CXV.—*Constituents of Acacia and Gambier Catechus. Part I.*

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Acacia catechu is the tree, common in most parts of India and Burma from which the drug acacia catechu (cutch, Pegu, or Bombay catechu) is obtained. This product, present in the red heart wood, is isolated by extraction with water and evaporation of the extract to a pasty condition. A purer substance known as "kath," or "the pale catechu of India" is prepared by suspending twigs in the hot concentrated extract and collecting the adhering crystals which separate on cooling. This is rarely exported to Europe, but is used by the natives for chewing with the betel nut.

Uncaria Gambier, an extensive scandent bush which is met with both wild and cultivated in Malacca, Penang, and Singapore is the source of gambier catechu (pale catechu or *Terra japonica*); this is isolated by extracting the leaves and twigs with hot water. As is the case with the acacia variety a purer product, or "kath" is also prepared.

Gambier catechu is very largely employed in the tanning industry and also to a considerable extent for dyeing; the acacia variety, however, gives but a hard leather, and is principally used for dyeing browns and blacks with chrome and iron mordants.

These catechus contain a colourless, crystalline substance, which, according to some chemists, is homogeneous and consists of one substance named catechin; on the other hand, however, five distinct catechins have been described. Catechutannic acid, a derivative of catechu, is also present in varying amount, together with quercetin (Löwe, *Zeit. anal. Chem.*, 1873, **12**, 134; Perkin, Trans., 1897, **71**, 1135), some ill-defined, amorphous products, and mineral matter.

Areca catechu, prepared from the betel nut palm and mangrove cutch, do not appear to contain catechin.

Summary of Previous Work.

Although catechu has perhaps received greater attention than other natural products, the results have been so varied that the chemistry of the subject is still in an unsatisfactory condition. Catechin appears to have been first described by Nees van Esenbeck (*Ann. Pharm.*, 1832, **1**, 243), was subsequently examined by Berzelius (*Jahresber.*, 1837, **14**, 235), and more recently by at least sixteen other chemists.

The following formulæ have been assigned to catechin: $C_{15}H_{12}O_6$, air-dried (Svanberg, *Ann. Pharm.*, 1837, **24**, 215). $C_{18}H_{10}O_8$, at 100° (Zwenger, *Ann. Chem. Pharm.*, 1841, **37**, 320). $C_{16}H_8O_8 + 2H_2O$, air-dried (Hagen, *ibid.*, 336). $C_{16}H_{18}O_8 + H_2O$, dried in a vacuum over sulphuric acid (Dellfs, *Pharm. Centr.*, 1846, 604). $C_{17}H_{12}O_{10}$, air-dried (Neubauer, *Ann. Chem. Pharm.*, 1855, **96**, 337). $C_{12}H_{12}O_5$, at 100° (Kraut and Delden, *ibid.*, 1863, **128**, 285). $C_{19}H_{18}O_8$ (Hlasiwetz, *ibid.*, 1865, **134**, 118). $C_{19}H_{18}O_8$, dried at 90° (Etti, *Annalen*, 1887, **186**, 327). $C_{22}H_{22}O_9$ (Schützenberger and Back, *Bull. Soc. Chim.*, 1865, [ii], **4**, 5). $C_{15}H_{14}O_7$, at 100° (Löwe, *Zeit. anal. Chem.*, 1874, **13**, 113). $C_{21}H_{20}O_9 + 5H_2O$, air-dried (Liebermann and Tauchert, *Ber.*, 1880, **13**, 964). $C_{18}H_{18}O_8$, dried over sulphuric acid (Etti, *Monatsh.*, 1880, **2**, 547). In regard to percentage of carbon, the formulæ $C_{15}H_{12}O_6$, $C_{18}H_{10}O_8$, $C_{12}H_{12}O_5$, $C_{19}H_{18}O_8$, $C_{22}H_{22}O_9$, and $C_{21}H_{20}O_9$ are in fairly close agreement, but it seems likely that the remainder represent analyses of substances not completely devoid of water of crystallisation.

