

On The Chemical Constituents Of The Heart Wood Of *Distylium Racemosum* S. ET Z. (Second Report)

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<https://doi.org/10.5109/22647>

出版情報：九州大学大学院農学研究院紀要. 10 (1), pp.101-117, 1951-10. Kyushu University
バージョン：
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ON THE CHEMICAL CONSTITUENTS OF THE HEART
WOOD OF *DISTYLIUM RACEMOSUM* S. ET Z.

(Second Report)

TAMIO KONDO

CHAPTER V

Degradation Study of Distylin

The author gives distylin the molecular formula $C_{15}H_{12}O_7$, and its oxygen-function is shown as follows: two of them belong to those of the γ -pyron ring, in which the carbonyl group in the C_4 -position has more similar behaviour to one of the flavanone type than of the flavanone type in the chemical reactivity and the remaining five are of hydroxyl groups, and four of them are aromatic and the last one is aliphatic, because tetramethyl distylin can be prepared with diazomethane, deprived of the ferric chloride reaction and of the solubility in alkali reagents.

The positive Mg-HCl reaction of distylin suggests that the number of the carbon linkage of the pigment is 15, but it is not conclusive, for a few xanthone derivatives are also active to the Mg-HCl reaction. However the expected carbon number 15 may be properly supported from the following experimental results: with the action of dilute sulphuric acid, distylin gave quercetin in good yield and no sugar was found in the filtrate. With regard to the attachment-positions of the hydroxyl groups in the molecule it is considered that there is perhaps a close relationship with one of quercetin and the author treated distylin with degradative cleavage in order to clear off this point.

In general the action of alkali to the pigment is appreciated on the structural study of the flavone substances. Really each group of the pigments, flavone, flavonol, flavanone and flavanoneol, stands on each special behaviour against alkali reagents, so we

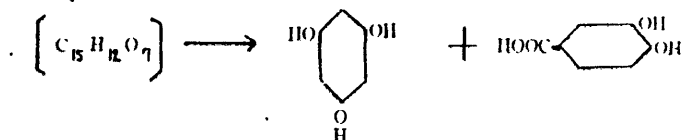
can obtain each characteristic reaction product from each peculiar degradative courses.⁶¹⁾

On flavanone homologues the action of conc. alkali gives derivatives of phenol and cinnamic acid, but dilute alkali yields derivatives of ortho-oxy-acetophenone and benzaldehyde. On flavone homologues it gives 2-oxy-benzoyl-acetophenone as the first product, from which acid cleavage will finally come in chief with a small side reaction of ketone cleavage. So we obtain each one mol of phenol, acetic acid and benzoic acid with a little quantity of salicylic acid and acetophenone which originated from ketone-cleavage. On the action of strong alkali it raised up mainly acid-cleavage and also on weak alkali or alcoholic alkali it aroused ketone-cleavage.

On flavonol pigments the type of degradation differs from the two above described courses, it yields phenol and benzoic acid over the intermediate product of ortho-oxy-acetophenone. Flavanonol pigments take a characteristic course of degradation as is described below.^{33, 35)}

In any cases it causes the cleavage of the γ -pyrone ring as the first step and by the action of strong alkali, in other words alkali fusion, we are able to obtain both phenol and phenol-carboxylic acid. Among them the phenol derivative is originated from the benzene ring of benzopyrone and phenol-carboxylic acid is also derived from the side-phenyl radical.

From the alkali-fusion of distylin the author obtained two substances in each crystalline form. The one was determined as protocathechuic acid and the other was identified as phloroglucin, respectively, through mixed melting-point determination with known preparations. So it is reasonable to conclude that distylin has phloroglucin nucleus in benzopyronering and orthodioxo-phenol nucleus in side the phenyl radical.



