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I hereby recommend that the thesis prepared under my supervision by Shu-Tung Tu

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Approved by:

Fred O'Flaherty

Robert M. Lollar

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A THEORY OF THE MECHANISM OF ORGANIC TANNAGE

A dissertation submitted to the

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by

Shu-Tung Tu

B.S. West China Union University, Chengtu, China 1940

M.A. Oberlin College, Oberlin, Ohio 1944

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Introduction

Nature of Vegetable Tanning Materials

Many types of leather, especially heavy leathers such as sole or belting, are tanned with natural vegetable tanning materials. The exact nature of the active principles in these materials is as yet not established. However, we may classify the vegetable tannins as either hydrolyzable pyrogallol or condensed catechol tannins. Among the hydrolyzable tannins, the active principle of Chinese nut gall tannin has been said by Fischer (8,9) to be isomer of penta-meta-digalboyl-betaglucose. Chestnut tannin, a hydrolyzable (ellagi) tannins, has been described by Flinn (11) as quercitin derivative of monogallol-ellagic acid, Russel (41,42,43) has synthesized bis-polyhydroxy-flav-pinacols, which he maintains are identical with the active principles of such condensed tannins as wattle and quebracho. These identification of the structures of the various natural tannins have been questioned by such authors as Perkin (33), Freudenberg (12), and Nierenstein (29). However it is beyond doubt that vegetable tannins are compounds of polyhydroxy phenolic nature.

Nature of Synthetic Tanning Materials

In 1911, Stiasny (50) developed a synthetic tanning material. Stiasny's patent claims comprise water-soluble formaldehyde condensation products of phenol or cresol sulfonic acids and also condensation products of phenol or cresol with subsequent sulfonation to obtain water solubility. Further work by many investigators has demonstrated that many materials possess tanning potentials. Wolesensky (55) demonstrated that resorcinol furfural condensation products possessed very excellent tanning properties. Ruppenthal (24) has reviewed the nature of the various syntans and has noted that in addition to the phenolic, the methylene bridges, and the sulfonic acid groups which may be functional in the presence of chlorine substitution in phenyl rings, the use of sulfone and sulfonyl imide bridges, as well as miscellaneous groups such as maleic anhydride, abutic acid or urea-formaldehyde condensates. Ruppenthal emphasized Otto's (31) classification of the syntans into auxiliary, condensation, and exchange tannins. In this classification it is emphasized that the sulfonation is necessary for its solubilizing influence, and that it does promote the optimum tanning properties. The true tanning function seems to be associated with the presence of groups dissiciating in an alkaline pH range such as the phenolic hydroxyl groups. This does not imply that certain other groups such as the sulfone bridges or the sulfonylimide bridges, may not contribute to the tanning potential, but it places the proper emphasis on the phenolic hydroxylation on the syntans. In fact, taking these ideas under consideration, true replacement synthetic tannins have been manufactured in Germany (3) and in the United States (53).

Theory of Vegetable Tannage

It is noticed that with both the syntans and the natural tannins, their phenolic hydroxylation has been thought to be responsible for their tanning potential. However, there is not agreement upon the mechanism of the tannage. We must therefore consider the possible mechanism of tanning that takes place. Fundamentally, there are two extreme theories, i.e. the chemical and the physical theories. The former holds that there are specific chemical (stiochiometric) relations between certain groups in the tannin and certain groups in the protein. In contrast, the physical deposition theory holds that tannage is merely a surface phenomenon in that the tannin is deposited onto the protein fibrils in agreement with adsorption isotherms of the type developed by Freundlich (13) or Langmiur (18). Of course, there are also the various intermediate theories between these two extremes.

Chemical Theory Seguin (47) considered the union of tannin extract and hide protein involves a kind of specific combination. Fahion (6) assumed that in vegetable tannage the primary tanstuffs are polyphenols which are oxidized to the quinones, and tannage takes place through chemical combination of the amino group of hide with these formed quinones. Nierenstein (30) supported Fahrion's idea in many cases. Powarnin (38) objected to the assumption of the formation of quinones by oxidation and suggested that they are formed by a tautomeric change and this constitutes the active carbonyl theory. Wilson (54) considered a possible chemical combination of the collagen and tannin. The collagen first takes up acid from the liquor with the formation of cation complex bring probably the free amino groups in the hide combining with the negatively charged tannin particles. Thomas and Foster (51) in their work on deaminized collagen also favor the chemical theory.

Physical Theory Knapp (16) was the first to claim that tanning is a process of colloidal adsorption in which the fibers of the collagen are mechanically coated by the tannin particles so as to prevent them from adhesion and hydration. This in a sense is the physical deposition theory. This theory of tanning was supported by Stiasny (48) and Ricevuto (34). The former emphasized the adsorption of a semi-colloidal substance and that the irreversibility of the tannins and skins is caused by a secondary change taking place after adsorption. The latter considered the neutralization of charges by colloidal particles of tannin with collagen. Mueller (27) viewed the above theory from the phenomenon of peptization. He considered that tannin is the peptizer, which penetrates the fibers of the hide, forming with them a solid solution without tanning them. The tannage is produced by the peptized substances deposited on the surface of the fibers.

Proctor and Wilson (39) explain the colloidal phenomenon existing between the hide substance and tannin when in equilibrium with a tan liquor, having a pH value in the range of 2 to 5. Collagen may be looked upon as an aggregate of complex cations balanced by much simpler anions held in the solution immediately in contact with the collagen structure by the same forces that hold all oppositely charged ions together. Under such conditions, there exists two electrical potential differences, i.e. the potential difference E_1, between the jelly phase and external solution, and the potential difference E_2 between the surface film on the tannin particle and the hide of solution. E_1 and E_2 are opposite in sign. According to this theory, the first important action in the mechanism of tanning results from the tendency of E_1 and E_2 to neutralize each other, and the initial rate of tanning will therefore be measured by the sum of the absolute values of the potential differences. Following the Proctor-Wilson theory of the colloidal phenomenon in the liquor, Wilson (54) considered a possible chemical combination between the collagen and tannin as shall be stated in the next paragraph. Thomas and Kelly (52) state that the data they obtained on the amount of gallotannic acid uptake by hide powder at various concentrations and pH values illustrate the validity of the Proctor-Wilson theory of vegetable tannage. Chang and Doherty studied the combining qualities of tannic acid and Chinese nut gall tannin (5) by hide powder. Lollar

(20,22) and his associates have studied the uptake of ordinary quebracho by hide powder and calf skin squares respectively. All showed that when the combining qualities of these tannins with hide substance are plotted according to the method of Langmiur a straight line results which may be cited in support of the sorption theory for vegetable tanning.

Hydrogen Bonding Theory It has been noticed that hydroxyl group is one of the tanning potential groups. In vegetable tannage it is probably the only functional group that is present in the tannin molecule. The present work of Mathur (23) on oil tannage has suggested that tanning with oil is due to the formation of hydroxy compounds during the tannage. Not only the organic tanning agents are mostly hydroxy compounds, but the mineral tannages are also associated with hydroxy compounds. According to Cameron, McLaughlin and Adams (4) in chromium tannage, the deposited chrome is always the 66 2/3 per cent basic chrome salt. According to Fleming (10) the iron-tanning mechanism is the absorption of acid from the basic ferric sulfate liquor by the hide protein, thus causing a deposition of iron compound (which is probably ferric oxide) with a varying amount of occluded sulfate. The free oxide is not a tanning material and the deposited oxide is therefore probably the hydrated ferric oxide with a varying amount of sulfate. Ruppenthal (40) used basic ferric sulfate with some masking agents and succeeded in making iron tanned leather on a pilot scale production. The best masking agents are hydroxy acids. Here again additional hydroxy groups are introduced to the iron complex.

However, the "hydroxy theory" of tanning must not be over emphasized by assuming that all hydroxyl compounds must tan by virtue of their possible affinities with the active groups of the collagen, because many hydroxy compounds are not active toward tanning, such as alcoholic-hydroxy groups. Not only alcoholic hydroxy compounds do not tan, but also a number of phenolic hydroxy compounds. Although quercetin (3,5,7,3',4'-pentahydroxy flavone) possesses four phenolic hydroxy groups in the molecule it has been found in this investigation to possess very little tanning action. Li (19) in 1927 published an article of the hydroxy theory of tanning of naphthalene derivatives and other organic compounds. He found the isomeric effect on tanning of alpha- and beta-naphthalene and their derivatives. All non-condensed derivatives of alpha-naphthol showed tanning effect. Non-condensed derivatives of beta-naphthol did not produce tannage. They had no action on the skins and did not penetrate the skins or penetrated without tanning. Li also extended his work to a number of dyes derived from the naphthols. All the dyes derived from alpha-naphthol produced a tannage, while those from beta-naphthol did not have such effect. From a theoretical standpoint the writer agrees with the above findings. However, when Li extended his work to a number of miscellaneous dyes, he noticed that those dyes which had the structure of triphenyl carbinol were particularly notable for their tanning effects. He concluded that the carbinol group present in the molecule of the dyes, is an essential group which gives tannage. According to our experimental evidence, this statement by Li is not correct and we shall discuss it in the later sections of this paper.

According to the current investigations on lignosulfonate tannage, tanning mechanism is probably not a single pure chemical origin. Kremen and Lollar (17) showed that the presence of the free amino group exercises a substantial influence on the fixation of lignosulfonates. The presence of the free amino group is of slight importance when using quebracho, except as it affects the swelling properties of the protein (51). Lignosulfonates practically have no ability to raise the shrinkage temperature and according to Gustavson (15) the shrinkage temperature of lignosulfonate retanned leather, pretanned with vegetable tannins depresses to some extent in every case. The absence of the free amino group seems to raise the shrinkage temperature slightly and this is probably due to its effect on the swelling and hydration characteristics of the protein. On further evoluation of the lignosulfonate tannage, Lipsitz, Kremen and Lollar (17) demonstrated that with proper adjustment of the tanning condition, both normal and deaminized hides can be tanned successfully with lignosulfonates. The leather thus produced resembles in every respect vegetable tanned leather, except that the shrinkage temperature is not raised from that of raw skin. Since lignosulfonates do not precipitate the special reagent, a soluble urea-formaldehyde condensation product, Grassman and associates (14) were led to believe that actual chemical combination takes place between the sulfonate and the free amino groups of the collagen. However, even though such chemical combination may take place in the tanning process, the actual leather formation mechanism is probably not contributed to the salt formation reaction, because deaminized skin gives just as good leather as the normal skin. Disregarding the activity of the free amino groups in this respect, the actual tanning functional groups that exist are probably the peptide linkages. Further demonstration with ninhydrin test* showed that vegetable tanned leather gives positive existance of free amino groups. Again recent investigation (25) of the moisture absorption of polyglycine polymers showed that hydrogen bonding between water molecules and glycine polymers takes place at the polypeptide linkages contributed by the -CO-NH- groups. Applying the same analogy, it is logical to say that the same mechanism of hydrogen bonding in tanning takes place between the polyhydroxyl groups of the tanning molecules and the peptide linkages of the protein.

*The writer expresses his appreciation to Miss Jean Jacobs, who made this test.

Development of the Present Investigation

"Hydroxylation Theory" With the "hydroxy theory" of tanning in mind, it is the purpose of the present investigation to study the significance of hydroxy groups present in the molecule of compounds of known structures on the tanning action. Also to study the effects on tannage with different numbers of hydroxy groups present as well as with some other non-polar radicals present in the molecules. Two series compounds were used, xanthenes and triphenylmethanes. The xanthenes were synthesized by zinc chloride condensation method. The triphenylmethanes are made by some known procedures.

In order to find the position effect of the hydroxy groups in the molecules on the tannage, some isomeric hydroxy compounds were also synthesized and their tanning actions studied likewise.

Solvent Tannage On account of the insolubilities of these compounds in water, the solvent system of tanning was adopted for the work. Solvent tanning system was first introduced by Roddy (35) in 1943. This system of tanning consists of two processes, penetration and fixation. Usually the penetration is completed within forty eight hours. This is then followed by fixation with water. According to Roddy, acetone is found to be the best among a number of organic solvents. Roddy claimed that solvent tannage has certain advantages over aqueous tannage. It is easy to see that the solvent system requires a shorter tanning operation period and is easier to control than the traditional aqueous system. Besides these advantages, Roddy also claimed that the quality of the leather thus produced is better then that produced by an aqueous system.

In the following year, Lollar (21) made use of the solvent system of tanning in a study of vegetable tanning. He showed that the take-up of quebracho from acetone systems by hide powder is significant only when water is present. In an acetone system, the take-up of quebracho tannin by hide powder is negligible. However, as water is added to the acetone quebracho system, uptake of quebracho tannin by hide powder develops. Applying this information to rapid tannage with acetone, as the solvent, it would seem that the quebracho-acetone systems serve as penetrates for carrying the tannin into the hide but that the fixation of the tannin in hide occurs by virtue of the water present.

In order to obtain conclusive and representable results for this investigation, the functions of both the penetration and fixation baths and the nature of the solvents are studied. The skin used in these experiments are dehydrated, bated calf skin squares, which are isoelectric around pH 4.8 and have a shrinkage temperature of 64°C. The method of preparation of these squares are described by Ma (22) in his dissertation for his degree of Master of Science.

The evaluation of the tanning character is based on the criteria of both shrinkage temperature and the visual observation of the leather tanned.

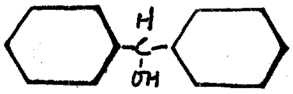
In addition, the physical characteristics of some of the solvent tanned leather with new synthetic compounds have been studied.

Experimental Procedures

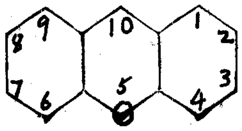
Syntheses

The compounds whose tanning functions we studied were derivatives of three parent compounds, i.e. benzhydrol (I), xanthene (II), and triphenylmethane (III).

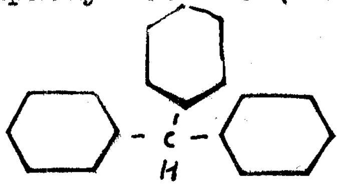
Benzhydrol (I)



Xanthene (II)

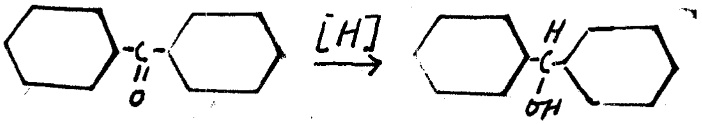


Triphenylmethane (III)



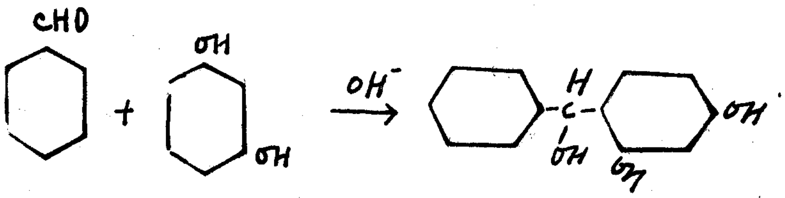
A. Synthesis of benzhydrol and its derivative.

1. Synthesis of benzhydrol



Synthesis of benzhydrol was accomplished by the method of Montague (28) from benzophenone (50 g.) in anhydrous (50 g.) ethanol (400 ml.) solution using zinc dust (60 g.) for reduction. Purification through precipitation by addition of water, followed drying and recrystallization from petroleum ether (40-60°C.), gave long colorless needles, yield 70%, m.p. 68-69°C.

