ON TECTOQUINONE, THE VOLATILE PRINCIPLE OF THE TEAK WOOD.

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It was Romanis,(1) who first studied the volatile constituents of the teak wood and isolated a crystalline component of quinonic nature which he named "tectoquinone". According to Romanis, this substance had a composition $C_{18}H_{16}O_2$, melted at 171°C., and represented an anthraquinone derivative. His studies, which were made as early as 1887, were rather limited and it remained altogether unsettled whether his view for this substance was correct or not. The chemistry of this substance, somehow or other, was left untouched for nearly half a century ever since, when the present authors, happening to possess a quantity of reliable material, took up this old problem, and after a series of experiments, have at last succeeded in establishing the true nature of tectoquinone, the detailed account of which will be reported in the following.

If teak saw dust is extracted with ordinary organic solvents such as alcohol, acetone, petroleum ether, benzene, or toluene, about 5–9 % of a viscid semisolid resinous mass will be obtained. These extracts, on distillation with superheated steam, give a small amount of golden yellow needle-like crystals together with a large quantity of aqueous distillate. These crystals represent Romanis's tectoquinone, melt exactly at 171°C., and show all the behaviours of tectoquinone as described by him. After repeated

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(1) R. Romanis, *J. Chem. Soc.*, **51** (1887), 869; *Proc. Chem. Soc.*, **4** (1888), 116.

purifications, it became almost colourless, and its melting point rose to 174–175°C. This process is, however, extremely slow and uneconomical on account of the poor volatility of the substance in question, so the authors tried the other way, viz., the dry distillation. As a result, an oily distillate of strongly empyreumatic smell was obtained, from which tectoquinone could be isolated on standing for a while at a cool place. The yield of the crystalline component amounted to 0.5 % as referred to the weight of the starting material used.

These crystals also melted at 171°C. at first, and was of bright golden yellow colour, but after purifications they became colourless and melted at 175–176°C. By testing the mixded melting point of these crystals with those obtained by steam distillation, the authors could prove the identity of these two. Romanis, in his paper, expects tectoquinone to be structurally identical with retene quinone of the present day, which, at his time, was yet unknown, but such is not the case, now that retene quinone is already known which in every respect differs from tectoquinone. Moreover, according to the authors' analyses, the hydrogen content in tectoquinone turned out to be much smaller than corresponding to Romanis's proposed formula $C_{18}H_{16}O_2$, but to conform to $C_{15}H_{10}O_2$ or $C_{16}H_{12}O_2$. Furthermore, on treating tectoquinone repeatedly with excess of chromic acid, only one carboxylic acid resulted. This acid, on heating with soda-lime, yielded ordinary anthraquinone, whereas, if preliminarily reduced and then treated with soda-lime, it gave anthracene. Comparison of the derivatives of these carboxylic acids with those of anthraquinone and anthracene carboxylic acids led to the conclusion that tectoquinone should represent a β-alkylated anthraquinone. The following table shows the melting points of such derivatives as are related to the chemistry of tectoquinone. For the sake of brevity, the names "tectonic acid", "hydrotectonic acid" and "tectonene" are used to represent the carboxylic acid produced by oxidizing tectoquinone, that which is obtained by reducing the former, and the hydrocarbon which is formed by completely reducing tectoquinone, respectively.

Table

Substance	Melting Point
Tectoquinone	175–176°
Tectonic Acid	284–285°
Methyl Tectonate	164–165°
Ethyl Tectonate	147°
Tectonyl Chloride	146–147°

Table—(*Concluded*).