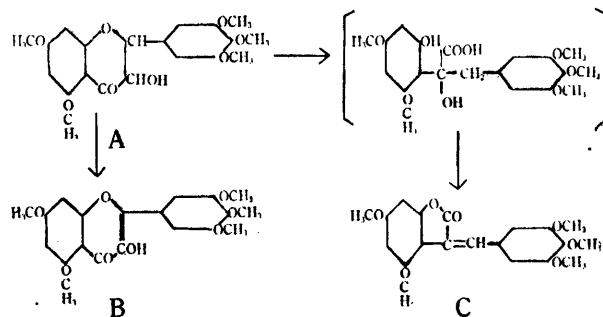
In the literature it is reported that quercetin gives the same two substances, phloroglucin and protocathechuic acid on the alkali-fusion. Here the author cleared off the constitutional relationship

and proved that distylin has the same structural components as that of quercetin.

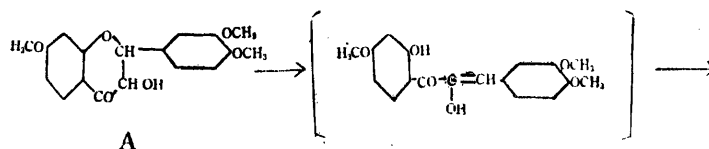
With the action of alcoholic potassium hydroxide, distylin gives protocathechuic acid and one more substance that crystallizes in colourless plates. The plates are insoluble in usual organic solvents and soluble in hot water. On ignition with a platin plate it leaves appreciable ash. The aqueous solution develops neutral reaction to the litmus paper, a green coloration to ferric chloride, and negative to the Mg-HCl reaction. From the results of the elementary analysis and the measurement of potassium it is in agreement with the molecular formula $C_{16}H_{13}O_8K \cdot H_2O$. When it is heated in a capillary tube, it melts at about $210^\circ C$ under decomposition.

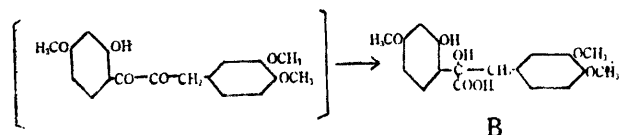
From the above described qualities the product can be recognized as the potassium salt of a phenol-carboxylic acid.

In the literature we find an interesting report that H. Kubota observed on ampeloptin from "shirocha" the following phenomena³⁵⁾: When pentamethyl-ampeloptin (A) was treated with 10% alcoholic potassium hydroxide for one hour, it gave anhydro-pentamethyl-ampeloptinlactone (C) with myricetin-5, 7, 3', 4', 5'-pentamethylether (B).

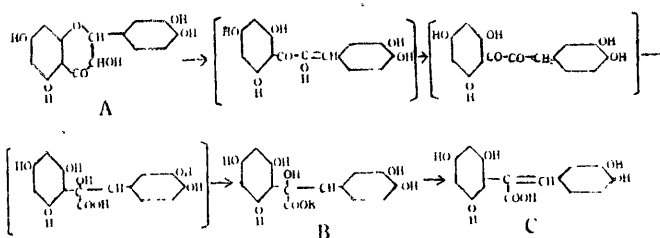


And also T. Oyamada treated trimethyl-fustin (A) with 10% alkali and obtained trimethyl-haseinic acid (B). So he illustrated this reaction in the following schema:³³⁾





It is generally recognized that such a cleavage-type is a characteristic for the flavanone pigment.⁶¹⁾ With reference to these observations one may safely say that the formation of potassium salt of phenol-carboxylic acid from distylin took place as the product of α -diketone after the benzilic acid rearrangement. And so the author provisionally propose 3,4-dihydroquercetin (A) as the structural formula of distylin and according to this formula he illustrates this product in the following schema :



So the potassium salt (B) was dissolved in hot water, acidified with dilute sulphuric acid, on shaking out with ether, the ether extract yielded light brown short prismatic crystals, m.p. 228°C. The product dissolved in aqueous sodium bicarbonate solution under bubbling of carbon dioxide and the aqueous solution developed acidic reaction to the litmus paper and gave green coloration to ferric chloride.

And this green coloration changed into reddish violet on addition of a few drops of soda solution. It is inactive to the Mg-HCl reaction. From the figures of the elementary analysis it corresponds with the molecular formula $C_{18}H_{12}O_7(C)$.