With the majority of workers, it appears to have been taken for granted that but one catechin exists, and Etti (*loc. cit.*) and Neubauer (*loc. cit.*) state that gambier and acacia catechus contain one and the same catechin. This, according to Etti, melts at 140°, and at 150—160° is converted into catechutannic acid. Gautier (*Bull. Soc. Chim*, 1878, [ii], **30**, 567) states, on the other hand, that gambier catechu itself contains three catechins, namely, (*a*) catechin, $C_{40}H_{38}O_{18},2H_2O$, m. p. 204—205°; (*b*) catechin, $C_{42}H_{38}O_{16},H_2O$, m. p. 176—177°; and (*c*) catechin, $C_{40}H_{28}O_{16},H_2O$, m. p. 163°. Further, he isolated from acacia catechu a catechin, m. p. 164—165°; from brown catechu, a catechin, m. p. 140°; and from yellow catechu, a catechin, m. p. 188—190°. Zwenger (*loc. cit.*) gives the melting point of his catechin as 217°, but the majority of workers, as Wackenroder (*Ann. Pharm.*, 1839, **31**, 72; 1841, **37**, 306), Hagen, Neubauer, Kraut and Delden, Cazeneuve, and Liebermann and Tauchert, do not state the melting point of their substances.

The most important decomposition products have been obtained from catechin by means of dry distillation and by fusion with alkali. By the former method, Wackenroder detected catechol, and A. Miller (*Annalen*, 1883, **220**, 115), acetic acid, catechol, and phenol; whereas by the second Hlasiwetz, and also Etti, isolated phloroglucinol and protocatechuic acid, and Gautier the same products together with formic acid. From his results, Etti considered the following constitution for catechin as probable:

$$C_6H_7(OH)_2\cdot CO\cdot O\cdot C_6H_3(OH)\cdot O\cdot C_6H_3(OH)_2,$$

and regarded the analytical results of Zwenger, Svanberg, Kraut and Delden, and Neubauer as too high because these chemists dried their substances at 100°, for he found that on long exposure to this temperature catechin becomes yellowish-brown. Neubauer (*loc. cit.*) found that catechin was not a glucoside, and considered that this substance and catechutannic acid were related to one another, similarly as gallic acid is to ordinary gallotannin.

Derivatives.—Weselsky (*Ber.*, 1876, **9**, 217) first prepared an azobenzene derivative of catechin and this Etti subsequently obtained in a crystalline condition and gave it the formula $C_{18}H_{16}O_8(N_2\cdot C_6H_5)_2$. Liebermann and Tauchert describe a diacetylcatechin, $C_{21}H_{18}O_9(C_2H_3O)_2$, and its dichloro- and monobromo-derivatives, showing that the molecular composition of catechin is represented by $C_{21}H_{20}O_9$. Amorphous products have been prepared by others, of which Etti's four anhydrides appear to be most important; the discussion of these, however, would have no bearing on the present communication.

The results obtained clear up, we hope, to some extent the vexed question as to the existence of one or more catechins, but their investigation is still incomplete, as, unfortunately, our joint work has now to cease. The subject, however, will be further studied by one of us, as it possesses considerable interest, not only from a dyeing, but also from a tanning, point of view.

Gambier Catechu.

The raw material employed was the well-known "cube gambier," and was obtained by purchase.

The finely powdered substance was extracted with ten times its weight of boiling ethyl acetate, a solvent suggested by Löwe and subsequently employed by Liebermann and Tauchert (*loc. cit.*). The brown extract was evaporated, the residue dissolved in ten times its weight of boiling water, and the crystals which separated on cooling collected on the pump and washed with a little water. This product was again dissolved in boiling water and lead acetate solution added drop by drop until a coloured precipitate no longer formed and the filtrate was almost colourless; the latter, while hot, was treated with sulphuretted hydrogen, the lead sulphide removed, and the crystals which separated on cooling collected, washed, and drained on a porous tile. This process, which is due to Berzelius, was found to be most advantageous, the substance being now practically colourless, and the yield greater than if this had been effected by frequent recrystallisation from water. After crystallisation from 25 per cent. alcohol, the product was dissolved in boiling ethyl acetate (10 parts), boiling benzene then added (6 parts), and the mixture treated with animal charcoal and rapidly filtered. On cooling, colourless, glistening needles separated which were washed with benzene and dried at 100°. Thus obtained, it sintered slightly at about 140° and melted at 175—177°; evidently it was a pure substance, for fractional crystallisation from water, and from dilute alcohol, and fractional precipitation from ethyl acetate with benzene did not effect any change in its melting point or other properties. As regards melting point, this product coincides with the (*b*) catechin which Gautier isolated from gambier (catechu); employing this process, however, no (*a*) catechin (m. p. 204—205°), which he describes as present in considerable quantity, could be detected.