Substance	Melting Point
Hydrotectonic Acid	278–279°
Ethyl Hydrotectonate	135°
Hysrotectonic Acid Amide	278–279°
Tectonene	202–203°
α–Methyl-anthraquinone⑴	166–167°
Anthraquinone–α–carboxylic Acid	293–294°
Anthraquinone–α–carboxylic Acid Methyl Ester	293–294°
Anthracene–α–carboxylic Acid	245°
β–Methyl-anthraquinone⑵	175–176°
β–Ethyl-anthraquinone	108°
Anthraquinone–β–carboxylic Acid	285–292°
Anthraquinone–β–carboxylic Acid Ethyl Ester	147°
Anthraquinone–β–carboxylic Acid Chloride	146°
Anthracene–β–carboxylic Acid	245°
Anthracene–β–carboxylic Acid Ethyl Ester	135°
Anthracene–β–carboxylic Acid Amide	280°
β–Methyl-anthracene	200–207°

On reduction of tectoquinone with zinc and ammonia, a hydrocarbon, tectonene resulted, which in all probability is identical with β-methyl-anthracene. This hydrocarbon, on treatment with bromine, gave a difficultly recrystallizable dibromide, which after careful purifications melted at 166–167°C., agreeing with the melting point of meso-dibromo-β-methyl-anthracene. The reduction of tectoquinone by means of tin and hydrochloric acid in glacial acetic acid solution led to the formation of an unstable, difficultly crystallizable substance of undefined melting point, the analytical data agreeing with the composition $C_{15}H_{12}O$, probably identical with β-methyl-anthrone. The handiest product of reduction in this case is β-methyl-anthrahydroquinone, which can easily be obtained in form of its diacetate by boiling tectoquinone with zinc dust and anhydrous sodium acetate in acetic anhydride. This diacetate melts at 217°C. and its identity as such was proved by observing the mixed melting point with a known sample of the substance prepared from β-methyl-anthraquinone.

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(1) O. Fischer, Sapper *J. prakt. Chem.*, [2] **83** (1911), 202.

(2) Kempf, *J. prakt. Chem.*, [2] **78** (1908), 257; Börnstein, *Ber.*, **15** (1882), 1821; Römer, Link, *Ber.*, **16** (1883), 695.

Nitration of tectoquinone afforded yellow-coloured crystalline needles melting at 263–265°C., the analyses agreeing with the composition $C_{15}H_9NO_4$, and was proved to be identical with 1-nitro-2-methyl-anthraquinone.

Aside from tectoquinone, a crystalline hydrocarbon, m.p. 199–200°C., was obtained from the oily distillate of dry distillation which was identified as β-methyl-anthracene, but the hydrocarbon melting at 94°C., which Romanis had reported to have isolated, could in no way be found in the present case. Also, attempts were made, to catch the oxy-derivatives directly from the wood by extraction with dilute alkali, but it proved altogether fruitless.

Experimental.

Extraction of Teak Saw Dust. 100 Gr. each of teak saw dust was extracted by means of 500 c.c. each of various solvents in the warm under reflux for six hours, and then the solvent evaporated, when 4.2 to 9.2 gr. of blackish semisolid resinous mass was left behind. All these residues melted around 100°C., and on cooling, coalesced into vitreous masses from which no crystalline component could be separated by filtration, recrystallization, or vacuum distillation. Only by prolonged distillation with superheated steam, however, it was possible to liberate the volatile crystalline substance, but it required too long a time to be practicable. The crystalline substance so obtained represented golden yellow needles with silky lustre, not uncontaminated with resionus impurities, but melted exactly at 171°C. as stated by Romanis. This was then purified by recrystallization from glacial acetic acid containing a little chromic acid so as to destroy resinous impurities present. After repeated treatments the melting point of the pure product rose to 174–175°C. and it became almost colourless. The yield of such pure product amounted to 0.3 % as referred to the whole weight of teak was dust used.