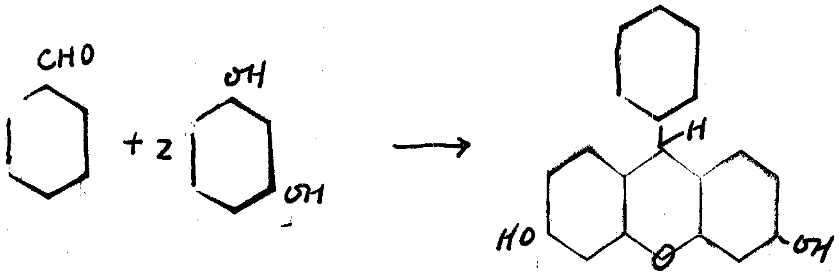
2. Synthesis of 2,4-dihydroxybenzhydrol



2,4-dihydroxybenzhydrol was synthesized by the method of Pope and Howard (37). Resorcinol (440 g.) was agitated with benzaldehyde (424 g.) in 10 L. of aqueous 10% NaOH solution. The color became deep red and then the odor of benzaldehyde disappeared during the 24 hour reaction period. The product was purified by four precipitations with dilute HCl, followed by filtration, washing and resolution in dilute NaOH. The product is soluble in pyridine, and acetone and is somewhat soluble in ethanol or glacial acetic acid. Yield was 80%, d.p. 200°C.

B. Synthesis of xanthenes.

The first series of xanthene compounds were prepared according to the literature (37). Their formation was accomplished by the condensation of the intermediate compound 2,4 dihydroxybenzhydrol with the corresponding components desired. The formation of this intermediate 2,4 dihydroxybenzhydrol was likewise condensed by the reaction of benzaldehyde and resorcinol in the presence of sodium hydroxide. However, applying the same procecure for the preparation of some other benzhydrol derivatives, the second series, there was no success. We began to investigate some other procedures and we found that the direct zinc chloride condensation method is very satisfactory. In this reaction two moles portion of hydroxyl was used and the formation of the xanthenes is direct without the isolation of the intermediate product. The reaction may be represented as follows:

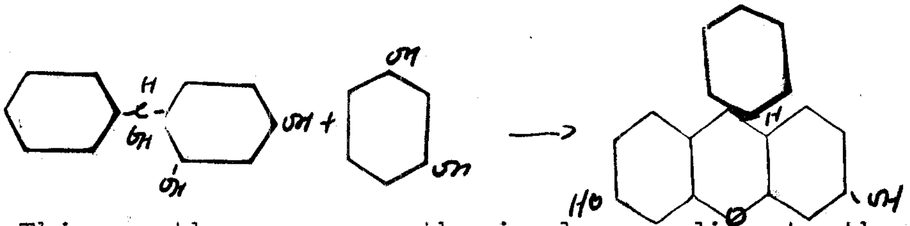


We found also that the preparation of 2,8-dihydroxy-3'-methoxy-4'-hydroxy phenylxanthene was more satisfactorily accomplished by the closed system method, using glacial acetic acid as the condensing agent.

On account of the difficulties of crystallization of these polyhydroxy compounds, their identifications were made by analysis of both carbon and hydrogen contents of their crystalline acetyl derivatives. The procedure used is the esterification which was the pyridine technique (48). The procedure is as follows:

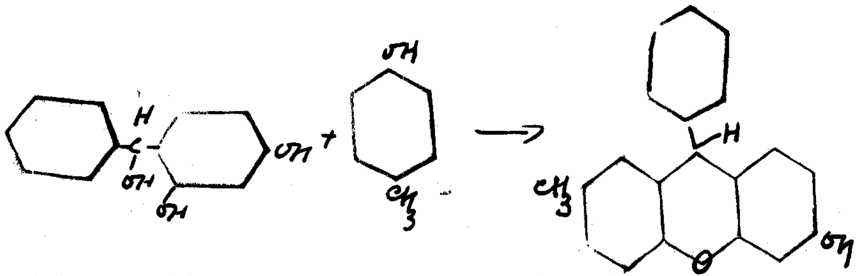
Two grams of the compounds was added to 20 ml. of anhydrous pyridine. Eight grams of acetic anhydride was added with shaking and after any initial reaction had subsided the solution was boiled for half an hour under a reflex condenser. The mixture was cooled and poured into 50 to 75 ml. of ice water. The acetyl derivative was removed by filtration, washed with cold, 2 per cent hydrochloric acid, and then with water. It was purified by recrystallization from alcohol.

3. Synthesis of 3,7-dihydroxy-10-phenylxanthene



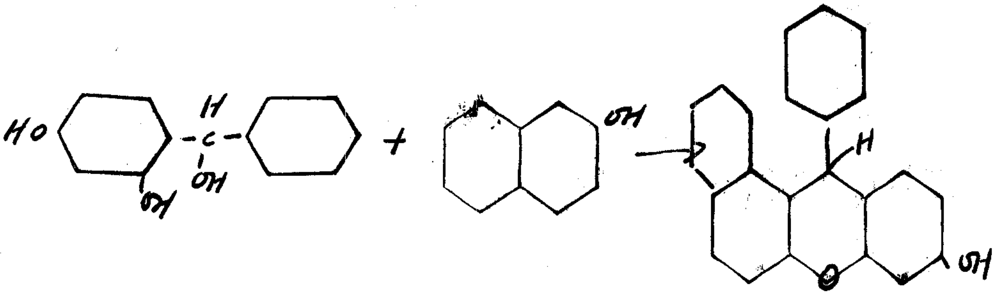
This xanthene was synthesized according to the method of Pope (37). It was made by the condensation of 2,4-dihydroxybenzhydrol (100 g.) and resorcinol (50 g.) in the presence of zinc chloride (100 g.). It was crystallized from 95% ethanol in small red crystalline needles. It is soluble in alcohol, pyridine, glacial acetic acid and is very slightly soluble in hot benzene. Yield 50%, m.p. 136°C.

4. Synthesis of 3-hydroxy-8-methyl-10-phenylxanthene



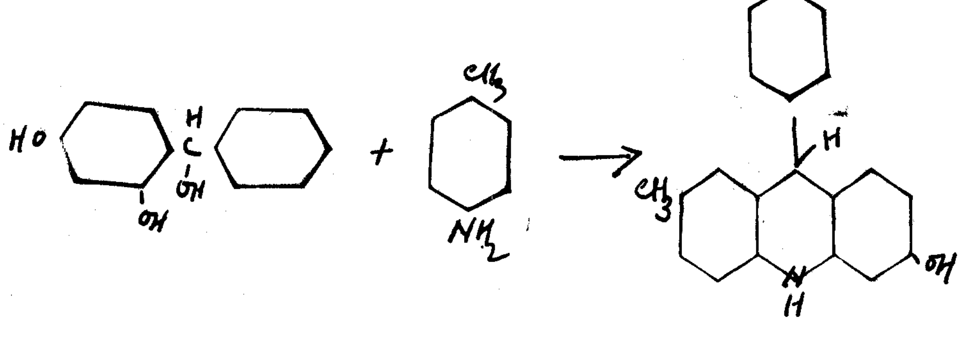
This xanthene was prepared in the same manner according to the above reference. It was synthesized by the condensation of 2,4-dihydroxybenzhydrol (100 g.) and p-cresol (50 g.) in the presence of zinc chloride (100 g.). It was then crystallized from 95% ethanol. It is soluble in most polar organic solvents. Yield 60%, m.p. 112°C.

5. Synthesis of 3-hydroxy-8,9-phenyl-10-phenylxanthene



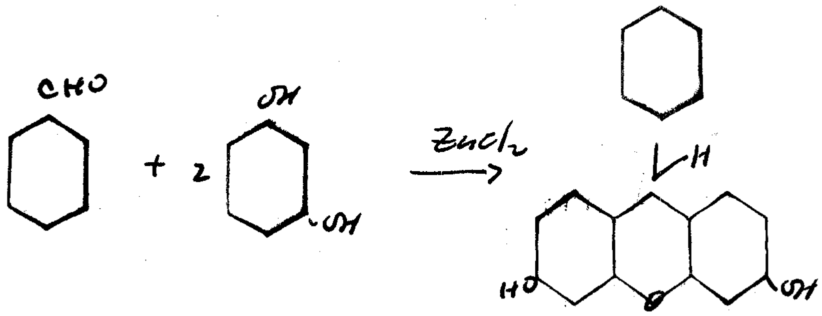
This compound was synthesized according to the method of Pope (37), by the condensation of 2,4-dihydroxybenzhydrol (100 g.) and b-naphthol (73 g.) in the presence of zinc chloride (75 g.). It was crystallized from 95% ethanol in dark red crystalline powder. It is soluble in alcohol, pyridine. Yield 60%, m.p. 84°C.

6. Synthesis of 3-hydroxy-8-methyl-10-phenylacridine



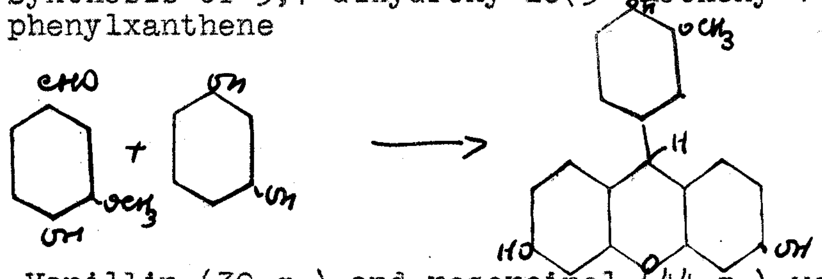
This compound was made according to the above reference by the condensation of 2,4-dihydroxybenzhydrol (17 g.) and p-toluedine (8.5 g.) in the presence of zinc chloride (20 g.). It was crystallized from dilute ethanol in light brownish powder. It is soluble in most polar organic solvents. Yield 50%

7. Synthesis of 3,7-dihydroxy-10-phenyl-xanthene by direct condensation of benzaldehyde and resorcinol



Benzaldehyde (100 g.) was mixed with resorcinol (200 g.) to 120°C., when freshly fused anhydrous zinc chloride powder (150 g.) was added. Due to heat of reaction, the temperature was raised up to 160°C. The content was well stirred with a mechanical stir at 160°C. for half an hour. At the end of the reaction, boiling water was added to extract the zinc salt. Washing was repeated for several times and the product was dissolved in 95% ethanol. The product was separated out in micro-crystalline precipitate by addition of water. This was repeated several times, and was finally crystallized from alcohol. This product checked with that prepared by the intermediate method. Yield 60%, m.p. 130°C.

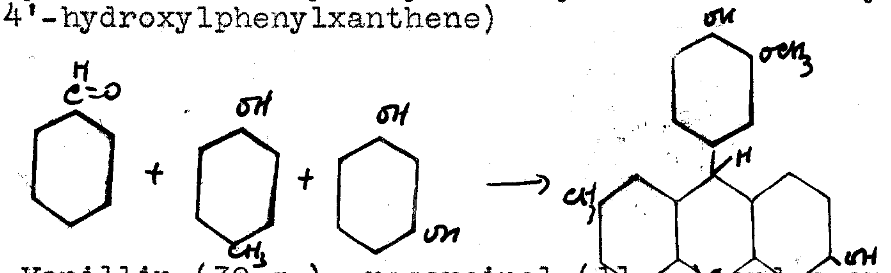
8. Synthesis of 3,7-dihydroxy-10(3'-methoxy-4'-hydroxy phenylxanthene



Vanillin (30 g.) and resorcinol (44 g.) were heated to 160°C. with a mechanical stir. Anhydrous zinc chloride (40 g.) was added slowly. The reaction became very vigorous and the temperature raised up to 200°C. due to heat of reaction. The temperature was kept at 160°C. for half an hour. At the end of the reaction, boiling water was used to dissolve the zinc salt and this was repeated several times. The residue was dissolved in 95% ethanol and the solution was filtered. The product was collected by addition of water to the alcoholic solution. Precipitation was repeated several times. It is a red dye, soluble in acetone, alcohol, pyridine, and glacial acetic acid; insoluble in benzene. Yield 60%

	Calculated as $C_{26}H_{22}O_6$	Found
	(triacetyl deriv. m.p. 174°C.)	
C%	67.5	68.1
H%	4.80	5.10

9. Synthesis of 3-hydroxy-8-methyl-10-(3'-methoxy-4'-hydroxylphenylxanthene)

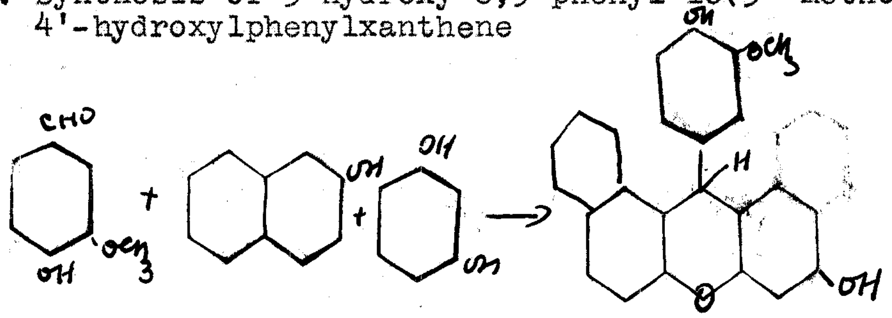


Vanillin (30 g.), resorcinol (11 g.) and p-cresol (22 ml.) were heated up to 140°C. Anhydrous zinc chloride (22 g.) was added and the temperature was raised up to 185°C. and this temperature was kept for an hour. The whole system is stirred with a mechanical stir. At the end of the reaction, the content was treated with hot water and the residue was dissolved in 95% ethanol. This product was precipitated by addition of water. It is a red dye and is soluble in alcohol, acetone, pyridine, and glacial acetic acid. Yield 50%

Analysis:

	Calculated as $C_{25}H_{22}O_6$ (diacetyl deriv. d.p. 221-225°C)	Found
C%	71.8	71.8
H%	5.30	5.50

10. Synthesis of 3-hydroxy-8,9-phenyl-10(3'-methoxy-4'-hydroxylphenylxanthene

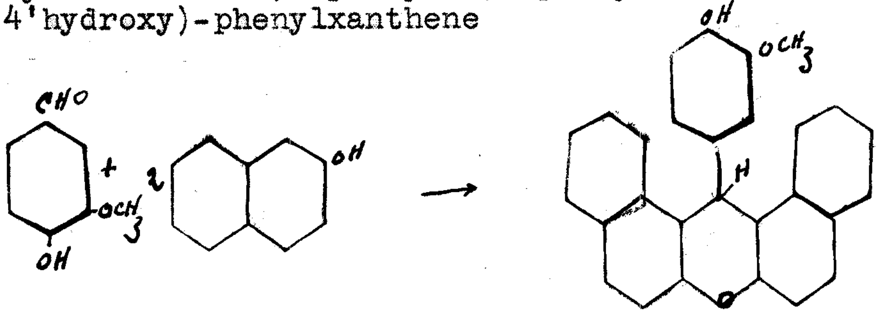


Vanillin (30 g.), resorcinol (22 g.) and bata-naphthol (15 g.) were mixed with a mechanical stir. This mixture was heated up to 150°C., and 22 g. anhydrous zinc chloride were added gradually. The temperature was raised up to 180°C. and this was kept for half an hour. At the end of the reaction the content was treated with boiling water and the residue was dissolved in 95% ethanol. The precipitation was carried out by addition of water. It is a red dye soluble in most polar organic solvents, insoluble in non-polar organic solvents. Yield 50%

Analysis:

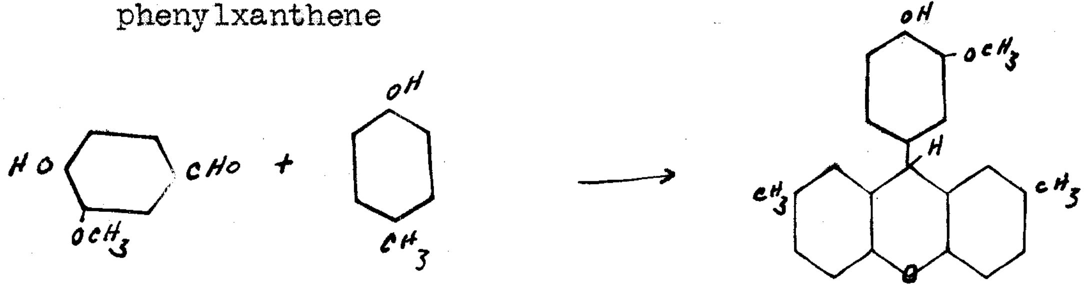
	Calculated as $C_{30}H_{24}O_7$	Found
(10-aceto diacetyl deriv. m.p. 205°C.)		
C%	72.5	72.0
H%	4.84	5.33

11. Synthesis of 1,2-phenyl-8,9-phenyl-10-(3'-methoxy-4'hydroxy)-phenylxanthene



This compound was synthesized according to the method of Rogow (36). It was prepared by the condensation of vanillin (3 g.) and -naphthol (6 g.) in the presence of glacial acetic acid (6 g.) in a 200 ml. pressure bottle. This was heated for 10 hours at 200°C. At the end of the reaction the bottle was opened and the content was allowed to crystallize. The crystals were filtered and washed with absolute alcohol and ether. It was recrystallized from hot alcohol, and was dried in a vacuum over concentrated sulfuric acid. It is soluble in acetone, chloroform, glacial acetic acid and is insoluble in ligrom and ether. Yield 80%, m.p. 211°C.