Crystallised from water and allowed to dry at the ordinary temperature, the catechin contained water of crystallisation. The following determinations were made with substance which had been left exposed to the air for 2, 4, and 6 weeks respectively:

(i) 1·2943, at 100°, lost 0·2665 H_2O. $H_2O = 20·59$.
(ii) 1·2805 „ 0·2600 H_2O. $H_2O = 20·31$.
(iii) 1·1790 „ 0·2370 H_2O. $H_2O = 20·10$.

On again heating to 110° and subsequently to 160°, (i) and (ii) respectively lost 0·0015 and 0·0037 gram H_2O, and although at the latter temperature the substance became faintly brown, it is evident that practically no decomposition had thus ensued:

0·2648, dried at 100°, gave 0·5992 CO_2 and 0·1164 H_2O. C = 61·71; H = 4·88.
0·1075, dried at 100°, gave 0·2443 CO_2 and 0·0470 H_2O. C = 61·97; H = 4·85.
0·1140, dried at 160°, gave 0·2588 CO_2 and 0·0492 H_2O. C = 61·91; H = 4·79.
$C_{15}H_{14}O_6$ requires C = 62·06; H = 4·82 per cent.
$C_{15}H_{14}O_6, 4H_2O$ requires $H_2O = 19·89$ per cent.

As regards percentage composition, these numbers are slightly higher than those of Liebermann and Tauchert, but approximate to those of Svanberg ($C_{15}H_{12}O_6$) and Schützenberger ($C_{22}H_{22}O_9$); on the other hand, the water of crystallisation is also in excess of that given by Liebermann and Tauchert ($C_{21}H_{20}O_9,5H_2O$), which is 17·78 per cent. Etti's statement that at and over 100° catechin commences to lose water of constitution appears to be incorrect, and the low temperature at which he dried his substance accounts for the considerably lower percentage of carbon which his analyses show.

This catechin is sparingly soluble in cold water, but readily in alcohol, and if air-dried it dissolves in ethyl acetate and to some extent in pure ether; on the other hand, when dried at 100° it is practically insoluble in the latter solvents. Previous statements as to its ready solubility in ether must refer to a commercial ether containing alcohol. Aqueous lead acetate gives a colourless precipitate, aqueous ferric chloride a green liquid, and the same reagent in the presence of sodium acetate a deep violet coloration. With pine wood and hydrochloric acid, it gives the phloroglucinol reaction, and with boiling dilute sulphuric acid brown products resembling Etti's third and fourth anhydrides (*loc. cit.*) are formed. It gives no insoluble salt with alcoholic potassium acetate, and no compounds with mineral acids in the usual manner; moreover, it contains no methoxy-group, and is optically inactive. This catechin and also the other catechins here described can hardly be considered as mordant dyestuffs, and their employment as colouring matters depends on the fact that they yield certain brown oxidation products (the so-called rubinic and japonic acids). Thus dyed in the usual manner upon wool, chromium mordant gives a pale olive, aluminium a very pale buff, and iron a pale dull black colour. The other catechins described in this paper behave in a similar manner.

Azobenzene Derivative, $C_{15}H_{12}O_6(N_2{\cdot}C_6H_5)_2$.—The catechin dissolved in one hundred times its weight of a boiling dilute solution of sodium or potassium acetates was cooled by ice and treated with diazobenzene sulphate as long as a precipitate formed. This, which had a bright red colour, was collected, well washed, transferred to a dish, and dried on the steam-bath. The yield was 170 per cent. by weight of the catechin employed. The finely ground product was extracted with boiling alcohol to remove a trace of resinous matter, the residue then dissolved in hot nitrobenzene, and treated first with a few drops of acetic acid and subsequently with about one-fourth its bulk of boiling alcohol. Crystals rapidly separated which were collected, washed with alcohol, and recrystallised in a similar manner, animal charcoal being employed:

0·1162 gave 0·2764 CO_2 and 0·0464 H_2O. C = 64·87; H = 4·43.
Found N = 11·50; 11·27; 11·29.
$C_{27}H_{22}O_6N_4$ requires C = 65·06; H = 4·41; N = 11·24 per cent.