So the author attempted to obtain its lactone-derivative with dilute mineralic acid, but contrary to his expectation the original substance was only obtained. The reason of the unsuccessful ring-closure may be cleared off by the following explanation: in the cases of fustin and ampeloptin each methyl derivative was treated with alkali, so the two hydroxyl groups in 5,7-positions of

benzopyron nucleus were covered with methyl radicals, but on the other hand the author treated free distylin with alkali, so the two hydroxyl groups in 5,7-positions are mainly in the type of chinoide in acidic solvent.

If it is assumed that distylin will be formulated as 3, 5, 7, 3', 4'-pentaoxy-flavone, its tetramethyl-derivative must be naturally 5, 7, 3', 4', -tetramethoxy-3-oxy-flavanone. About fifteen years ago Y. Kimura reported the 5, 7, 3', 4'-tetramethoxy-3-oxy-flavanone, m.p. 176°C, which was synthesized through condensation of 2-oxy-4, 6, ω -trimethoxy-acetophenone and veratricaldehyde.⁶²⁾ The interval between both melting points could not be diminished by the repeating recrystallization. Here we shall notice two asymmetric carbon atoms in the assumed 3, 5, 7, 3', 4'-pentaoxy-flavanone molecule. So the existence of optical epimer is naturally considered, as in the case of crystalline catechine⁶³⁾ that has close structural relationship with flavone pigment. Then the author treated natural tetramethyl-distylin, m.p. 170°, with 10% methanolic potassium hydroxide for a few minutes, and obtained one crystal, m.p. 176°C which has the same crystalline form, qualitative reactions with Kimura's 5, 7, 3', 4'-tetramethoxy-3-oxy-flavanone.

Dr. Kubota reported the similar experiment on ampeloptin; on the treatment of pentamethyl-ampeloptin that derived from natural ampeloptin with 10% methanolic potassium hydroxide, he obtained a product which corresponded with synthetic pentamethyl-ampeloptin and he interpreted this phenomena by the opimerization.³⁶⁾ According to Kubota's nomenclature this acquired product, naturally also synthesized tetramethyl-flavanone, should be named 5, 7, 3', 4'-tetramethyl-epi-distylin.

Experimental

Alkali-fusion of distylin:

25 g of potassium hydroxide were weighed in the nickel basin, added to water (10 c.c.) and fused in the oil bath. In the fused alkali solution distylin (4.1 g) was thrown little by little with gentle stirring, and decomposed presenting a darkish red colour. The reaction was continued for 20 minutes at 190–200°C and for 10 minutes at 200–210°C. After cooling the mixture was added to a large volume of water, acidified with dilute sulphuric acid and extracted with ether. The darkish ether extract was

shaken with bicarbonate solution. The bicarbonate fraction was again extracted with ether, after acidification with dilute sulphuric acid. The ether extract was dried with Glauber's salt, and evaporated to dryness. The violet resinlike residue gave nearly colourless needles, m.p. 193°C. The aqueous solution of this product gave indigo coloration to ferric chloride and this coloration changed to red on the addition of the soda solution.

When lead acetate solution was added it gave a white precipitate which is soluble in acetic acid. It also reduced the ammonia-alkaline mercuric nitrate solution and strongly reduced Fehling's solution on heating. It was reliably identified as protocatechuic acid through the mixed melting point determination with known one that obtained from the alkali-fusion of quercetin.

The phenolic fraction, namely the ether extract free from the soda-soluble portion, gave a yellowish tar-like mass. Upon treatment with hot water the mass yielded a few plates of yellowish tar. The crystalline substance was smeared on a porous plate, and recrystallized by the use of hot water. When the product was dried at the boiling point of toluene it melted at 209°C. Its aqueous solution gave a bright violet colour to the ferric chloride solution, also a rose colour to the HCl-vanilline reaction, and a reddish violet to the fichten-span reaction. With the mixed melting-point determination with phloroglucin specimen that dried under the above described condition, no depression was observed (The mixed melting point: 213°C).