The Dry Distillation. A preliminary experiment with 100 gr. of teak saw dust has shown that the product of dry distillation was practically the same as in the case of Romanis. They came over in the following proportions :—

Tar heavier than water	12 %
Water and Water-solubles.	35 %
Carbonaceous Residue	33 %

The dark brown tar consisted for the most part of phenols and acids, the greater part dissolving in dilute alkali with evolution of heat. It was shaken with ether and dilute alkali several times and the neutral ethereal solution remaining behind was evaporated on the water-bath. The gruel-like mass thus obtained, on cooling, congealed into a vitreous mass conglomerated with crystalline needles. This was then fractionally distilled under 7 mm. pressure, when the following fractions distilled over :—

Up to 150°	150–190°	190–235°	235°–265°	Residue
27.4%	16.4%	3.8%	23.6%	24.0%

The first fraction represented a yellow-coloured mobile liquid with the peculiar odour of the teak wood, while the second fraction was more viscous than the former and on cooling deposited a small quantity of beautifully yellow-coloured needles. The third fraction was practically solid while the fourth was a dark brown viscous oil with a little crystalline precipitate in it. The third fraction was weell-cooled and freed from the adhering oily matter by allowing it to drain on the porous porcelain plate, the crude crystals obtained in this way were recrystallized from glacial acetic acid to which a little active carbon had been added. The pure product thus obtained showed a melting point 175–176°C., and was proved to be identical with tectoquinone by 'mischproben'.

Thus, from 150 kg. of teak saw dust, about 400 gr. of such crystals were obtained, purified as above-stated, and were used in the experiments described below.

Properties of Tectoquinone. At ordinary temperatures, tectoquinone represents pale yellow needle crystals with silky lustre, which melt at 175–176°C., and boil at 215–220°C. under 4 mm. pressure. Under atmospheric pressures it sublimes but with decomposition. It is soluble in most organic solvents such as alcohol, ether, benzene, or acetone. It is also slightly soluble in hot water. It does not react with hydroxylamine or semicarbazide. When shaken with zinc dust and concentrated ammonia water, a deep blood-red colouration ensues, but it quickly discolours on exposure to the air and the original substance can be recovered unchanged from the solution. It is neither an alcohol nor a phenol, but represents an anthraquinone derivative. The colour reaction for phenanthrene was tried but with negative results.

Anal. Subst. = 0.0912, 0.0958; CO_2 = 0.2706; 0.2844; H_2O = 0.0400, 0.0418 gr. Found: C = 80.80, 80.96; H = 4.87, 4.84%. Calc. for $C_{15}H_{10}O_2$: C = 81.08; H = 4.50%. Calc. for $C_{16}H_{12}O_2$: C = 81.38; H = 5.09%.

The Crystalline Substance from Lower Fractions. From lower boiling fractions another crystalline component was obtained which after due purifications melted at 199–200°C. It boils a little lower than tectoquinone, viz., at 190–200°C. under 4 mm. pressure. It sublimes easily on heating it in vacuo and gives bluish green tiny needles which fluoresce. It dissolves easily in hot alcohol or acetic acid from which it can be recrystallized. Its dilute solutions also fluresce beautifully.

Anal. Subst. = 0.1042; CO_2 = 0.3550; H_2O = 0.0646 gr.
Found: C = 92.91; H = 6.89%. Calc. for $C_{15}H_{12}$: C = 93.75; H = 6.25%. Calc. for $C_{16}H_{14}$: C = 93.21; H = 6.78%.

On oxidizing this substance with strong chromic acid in glacial acetic acid, the same monocarboxylic acid as that obtained by the oxidation of tectoquinone, resulted. Furthermore, it showed no lowering of its melting point on admixture with the hydrocarbon obtained by the reduction of tectoquinone, and its other behaviours towards bromine or picric acid etc. agreed perfectly with those of the hydrocarbon above-mentioned. From these, it appears probable that this hydrocarbon must have been formed during the process of dry distillation from tectoquinone through the reducing action of carbonaceous matter, so that it should represent β-methyl-anthracene, although the analytical data are not satisfactory enough.

Oxidation of Tectoquinone. 12 Gr. of tectoquinone was dissolved in 300 c. c. of boiling glacial acetic acid and then a solution of 20 gr. of chromic acid in a suitable quantity of the same solvent was gradually added unto the boiling mixture and kept at boiling for two hours until the solution assumed a pure green colour. The whole solution was then cooled and the canary-yellow coloured needle crystals thereby precipitating were filtered on the pump. By evaporating the mother liquor, another crop of the same crystals was obtained, the total yield amounting to 13 gr. After several recrystallizations from glacial acetic acid it was observed to melt at 284–285°C.