12. Synthesis of 2,8-dimethyl-10-(3'-methoxy-4'-hydroxy) phenylxanthene

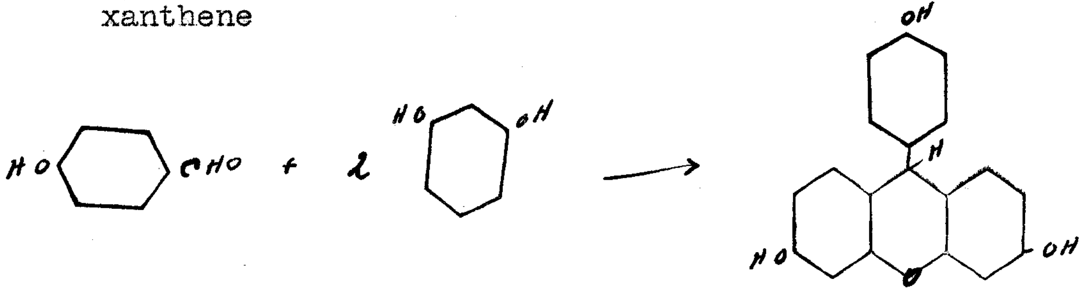


Vanillin (9 g.), p-cresol (13.2 g.), and glacial acetic acid (18 ml.) were mixed in a pressure bottle, (200 ml. capacity). This was heated for 5 days at 200°C. At the end of the reaction, water was added to the content and the product turned red gummy-like material. The material was then dissolved in chloroform to which anhydrous sodium sulfate was added to remove water present. The solution was allowed to stand overnight and was filtered. To the chloroform solution, petroleum ether was added to precipitate the product. It is a light reddish powder, soluble in benzene, chloroform, acetone, alcohol and insoluble in water and petroleum ether. Yield 70%

Analysis:

	Calculated as $C_{26}H_{24}O_5$ (menoacetyl-10 aceto-deriv. m.p. 170°C.)	Found
C%	75.0	75.0
H%	5.77	5.85

13. Synthesis of 3,7-dihydroxy-10 (p-hydroxy) phenyl-xanthene

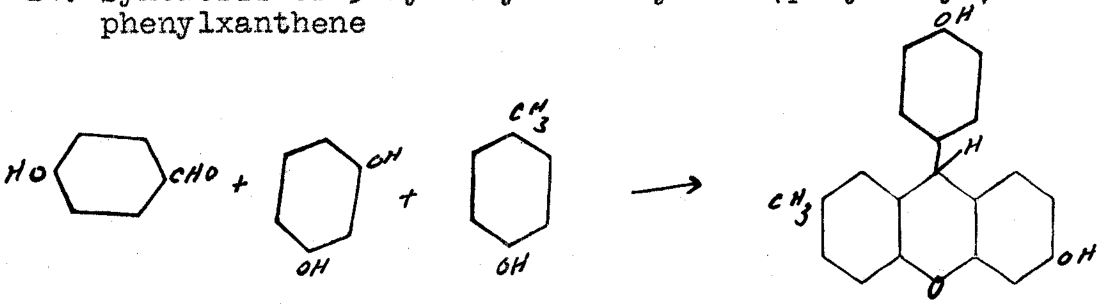


Resorcinol (44 g.) and p-hydroxy-benzaldehyde (21.5 g.) were heated with constant stirring up to 160-170°C. Powderous and freshly fused zinc chloride (40 g.) was added slowly and the temperature was kept at 170°C. for 30 minutes. At the end of the reaction boiling water was used to wash the zinc salt, and the residue was dissolved in 95% ethanol. This was precipitated out by addition of water. This was repeated several times. It is a red dye, soluble in most polar organic solvents but not soluble in non-polar solvents. Yield 50%

Analysis:

Calculated as $C_{25}H_{20}O_7$ (triacetyl deriv. m.p. 217°C.)		Found
C%	69.5	69.6
H%	4.62	4.82

14. Synthesis of 3-hydroxy-8-methyl-10 (p-hydroxyl)-phenylxanthene

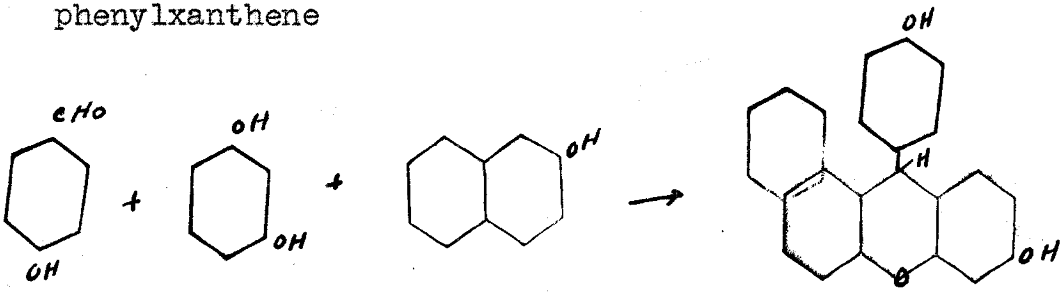


Resorcinol (32 g.), p-cresol (21.6 g.), and p-hydroxylbenzaldehyde (12.2 g.) were heated with constant stirring up to 180-190°C. Anhydrous zinc chloride (40 g.) was added slowly and this temperature was kept at 180°C. for 30 minutes. The residue was washed several times with hot water and was finally dissolved in 95% ethanol. The solution was filtered and the product was separated out by addition of water. This was repeated several times and was dried in an oven at 70°C. It is soluble in most polar organic solvents, insoluble in non-polar ones. Yield 60%

Analysis:

Calculated as $C_{24}H_{20}O_5$		Found
(diacetyl deriv. m.p. 185°C.)		
C%	74.3	74.2
H%	5.16	5.06

15. Synthesis of 3-hydroxy-8,9-phenyl-10 (p-hydroxyl)-phenylxanthene

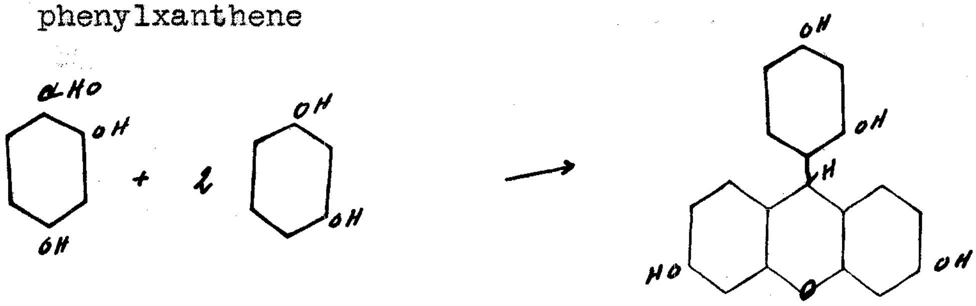


Resorcinol (22 g.), p-hydroxy-benzaldehyde (12.2 g.), and b-naphthol (28 g.) were heated with constant stirring up to 180-190°C. Anhydrous zinc chloride (40 g.) was added slowly and this temperature was kept at 180°C. for 30 minutes. The residue was washed several times with hot water and was finally dissolved in 95% ethanol. This was filtered and the product was collected by addition of water. Precipitation was repeated several times. It is a red dye possessing the same solubilities as those other hydroxyxanthenes described. Yield 50%

Analysis:

	Calculated as $C_{29}H_{22}O_6$	Found
(10-aceto-diacetyl deriv. m.p. 260°C.)		
C%	74.6	74.2
H%	4.72	5.15

16. Synthesis of 3,7-dihydroxy-10 (2',4'-dihydroxy) phenylxanthene

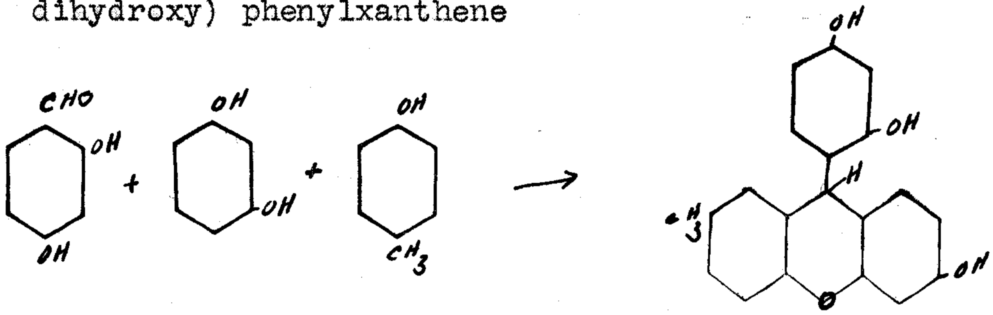


Resorcinol (22 g.) and 2,4-dihydroxy-benzaldehyde (13.8 g.) were heated up to 160-170°C. Anhydrous zinc chloride (20 g.) was added slowly and this temperature was kept for 30 minutes. Then the residue was treated with hot water and dissolved in 95% ethanol and precipitated by the addition of water. It is a red dye, possessing similar solubilities as the other xanthenes described. Yield 50%

Analysis:

	Calculated as $C_{23}H_{18}O_7$ (diacetyl deriv. m.p. 218-220°C.)	Found
C%	68.0	68.0
H%	4.44	4.33

17. Synthesis of 3-hydroxy-8-methyl-10 (2',4'-dihydroxy) phenylxanthene

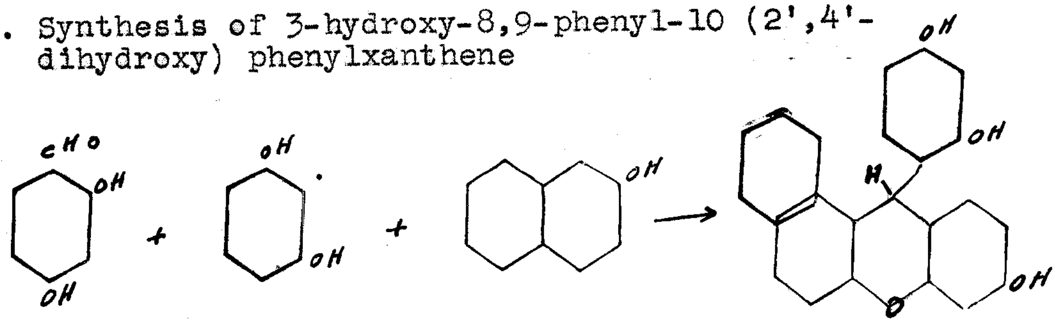


Resorcinol (11 g.), 2,4-dihydroxybenzaldehyde (13.8 g.), and p-cresol (10.8 g.) were heated up to 180-190°C. Anhydrous zinc chloride (20 g.) was added slowly at this temperature. This temperature was held for another 30 minutes. Finally the residue was washed with hot water and dissolved in 95% ethanol, filtered and precipitated. The procedure was the same as in the previous cases. It is also a red dye possessing similar solubilities of the xanthenes. Yield 50%

Analysis:

Calculated as $C_{22}H_{18}O_5$ (mono-acetyl deriv. d.p. 270°C.)		Found
C%	73.0	73.0
H%	4.98	4.86

18. Synthesis of 3-hydroxy-8,9-phenyl-10 (2',4'-dihydroxy) phenylxanthene

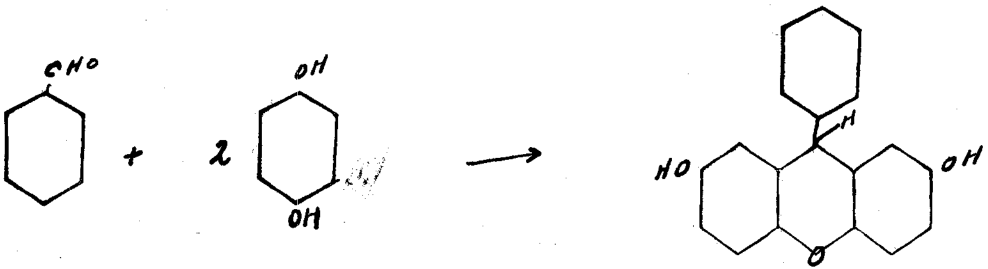


Resorcinol (11 g.), 2,4-dihydroxybenzaldehyde (13.8 g.), and b-naphthol (14.4 g.) were heated up to 180-190°C. Anhydrous zinc chloride was added gradually. The melt was stirred at this temperature for 30 minutes. The material was washed with hot water and dissolved in 95% ethanol and filtered as usual. It may then be precipitated by addition of water. It is a red dye possessing similar solubilities as other xanthenes described. Yield 60%

Analysis:

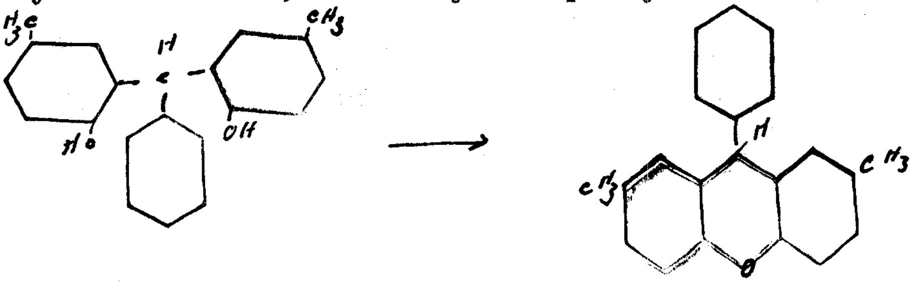
	Calculated as $C_{29}H_{22}O_7$	Found
	(10-aceto-diacetyl deriv. d.p. 250°C.)	
C%	72.2	72.3
H%	4.57	4.22

19. Synthesis of 2,8-dihydroxy-10-phenylxanthene



This compound was made according to the method of Meyer (26). It was prepared by the condensation of hydroquinone (100 g.) and benzaldehyde in the presence of dilute sulfuric acid. It was crystallized from dilute ethanol. It is a colorless, crystalline substance soluble in glacial acetic acid, methanol and slightly soluble in benzene. Yield 40%, m.p. 259°C.