It formed minute, salmon-red needles which, on heating, commenced to sinter at 185° and melted at 193—195° with decomposition. It is almost insoluble in boiling alcohol, but soluble in dilute alkalis with an orange-red coloration. The calculated yield of this compound according to the above formula is 171 per cent. It is remarkable that this compound neither in percentage composition nor in solubility in alcohol agreed with Etti's (*loc. cit.*) disazobenzene catechin. As Etti's method differed somewhat from the above, especially in the respect that he did not employ sodium acetate, his experiments were repeated. It was found that the resulting crude azobenzene derivative, which, as he recommends, was dried at the ordinary temperature, is in this condition somewhat readily soluble in boiling alcohol; the crystals, however, which separate on cooling or by boiling the solution for a few minutes, are almost insoluble in boiling alcohol. It melted in a similar manner to that described above and there could be no doubt that they consisted of one and the same substance. To his compound, Etti assigned the formula $C_{18}H_{16}O_8(N_2 \cdot C_6H_5)_2$, and the lower numbers which he obtained can only be accounted for on the assumption that his substance was not entirely free from alcohol or water of crystallisation; this, experiment showed, is retained with much obstinacy, for the substance is not always constant in weight after drying for six hours at 100°, and when subsequently dried at 160° frequently lost as much as 2 per cent. in weight. There was no evidence of decomposition during these drying operations.

Acetyl Compound, $C_{15}H_9O_6(N_2 \cdot C_6H_5)_2(C_2H_3O)_3$.—The azobenzene compound dissolved slowly in boiling acetic anhydride and the solution, after digestion for 5 hours, was poured into alcohol. A small quantity of a crystalline powder separated, and as the mother liquors were dark coloured it appeared likely that the small yield was due to the occurrence of some secondary reaction. The product was again digested with acetic anhydride for 1 hour, precipitated by alcohol as before, and recrystallised by adding alcohol to its solution in hot benzene, animal charcoal being employed:

0·1229 gave 0·2852 CO_2 and 0·0487 H_2O. C = 63·27; H = 4·40.
0·1037 „ 8·3 c.c. nitrogen at 18° and 756 mm. N = 9·19.
$C_{33}H_{28}O_9N_4$ requires C = 63·46; H = 4·48; N = 8·97 per cent.

It forms glistening, orange-red needles melting at 253—255°, and is readily soluble in benzene but almost insoluble in alcohol. Judging from the behaviour of the azobenzene derivatives of maclurin (Trans., 1897, **71**, 187), phloretin, &c., it had been anticipated that the acetyl groups in this compound could be readily determined by Liebermann's method. The sulphuric acid, however, caused some secondary reaction, and the product was not disazobenzene catechin, for on heating it commenced to darken at 220° and had not melted at 275°. From the percentage of nitrogen, there was little doubt that this compound is a triacetyl derivative, and, consequently, this catechin contains five hydroxyl groups (compare acetylmaclurin disazobenzene, *loc. cit.*).

Pentabenzoylcatechin, $C_{15}H_9O_6(C_7H_5O)_5$.—Attempts to prepare a benzoyl derivative by heating the catechin with benzoic anhydride, and by the Schotten-Baumann method, were unsuccessful, but Deninger's method gave a good result. Two grams of the catechin dissolved in 30 grams of pyridine were treated with 23 grams of benzoyl chloride, added a little at a time, rise of temperature being avoided. After standing 24 hours, the product was washed with water and placed aside until it became semi-solid owing to the separation of crystals. It was now dissolved in about twice its bulk of methyl alcohol, and the crystals which slowly separated were collected on the pump, washed with alcohol, and recrystallised twice by adding alcohol to its solution in acetone. In case the mixture became turbid on cooling, acetone was added drop by drop until this disappeared:

0·1134 gave 0·3078 CO_2 and 0·0432 H_2O. C = 74·02; H = 4·23.
$C_{50}H_{34}O_{11}$ requires C = 74·07; H = 4·19 per cent.

Thus crystallised, it separates in spongy masses of colourless needles melting at 151—153°, and is readily soluble in acetone, but insoluble in cold alcohol. Alkaline solutions do not dissolve it.

A molecular weight determination of this substance by the cryoscopic method, naphthalene being employed as solvent, gave the following result:

0·6249 gram in 11·95 grams of naphthalene depressed the freezing point 0·45°. Mol. wt. 813.
0·5272 gram in 13·21 grams of naphthalene depressed the freezing point 0·35°. Mol. wt. 798.
The molecular weight of $C_{15}H_9O_6(C_7H_5O)_5$ is 810.

This result indicated, therefore, that this catechin has the formula $C_{15}H_{14}O_6$, and cannot have the high molecular weight required by the formulæ proposed by Schützenberger ($C_{22}H_{22}O_9$) or Liebermann and Tauchert ($C_{21}H_{20}O_9$).