Anal. Subst. = 0.0990; CO_2 = 0.2582; H_2O = 0.0318 gr.
Found: C = 71.13; H = 3.57%. Calc. for $C_{15}H_8O_4$: C = 71.4; H = 3.2%.

It is almost insoluble in ether, chloroform, benzene or water, but is moderately soluble in hot alcohol or acetic acid. On treatment with zinc dust and concentrated aqueous ammonia, it displays the characteristic blood-red colouration peculiar to anthraquinone derivatives, showing that the quinone grouping is left unaffected throughout the oxidative process.

Nextly, 2 gr. of the acid was intimately mixed with an equal amount of soda-lime and heated in a test-tube in a paraffin-bath at 290°C., when a sublimate was seen to form on the wall of the test-tube, which was collected, purified by recrystallization, and its melting point tested. It was observed to melt at 272–274°C. and showed no lowering of the melting temperature on admixture with a sample of pure anthraquinone. It follows that the original carboxylic acid represents one of the two anthraquinone carboxylic acids.

The Chloride and the Amide of the Acid. In order to identify the acid, its chloride and amide were prepared in the following way. 3 Gr. each of the acid, phosphorus pentachloride were weighed out into a flask to which 50 c. c. of carbon disulphide was added and boiled for half an hour under reflux until the solid matter in the flask disappeared. Then the solvent and the excess of phosphorus pentachloride were distilled off and the residue was thrown into cold water. The crystalline solid sesarating thereby was filtered, dissolved in chloroform, the chloroform layer separated, dried and evaporated. The residue was then dried on the porous porcelain plate and finally recrystallized from glacial acetic acid. The chloride thus obtained melted at 146–147°C. It was readily soluble in alcohol, benzene, chloroform or carbon disulphide, but was only slowly acted on by cold water or alcohol. 2 Gr. of it was dissolved in 50 c. c. of benzene, a current of dry ammonia gas was passed through, the white precipitate forming thereby was filtered, washed with hot aqueous ammonia to remove the simultaneously produced ammonium salt, allowed to dry on the porous porcelain plate, and then recrystallized from benzene. The pure acid amide thus obtained melted at 278–279°C. It is very sparingly soluble in such solvents as alcohol, benzene, chloroform or carbon disulphide, and produces the characteristic blood-red colouration on treatment with zinc and ammonia water, showing that the quinonic structure is still left unchanged.

As for the melting points of anthraquinone carboxylic acids and their derivatives, we have in the literature, 293–294°C. for the α-acid,(1) and several date ranging from 285°C. to 292°C. for the β-acid,(2) 147°C. for the β-acid chloride,(3) 280°C. for the α-acid amide,(4) and another datum that the β-acid amide melted higher than 280°C.(3) With these data it is not yet sufficient to determine which of the two anthraquinone carboxylic acids represents tectonic acid—the acid obtained from tectoquinone, but it may certainly be regarded as likely that tectonic acid must be either the one or the other.

Preparation of Tectonic Esters.

(a) **Methyl Tectonate.** One gram of tectonic acid was dissolved in 50 c.c. of methyl alcohol, saturated with cold, dry hydrogen chloride, warmed

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(1) Graebe, Leonhardt, *Ann.*, **290** (1896), 231.

(2) Liebermann, Bischof *Ber.*, **13** (1880), 49; O. Fischer *J. prakt. Chem.*, [2] **79** (1909), 558; Limpricht, *Ann.*, **309** (1899), 122.

(3) Liebermann, Glock, *Ber.*, **17** (1884), 889, 890.

(4) Graebe, Blumenfeld, *Ber.*, **30** (1897), 1116.

on the water-bath for thirty minutes, this treatment repeated again and again until all the solid dissolved away on warming, filtered while hot, and allowed to cool. In this way the methyl ester was obtained in form of pale yellow crystalline needles melting at 164–165°C. after purifications.