20. Synthesis of 2,8-dimethyl-10-phenylxanthene



This compound was prepared by dehydrating of 2,2'-dihydroxy-5,5'-dimethyl triphenyl methane (7). Dehydration with ring closure was carried out by vacuum distillation at 150°C. The distillate was treated with warm dilute sodium hydroxide and was crystallized from chloroform and ligrom. It is a white crystalline needle. Yield 70%, m.p. 191.5°C.

Because of short time, the optimum conditions of synthesis of the above compounds were not obtained. In general the yield was very low. They are generally soluble in alcohol, acetone, and insoluble in benzene and ether, with the exception of 1,2-phenyl-8,9-phenyl-10 (3'-methoxy, 4'-hydroxy) phenylxanthene and 2,8-dimethyl-10-phenylxanthene, which are also soluble in benzene and chloroform and insoluble in petroleum ether and ether.

For the esterification, in some cases incomplete acetylation resulted. This is, of course, due to the difference in reactivities of these hydroxy compounds. However, in general, for most of these compounds, complete acetylation took place, with those xanthenes possessing a lesser degree of hydroxylation.

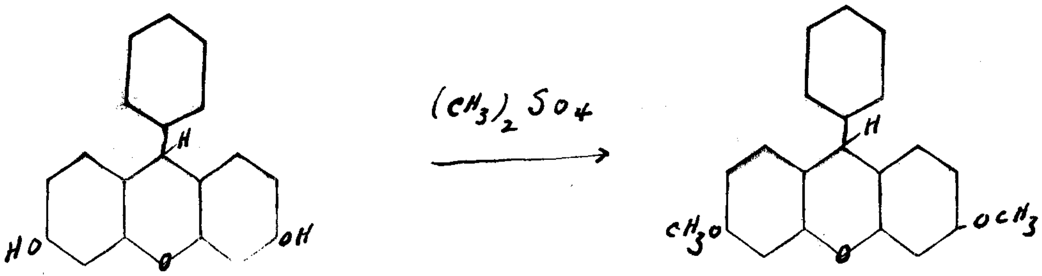
It is also noted that the acetyl derivative of those xanthenes having a naphthyl radical in the molecule, gave additional substitution of hydrogen of the 10-Carbon (central) aceto ($CH_3\underset{O}{\overset{}{\underset{\|}{C}}}-$) group. This is probably due to the influence of the presence of large aromatic radicals of the naphthyl group which activates the reactivity of the central hydrogen atom. There was incomplete acetylation in the 2',4'-dihydroxy-10-phenylxanthenes. This is probably due to the steric effect that the 2'-hydroxyl of the 10-phenyl radical is not acetylated.

The hydrogen atom of the central carbon in 2,8-dimethyl-10 (3'-methoxy-4'hydroxy) phenylxanthene was also substituted by aceto radical. This is probably due to the presence of two additional methyl groups in the 2,8 positions of the molecule.

C. Synthesis of triphenyl methanes.

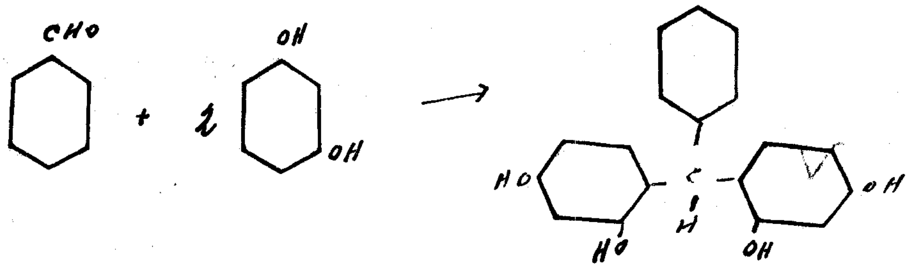
Compounds of this series are all known except one, the 2,4,2',4'-tetrahydroxy-triphenyl methane, in the literature. These preparations were made according to the literature cited.

21. Synthesis of 3,7-dimethoxy-10-phenylxanthene



Methylation of this compound was made according to Pope (37). 3,7-dihydroxy-10-phenylxanthene (10 g.) were mixed with 33 per cent potassium solution (20 ml.). This was stirred on a steam bath. Drops of dimethyl sulfate were added slowly. The alkalinity was checked from time to time. An alkaline solution was maintained. A termination addition of both alkali solution and dimethyl sulfate was kept going for about an hour until the color of the dye disappeared and a light yellowish product was obtained. At the end of the reaction, the product was washed with water, and crystallized from hot ethanol. Yield 60%, m.p. 126°C.

22. Synthesis of 2,4,2',4'-tetrahydroxy-triphenylmethane



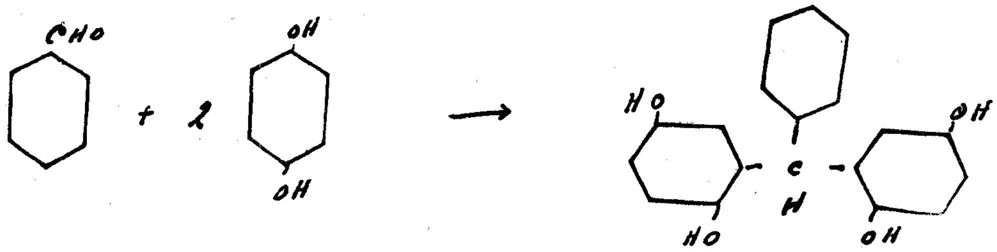
Resorcinol (220 g.) and benzaldehyde (106 g.) were heated to melting, with constant stirring. A few crystals of anhydrous zinc chloride were added to the mixture and the temperature was kept below 160°C. for 10 minutes.

The yellowish mass was dissolved in dilute sodium hydroxide solution. After filtering, dilute acetic acid was added and the precipitate was collected. This was then decolorized with bone black and recrystallized several times from dilute alcohol. It is a slight yellowish crystalline substance, soluble in most organic solvents. Characterization was made by analyzing its diacetyl derivative. Yield 90%

Analysis:

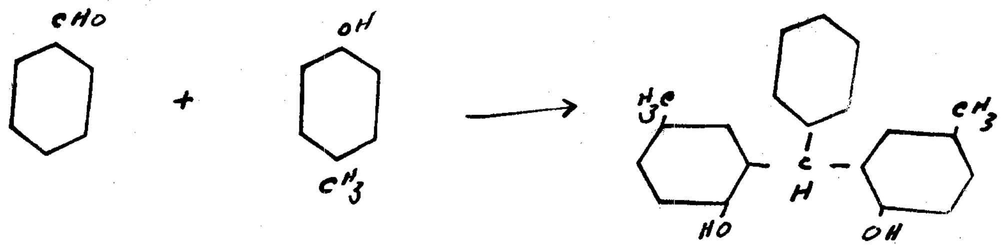
	Calculated as $C_{23}H_{20}O_6$ (diacetyl deriv. m.p. 107-108°C.)	Found
C%	70.5	70.7
H%	5.07	5.01

23. Synthesis of 2,5,2',5'-tetrahydroxy-triphenylmethane



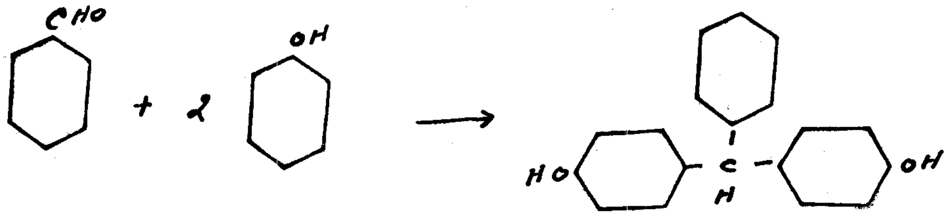
This compound was made according to the method of Schorygin (46) by the condensation of hydroquinone (50 g.) and benzaldehyde (24 g.) in an acidic ethanol solution (200 ml.). It is a yellow powder, soluble in alcohol, acetone, and pyridine, and insoluble in water or benzene. Yield 80%

24. Synthesis of 2,2'-dihydroxy-5,5'-dimethyl-triphenylmethane



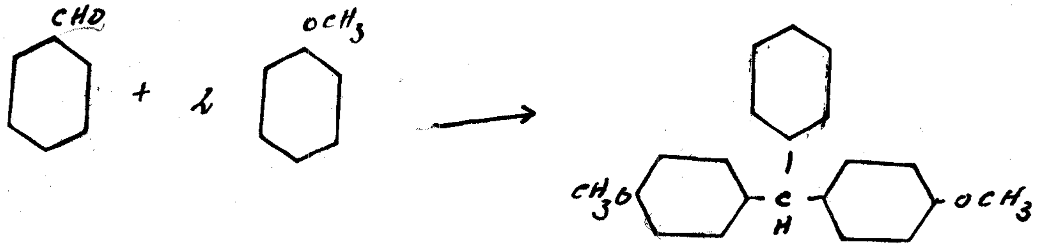
This compound was made according to the method of Feuerstein (7) by the condensation of p-cresol (100 g.) and benzaldehyde (50 g.) in a glacial acetic acid (250 g.) and sulfuric acid (500 g.) medium. It is a slightly yellowish powder crystallized from benzene and ligroin mixture. It is soluble in alcohol and in acetone. Yield 80%, m.p. 160°C.

25. Synthesis of p,p'-dihydroxy-triphenylmethane



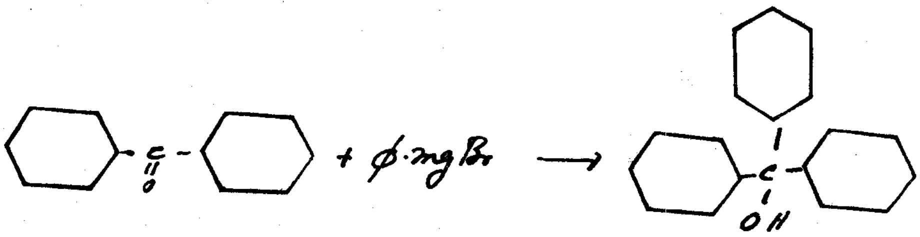
This compound was made by the method of Rossanow (45) by the condensation of benzaldehyde (20 g.) and phenol (36 g.) in the presence of dilute sulfuric acid (8 ml.). It was crystallized from glacial acetic acid and recrystallized from dilute alcohol. It is soluble in most polar organic solvents. Yield 80%, m.p. 160-161°C.

26. Synthesis of p,p'-dimethoxy-triphenylmethane



This compound was made according to the method of Feuerstein (7) by the condensation of benzaldehyde (10 g.) and anisol (20 g.) in a glacial acetic acid (70 ml.) and sulfuric acid (120 ml.) medium. It was crystallized from 95% ethanol. Yield 80%, m.p. 101° C.

27. Synthesis of triphenylcarbinol



This compound was made according to Acree (1) by the Grignard reaction. The Grignard solution was made by using bromobenzene (5 g.) and this was condensed with benzophenone (5.5 g.). The product was crystallized from alcohol. It melts at 162.5°C.

A summary of the compounds prepared was presented in Table I.

Systematic Study of the Organic Solvent Tanning System

Since the compounds we had synthesized were not appreciably soluble in water, we employed the organic solvent tannage procedure described by Roddy (35) for natural vegetable tannins. This tannage system with the vegetable tannins involves two steps as Lollar (21) has shown: penetration of the skin by the solvent-tannin infusion, and fixation of the tanning material in the skin by an aqueous fixing bath. Roddy and also Lollar used acetone as the penetration solvent. Lollar has shown that in the absence of water in the acetone penetration system, there is no fixation of tannin by the skin substance. However, Roddy used bated stock for his tannages and followed the penetration with an aqueous fixing bath. Under these conditions, it is possible to secure tannage from the organic solvent system to the same extent that it is possible with aqueous tannages.

In our research we used two types of skin substance for tannage. For preliminary evaluations we used calf skin squares prepared as described by Ma, Peierle, and

Lollar (22). The calfskins used were green salted skins. The salted skins were trimmed and then soaked for 24 hours at room temperature with 0.4 per cent sodium polysulfide (40 per cent solution of $Na_2S_{4.5}$) and 400 per cent distilled water on the trimmed stock weight basis. Liming was carried out with 4 per cent calcium hydroxide and 400 per cent distilled water on the stock basis for 5 days at room temperature, with intermittent paddling. After unhairing and fleshing, the skins were bated with 1.0 per cent commercial bate (pancreatic tryptic enzyme, NH_4Cl delimer) and 400 per cent distilled water for 3 hours at 35°C. with continuous paddling. The skins were then delimed by drumming them with dilute hydrochloric acid until the pH of the wash water was at an equilibrium value of pH 4.8, the probable isoelectric point of the limed collagen. Successive passage of the skins through acetone dehydrated and partially defatted them. The acetone dehydrated skins were cut up into one inch squares and air dried at room temperature without exposure to direct sunlight for one week. Analysis of the squares (on dry basis): 0.4 per cent ash, 1.0 per cent petroleum ether extract and 98 per cent hide substance. Generally the air dried skin squares contain approximately 10 per cent moisture. The shrinkage temperature of these squares is 64°C.

For final evaluations it was necessary to employ larger pieces of calf skin so that a more valid determination of the tanning potential could be made. In these cases we used 10X6 square inch rectangles of calf skin cut from the bend area of the skin. On these larger pieces we could, of course, determine the physical properties of the leather with more precision than we could on the small squares.

Both the squares and the larger rectangles were used in two conditions of hydration. Most of the work was done on the air dried solvent dehydrated skin containing about 10 per cent moisture. Since an excess of the organic solvent solution of the tanning material was used, the penetration bath was essentially anhydrous with these air dried squares. However, we also wished to establish the effect of water in the skin on the tannage so that we also used hydrated skin pieces containing about 75 per cent water.

Our evaluation of the leathering potential of any tannage system was based upon the integrated result of three criteria:

a. Chemical analysis to indicate the tanning material fixed by the skin substance.

b. Shrinkage temperature.

c. Visual observations for leathery "feel" supplemented by physical testing.

For our chemical and physical analyses we employed the A. L. C. A. Official Methods (2) unless otherwise noted. Since the water solubles in our leather were insignificantly low, we could eliminate this determination. Further, we ran petroleum ether extractives only on those leathers which we fat-liquored, since the solvent dehydration procedure leaves such a small residue skin lipid content. In the tannages of the calf skin squares therefore we could analyze for moisture and hide substance and then calculate combined tannin (100 minus hide substance on the dry basis) and degree of tannage (combined tannin devided by hide substance). Shrinkage temperature was determined in water using the Theis shrinkage meter (24).

From this discussion it is obvious that the following variables may control the organic solvent tannage system. First, the state of hydration of the skin entering the penetration bath must be considered. This could be significant because the addition of water to these organic solvent infusions of tanning materials could cause the penetration bath to be modified so that fixation could occur in the penetration, as Lollar (21) has shown for the quebracho acetone system. Secondly, the nature of the organic solvent could influence the tannage. It is conceivable that an organic solvent such as methyl alcohol with relatively high dielectric constant could permit fixation in the penetration bath in the absence of water. Of course the concentration of tanning material in the penetration bath is also a factor. Again, the nature of fixation bath could influence the tannage. If the material was very insoluble in water it could be deposited from an aqueous fixing bath so rapidly that fixation could not occur. Thus the tanning would be deposited, but not fixed in the skin. Under these conditions the use of a fixing bath such as mixed water-organic solvent bath could promote tannage. We therefore had to study these variables as well as to evaluate a variety of synthetic products.