Action of methanolic potash:

Distylin (2 g) was dissolved in 40% methanolic potash (15 c.c.), the yellowish mixture became gradually brown on warming with the reflux condenser for one hour. After evaporation of the solvent it separated into colourless crystals with the lapse of time, which yielded about 1 g. It was recrystallized from hot water. The product was colourless plates that on heating changed to a light brown colour at about 180°C, became red at about 200°C and decomposed presenting a blackish brown colour at about 210°C. It was almost insoluble in the usual organic solvents and the aqueous solution was neutral to the litmus, and it developed green coloration to the ferric chloride solution. It gave voluminous yellowish white precipitate with lead acetate solution, reduces Fehling's solution and it was inactive to the Mg-HCl reaction. In

conc. sulphuric acid it dissolved into a brown solution, and this coloration though it became remarkably pale on addition of water, did not disappear. And the second addition of sulphuric acid gave again a deep brown coloration. After standing on the table for a long time its surface became a light reddish colour.

Sample : (air-dried)

Subst.	CO ₂	H ₂ O	C %	H %
19.5 mg	33.7 mg	7.2 mg	47.25	4.12
Calc. for C ₁₅ H ₁₃ O ₈ K. H ₂ O			47.61	3.96

Measurement of potassium :

Subst.	K ₂ SO ₄	K %
10.5 mg	2.4 mg	10.23
Cal. for C ₁₅ H ₁₃ O ₈ K. H ₂ O		10.31

Further, the mother liquor from the potassium salt, gave a little protocatechuic acid from its ether extraction.

The potassium salt in hot water was acidified with dilute sulphuric acid and extracted with ether. The ether solution was dried with Glauber's salt and yielded light brown crystals on evaporation of the solvent. The residue was purified from methanol, but remained only as oily substance. From using hot water it was successfully crystallized in light brown needles, m.p. 228°C. The aqueous solution was evidently acidic to the litmus. It dissolved in the bicarbonate solution under bubbling of carbon dioxide. And it gave no ash on ignition. In the aqueous solution ferric chloride gave a green coloration, which became a reddish violet colour on addition of soda. The author attempted to force the lactonering closure, but obtained only the unchanged original substance.

Subst.	CO ₂	H ₂ O	C %	H %
14.7 mg	32.3 mg	6.07 mg	59.97	4.58
Calc. for C ₁₅ H ₁₂ O ₇			59.21	3.94

Epimerisation of tetramethyl-distylin.

0.3 g of tetramethyl-distylin, m.p. 170°C was mixed with methanolic potash solution (3 c.c.) in which potassium hydroxide (1 g) was dissolved in 50% methanol (10 c.c.), and the mixture was warmed on a water bath for 6 minutes. After cooling it was poured into a large quantity of ice water and acidified with dilute sulphuric acid. After standing overnight it separated into light reddish white precipitates. It was filtered and the product was

unfortunately separated from alcohol in milky emulsion. So the solvent was dried off and extracted with ether. The product from ether extract was kneaded on the porous plates with acetone. Through this procedure it was crystallized in a nearly colourless substance and purified two times from alcohol. It was light yellowish, sandy-formed crystals and melted at 176—177°C. The alcoholic solution was neutral to the litmus and gave no coloration to ferric chloride and to the Mg-HCl reaction. It was negative to both the phloroglucin-HCl and the vanilline-HCl reactions. In fuming nitric acid it dissolved into a bloody red colour. From the comparison of the melting point, the crystalline form and other colour-reactions it was identical with Kimura's synthetic 5, 7, 3', 4'-tetramethoxy-3-oxy-flavanone. So according to the Kubota's preceding nomenclature it should be properly named tetramethyl-epi-distylin.

Subst.	CO ₂	H ₂ O	C %	H %
20.6 mg	48.0 mg	10.4 mg	63.58	5.65
* Calc. for C ₁₅ H ₈ O ₇ (CH ₃) ₄			63.33	5.55

CHAPTER VI

The Structural Formula of Distylin

From the above described experimental results, the author proposed 3, 5, 7, 3', 4'-pentaoxyflavanone as the structural formula of distylin. Now in comparing the chemical and physical properties of distylin with other flavanonol pigments, such as fustin, ampeloptin and Katuranin, the author will generally try to reexamine the reasonableness of his proposal.