Tetrabenzoyl Compound, $C_{15}H_{10}O_6(C_7H_5O)_4$.—In the earlier experiments on the preparation of a benzoyl compound, a crystalline product, not identical with the above, was obtained. Employing substantially the same amounts of the catechin and reagents, a compound was isolated in the form of colourless prisms melting at 171—172° and readily soluble in acetone but almost insoluble in alcohol:

0·1144 gave 0·3066 CO_2 and 0·0423 H_2O. C = 73·09; H = 4·10.
0·1087 „ 0·2923 CO_2 „ 0·0415 H_2O. C = 73·34; H = 4·24.
$C_{43}H_{30}O_{10}$ requires C = 73·08; H = 4·24 per cent.

A molecular weight determination gave the following result:

0·7880 gram in 12·08 grams of naphthalene depressed the freezing point 0·637°. Mol. wt. = 716. $C_{43}H_{30}O_{10}$ requires 706.

It was consequently a tetrabenzoyl derivative. Subsequently it was noted that the benzoyl chloride here employed, a somewhat old sample, had, through leakage of moisture, been partly decomposed, for on obtaining a fresh supply the pentabenzoyl derivative (m. p. 151—153°) was always formed in this manner.

Fusion with Alkali.—The fusion was carried out in the usual manner at 210—220° and gave phloroglucinol (m. p. 210°) and protocatechuic acid (m. p. 194—196°), as was to be anticipated from the earlier work of others. An acid resembling acetic acid is simultaneously formed, but its identification was reserved until a larger quantity of the pure catechin was available.

Lead Salt.—If a hot aqueous solution of this catechin containing a little acetic acid be treated with lead acetate solution and the precipitate removed, the filtrate on cooling deposits catechin together with a small quantity of a crystalline lead salt. On extraction with hot water, the latter remains undissolved, and is collected, well washed with alcohol, and dried:

0·5247 at 160° gave 0·2640 $PbSO_4$. Pb = 34·17.
0·5900 „ 160° „ 0·2930 $PbSO_4$. Pb = 33·91.
0·2988 „ 160° „ 0·1468 $PbSO_4$. Pb = 33·53.

It appears likely that this salt has the formula $C_{15}H_{14}O_6,Pb(C_2H_3O_2)_2$, which requires Pb = 33·66 per cent. It formed minute, colourless, glistening, prismatic needles, and was seen under the microscope to be homogeneous. A somewhat similar salt was obtained by Löwe (*loc. cit.*), who assigned to it the formula $2C_{21}H_{20}O_9,3PbO$.

The Catchin of High Melting Point.

The aqueous mother liquors obtained during the purification of the preceding catechin (m. p. 175—177°) were examined with the object of isolating Gautier's (*c*) catechin (m. p. 163°) if such were present. By spontaneous evaporation and by other methods, a further quantity of crystalline product was isolated, but this, on purification, melted at 175—177° and had all the reactions of the catechin described above. From the final mother liquors, however, a new substance separated. Addition of salt caused the separation of a brown, viscous product, which was removed, the clear liquid then extracted with ethyl acetate, the extract evaporated, and the residue dissolved in a little hot water. On standing, crystals separated which were recrystallised several times from water with the aid of animal charcoal. The yield of this substance was poor, for at most only two grams of the pure catechin have as yet been obtained, but this may to some extent be due to the methods employed. Allowed to dry for 10 days at the ordinary temperature, it was *devoid of water of crystallisation*, and experienced no loss even when heated at 160°.

0·1038 gave 0·2348 CO_2 and 0·0459 H_2O. C = 61·68; H = 4·91.
0·1096 „ 0·2480 CO_2 „ 0·0479 H_2O. C = 61·70; H = 4·85.
$C_{15}H_{14}O_6$ requires C = 62·06; H = 4·82.

It was obtained as small prisms, as a rule possessing a faintly yellow tint, and melted at 235—237°. In its reactions with lead acetate, ferric chloride, pine wood and hydrochloric acid, in fact in all its properties with the exception of melting point and solubility, it is indistinguishable from the catechin melting at 175—177°. It does not appear to contain a methoxy-group, but until larger quantities are available this cannot be decided. There is no record by previous workers of a catechin of so high a melting point, although the product to which Zwenger assigned the melting point 217° might have contained this substance.