As example of the influence we present the data in Table II. In these experiments, calf skin squares were used, and tannages of 2,4,2',4'-tetrahydroxytriphenylmethane and p,p'-dihydroxytriphenylmethane were used. In each case 50 ml. a saturated solution of (about 10 per cent) these tanning materials were added to 6 g. of the air dried squares for 48 hours. Samples designated as air dried squares contains approximately 10 per cent moisture. Samples designated as wet squares are rehydrated, air dried squares which contain approximately 70 per cent moisture. In the fixation process, both fixation in H_2O and in air were studied. In the former case, skin squares after penetration were put in pure water for 24 hours, and in the latter case, they were left in the air at room temperature for 24 hours. The shrinkage temperature was determined the next day and the samples were air dried and quartered and analyzed. Table II shows that methanol is a better solvent than acetone in both air dried skin and wet skin samples. Fixation in water is much better than that in air. Acetone, on the other hand, is not a good solvent in all cases even though it permits a high up-take of the tanning materials. Although the shrinkage temperature of the skin squares penetrated with acetone and air-dry fixed was high, yet the leather character was very poor. This is probably a matter of poor fixation.

We also made an extensive study of the influence of the penetration solvent on the tannages. In these experiments, tannages with quebracho, 2,4-dihydroxybenzhydrol, p.p'-dihydroxytriphenyl methane and 3,7-dihydroxy-10(p-hydroxy) phenylxanthene were investigated. It has been seen that air-dried skin squares give satisfactory evaluation, so that they were used in this experiment. Water fixation gave good results and it was also adopted. The concentration of the solutions were also determined, however, they may not the saturated values. The results are represented by Table III, IV, V, and VI for the different tanning materials. Generally speaking, as far as leather character is concerned, alcohols gave better tannages than cellosolve and calbitol, which are again better than acetone and dioxane as penetration solvents. Considering, now, from both points of fixation and the hydrothermostability of the tanned skin squares, the degree of tannage and the shrinkage temperature ran from high to low with the above order of the solvents. This is probably due to the difference of the polar properties of these solvents. It was also noticed that a good tanning material gave good tannage even when the tanning is carried out in low concentration of the material. Again a solvent with a high dielectric constant gives greater fixation than those with low dielectric constants.

According to histological study of the sections of the leather squares, more uniform fixation took place in the alcohol solvent tannages. Therefore, alcohol does not only give higher fixation but also gives more uniform fixation than the other solvents investigated. Acetone and dioxane systems gave surface deposition, while cellosolve and carbitol gave heavy deposition in the middle layer of the skin squares. From histological examination, it is shown that such an heterogeneous deposition of tanning materials is not due to the penetration factor, but is due to the manner of fixation, resulting from differences in the nature of solvent.

Anhydrous acetone did not give satisfactory results to the tannage as a good penetrating solvent in the above experiments. On the other hand, Roddy (35) had shown that when wet bated skin was used, acetone had been proved to be a good penetrating solvent. It therefore appeared to us that a thorough study of the variables of the fixation condition of the acetone system is desirable. In this series of investigations, 2,4-dihydroxybenzhydrol, and quebracho were chosen as tanning materials to be studied. A 20% tanning liquor of these materials was used. The source of skins were rectangular cuts already described. Samples under treatment "conditioned" were accomplished by putting the solvent penetrated skins in the conditioning room, maintained at constant relative humidity (65%) and constant temperature (70°F.). Samples under treatment "air dried over saturated water vapor" were exposed, after penetration over water, to a constant current of air passing through water. This is to obtain 100 per cent relative humidity at that temperature. Tannage determined under treatment "air dried over phosphorous pentoxide" was carried out in a chamber with the reagent present. This is to obtain a condition of anhydrous atmosphere.

The results are shown by Table VII and VIII. It was seen that the presence of moisture in the skin during penetration exerts favorite results to the leather character on the quebracho tannage. The presence of water exerts little effect to the 2,4-dihydroxybenzhydrol tannage. It is also noticed that fixation with a solution containing 40 per cent acetone (by volume) in water gave good results in the 2,4-dihydroxybenzhydrol tannage, but detannized the quebracho tannage. This illustrated the specificity of the tanning materials. Both the shrinkage temperature and the degree of tannage of the quebracho leather of the wet skin system were higher than that of the dehydrated skin system. Again, this illustrated the significance of proper fixation, which was different for different tanning materials.

It was noticed that the manner of fixation is very significant to influence the leather character. In this experiment the volume ratio effect of organic solvent to water was varied and the character of the final leather was observed. Wet rectangular skin cuts were used in this experiment. A 20 per cent 2,4-dihydroxybenzhydrol acetone solution was used as tanning liquor. In addition, the "Wilson-Kern water solubles" analysis was carried out. In this analysis 2 g. of the ground hide powder was treated to a continuous water washing for a period of 72 hours at a rate of 250 ml. per hour. The results were represented by Table IX. It was shown that both 40 per cent acetone solution and 30 per cent methanol solution are the most satisfactory fixation solutions thus studied. Under these conditions of fixation, the leather possessed both higher shrinkage temperature and higher degree of tannage.

The leather produced from the acetone system, however, appeared cracky grain phenomenon. This probably can be corrected by the following fatliquoring process. Histological section examination showed that the fixation of tanning material were more uniform in these cases. The leather also showed more water resistance than that of ordinary aqeous tannage.

The effect of "build-up" tannage, i.e. tannage with progressively tanning solutions, on the leather character was also studied. Hide piece used in this experiment was wet rectangular cut. It was first treated with a 20 per cent 2,4-dihydroxybenzhydrol acetone solution for 48 hours and was then followed by a second bath with a 30 per cent solution for an additional 24 hours. Fixation was carried out in a 40 per cent acetone solution. The result was shown in column a, Table X. Tanning by this process, gave a piece of leather which stands boiling for 5 minutes. This again pointed out the significance of fixation. Acetone, in the presence of moisture, served more or less as a fixation solvent.

Among the fixation variables, air fixation with high humidity was made with wet rectangular skin cut. Tanning liquor was a 20 per cent 2,4-dihydroxybenzhydrol acetone solution. The procedure of tanning remained the same, with the exception that instead of a solvent fixation, a high humidity air fixation was used. This was carried out over water with a current of air passed through. From the result in column 6, Table X, it appeared that this procedure had no advantage over medium fixation. It possessed piping grain phenomenon.

Acetone and dioxane were found to be poor penetrating solvents in the anhydrous state in the organic solvent tannages. This might be due to the poor fixation when the penetrated skin entered the fixation bath. However, this could also be due to the poor penetrating phenomenon in the penetration bath. Confirmatory tests were therefore desirable. In this section concentrated tanning solutions were made by shaking the tanning materials with dioxane and acetone respectively. In this way liquors of 30 per cent concentration were obtained after 6 hours shaking. Tannage was carried out as in the usual manner. The dehydrated skin cut contained negligible moisture content. In the case of quebracho tannage direct fixation with water was made. In the case of 2,4-dihydroxybenzhydrol tannage both water fixation and acetone-water fixation were made. The results were shown in Table I and XII. Under such conditions, both acetone and dioxane, showed complete penetration of the tanning materials. In the quebracho tannage, both dehydrated and air-dried hides produced very good leather. Wet skin, which was acid swollen, caused case hardening phenomenon, and the leather character was only fair. There also showed a high degree of depositions of quebracho in the wet skin system. Wet skin with dilute quebracho liquor (20%) showed good tannage (Table VIII), while dehydrated skin with strong quebracho liquor (30%) showed very good tannage. This pointed out the significance of concentration of the tanning liquor and also the significance of fixation. In the benzhydrol tannage, neither solvents showed good tannage, although acetone-water fixation showed higher shrinkage temperature of the leather thus produced. On the contrary, as showed by Table VII, wet skin cut did improve the leather character, especially when properly fixed. All these facts pointed out the specificity of the tanning materials and the significance of fixation.

It was recognized from previous studies that the nature of a tanning material determined the leather property. The concentration of the tanning solution and the way of fixation also exerted significant effect to the tannage. If a material was not a tanning agent, no matter how good you processed it, no leather would be produced. In this experiment studies were made to demonstrate the relationships that existed between the concentration of tanning liquor and the tannin up-take. The shrinkage temperature and the leather character thus produced were also correlated. Wet rectangular skin cuts were used. Fixation took place in the acetone-water medium. The data were presented by Table XIII, and Curves 1 and 2. It was shown that the greater the degree of tannage the higher the shrinkage temperature of the leather produced. The higher the concentration of the tanning liquor, the greater the fixation of the tanning material.

In this evaluation of the hydroxy theory of tannage, the following compounds were employed:

a. Nonhydroxyxanthenes and nonhydroxy-triphenylmethanes.

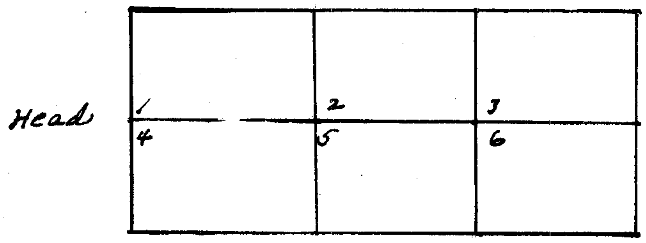
b. Alcoholic or carbinol hydroxy compounds.

c. Simple dihydroxybenzenes.

d. Polyhydroxyxanthenes.

e. Polyhydroxy-triphenylmethanes.

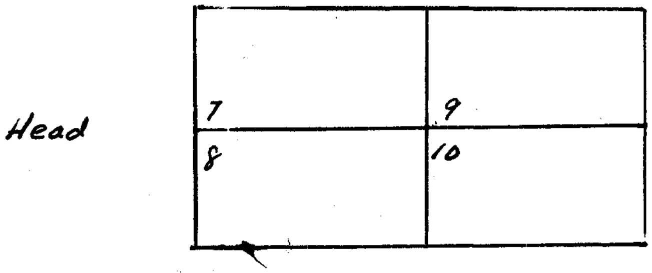
As was indicated by Table XIV, nonhydroxy-xanthene such as 2,8-dimethyl-10-phenylxanthene, 3,7-dimethoxy-10-phenylxanthene and p,p'-dimethoxy-triphenylmethane did not show any tanning property. The acetyl derivatives of the xanthenes did not have significant tanning properties either. Hydroxyl groups in the molecule appeared to be the essential functional groups for the tannage. Benzhydrol and triphenylcarbinol did not show any tanning action, even though there were hydroxy groups present in the molecules. Alcoholic hydroxyl groups were therefore ruled out as groups with tanning potential. Catechol, hydroquinone and resorcinol, although possessing two phenolic hydroxyl groups in the simple benzene ring did not show any improvement of the tannage. All the hydroxyxanthenes and hydroxytriphenylmethanes showed tanning action, except 2,8-dihydroxy-10-phenylxanthene. Their tanning potentials ran more or less in parallel with the degree of hydroxylation of the compounds. It was noticed that, although 3,7-dihydroxy-10-phenylxanthene was a tanning agent, 2,8-dihydroxy isomer did not show any tanning ability. Because of this difference, the author was lead to consider other factors that might influence the tannage of 2,8-dihydroxyxanthene. Among the possible factors, the solubility and ionization character of these isomers in methanol-water system were studied. It was observed that there was a lower up-take of 2,8-dihydroxy-10-phenylxanthene than that of its 3,7-dihydroxy isomer. Since the concentration of the tanning liquor determined the degree of tannage that the skin could take up and since the solubility of the tanning material determined the concentration of the liquor that could be built, the solubility study was thus desirable. In this experiment, both compounds were as saturated methanol solutions at 25°C. Various volume portions of water were added to these methanol solutions. The compounds began to precipitate on addition of water. After mixing and centrifuging the solutions were filtered and the solubilities of these xanthenes were determined. The results were shown by Table XVI and Curve 4. The two curves appeared similar in shape and the 2,8-dihydroxytriphenyl-methane was only about one per cent less soluble than its isomer. A good tanning material at such concentration or lower would give tanning action. Hence the fact that 2,8-dihydroxy-10-phenylxanthene was not a tanning material could not be caused by its slightly lower solubility. The next factor that might influence the 2,8-dihydroxy-xanthene tannage was the ionization character of this compound itself. Since ionization bears close relationship to the conductance of the material, the specific conductance of these two isomers in methanol-water solutions were determined by means of a Wheatstone bridge set-up. The specific conductance of the solvent systems without the presence of tanning materials was also determined. The results are shown by Table XVI and Curve 5. In this experiment the specific conductance of the saturated tanning solutions in the methanol-water mixtures obtained from the solubility determination, were measured. There were evident differences in ionic character between these two compounds in methanol-water solutions. The 3,7-dihydroxy-10-phenylxanthene has about one hundred times greater conductance than the 2,8-dihydroxy isomer. It was also shown that where the concentration range of the methanol solution was about 70-90 per cent the specific conductance of the 3,7-dihydroxy-10-phenylxanthene attained a maximum value, while its isomer attained a minimum value. This concentration range of methanol in water is more or less identical with condition that might exist in the skin during fixation with water. From the conductance measurement, there was a definite difference in the ionic character between these two xanthenes in methanol-water solution. Further, it was found that the synthetic tanning materials tested did not tan very well, when cellosolve and dioxane were used as penetration solvents. On account of the differences in dielectric constants of these organic solvents, the ionic character of a tanning material, in these organic-solvent-water solutions could therefore be different. Hence the tanning action of a compound might therefore be varied from one medium to the other. With this idea in mind, the specific conductance of 3,7-dihydroxy-10-phenylxanthene in both cellosolve-water and in dioxane-water solutions were measured in the same manner that it was for the methanol-water system. The solubilities of 3,7-dihydroxy-10-phenylxanthene in the corresponding organic solvent-water solutions were determined as described for the methanol-water system. The results are presented in Table XVII and Curve 6 and 7. It is seen that the conductance of 3,7-dihydroxy-10-phenylxanthene in both cellosolve-water and in dioxane-water solutions is much less than that in the methanol-water system. Therefore, 3,7-dihydroxy-10-phenylxanthene is a good tanning material in methanol-water fixation system and does not show good tannage in the cellosolve-water nor in the dioxane-water fixation system. For the final evaluation of the tanning potentials of the synthetic materials, several compounds were taken for demonstration. The skin sources were rectangular dehydrated calf skin cuts. The samples were located as shown in the following diagram:



They were tanned in 2 liters methanol solutions respectively saturated with each tanning material. The tanning operations were the same as in the usual manner. Quebracho and 2,4,2',4'-tetrahydroxy-triphenylmethane were fixed with water, while 3,7-dihydroxy-10(p-hydroxy)-

phenylxanthene, 3-hydroxy-8-methyl-10(3'-methoxy-4'-hydroxy)phenylxanthene and 2,4-dihydroxybenzhydrol were fixed with a 30 per cent methanol solution in water. The tanned leather was fatliquored with 1.5 per cent cod oil and a 1.5 per cent sulfated cod oil (wet skin basis). They were then tacked and air dried. After being conditioned they were subjected to physical testing and chemical analyses. The data are presented in Tables XVIII and XIX. Samples 2b and 4b were supplementary samples from another piece of hide. It was seen that 2,4-dihydroxybenzhydrol possessed Class 1 leathering potential and 2,4,2',4'-tetrahydroxy-triphenylmethane possessed Class II leathering potential. They all showed better leathering action than that of quebracho, taken as standard. 3,7-dihydroxy-10(p-hydroxy)phenylxanthene fell in Class III tannage, which was about the same as quebracho, and 3-hydroxy-8-methyl-10(3'-methoxy-4'-hydroxy)phenylxanthene fell in Class IV tannage. Among the physical characteristics, the tensile strength and stitch tear tests of the leather tanned with these synthetic materials showed comparable values as that of ordinary quebracho leather. However, 2,4-dihydroxybenzhydrol and 3,7-dihydroxy-10(p-hydroxy)-phenylxanthene and 3-hydroxy-8-methyl-10(8'-methoxy-4'hydroxy) phenylxanthene leather were less readily detanned than 2,4,2',4'-tetrahydroxytriphenylmethane leather which was about the same as quebracho leather.