1) Crystalline form and colourlessness of distylin. In general almost all of the natural flavone pigments are coloured and accordingly have been called "pigment" from this physical quality. Naturally some pigments are deep coloured and some light coloured. In the literature we find three groups of colourless substances which are called "pigment", the first is flavanone pigment, such as sakuranetin and butin, the second is a few glucoside of the pigment, such as acacetin, and the last is flavanonol pigment that was found in comparatively recent times. So the colourlessness of distylin suggest to us that distylin may be one of the above three groups. However in the inactivity of

the carbonyl group and the cleavage-form with alkali reagent, distylin is considered neither glucoside nor flavanone. So distylin may be one of flavanone homologues. Furthermore distylin has two crystalline forms, needles and plates under the crystallizing conditions. But it is not an unprecedented matter in flavanone pigment, such as ampeloptin which is also in two crystalline forms. Now the crystalline forms and melting points of the known natural flavanones are shown as follows :

Substance	crystalline form	m.p.
Fustin $C_{15}H_{12}O_6$ ³³⁾	colourless needles.	faintly brown at about 200°C, melts at 216–218°C under decomposition.
Alpinon $C_{17}H_{16}O_8$ ³⁴⁾	colourless long needles.	178°C
Ampeloptin $C_{15}H_{12}O_8$ ³⁵⁾	colourless needles or square plates.	245–246°C under decomposition.
Katuranin $C_{15}H_{12}O_6$ ⁷⁾	colourless needles.	faintly colours at about 200°C, melts at 224–225°C under decomposition.
Distylin $C_{15}H_{12}O_7$	colourless needles or plates.	faintly colours at about 200°C, melts at 228–229°C under decomposition.

2) Coexistence of flavanone with flavonol. It is notable that all known natural flavanones have been always found together with those corresponding flavonols in the same plant tissue. In addition the content of flavanone pigments is generally larger than flavonol's and its ratio is approximately 1:3. These simple experimental observations suggest to us an interesting physiological significance of the pigments in the plant metabolism. The following table shows the coexistence of both pigments and its round ratio.

Original plants	substance	yield	ratio	authors
<i>Rhus succedanea</i> L.	Fisetin $C_{15}H_{10}O_6$	of the raw subst.	20% 1	: T. Oyamada
(in heart wood)	Fustin $C_{15}H_{12}O_6$	of the raw subst.	50% 2.5	
<i>Ampeleopsis neliifolia</i> Kudo	Myricetin $C_{15}H_{10}O_8$	of the original material.	2.5% 1	: H. Kubota
(in leaves)	Ampeloptin $C_{15}H_{12}O_8$	of the original material.	7.4% 3	
<i>Alpinia japonica</i> Miquel	Izalpinin $C_{16}H_{12}O_5$		1	: Y. Kimura : M. Hoshi
(in seeds)	Alpinon $C_{17}H_{16}O_5$		4	

Geracidiphyllum

<i>japonicum</i> S. et Z.	Kaempferol $C_{15}H_{10}O_6$ of the material.	0.03%	1	H. Uota
(in wood)	Katuranin $C_{15}H_{12}O_6$ of the material.	0.10%	3	T. Fukushima
				T. Kondo

Distylium racemosum

S. et. Z.	Quercetin $C_{15}H_{10}O_7$ of the material.	0.7%	1	T. Kondo
(in heart wood)	Distylin $C_{15}H_{12}O_7$ of the material.	2.3%	3	

3) Distylin has an intermediate quality between flavonol and flavanone in chemical behaviour. On flavanone compound its carbonyl group of γ -pyrone is usually active to the carbonyl reagents and gives its oxime and semicarbazone. And with conc. sulphuric acid flavanone yields an oxonium compound in the glacial acetic acid solution. Distylin gives no carbonyl derivative through the usual treatment, so from this result it may be considered rather as one of flavonol homologues. But it also gives no characteristic oxonium salt of flavonol pigment. So the chemical quality of distylin must be considered as being in the intermediate position between both pigments.