Fusion with alkali gave *phloroglucinol* (m. p. 210°) and protocatechuic acid (m. p. 194—196°) and a volatile acid having the odour of acetic acid.

The *azobenzene* compound, $C_{15}H_{12}O_6(N_2{\cdot}C_6H_5)_2$, was prepared and purified by identical methods to those employed with the catechin melting at 175—177°. The yield of pure substance was 100 per cent. by weight of the catechin employed:

0·1061 gave 10·4 c.c. nitrogen at 16° and 754 mm. N = 11·33.
$C_{27}H_{22}O_6N_4$ requires N = 11·24 per cent.

It formed glistening, orange-red needles melting at 215—217° and was almost insoluble in alcohol, but soluble in alkaline solutions with an orange-red coloration. Its *acetyl* derivative crystallised in glistening needles melting at 250—253°, was readily soluble in benzene, and closely resembled the analogous derivative of the catechin melting at 175—177°:

0·1008 gave 8·5 c.c. nitrogen at 18° and 754 mm. N = 9·66.

Owing to lack of material, it was not possible to prepare a benzoyl compound, and consequently the molecular composition of this catechin must remain uncertain for the present. This, however, appears to be, or is closely represented by, $C_{15}H_{14}O_6$.

Acacia Catechu.

For the material employed we are indebted to the authorities of the Imperial Institute. The sample was labelled "Catechu Extract, Acacia Catechu, Surat, Bombay," and had a pale, flesh-coloured appearance ; from its comparatively pure nature, it was evidently identical with the "kath" referred to in the introduction. To isolate the catechin, the method employed was similar to that adopted with the gambier catechu, with the exception that the lead acetate treatment was omitted. The product was finally purified by crystallisation from water until no alteration in the melting point could be observed. Dried in the air :

1·3878 at 100° lost 0·2180 and at 160° 0·2200 H_2O. $H_2O = 15·85$.
1·2966 „ 100° „ 0·2018 H_2O. $H_2O = 15·56$.
1·1378 „ 160° „ 0·1808 H_2O. $H_2O = 15·90$.

This catechin, when heated, behaves somewhat peculiarly, as it sinters at about 140°, resolidifies on slowly raising the temperature, and finally melts at 204—205° with decomposition. That this preliminary fusion or semifusion was not due to the presence of water of crystallisation was determined by experiment, and although the substance, when thus treated in quantity, assumed a faintly brown tint, the decomposition, if any, which had ensued was practically infinitesimal. In the melting-point tube, the sintering at 140° might almost escape notice, but if the tube was at once plunged into the sulphuric acid bath at 160°, complete fusion followed by gradual solidification ensued. The difficulty now arose as to whether the catechin should be considered anhydrous at 100° or at 160°, for although the loss in weight between these temperatures is very small, the analytical numbers are affected thereby, as regards the carbon, by about 1 per cent. As the substance appears to remain quite constant at 160°, this temperature seemed preferable to use, but as at present there is nothing definite to decide this point, the distinct analyses are given :

0·1186 at 110° gave 0·2648 CO_2 and 0·0514 H_2O. C = 60·89 ; H = 4·82.
0·1205 „ 100° „ 0·2690 CO_2 „ 0·0564 H_2O. C = 60·88 ; H = 5·20.
0·1275 „ 160° „ 0·2895 CO_2 „ 0·0568 H_2O. C = 61·92 ; H = 4·94.
0·1242 „ 160° „ 0·2827 CO_2 „ 0·0540 H_2O. C = 62·07 ; H = 4·83.
$C_{15}H_{14}O_6$ requires C = 62·06 ; H = 4·82 per cent.
$C_{14}H_{14}O_6$ „ C = 60·43 ; H = 5·04 „
$C_{15}H_{14}O_6,3H_2O$ requires $H_2O = 15·69$; and $C_{14}H_{14}O_6,3H_2O$ requires $H_2O = 16·36$ per cent.