Anal. Subst. = 0.1254; $CO_2 = 0.3304$; $H_2O = 0.0438$ gr.
Found: $C = 71.85$; $H = 3.88\%$. Calc. of $C_{16}H_{10}O_4$: $C = 72.18$; $H = 3.76\%$.

(b) **Ethyl Tectonate.** The ethyl ester was prepared exactly in the same manner as described above, using ethyl alcohol in place for methyl alcohol. The crystalline ester so obtained melted after purifications at 147°C., the yield amounting to 2 gr. starting from 2 gr. of the acid.

Anal. Subst. = 0.1022; $CO_2 = 0.2720$; $H_2O = 0.0410$ gr.
Found: $C = 72.60$; $H = 4.45\%$. Calc. for $C_{17}H_{12}O_4$: $C = 72.86$; $H = 4.28\%$.

These esters are both very soluble in benzene or chloroform, also in hot alcohol or hot glacial acetic acid, and show the characteristic colour reaction on treatment with zinc and ammonia.

According to literature, the ethyl ester of anthraquinone-α-carboxylic acid(1) melts at 169°C., while that of the β-acid(2) does at 147°C. The melting point of methyl ester of the α-acid is reported to be 189°C., which is decidedly higher than that of methyl tectonate. Thus, the identity of tectonic acid with anthraquinone-carboxylic acid looks very probable.

Reduction of Tectonic Acid.

(a) **Reduction with Zinc and Ammonia.** Two grams of tectonic acid was intimately mixed with 3 gr. of zinc dust and was added to 100 c. c. of 12 % aqueous ammonia under stirring and was warmed on the water-bath for two hours. The reaction mixture, which at first assumed an intense blood-red colour, gradually discoloured into pale greenish blue, and a remarkable fluorescence set in. It was filtered while hot, and allowed to cool. On acidification, a bulky precipitate separated out which gradually passed into crystalline needles. It was filtered on the pump, dried, and recrystallized from glacial acetic acid. The beautiful yellowish green crystals thus obtained, which amounted to 1.5 gr., melted at 274–275°C. This acid, if once transformed into its acid chloride and then restored to the original acid, then its melting point rises to 278–279°C., but never by repeating simple recrystallizations.

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(1) Graebe, Blumenfeld, loc. cit.

(2) Liebermann, Glock, *Ber.*, **17** (1884), 889.

Anal. Subst. = 0.1400; CO_2 = 0.4148; H_2O = 0.0704 gr.
Found: C = 80.81; H = 5.58%. Calc. for $C_{17}H_{14}O_2$: C = 81.60; H = 5.60%.

The data on the melting point of anthracene carboxylic acid are as follows. 245°C. for anthracene-α-carboxylic acid,⑴ 275–280°C. for the β-acid,⑵ 135°C. for the ethyl ester of the β-acid.⑵ These date for the β-acid and its ethyl ester are in good accord with the authors' substances, so the product in question, viz.—the hydrotectonic acid in the table—should be regarded as anthracene-β-carboxylic acid.

(b) **Reduction with Zinc and Acetic Anhydride.** 2 Gr. of tectonic acid was boiled with 30 c. c. of acetic anhydride together with 2 gr. of anhydrous sodium acetate and 4 gr. of zinc powder under reflux for 15 minutes. This mixture, which at first showed yellowish brown colour, soon clarified into bluish green fluorescent liquid and deposited a quantity of tiny orange-coloured needles, which after recrystallization from glacial acetic acid melted at 219–220°C.

Anal. Subst. = 0.1468; CO_2 = 0.3590; H_2O = 0.0358 gr.
Found: C = 66.70; H = 4.38%. Calc. for $C_{19}H_{14}O_6$: C = 67.45; H = 4.16%.