4) Distylin has the characteristics of flavanone pigment. Through the action of dilute mineralic acid, or rarely of dilute alkali, flavanone compound is converted into the flavonol. Accordingly it will be reasonable to assume that distylin is a corresponding dihydro-derivative of quercetin, because it gives quercetin with the action of mineralic acid. The second characteristic of flavanone was observed on the acetylation with sodium acetate and acetic anhydride. In this treatment it gives an amorphous reddish substance that could not be obtained in crystalline form. Distylin gives the same reddish substance under the same condition of acetylation. However flavanone yields crystalline chalcone derivatives on the same acetylation.

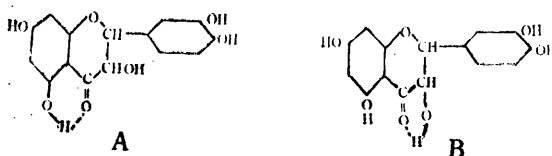
The cleavage-type of the pigment, which is developed by alkali reagent, is the most characteristic aspect of flavanone homologues. It appears to be produced 1,2-diketone derivative as the intermediate product of this reaction, and we obtain one phenol-carboxylic acid as the final product of the secondary reaction of like-benzilic acid rearrangement.

Distylin gave one phenol-carboxylic acid that may be explained by the above mechanism.

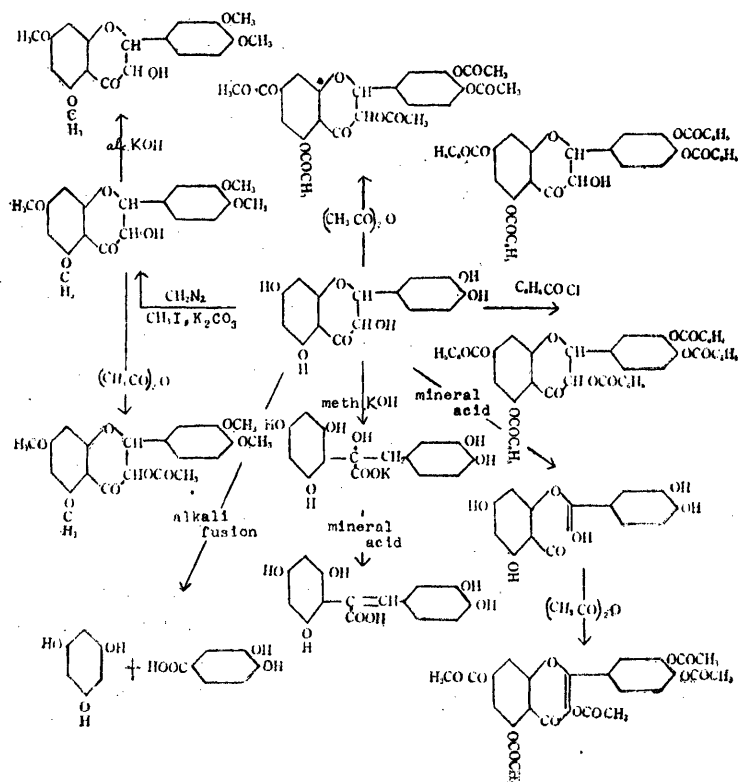
Furthermore it is reported that 3-oxy-flavanone compound develops reddish coloration on the treatment with granulated zinc and hydrochloric acid,⁴³⁾ while distylin is positive to this colour reaction.

5) The hydroxyl group, in the 3-position of distylin, is an alcoholic one. Five hydroxyl groups of distylin are divided in two forms, to one of which four belong to the phenolic group and the other to the alcoholic group. And from the fact that tetramethyl derivative was barely obtained, when an excess of diazomethane was employed on the methylation, it is obvious that one of the four phenolic hydroxyls resisted to the methylation.