Since 2,4-dihydroxybenzhydrol was a very good tanning material, its leather characteristics were further investigated. In this experiment wet skin rectangular cuts were used. The location of these skin cuts were shown as follows:



They were tanned in the usual manner as described before. They were fixed with a 40 per cent acetone solution. Sample No. 10 was the only sample that was not fatliquored. Both the chemical analyses and the physical tests are presented by Tables XX and XXI. 2,4-dihydroxybenzhydrol leather was very water resistant. It was even more so to acidic washing, but was less resistant to alkaline buffer washing. It was again much less resistant to aqueous acetone washing. It was shown by Table XXII that the degree of tannage decreased when the time of washing increased.

In order to investigate the mechanism of organic tannage, deaminized air dried calf skin squares were used. These squares contained less than 0.53 per cent nitrogen in comparison to normal limed squares containing 18.16 per cent nitrogen and had a 5°C. higher shrinkage temperature than that of normal skin squares. From the results presented in Table XXIII there is no difference in shrinkage temperature between normal and deaminized squares in both quebracho system and 2,4-dihydroxybenzhydrol systems. Degree of tannage also showed little difference. By visual observation, the leather character of deaminized leather was not inferior to that of normal squares. It is therefore logical to infer that -CO-NH- linkages of the hide protein play an important role in the tannage.

Discussion

Synthesis All the new xanthenes were prepared by the direct zinc chloride condensation method, except the 3,8-dimethyl-10(3'-methoxy-4'-hydroxy)-phenylxanthene, which was more satisfactory made by the closed system method, using glacial acetic acid as condensation agent. Zinc chloride condensation procedure was found to be very convenient. However, due to shortage of time, the optimum condition for each synthesis was not obtained. In general, the yield of the product was rather low. All the polyhydroxy xanthenes are soluble in most polar solvents and insoluble in non-polar solvents. Xanthenes with least hydroxylation are soluble to some extent in non-polar solvents. However, most of them are not readily crystallizable. On account of the difficulties of crystallization of these polyhydroxy compounds, their identifications were made by analyzing their crystalline acetyl derivatives, which were easily prepared by the pyridine procedure (48). All these new xanthenes, except the 2,8-dimethyl-10(3'-methoxy-4'-hydroxy)phenylxanthenes are dyestuffs whose color range run from light red to dark red depends on the degree of hydroxylation of the molecules. As a general rule, all hydroxyxanthenes which show dyeing properties are capable of existing in the chromophoric quinoid structure. The hydroxyl groups present in the molecule serve as auxochromes to intensify the dye color. It is, therefore, those hydroxyl groups that occupy either the para or the ortho positions to the carbon atom of the benzene ring that is attached to the 10-carbon atom of the xanthene, that are capable of reinforcing the quinoid structures. Xanthenes having meta hydroxyl groups in the molecules, are colorless crystalline substances and they do not have dye properties.

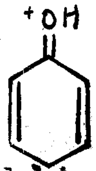
<u>Acetylation of the hydroxyxanthenes</u> The degree of acetylation depends on the condition of the experimental procedure. Complete acetylation took place, with all dihydroxyxanthenes under our experimental condition. Symmetrical trihydroxyxanthene was acetylated to completion, while unsymmetrical ones remained only diacetylated. Tetrahydroxyxanthene was also diacetylated. Phenylhydroxyxanthene gave additional substitution of the active hydrogen atom of the 10-carbon atom of the xanthenes. Such an activation of the hydrogen atom is probably caused by the presence of the naphthyl ring according to the free radical principle. Dimethylxanthene also showed the

additional substitution of the 10-carbon atom. This is probably due to the same fact as described in case of phenylxanthenes.

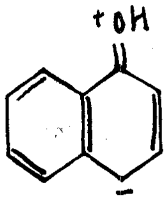
Solvent tannage It was found that the first bath of the solvent tanning system served as penetrating bath of the system. It was only the fixation bath that tanning fixation takes place. With proper procedure and technique real fixation takes place and the leather thus formed showed good leather quality. With poor procedure and technique, hetergeneous tannin deposition takes place and the leather thus formed showed poor leather quality. By proper fixation, it means that weak ionization of the hydroxyl groups of the tanning materials takes place in the hide protein, which are thus possible to act with the active groupings of the polypeptide linkages of the collagen. From this respect, alcohol with a high dielectric constant is therefore better fixation solvent than those having low dielectric constants. Acetone in the presence of small amount of water served as a good penetrating solvent for some tannin materials is probably because of the reinforcement of its dielectric constant caused by the presence of water. The optimum fixation condition is rather specific for different tanning materials. The water solubility of the tanning materials is one of the important properties that controlling the condition of fixation. Usually, the more uniform the fixation of the tannin material, the higher the shrinkage temperature and the better the quality of the leather. The more the concentration of the tanning liquor, the more the tannin take-up by the skin and the higher the shrinkage temperature of the leather.

<u>The hydroxy theory of tannage</u> It was noticed that alcoholic hydroxyl groups did not have tanning potential. Phenolic hydroxyl groups at the meta-positions to the carbon atom of the benzene ring that attached to the central carbon atom did not have any tanning action. With the elimination of these inactive hydroxyl groups in the molecule of the tanning materials, a paraboa was obtained by plotting the percentage of hydroxylation of the tanning molecule against the shrinkage temperature of the leather (Curve 3). It was demonstrated, that the greater the degree of hydroxylation of the molecule, the higher the shrinkage temperature of the leather. The leather character ran more or less in parallel with the

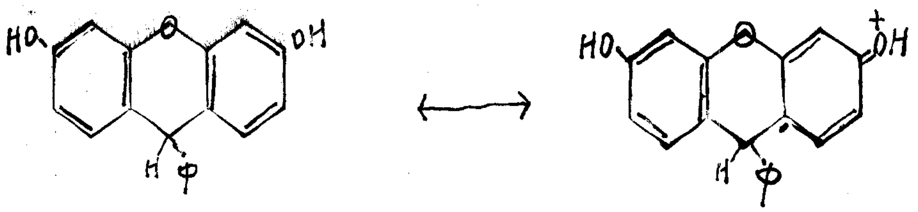
shrinkage temperature. Of course, this does not apply to the simple hydroxy benzenes. From the conductance measurement, it was demonstrated that active hydroxy groups possessed more electrostatic character than that of the inactive groups. We can, therefore attribute the tanning potential of a compound to the modern Resonance' concept of hydrogen bonding. According to Pauling (32) the hydrogen bond is a bond by hydrogen between two atoms, since the coordination number of hydrogen does not exceed two. It is known that only the most electronegative atoms can form hydrogen bonds, and that the strength of the bond should increase with increase in the electronegativity of the two bonded atoms. Increasing the electronegativity of an atom increases its power of forming hydrogen bonds. The phenols form stronger hydrogen bonds than aliphatic alcohols because of the increase in electronegativity of the oxygen atom resulting from resonance with structure such as:



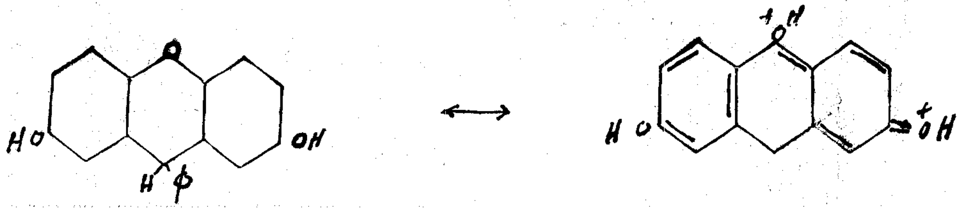
Alpha-naphthol and derivatives possess tanning action, is probably due to the hydrogen bonding ability of the oxygen atom resulting from resonance with structure such as:



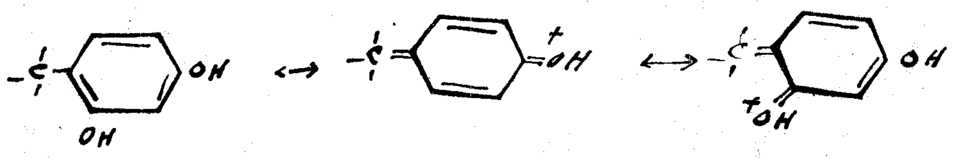
Beta-naphthol and derivatives do not give the quinone structure because of its symmetrical bond structure and therefore the oxygen atom is not as electronegative. 3,7-dihydroxy-10-phenylxanthene is a red dye and the contribution of the quinoid resonance form is also great, while 2,8-dihydroxy-10-phenylxanthene possesses meta hydroxyl group to the central carbon atom and therefore has less electronegativity on the oxygen atom. Thus we have:



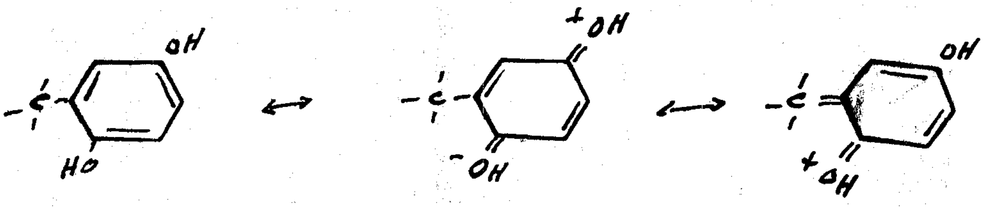
It can be readily understood by observing their structural formuli, that all hydroxyxanthenes possessing tanning action possess hydroxy groups, either para or ortho to the central carbon atom. 2,8-dihydroxy-10-phenylxanthene, having meta hydroxyl groups, does not form quinoid structure. The electronegativity of the oxygen atom may be increased due to resonance in the following manner:



In this way the oxonium ion is formed but this can only happen when strong acid is present. Using the same reasoning the tanning action of triphenyl methanes can be explained. The contribution of the quinoid structure, either para or ortho through the central methane carbon atoms, resulting from resonance, apparently increases the electronegativity of the oxygen atom. In the case of 2,4-dihydroxyphenylmethane system that both oxygen atoms are electronegative as illustrated below:



In the case of 2,5-dihydroxyphenylmethane system, the contribution of the quinoid structure through the benzene ring increases the electronegativity of one oxygen, but at the same moment, decreases the electronegativity of the other. The following illustration shows the relationship:



Thus in 2,4-dihydroxyphenyl-methane system we have two active hydroxyl groups capabel of hydrogen bonding, and in 2,5-dihydroxyphenyl system, although there are two hydroxyl groups present, the actual active ones is only one. Therefore 2,4,2',4'-tetrahydroxytriphenyl-methane is a better tanning agent than its 2,5,2',5'-tetrahydroxy isomer, whose tanning action is equivalent to 2,2'-dihydroxy-5,5'-dimethyltriphenylmethane. In this case the two meta hydroxyl groups exert the same effect as the two methyl groups.

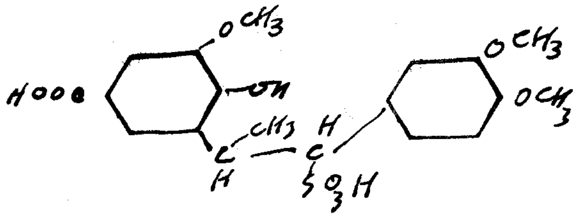
According to this resonance theory alcoholic hydroxyl groups are not capable to form hydrogen bond and they are therefore possessing no tanning potential. However, Li (19), who studied a number of triphenyl carbinol dyes concluded that the carbinol group possesses tanning action. In our investigation on the tannages of both benzhydrol and triphenylcarbinol, no tanning function of these compounds was observed. Li was therefore, we believe, mislead on this aspect, because there is neither theoretical nor experimental support. If we check the carbinols he used we will note that they possess other groups in addition to the carbinol hydroxyl group; these groups may have tanning potential.

If the tanning action is due to hydrogen bonding effect of the hydrogen groups of the tanning material, removal of such hydrogen atoms from the molecule should destroy the tanning action of the material. Actually this was found to be the case. Both the acetyl derivatives and the methoxy derivatives of these compounds synthesized did not show any tanning property. However, the solubility of these derivatives in methanol was only slight, small amount of ethyl acetate was used to solubilize these materials. This may, of course, exert some indifferent effect on the tannage, but we may rule out their possible tanning action by considering their alcohol insolubility.

Even though dihydroxybenzenes are capable for hydrogen bonding, they possess no tanning potential. This may be a matter of molecular size. It was found that the limiting molecular size is restricted to di-phenyl nucleous systems. Either di-phenyl methane or naphthalene (19) with proper hydroxylation possesses tanning potential.

The mechanism of tanning action It was recognized that hydrogen bonds restrain protein molecules to their native configurations. According to a recent investigation (28) on the water absorption of protein, the water absorption of polyglycine polymers is primarily due to the polypeptide groups. Free amino groups present in the shorter glycine polymers exerts some water absorption power, but when the number of polymer units are built up to 44, its contribution is nil. Applying the same anology that the main hydrogen bonding power of the hide protein is probably mainly contributed by the -CO-NH- groups of the polypeptides. Based on these facts, tanning action is probably a hydrogen bonding effect of the -CO-NH- groups with hydroxy groups of the tanning materials. If this is the case, elimination of the free amino groups of the hide protein would not influence the leather forming character of the hide. Since this was the case, tanning action is therefore likely to be union of the hydroxyl groups of the tanning material and the polypeptide linkages of the protein through hydrogen bonding.

This statement agrees to the findings of lignosulfonate tannage. According to Russell (44), gymnosperm lignins are a polymeric-8-methoxy-dihydrobenzopyrone. Its degradation product from sulfite cellulose process waste liquors may consist of a substituted-phenyl ethane sulfonic acid:



This aliphatic sulfonic acid reacts with the amino group of the hide, splitting the hydrogen bonding between the zwitter ions with the formation of more stable salts. This results in a lower degree of shrinkage temperature of the leather. However, hydrogen bonding effect of the hydroxy groups tends to raise it and thus showed a compensation balance in shrinkage temperature. The degree of hydroxylation in this compound is low and hence the shrinkage temperature of the leather is low. Again it was shown in this laboratory, that deaminized skin tanned with lignosulfonate appeared all good leather characteristics, except that its shrinkage temperature is low. Therefore, the polypeptide linkages played the most significant role in the tannage. Considering the hydrogen bonds, both bonds -O-H-O- and -O-H-N- are probably more important than bond -N-H-O because that the methoxy and acetyl groups are not tanning functional groups.

Summary

A series of new 10-phenylxanthenes were synthesized by the direct condensation of hydroxybenzaldehyde and hydroxybenzenes or naphthols in the presence of zinc chloride.

A series of hydroxytriphenylmethane derivatives were prepared, according to the known procedures.

In the organic solvent tanning system, the first bath serves the penetration and the second bath serves the fixation of the tanning material. Organic solvents with fairly high dielectric constants are better solvents for the penetration bath than those with very low dielectric constants. This is because the polar solvent ionizes the tanning material to some extent and thus fixation of the tannin occurs. Non-polar solvents ionize the tanning material very little and thus, instead of deposition of tanning takes place without fixation. Among these organic solvents studied, alcohol (methanol and ethanol) are better than both cellosolve and carbitol, which are again better than acetone and dioxane as penetration solvents. Methanol has a greater dielectric constant, is a better solvent, than ethanol, having a smaller dielectric constant.