This substance, as dilute solutions in alcohol or acetic acid, fluoresces blue-green. On addition of alkali to the dilute alcoholic solution, it acquires red tinge, but it rapidle fades away to give anthraquinone-β-carboxylic acid. It has been reported that anthraquinone-α-carboxylic acid on treatment as above, gives the lactone of acetyl-anthrahydroquinone-α-carboxylic acid,⑶ whereas the acid under investigation led to the formation of a diacetate instead of a lactone, it follows that in the present case the carboxyl group must be attached to the β-position and not to α-.

Derivatives of Hydrotectonic Acid.

(a) **Anthracene.** 1.5 Gr. hydrotectonic acid was carefully mixed with 3 gr. of soda-lime and was heated in a test tube in the paraffin bath at 300°C. for half an hour, the crystalline sublimate thereby forming, was collected, recrystallized from alcohol, and resublimed in vacuo. It melted at 212–213°C. On mixing this substance with some pure specimen of anthracene, no depression of the melting point was to be perceived.

Anal. Subst. = 0.0944; CO_2 = 0.3233; H_2O = 0.0503 gr.
Found: C = 93.99; H = 5.48%. Calc. for $C_{14}H_{10}$: C = 94.38; H = 5.62%.

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(1) Graebe, Blumenfeld, loc. cit.

(2) Börnstein, *Ber.*, **16** (1883), 2610; Limpricht, loc. cit., Liebermann, Bischof, *Ber.*, **13** (1880), 49.

(3) Scholl, Böttger, *Ber.*, **62** (1929), 625.

(b) **The Chloride and the Amide.** One gram of hydrotectonic acid was treated with 1 gr. of phosphorus pentachloride in 40 c. c. of carbon disulphide in the warm for half an hour, and finally the excess of the solvent and phosphorus pentachloride was distilled off, and the residue thrown into cold water. The brilliant golden yellow needles thereby crystallizing were filtered, dissolved in chloroform, dried on anhydrous sodium sulphate, chloroform evaporated, the residue was allowed to drain on the porous porcelain plate. It was found to melt at 172–173°C. This chloride is pretty stable, and is not acted on by cold water, but on being kept for a long time in the desiccator, or on being recrystallized from alcohol or acetic acid, it is liable to be transformed back into its mother acid or its ester, so it was quickly dried on the porous plate, and at such stage it was found to melt at 172–173°C. 0.5 Gr. of this acid chloride was treated with ammonia gas in benzene solution (100 c. c.) when a deposit in form of yellow leaflets separated out, which was filtered, washed with water and aqueous ammonia one after the other, and finally recrystallized from acetic acid. It represented beautiful yellow-green laminae and melted at 293°C. Its solutions in alcohol or glacial acetic acid showed a blue fluorescence.

Anal. Subst. = 0.1160; CO_2 = 0.3450; H_2O = 0.0536 gr.
Found: C = 81.12; H = 5.12%. Calc. for $C_{15}H_{11}NO$: C = 81.45; H = 5.00%.

The melting points of anthracene carboxylic acid amides are reported as 256° or 260°C. for α-acid amide,(1) and 293–295°C. for the β-acid amide.(2) Thus the amide obtained here from hydrotectonic acid is most likely identical with anthracene-β-carboxylic acid amide.

The Reduction of Tectoquinone.

(a) **The Reduction by means of Zinc and Ammonia.** Four grams of tectoquinone and 8 gr. of zinc dust were stirred in aqueous ammonia (50 c. c. concentrated ammonia and 50 c. c. of water) on the water-bath under reflux, the blood-red coloured solution gradually bleached in course of two hours, which on cooling deposited a crystalline precipitate. The precipitate was filtered, redissolved in glacial acetic acid, refiltered while hot to get rid of excess of zinc dust and then allowed to cool. Thus, about 3 gr. of scaly crystals of yellowish green colour were obtained from the filtrate. After recrystallizations the substance melted at 202–203°C. with partial sublima-

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(1) Dienel, *Ber.*, **39** (1906), 932; Graebe, Blumenfeld, loc. cit.

(2) Börnstein, loc. cit.

tion. It was difficultly soluble in cold glacial acetic acid but more soluble in the hot state. Its dilute solutions displayed a green-violet fluorescence.

