. (after one recrystallisation from water) 141—146° (Found : equiv., 198—200). The mixture was separated (cf. Eggert and Corbett, Theses, Rhodes University College, Grahamstown) by making use of the different solubilities of the silver salts in water; in this way veratric acid, m. p. 176·5—178° (Found: equiv., 182. Calc. for $C_9H_{10}O_4$: equiv., 182), and *O*-trimethylgallic acid, m. p. and mixed m. p. 166°, were identified. Oxidation of methylated tannin (4 g.) in acetone and then water for 3 hours gave a better yield (0·6 g.) of the acids. After 3 crystallisations from water (charcoal), 0·2 g. of acid (Found: equiv., 201) was obtained. More prolonged treatment, especially when boiling aqueous permanganate was used, completely destroyed the aromatic methoxy-acid fragments. Oxidation in acetone alone, on the other hand, or such oxidation followed by a brief treatment with hot aqueous permanganate, was insufficient.

Action of Alkalis.—The best yield of ether-soluble products was obtained by heating tannin (30 g.) with 8 times its weight of mixed sodium and potassium hydroxides in a nickel crucible at 240° for 1½ hours. After cooling and acidification, the ether extract afforded a mixture of acids (13·8 g.), phenols (3·5 g.), and neutral material (0·4 g.). From the tarry acid fraction, gallic acid was isolated [m. p., with slight decomposition, at 225° (meniscus at 237°), unchanged by admixture with an authentic specimen (Found: equiv., 180. Calc. for $C_7H_6O_5,H_2O$: equiv., 188)]. Colour tests confirmed the identity. It was not possible to separate the small quantity of other acidic material which causes a low m. p. (170—182°) and the somewhat higher equivalent weight of the crude product. From the syrupy phenolic fraction, resorcinol, m. p. and mixed m. p. 108—109°, was isolated, by extraction with benzene and recrystallisation or by sublimation at 20 mm. (bath temperature, 110—140°) (yield, 3½% by wt. of tannin). No other phenol was detected. The alkaline oxidation of lignin to give vanillin, syringaldehyde, and numerous ketonic products (cf., *e.g.*, Tomlinson and Hibbert, *J. Amer. Chem. Soc.*, 1936, **58**, 345; Creighton, McCarthy, and Hibbert, *ibid.*, 1941, **63**, 3049; Freudenburg, Lautsch, and Engler, *Ber.*, 1940, **73**, 167) suggested a similar series of experiments on tannin, sulphited tannin, and sulphited-methylated tannin. No volatile or trichloroethylene-soluble substances were detected in the form of their 2 : 4-dinitrophenylhydrazones, from which it was concluded that the mode of linkage of the gallic acid residues in tannin differs from that of the aromatic portion of the lignin molecule.

Action of Acids.—When boiled with 5N-hydrochloric acid, tannin gives, on cooling, a precipitate of a brown solid which, though insoluble in cold water, ethanol, and acetic acid, is slightly soluble in hot water and boiling pyridine. The exceedingly high molecular weight (the f.-p. depression of dioxan is negligible) indicates condensation, possibly between adjacent hydroxyl groups with elimination of water. Acetylation and bromination, however, indicate little change in the total number of hydroxyl groups and positions reactive towards substitution by electrophilic reagents. Dry hydrochloric acid catalysed methylation of tannin in methanol to a small extent (2%) (the product being insoluble in water), and acetylation in acetic acid (product contains OAc, 2%).

Nitric acid up to 3N. has no effect on tannin in the cold, but causes precipitation accompanied by evolution of brown fumes on warming. After a few minutes the colour of the solution lightens, and on concentration a viscous syrup remains which crystallises on storage. Oxalic acid dihydrate (4 parts) and styphnic acid (1 part), m. p. and mixed m. p. 174—175° (Found: equiv., 128. Calc. for $C_6H_3O_8N_3$: *M*, 245) were isolated. Acetylated tannin decomposed similarly, but brominated tannin resisted oxidation by this reagent.

The action of bromine in a number of solvents on tannin yielded dark-brown products (Found: total Br, 57—61; labile Br, precipitated by Ag^+ in ethanol, 10—19%) containing 4—5 Br in each C_{15} unit.

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