In the study of the tannages of the xanthenes and triphenylmethanes, degree of hydroxylation of these compounds is the significant factor that controls the leather potential of these tanning materials. However, not all hydroxyl compounds are tanning materials, simple dihydroxybenzenes, alcohols or carbinols, quercetin, and both hydroxyxanthenes and hydroxytriphenylmethane, whose hydroxyls are not properly substituted in the benzene rings of the molecule do not give tanning action. It is only those hydroxy compounds, whose hydroxy groups occupying the para and ortho positions to the central carbon atom of the molecules, give tannage. In such a system, the electronegativity of the oxygen atom of the hydroxyl groups, is increased on account of the existing of the quinoid structure of the molecule resulting from resonance. Hydrogen bonding is therefore possible to occur between the tanning material and the hide protein.

The mechanism of vegetable tannage is probably a sorption type action that tannin is fixed in the hide protein by virtue of hydrogen bonding phenomenon. It is probably that the polypeptide linkages of the protein are the major active groups to form hydrogen bonds with the hydroxyl groups of the tannins.

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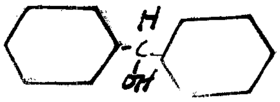
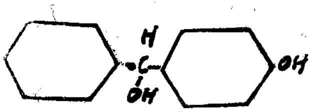
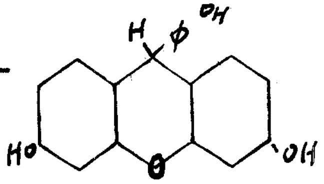
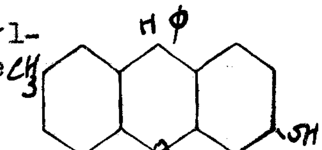
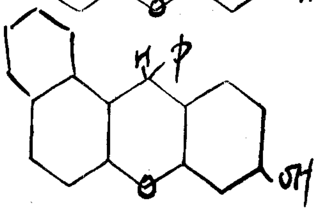
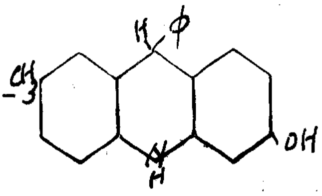
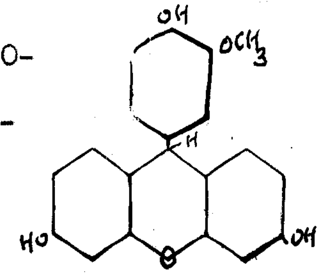
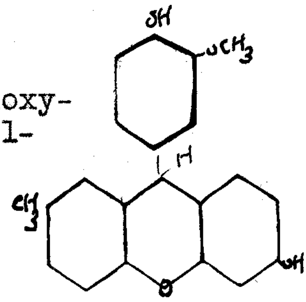
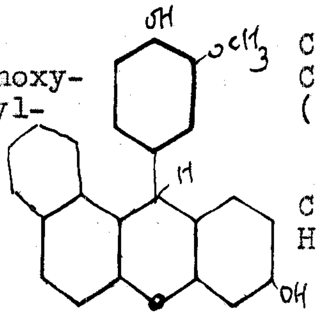
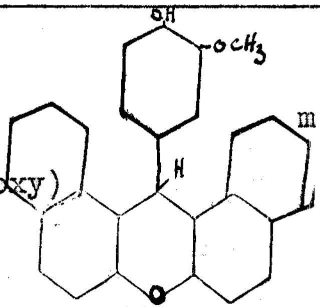
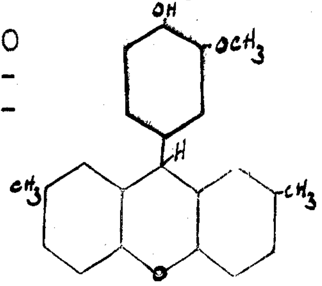
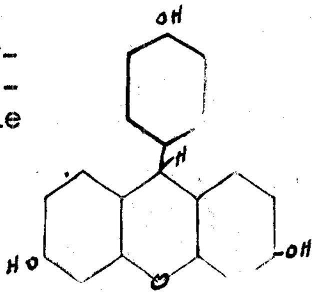
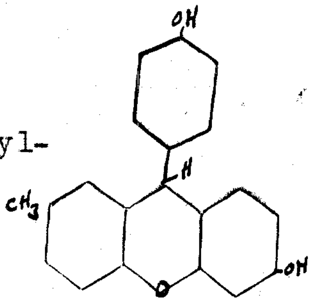
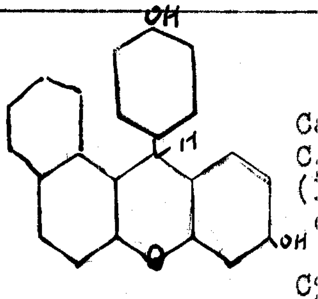
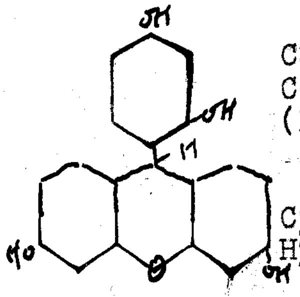
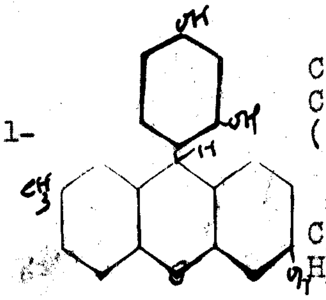
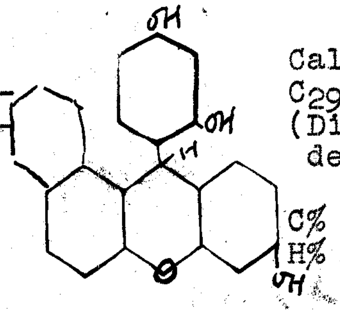
TABLE I.

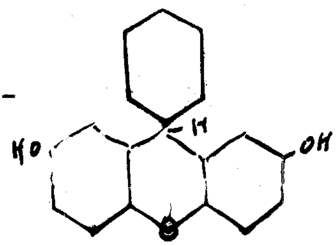
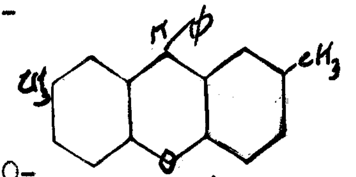
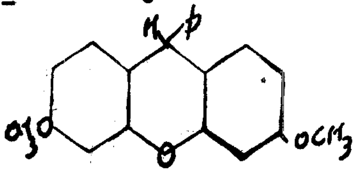
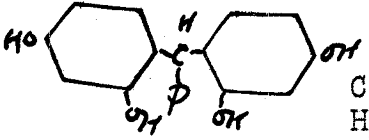
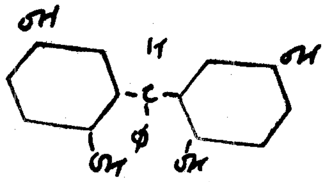
Compound Synthesized

Syn. No.	Compound	Structure	Remarks	Ref. No.
1.	Benzhydrol		m.p. 68-69°C.	(28)
2.	2,4-dihydroxybenzhydrol		Diacetyl deriv. d.p. 200°C.	(37)
3.	3,7-dihydroxy-10-phenylxanthene		m.p. 136°C.	(37)
4.	3-hydroxy-8-methyl-10-phenylxanthene		m.p. 112°C.	(37)
5.	3-hydroxy-8,9-phenyl-10-phenylxanthene		m.p. 84°C.	(37)

Syn. No.	Compound	Structure	Remarks	Ref. No.
6.	3-hydroxy-8-methyl-10-phenyl-acridine			(37)
8.	3,7-dihydroxy-10-(3'-methoxy-4'-hydroxy) phenyl-xanthene		Cal. as $C_{26}H_{22}O_6$ Found (triacetyl deriv. m.p. 174°C.) C% 67.5 68.1 H% 4.80 5.0	
9.	3-hydroxy-8-methyl-10(3'methoxy-4'-hydroxy)phenyl-xanthene		Cal. as $C25H22O6$ Found (diacetyl. deriv. d.p. 221-225) C% 71.8 71.8 H% 5.30 5.50	
10.	3-hydroxy-8,9-phenyl-10(3'-methoxy-4'-hydroxy) phenyl-xanthene		Cal. as $C_{35}H_{24}O_7$ Found (10-aceto-diacetyl deriv. m.p. 205°C.) C% 72.5 72.0 H% 4.84 5.33	

Syn. No.	Compound	Structure	Remarks	Ref. No.
11.	1,2-phenyl-8,9-phenyl-10(3'-methoxy-4'-hydroxy)phenylxanthene		m.p. 211°C.	(36)
12.	2,8-dimethyl-10(3'-methoxy-4'-hydroxy)phenylxanthene		Cal. as $C_{26}H_{24}O_5$ Found (Monoacetyl-10-aceto- deriv. m.p. 170°C.) C% 75.0 75.0 H% 5.77 5.85	
13.	3,7-dihydroxy-10(p-hydroxy)-phenylxanthene		Cal. as $C_{25}H_{20}O_7$ Found (Triacetyl deriv. m.p. 217°C.) C% 69.5 69.6 H% 4.62 4.82	
14.	3-hydroxy-8-methyl-10(p-hydroxy)-phenylxanthene		Cal. as $C_{24}H_{20}O_5$ Found (Diacetyl deriv. m.p. 185°C.) C% 74.3 74.2 H% 5.16 5.06	

Syn. No.	Compound	Structure	Remarks	Ref. No.
15.	3-hydroxy-8,9-phenyl-10-(p'-hydroxy)phenyl-xanthene		Cal. as $C_{29}H_{22}O_6$ Found (Diacetyl-10-aceto-deriv. m.p. 260°C.) C% 74.6 74.2 H% 4.72 5.15	
16.	3,7-dihydroxy-10(2',4'-di-hydroxy)-phenyl-xanthene		Cal. as $C_{23}H_{18}O_7$ Found (Diacetyl-deriv. m.p. 218-220°C.) C% 68.0 68.0 H% 4.44 4.33	
17.	3-hydroxy-8-methyl-10(2',4-dihydroxy)phenyl-xanthene		Cal. as $C_{22}H_{18}O_5$ Found (Mono-acetyl-deriv. d.p. 270°C.) C% 73.0 73.0 H% 4.98 4.86	
18.	3-hydroxy-8,9-phenyl-10-(2',4'-dihydroxy)phenyl-xanthene		Cal. as $C_{29}H_{22}O_7$ Found (Diacetyl-10-aceto-deriv. d.p. 250°C.) C% 72.2 72.3 H% 4.57 4.22	

Syn. No.	Compound	Structure	Remarks	Ref. No.
19.	2,8-dihydroxy-10-phenylxanthene			(26)
20.	2,8-dimethyl-10-phenylxanthene			(7)
21.	3,7-dimethoxy-10-phenylxanthene			(37)
22.	2,4,2',4'-tetrahydroxy-triphenylmethane		Cal. as $C_{23}H_{20}O_6$ Found (diacetyl deriv.) C% 70.5 70.7 H% 5.07 5.01	
23.	2,5,2',5'-tetrahydroxy-triphenylmethane			(46)

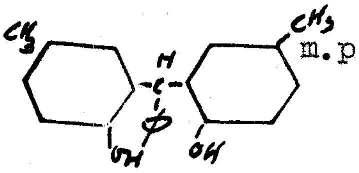
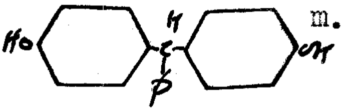
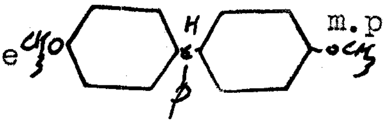
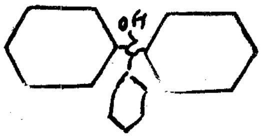
Syn. No.	Compound	Structure	Remarks	Ref. No.
24.	2,2'dihydroxy-5,5'-dimethyl-triphenylmethane		m.p. 100-101°C.	(7)
25.	p,p'-dihydroxy-triphenylmethane		m.p. 160-161°C.	(45)
26.	p,p'-dimethoxy-triphenylmethane		m.p. 109-110°C.	(7)
27.	triphenylcarbinol		m.p. 162.5°C.	(1)

TABLE II.

The Influence of Tannage Variables

Part a. 2,4,2',4'-tetrahydroxy-triphenylmethane tannage

Solvent	Methanol				Acetone			
Calf-skin Squares	Air Dried		Wet Skin		Air Dried		Wet Skin	
Fixation	Water	Air Dry	Water	Air Dry	Water	Air Dry	Water	Air Dry
Shrink. Temp. °C.	92	86	93	87	78	68	69	82
Degree of Tan. %	72.5	83.5	73.4	80.0	37.0	78.5	86.0	94.2
Leather Character	Very good	Fair Cracky Grain	Very good	Fair Cracky Grain	Good	Poor Harsh	Poor Harsh	Poor Harsh

Part b. p,p'-dihydroxy-triphenylmethane tannage

Shrink. Temp. °C.	85	83	84	82	67	73	68	74
Degree of Tan. %	52.2	52.0	41.8	38.0	40.7	45.6	38.0	47.0
Leather Character	Very good	Fair	Very good	Good	Poor Harsh	Poor Harsh	Raw Skin	Poor Harsh

TABLE III.

The Influence of Tannage Variables

Nature of Solvent Effect

Quebracho Tannage

Solvent	Methanol	Ethanol	Cellosolve	Carbitol	Acetone	Dioxane
Dielectric Constant of Solvent (20°C.)	31.2	25.8			21.2	
Con. of Liquor % g/ml.	7.2	7.6	8.6	8.3	9.0	9.4
Shrink. Temp. °C.	78	71	68	68	65	66
Degree of Tan. %	41.7	32.5	30.7	28.2	20.2	16.4
Leather Character	Good	Good	Poor	Poor	Poor	Poor

TABLE IV

The Influence of Tannage Variables

Nature of Solvent Effect

2,4-dihydroxybenzhydrol tannage

Solvent	Methanol	Ethanol	Cellosolve	Carbitol	Acetone	Dioxane
Dielectric Constant of Solvent (20°C.)	31.2	25.8			21.2	
Con. of Liquor % g/ml.	6.4	5.8	6.0	5.8	6.4	7.4
Shrink. Temp. °C.	90	82	79	78	65	65
Degree of Tan. %	37.9	38.3	21.9	22.9	15.1	14.4
Leather Character	Good	Good	Fair	Fair	Poor	Poor

TABLE V

The Influence of Tannage Variables

Nature of Solvent Effect

p',p'-dihydroxy-triphenylmethane tannage

Solvent	Methanol	Ethanol	Cellosolve	Carbitol	Acetone	Dioxane
Dielectric Constant of Solvent (20°C.)	31.2	25.8			21.2	
Con. of Liquor % g/ml.	10	10	10	10	10	10
Shrink. Temp. °C.	89	86	69	67	63	63
Degree of Tan. %	53.9	51.6	43.9	37.0	16.3	15.0
Leather Character	Good	Good	Fair	Fair	Poor	Poor

TABLE VI

The Influence of Tannage Variables

Nature of Solvent Effect

3,7-dihydroxy-10(p'-hydroxy)-phenylxanthene tannage

Solvent	Methanol	Ethanol	Cellosolve	Carbitol	Acetone	Dioxane
Dielectric Constant of Solvent (20°C.)	31.2	25.8			21.2	
Con. of Liquor % g/ml.	3.8	5.2	6.4	6.1	3.6	3.4
Shrink. Temp. °C.	92	84	68	77	63	63
Degree of Tan. %	54.8	38.9	36.1	39.5	25.7	9.90
Leather Character	Good	Good	Fair	Fair	Poor	Poor

TABLE VII.