Anal. Subst. = 0.0918; CO_2 = 0.3138; H_2O = 0.0541 gr.
Found: C = 93.20; H = 6.00%. Calc. for $C_{15}H_{12}$: C = 93.75; H = 6.25%.
Calc. for $C_{16}H_{14}$: C = 93.20; H = 6.80%.

One gram of this hydrocarbon was dissolved in 40 c. c. of carbon disulphide to which a calculated amount of bromine (4 Br against 1 Mol.) in 10 c. c. of the same solvent was slowly added and stood still. In an hour the reaction was complete, and on evaporating off the solvent, about 1 gr. of a yellowish crystalline substance was left behind, which on recrystallization from glacial acetic acid gave needle cryatals of bright yellow colour melting at 166–167°C., readily soluble in benzene, chloroform or carbon disulphide. Its dilute solutions also showed a green fluorescence.

Anal. Subst. = 0.1161; CO_2 = 0.2130; H_2O = 0.0287 gr.
Found: C = 50.05; H = 2.67%. Calc. for $C_{15}H_{10}Br_2$: C = 51.48; H = 2.88%.
Calc. for $C_{16}H_{12}Br_2$: C = 52.76; H = 3.32%.

According to literature, the melting points for methyl anthracenes are stated to be 85–87°C. for the α-,(2) and 202–207°C. for the β-modification,(2) while as regards the mesodibromo-compounds we find 138–140°C.,(3) 142–143°C.,(4) and 148°C.(5) for the β-derivative—these discrepancies seemingly arising from the difficulty of purification. In the present case, the mother hydrocarbon melts at 202–203°C., and the mesodibromide at 166–167°C. Thus it should be regarded as derived from β-anthracene, and the datum for the bromine compound as representing a purer specimen.

(b) Reduction by means of Tin and Hydrochloric Acid. To a boiling mixture of 4 gr. of tectoquinone, 10 gr. of granulated tin, and 100 c. c. of glacial acetic acid, 10 c. c. of concentrated hydrochloric acid was slowly added. After an hour, the reduction was complete, and the reaction mixture was filtered on the pump and the solution was poured into 500 c. c. of cold water. At first, an oily substance separated out which gradually coalesced into a crystalline deposit. This substance is very difficult to recrystallize and it was impossible to purify it so as to attain to the definite melting point. At any rate, it became indiffer-

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(1) O. Fischer, Sapper, loc. cit.

(2) Kraemer, Spilker, Eberhardt, *Ber.*, **23** (1890), 3272; O. Fischer, Sapper, *J. prakt. chem.*, [2] **79** (1909), 558; Lavaux, *Ann. chim. phys.*, [8] **20** (1910), 445.

(3) Liebermann, *Ann.*, **212** (1882), 35.

(4) Börnstein, *Ber.*, **15** (1882), 1822.

(5) Weller, *Ber.*, **7** (1874), 1186; O. Fischer, *J. prakt. chem.*, [2] **79** (1909), 558.

ent to the colour reaction peculiar to the anthraquinone derivatives, and showed a decided tendency to return to the original substance on keeping for a long while, regaining the property to produce blood-red colouration on treatment with zinc and ammonia. Thus, it was so far purified by deposition from its dilute alcoholic solution by the addition of a large quantity of water, the milky fluid produced thereby being stood still for a length of time. By repeating such treatment five times, the melting of the resulting product rose to 80–90°C.

Anal. Subst. = 0.0938; CO_2 = 0.2982; H_2O = 0.0506 gr.
Found: C = 86.70; H = 6.00%. Calc. for $C_{15}H_{12}O$: C = 86.54; H = 5.77%.

It dissolves easily in alcohol, benzene or glacial acetic acid, but not much in alkalies. This feature of solubilities together with the tendency of retransforming into the original substance, as well as the analytical data, agree with the properties of methyl-anthrone. As to the melting point of methyl-anthrone, there are reported.