This catechin, judging by its melting point, is identical with

Gautier's (a) catechin, $C_{40}H_{38}O_{18},2H_2O$ (m. p. 204—205°), but the water of crystallisation determined by him is much lower (4·27 per cent.), and the result difficult to understand. Again, the analytical numbers given by Liebermann and Tauchert (C = 60·85 and 60·49; H = 4·89 and 4·96 at 110°) at first indicate that the substance they employed was identical with the above, but, on the other hand, the water of crystallisation (18·14 per cent.) which they found to be present seems to show that they worked with a mixture of the catechins melting at 175—177° and 204—205° respectively. It is possible also that Svanberg's catechin ($C_{15}H_{12}O_6$, air-dried) was the catechin, m. p. 235—237°, previously described, and that those of Hagen ($C_{16}H_8O_8,2H_2O$, air-dried) and Gautier consisted of this substance admixed with a small quantity of another catechin. Zwenger has given the melting point of catechin as 217°, and this has been adopted by the text-books; at present, however, we have not found any catechin melting at this temperature, and have doubts as to the existence of such a substance in the pure condition. In view, however, of the extraordinary differences of opinion among previous workers on catechin, these suggestions are made with some reserve, pending an examination of other qualities of this dyestuff that have not been included in this investigation.

In general properties, this catechin (m. p. 204—205°) almost exactly resembles that previously described (m. p. 175—177°), which was isolated from gambier catechu; the former is, however, more sparingly soluble in water than the latter.

When *fused with alkali*, phloroglucinol (m. p. 210°), protocatechuic acid (m. p. 194—196°), and an acid resembling acetic acid were produced.

Azobenzene Derivative.—This was prepared and purified by methods identical with those given above. The yield was 159 per cent. by weight of the catechin employed :

0·1082 gave 0·2580 CO_2 and 0·0445 H_2O. C = 65·02; H = 4·57.
0·1274 ,, 12·4 c.c. nitrogen at 17° and 763 mm. N = 11·34.
$C_{15}H_{12}O_6(N_2{\cdot}C_6H_5)_2$ requires C = 65·06; H = 4·41; N = 11·24 per cent.
$C_{14}H_{12}O_6(N_2{\cdot}C_6H_5)_2$,, C = 64·20; H = 4·52; N = 11·52 ,,

It was obtained as a glistening mass of small, salmon-red needles melting with decomposition at 198—200°, and was very sparingly soluble in the usual solvents, but soluble in dilute alkalis with an orange-red coloration.

On digestion for 5 hours with boiling acetic anhydride, an *acetyl* compound was formed which, after purification, consisted of orange-red leaflets; these were readily soluble in benzene or acetic acid and melted at 227—229°;

0·1220 gave 0·2843 CO_2 and 0·0507 H_2O. C = 63·55 ; H = 4·53.
0·1618 ,, 12·9 c.c. nitrogen at 12° and 750 mm. N = 9·33.
0·1084 ,, 8·75 ,, 22° ,, 754 ,, N = 9·07.
$C_{15}H_9O_6(N_2{\cdot}C_6H_5)_2(C_2H_3O)_3$ requires C = 63·46 ; H = 4·48 ; N = 8·97 per cent.
$C_{14}H_9O_6(N_2{\cdot}C_6H_5)_2(C_2H_3O)_3$ requires C = 62·73 ; H = 4·57 ; N = 9·15 per cent.

An attempt to determine the acetyl groups according to Liebermann's method was not successful owing to the occurrence of a secondary reaction. The analyses, however, indicate that the substance is a *triacetyl* compound, and it therefore appears that the catechin from which it is derived contains *five* hydroxyl groups.

Pentabenzoyl Derivative, $C_{15}H_9O_6(C_7H_5O)_5$.—This was prepared by Deninger's method, employing 2 grams of the catechin, 30 grams of pyridine, and 23 grams of benzoyl chloride. After standing 24 hours, the product was isolated by the methods given on page 1166, and was thus obtained in beautiful, colourless, prismatic needles which melted at 181—183° and were readily soluble in acetone, but almost insoluble in cold alcohol. Three distinct experiments were carried out, and in each case the substance had the same melting point :

0·1143 gave 0·3098 CO_2 and 0·0442 H_2O. C = 73·93 ; H = 4·29.
$C_{50}H_{34}O_{11}$ requires C = 74·07 ; H = 4·19 per cent.

Molecular weight determinations by the cryoscopic method gave the following results :

0·6125 gram in 13·91 grams of naphthalene depressed the freezing point 0·395°. Mol. wt. 780.
0·5419 gram in 11·85 grams of naphthalene depressed the freezing point 0·400°. Mol. wt. 800.
$C_{15}H_9O_6(C_7H_5O_5)_5$ has a molecular weight of 810.

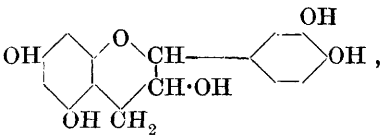
It therefore follows that this (*a*) catechin (m. p. 204—205°) is represented by the formula $C_{15}H_{14}O_6$.