So this one group is perhaps in the 5-position of the benzopyron linkage, in other words in the ortho-position to the carbonyl radical. On the other hand the hydroxyl group in the 5-position of flavonol resists strongly the methylation and it is barely methylated by the treatment with dimethyl sulphate and potassium hydroxide. But in the literature we find no reports that the hydroxyl group of the 3-position resists its methylation. Accordingly the resistance of the 3-position-hydroxyl group to the methylation may be explained as follows: the hydroxyl group may be considered with high probability as one of dihydro- γ -pyron linkage, so flavanonol compound acquires increasingly hydroaromaticity with the loss of aromaticity in its chemical activity. So beside hexacyclic linkage (A) the formation of pentacyclic linkage by the hydrogen bond (B) may be assumed, accordingly the methylation of 3-hydroxyl group becomes troublesome and simultaneously the resistance of the 5-hydroxyl group may appropriately diminish.



6) On the ground of the assumption that distylin is 3, 5, 7, 3', 4'-pentaoxy-flavanone, the above described experimental results are abstracted in the following scheme.

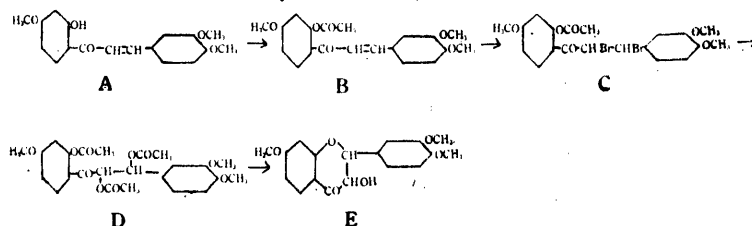


CHAPTER VII

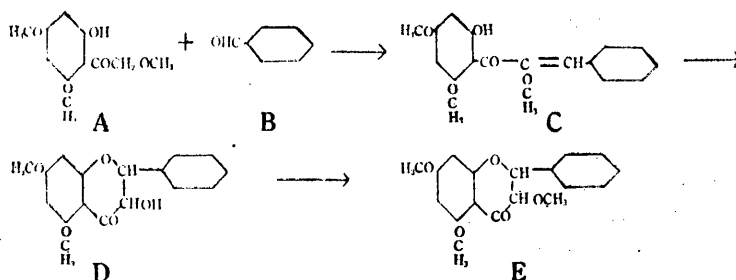
Synthesis of Distylin

There have been reported two different synthetic procedures of the flavanonol pigment. The one was executed by T. Oyamada as follows³³: He chose 2-oxy-4,3',4'-trimethoxy-chalkone (A) as the first material for his synthesis. The chalkone (A) was acetylated with acetic anhydride and anhydrous sodium acetate, and converted into 2-acetoxy-4,3',4'-trimethoxy-chalkone (B). Through the bromination of the product in the carbon bisulfide solution it gave 2-acetoxy-4,3',4'-trimethoxy-chalkonedibromide (C). For the substitution of bromine with acetyl group the halide was treated with silver acetate in the acetic anhydride solution, and thus obtained 2.α.β-triacetoxy-4,3',4'-trimethoxy-chalkone (D) was saponified and simultaneously closed in γ-pyrone compound,

trimethyl fustin (E), by the action of dilute mineralic acid in the alcoholic solution.



In the literature we find one more method, which Y. Kimura performed on the synthesis of apoalpinon-dimethylether.⁶²⁾ Namely he started from 2-oxy-4,6-dimethoxy-γ-methoxyacetophenone (A) and benzaldehyde (B). Through condensation of both compounds with the existence of alkali, 2-oxy-4,6-dimethoxy-α-methoxychalcone (C) was prepared. The chalcone was treated with the dilute solution of hydrochloric acid in alcohol for a long time and 3-oxy-5,7-dimethoxy-flavanone (D) obtained which was finally methylated with dimethyl sulfate and alkali. This methyl derivative was recognized as apoalpinon-dimethylether (3,5,7-trimethoxyflavanone) (E).