3-methyl-anthrone-9	80–84°C.,⑴ 86°–88°C.,⑵ 101°C.(22)
2-methyl-anthrone-9	103°C.⑶

According to Barnett and Frederick, the anthrones from β-methyl-anthraquinone represent a mixture of 3-methyl-anthrone-9 and 2-methyl-anthrone-9, and the separation of these two from one another by means of simple recrystallizations is practically impossible.

(c) **Reduction by means of Zinc and Acetic Anhydride.** One gram of tectoquinone was dissolved in 20 c. c. of acetic anhydride to which 2 gr. of zinc dust and 3 gr. of anhydrous sodium acetate were added and the whole was boiled under reflux for an hour, when the brownish yellow colour of the initial mixture faded almost completely and a slight fluorescence became perceptible. After cooling, it was slowly poured into cold water and kept still. The greenish yellow leaflets separating out therefrom, after recrystallizations from alcohol, showed a melting point 216–217°C., agreeing with the data for β-methyl-anthra-hydroquinone diactetate.⑷ It dissolved readily in alcohol or acetic acid in the warm, and the solutions fluoresced blue green.

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(1) Liebermann, Manlock, *Ber.*, **38** (1905), 1792.
(2) Padova, *Ann. chim. phys.*, [8] **19** (1910), 395.
(3) Barnett, Frederick, *J. Chem. Soc.*, **1929**, 1755.
(4) Liebermann, *Ber.*, **21** (1888), 1172.

Anal. Subst. = 0.1116; CO_2 = 0.2964; H_2O = 0.0522 gr.
Found: C = 72.44; H = 5.17%. Calc. for $C_{19}H_{16}O_4$: C = 73.05; H = 5.20%.

This substance, on treatment with alcoholic potash furnished a blood-red coloured solution which discoloured in course of time to be restored into tectoquinone again. Such tectoquinone was observed to melt at 176–177°C., and seemed to represent the substance of the highest purity as far as the authors' experiments are concerned.

The Nitration of Tectoquinone. Into a cold mixture of 20 c. c. concentrated sulphuric acid and 15 c. c. concentrated nitric acid, 2 gr. of tectoquinone was slowly introduced in small portions with constant stirring and cooling. After all the crystals dissolved away, the whole mass was warmed on the water-bath when a yellow crystals of the nitro-compound separated out. This nitro-compound was only sparingly soluble in most of the organic solvents and could only be recrystallized from a large volume of hot glacial acetic acid. After five consecutive recrystallizations it was observed to melt at 262–265°C. with decomposition.

Anal. Subst. = 0.1047; CO_2 = 0.2542; H_2O = 0.0327 gr.
Found: C = 66.26; H = 3.46%. Calc. for $C_{15}H_9NO_4$: C = 67.41; H = 3.37%.

The melting point and the analytical data agree with 1-nitro-2-methyl-anthraquinone.(1) An impure 1-oxy-2-methyl-anthraquinone of m. p. 170°C. could be obtained from this nitro-compound by treatment with tin and hydrochloric acid and subsequent diazotization etc.

Summary.

(1) Tectoquinone, the volatile crystalline ingredient of the teak wood, which was isolated by R. Romanis in 1887, represents β-methyl-anthraquinone.

(2) Tectoquinone, on oxidation, gives tectonic acid, which is identical with anthraquinone-β-carboxylic acid.

(3) Tectoquinone, on reduction, gives a hydrocarbon 'tectonene', which, on examination, was proved to be β-methyl-anthracene.

(4) Tectoquinone, on treatment with zinc and acetic anhydride, gives β-methyl-anthra-hydroquinone diacetate melting at 216–217°C., which is very easy to purify and thus may be used for the purpose of identifying tectoquinone.

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(1) Römer, Link, *Ber.*, **16** (1883), 697; Holdermann, *Ber*,, **39** (1906), 1257.

(5) β-Methyl-anthra-hydroquinone diacetate, on treatment with alcoholic potash and subsequent exposure to the air, regenerates tectoquinone of highest purity, melting at 176–177°C.

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