With lead acetate in the presence of acetic acid, this catechin gave a crystalline lead salt, almost identical in appearance with that obtained from the (*b*) catechin. As analyses gave 37·50 and 37·00 per cent. of lead, this did not appear to be quite pure, and will be further investigated as soon as a fresh supply of the raw material is available.

Summary.

This investigation shows that at least three catechins exist, namely, (*a*) m. p. 204—205°, (*b*) m. p. 175—177°, and (*c*) m. p. 235—237°. The two former correspond with the (*a*) and (*b*) catechins which Gautier isolated from gambier catechu, and although we have not found the (*a*) variety in our sample of gambier, there is evidence in the work of earlier investigators of its presence in some samples of this product. It is quite possible that the crude fractional crystallisation which is carried out in order to obtain *kath* may practically consist of the removal of this substance. This point remains to be investigated. The remarkable resemblance which these catechins bear to one another caused us at first to believe that they consisted of the same substance, and that the varieties of lower melting point were contaminated with some impurity. As, however, they differ, not only in melting point, but in water of crystallisation, and in the melting points of all their various derivatives, such cannot be the case, although it is evident that they possess an extremely close chemical relationship. There is considerable evidence that they all have the formula $C_{15}H_{14}O_6$, although it cannot be considered as decided in the case of the (*b*) catechin, which may be represented as $C_{14}H_{14}O_6$. This point will possibly be settled by a study of the volatile acids which these substances yield on fusion with alkali, for it is worthy of note that whereas A. Miller obtained acetic acid, Gautier described formic acid as one of the decomposition products of catechin. This discrepancy may have arisen owing to the fact that these chemists did not employ the same catechin.

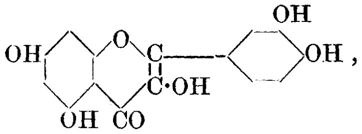
The remarkable similarity between the catechins and the quercetin which accompanies them in the plant, possibly as glucoside, is interesting; thus they contain the same number of carbon atoms, and the same number of hydroxyl groups, and give on decomposition phloroglucinol and protocatechuic acid. It is possible, indeed, that the catechins may be viewed as reduction products of quercetin, one or other being represented thus:



but much work is, of course, necessary before any definite constitution can be asserted. The fact that they give the phloroglucinol reaction with pine wood and hydrochloric acid is of some importance, and tends to demonstrate, in so far as evidence is available, that the phloroglucinol nucleus is attached to the remainder of the molecule by a single bond. A search has shown that this reaction is also possessed by such phloroglucinol derivatives as maclurin,

$$(OH)_3C_6H_2{\cdot}CO{\cdot}C_6H_3(OH)_2,$$

phloretin, $(OH)_3C_6H_2{\cdot}CO{\cdot}CH(CH_3){\cdot}C_6H_4{\cdot}OH$, and hesperitin, but that on the other hand quercetin,



morin, luteolin, and other compounds of the flavone group do not react in this manner. The value of this observation, however, cannot be certain until other phloroglucinol compounds are available for examination in this way.

The further investigation of these catechins and of the catechus, especially in regard to catechutannic acid, is in progress, and at the same time a study of cyanomaclurin (Trans., 1895, **67**, 939) is being continued. This substance, it is now found, contains a phloroglucinol group, and, like the catechin, readily gives the reaction of this phenol; most probably it is a member of the catechin group, and appears to differ mainly from the above compounds in that one of its hydroxyl radicles is situated in a different position.

Kinoin (Etti, *Ber.*, 1878, **11**, 979) from Malabar kino, has been considered by some as possibly identical with catechin, but as a trace which was prepared some years ago in this laboratory by Etti's method dyed a pale yellow with alumina mordant, this seems unlikely.

Addendum.—It is necessary to add that the results of this work were completed before the publications of Kostanecki and Tambor (*Ber.*, 1902, **35**, 1867 and 2408) and Kostanecki and Krembs (*ibid.*, 2410) appeared. These authors have obtained their catechin from Merck of Darmstadt, but give no melting point for their substance. A preparation from this firm, obtained some years ago, melted at 175—177° after purification, and as the water of crystallisation found by these authors coincides with that present in (*b*) catechin, it is evident they have worked with this substance. Under these circumstances and owing to the prior publication of their results, the further work will be chiefly concerned with the (*a*) and (*c*) catechins, the examination of which is reserved.

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