Independent of Kimura's study, H. Kubota synthesized 5,7,3',4'5'-pentamethyl-epi-ampeloptin with the same method.³⁶⁾ And he found that on the ring-closure of chalcone with alcohol-mineralic acid demethylation of the 3-position did not occur under some experimental conditions.

The author proposed 3,5,7,3',4'-pentaoxy flavanone as the structural formula of distylin and attempted to synthesize this compound by Kimura's method and set himself to this work. Namely he started from the cleavage of pentamethylquercetin.

with alcoholic potash and obtained 2-oxy-4, 6-dimethoxy-*o*-methoxy-acetophenone and 3,4-dimethoxy benzoic acid and from the latter he prepared 3,4-dimethoxy-benzoyl-chloride with the intention of synthesising 3,4-dimethoxy-benzaldehyde. However just at this time the author noticed the original report in which J. C. Pew has made from his studies on the pigment of Douglas Fir.⁴³⁾ From the heart wood of this tree he obtained an optically active flavanone, d-3, 5, 7, 3', 4'-pentaoxy flavanone and finally synthesized the corresponding racemic compound through direct reduction of quercetin. On various qualities of this racemic compound described in his report the pigment of Douglas Fir corresponded well to the one of distylin, so the author changed his synthetic project and synthesised his preparation with Pew's simple method. Accordingly the solution of quercetin in sodium carbonate was strongly reduced with sodium hydrosulfite and the product obtained was strictly identical with distylin in the physical and chemical properties. Furthermore it was also proved from the following experiment: the product was acetylated with acetic anhydride and pyridine, and acetyl derivative (m.p. 153°C) was mixed with penta-acetyl distylin and no depression of the mixed melting point was observed. Accordingly it is doubtless that distylin is racemi-Douglas Fir-flavanone, namely dl-3, 5, 7, 3', 4'-pentaoxyflavanone.

Experimental

Reduction of quercetin with sodium hydrosulfite: Synthesis of distylin. Quercetin (2.0 g) was sufficiently mixed with sodium carbonate (17 g), added to water (200 c.c.) and the mixture was dissolved in the homogeneous solution under warming in water bath. Sodium hydrosulfite (40 g) was added to the homogeneous solution in each 2-3 grams, under bubbling of hydrogen sulfide it was warmed in water bath. After fifteen minutes the mixture was added to 250 c.c. of water and some dilute sulfuric acid until a violet brown coloration of hydrosulfurous acid remained for some time. On cooling it separated into some precipitates of unchanged quercetin, filtered off and the filtrate was extracted with ether. The ether solution gave a light brown mass on evaporation of the solvent. On standing in the CaCl₂-desiccator under diminished

pressure it yielded light yellow crystals. The yield was 0.32 g, equal to 16% of the weight of the quercetin used. The product was recrystallized several times from hot water and developed into the form of plates or needles under conditions of recrystallization. On heating it lightly coloured at near 200°C and melted at 228—229°C with decomposition. However, on rapid heating the melting point was raised up to 238—239°C. In alcoholic solution it was positive to the Mg-HCl reaction and also to the reaction with granulated zinc and hydrochloric acid. The mixed melting point with distylin showed the same behaviour with one of distylin itself.

Subst.	CO ₂	H ₂ O	C %	H %
15.2 mg	33.4 mg	6.04 mg	59.95	3.95
Calc. for C ₁₅ H ₁₂ O ₇			59.21	3.95

On the acetylation with acetic anhydride and pyridine the reduction product gave colourless needles, m.p. 153°C after three times of recrystallization from methanol. The methanol solution of the acetyl derivative was negative to ferric chloride solution, but positive to the Mg-HCl reaction. On the mixed melting point determination with pentaacetyl-distylin no depression was observed.

ACKNOWLEDGMENT

The author is pleased to express his appreciation to Professor K. Nishida for sincere direction throughout this study; to the Forest chemistry division of the Faculty of Agriculture, Kyushu University for graciously extending its facilities for his scientific research, therefore making possible the execution of this work. And he acknowledges with deep thanks his indebtedness to Tsuma Forest Division for the donation of the material and to Mr. T. Fukushima for the isolation of the pigments.

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