The Influence of Tanning Variables

Fixation Effect

2,4-dihydroxybenzhydrol tannage

Treatment	Shrinkage Temp. °C.		Degree of Tan. %		Leather Character	
Skin pieces	Air Dried	Wet Skin	Air Dried	Wet Skin	Air Dried	Wet Skin
Water fixation (48 hours)	80	84	39.1	33,7	Good	Good
Conditioned (65% R.H., 70°F.)	80	89	41.0	45.2	Poor Cracking Grain	Fair Cracking Grain
Air dried over sat. water vapor	87	87	41.0	33.0	"	"
Dried over P_2O_5	82	83	47.1	30.6	"	"
Fixation with 40% (by volume) acetone in water	92	98	38.1	32.7	Very good	Very good

TABLE VIII.

The Influence of Tanning Variables

Fixation Effect

Quebracho Tannage

Treatment	Shrinkage Temp. °C.		Degree of Tan. %		Leather Character	
Skin pieces	Air Dried	Wet Skin	Air Dried	Wet Skin	Air Dried	Wet Skin
Water fixation (48 hours)	62	77	39.1	52.0	Poor	Good
Conditioned (65% R.H., 70°F.)	61	63	45.4	50.0	Poor	Poor
Air dried over sat. water vapor	68	70	37.7	50.6	Poor	Fair
Dried over P_2O_5	70	73	62.8	50.4	Fair	Fair
Fixation with 40% (by volume) acetone in water	62	65			Detanned	Detanned

TABLE IX.

The Influence of Tannage Variables

Fixation Effect

2,4-dihydroxybenzhydrol tannage

Volume % of Solvent in Water	Shrinkage Temp. Ts. oC.	Degree of Tannage %	Water Solubles % Wilson-Kern	Leather Char-acter
50% Acetone	95	48.9	2.2	Good, cracky grain
40% Acetone	92	60.5	3.2	Good, cracky grain
20% Acetone	85	38.3	2.5	Very good cracky grain
30% Methanol	92	61.3	4.0	Very good

The Influence of Tannage Variables

2,4-dihydroxybenzhydrol tannage

Part a. Build up tannage.

Part b. Air fixation under high limed atmosphere.

	Shrinkage Temp. °C.	Degree of Tan.	Water Solubles % Wilson-Kern	Leather Char-acter
a.	Boiling 5 minutes	79.0	2.2	Good, cracky grain
b.	89	58.5	3.4	Good, piping grain

TABLE XI

The Influence of Tannage Variables

Penetration and Fixation Effects

Quebracho Tannage

Tanning Liquor	30% Quebracho in acetone	30% Quebracho in acetone	30% Quebracho in acetone	30% Quebracho in dioxane
Skin cut	Dehydrated	Air-Dried	Wet skin	Air-Dried
Shrink. Temp. °C.	76	80	76	76
Degree of Tannage %	92.2	80.0	110	33.3
Leather Character	Very good	Very good	Fair, case-hardening	Very good

TABLE XII.

The Influence of Tannage Variables

Penetration and Fixation Effects

2,4-dihydroxybenzhydrol tannages

Solvent	30% 2,4-dihydroxybenzhydrol in acetone		30% 2,4-dihydroxybenzhydrol in dioxane	
Fixation condition	Water	40% Acetone	Water	40% Acetone
Shrinkage Temp. Ts °C.	79	90	75	78
Degree of Tanning %	80.0	64.4	34.4	29.1
Leather Character	Poor, cracky grain	Fair	Fair	Fair

TABLE XIII.

The Influence of Tannage Variables

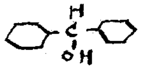
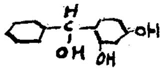
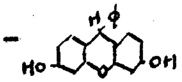
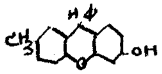
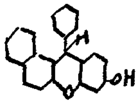
The Hydrothermostability and Fixation of the Leather

2,4-dihydroxybenzhydrol tannage

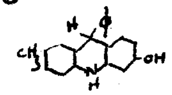
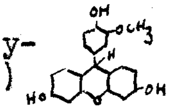
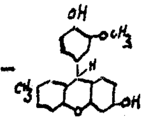
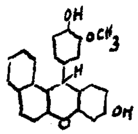
Concentration % g/100 ml. Acetone	Shrinkage Temp. °C.	Degree of Tan. %	Water sol. % (Wilson-Kern)	Leather Character
5	80	17.9	1.9	Fair, cracky grain
10	85	26.3	6.7	Very good
20	92	60.5	3.2	Very good cracky grain
30	96	79.9	3.8	Good, cracky grain

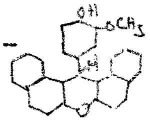
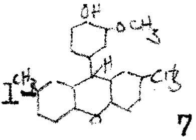
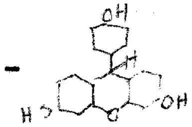
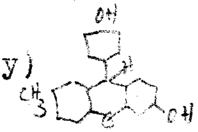
TABLE XIV.

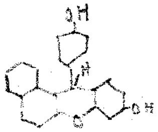
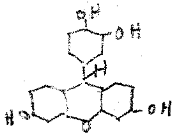
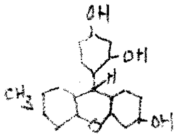
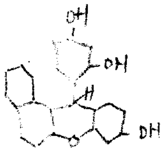
Effect of Degree of Hydroxylation on the Leather Character

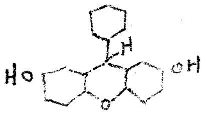
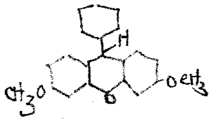
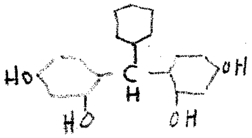
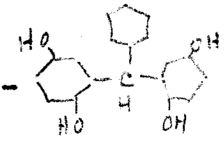
Syn. No.	Compound	Structure	Shrink. Temp. °C.	Degree of Tannage %	$\left(\frac{\text{Active OH radical wt}}{\text{mol. wt.}}\right)\%$	Leather Character
1	Benzhydrol		60	25.0	0 9.25*	Raw skin
2	2,4-dihydroxy-benzhydrol		90	37.9	15.7 23.6*	Very good
3	3,7-di-hydroxy-10-phenyl-xanthene		80	53.2	11.7	Fair
4	3-hydroxy-8-methyl-10-phenyl-xanthene		70	42.8	5.70	Poor
5	3-hydroxy-8,9-phenyl-10-phenyl-xanthene		75	67.0	5.25	Poor

* $\left(\frac{\text{Total OH radical wt.}}{\text{mol. wt.}}\right)\%$

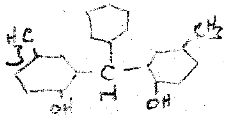
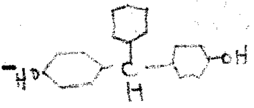
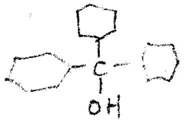
Syn. No.	Compound	Structure	Shrink. Temp. Ts °C.	Degree of Tannage %	(Active OH radical wt. / mol. wt.)	Leather Character
6	3-hydroxy-8-methyl-10-phenyl-acridine		68	39.0	5.92	Poor
8	3,7-di-hydroxy-10 (3'-methoxy-4'-hydroxy) phenyl-xanthene		91	35.1	15.2	Good
9	3-hydroxy-8-methyl-10 (3'-methoxy-4'-hydroxy) phenyl-xanthene		84	36.8	10.2	Good
10	3-hydroxy-8,9-phenyl-10(3'-methoxy-4'-hydroxy) phenyl-xanthene		77	48.2	8.95	Good

Syn. No.	Compound	Structure	Shrink. Temp. Ts °C.	Degree of Tannage %	$\left(\frac{\text{Active OH radical wt.}}{\text{mol. wt.}}\right)\%$	Leather Character
11	1,2-phenyl-8,9-phenyl-10(3'-methoxy-4'-hydroxy) phenyl-xanthene		60	41.0	4.21	Raw skin
12	2,8-dimethyl-10(3'-methoxy-4'-hydroxy)phenyl-xanthene		76	111	5.12	Fair
13	3,7-di-hydroxy-10 (p-hydroxy)-phenyl-xanthene		94	42.1	16.7	Good
14	3-hydroxy-8-methyl-10(p-hydroxy) phenyl-xanthene		80	25.0	11.2	Good

Syn. No.	Compound	Structure	Shrink. Temp. Ts °C.	Degree of Tan. %	$\left(\frac{\text{Active OH radical wt.}}{\text{mol. wt.}}\right)\%$	Leather Character
15	3-hydroxy-8,9-phenyl-10(p-hydroxy)phenyl-xanthene		82	42.0	10.0	Good
16	3,7-dihydroxy-10(2',4'-dihydroxy)phenyl-xanthene		92	35.1	21.2	Good
17	3-hydroxy-8-methyl-10(2',4'-dihydroxy)phenyl-xanthene		86	37.0	15.8	Good
18	3-hydroxy-8,9-phenyl-10-(2',4'-dihydroxy)phenyl-xanthene		84	42.1	19.2	Fair

Syn. No.	Compound	Structure	Shrink. Temp. Ts ^{o}C.	Degree of Tan. %	$\left(\frac{\text{Active OH radical wt.}}{\text{mol. wt.}}\right)\%$	Leather Character
19	2,8-di-hydroxy-10-phenyl-xanthene		60	31.2	0 11.7*	Raw skin
20	2,8-di-methyl-10-phenyl-xanthene		62	26.6	0	Raw skin
21	3,7-di-methoxy-10-phenyl-xanthene		60	7.90	0	Raw skin
22	2,4,2',4'-tetra-hydroxy-triphenyl-methane		92	50.0	22.1	Very good
23	2,5,2',5'-tetra-hydroxy-triphenyl-methane		79	78.0	11.1 22.1	Fair

*Total hydroxylation

Syn. No.	Compound	Structure	Shrink. Temp. Ts °C.	Degree of Tan. %	(Active OH radical wt. / mol. wt.)%	Leather Character
24	2,2'-dihydroxy-5,5'-dimethyl-triphenylmethane		78	50.0	11.2	Fair
25	p,p'-dihydroxy-triphenylmethane		85	52.2	12.3	Very good
26	p,p'-dimethoxy-triphenylmethane		60	12.0	0	Raw skin
27	triphenylcarbinol		60	15.6	0 6.54*	Raw skin

*Total hydroxylation

TABLE XV.

Tannages of Simple Phenols

Compound	Hydroquinone	Resorcinol	Catechol	Quercetin*
Shrink. Temp. Ts °C.	62	60	66	68
Degree of Tannage %	54.0	25.0	30.7	37.7
Leather Character	Poor	Poor	Poor	Poor

*Not a simple phenol

TABLE XVI.

Solubilities and Specific Conductances of Dihydroxy-10-phenylxanthenes

Methanol-water Fixation Systems

Volume % Methanol	Specific Con. (pure solution) 1/ohm 10^{-6}	3,7-dihydroxy-10-phenylxanthene		2,8-dihydroxy-10-phenylxanthene	
		Solubility % in solution g/ml.	Specific Con. 1/ohm 10^{-6}	Solubility % in specific sol. g/ml.	Specific Con. 1/ohm 10-6
100	0.88	8.7	82.0	7.8	1.9
97		7.8			
95		7.0	103	5.5	1.9
90	0.94	5.2	131	3.5	1.8
85			150	2.5	
80	0.99	2.5	154	2.0	1.5
70	1.1	1.7	144	1.0	0.58
60	1.1	0.75	142	0.35	2.8
50	1.1	0.50		0.15	
40	1.3				
30	1.3				
20	1.6				
10	1.6				
0 (100 water)	2.4		2.6		

TABLE XVII.

Solubilities and Specific Conductances of Dihydroxy-10-phenylxanthenes

Cellosolve-water and Dioxane-water Fixation Systems

Volume % Solvent	Specific Con. of Solution 1/ohm 10^{-6}		3,7-dihydroxy-10-phenylxanthene in dioxane-water system		3,7-dihydroxy-10-phenylxanthene in cellosolve-water system	
	Dioxane	Cellosolve	Solubility % in solution g/ml.	Specific Con. 1/ohm 10-6	Solubility % in solution g/ml.	Specific Con. 1/ohm 10^{-6}
100			6.2		7.4	1.3
95			6.2		7.2	2.6
90			6.1	(0.53)	6.8	5.3
80		3.9	5.4	1.9	6.2	8.8
70	0.53	12	5.2	4.4	5.2	16
60	2,8	26	4.6	6.2	4.7	23
50	6.6	49	0.50		0.60	
40	13	79.6	0.10		0.20	
30	19	112				
20	24	138				
15	24	143				
10	22	136				
5	15	101				
0 (100 water)	2.6	2.6				

TABLE XVIII.

Chemical Analysis of Leather

No. Sample	Tanning Material	Con. % of Liquor g/ml.	Moisture %	Pet. ether extract %	Degree of tannage %	Water Reversibility	
						Degree of Tan. %	Water Sol. % Wilson-Kern
1	Quebracho	11	13.0	2.5	74.5	40.3	16
2a	3,7-di-hydroxy-10(p-hydroxy) phenyl-xanthene	7.4	12.3	2.2	57.7	52.3	2.7
2b	"	7.4	14.2	0.60	62.1	60.5	7.6
3	2,4-di-hydroxy-benzhydrol	11	10.7	0.40	95.5	95.5	2.5
4a	2,4,2',4'-tetra-hydroxy-tri-phenyl-methane	11	10.3	1.8	77.3	50.7	17
4b	"	11	8.96	1.0	67.2	40.4	19
5	Quebracho	11	13.3	1.8	65.6	36.4	17
6	3-hydroxy-8-methyl-10 (3-methoxy)	11	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	4'-hydroxy phenylxanthene	7.4	11.9	1.8	49.5	44.4	4.5

TABLE XIX.

Physical Characteristics of Leather

No Sample	Compound	Tensile Strength lb./sq. in.	Stitch Tear lb./sq. in.	% Stretch	Shrink. Temp. °C.	Leather Character
1	Quebracho	3,350	667	20	70	Class III good
2a	3,7-dihydroxy-10-(p-hydroxy) phenyl-xanthene	2,665	754	30	80	Class III good
2b	"	3,255	625	25	93	
3	2,4-di-hydroxy-benz-hydrol	2,660	624	22	92	Very good, Class I
4a	2,4,2',4'-tetra-hydroxy-triphenyl-methane	2,710	485	26	86	Very good, Class II
4b	"	2,895	1431	29	89	
5	Quebracho	2,695	574	21	75	Good, Class III
6	3-hydroxy-8-methyl-10 (3'-methoxy-4'-hydroxy) phenyl-xanthene	3,625	1110	28	79	Fair, Class IV

TABLE XX.

Chemical Analysis of 2,4-dihydroxybenzhydrol Leather

No. of Sample	Con. of Liq. % (Acetone)	Ash %	Pet. Ether Ext. %	Degree of Tannage %	Water Solubles % (Wilson-Kern)
7	20	0.35	3.1	57.0	2.7
8	41	0.26	2.1	70.9	2.9
9	41	0.56	0.3	61.2	2.5
10	41	0.17	1.3	59.5	2.4

Reversibility

Aqueous Buffer (phosphate) Washables %

pH5.	Degree of Tan. %	pH8.9	Degree of Tan. %	pH9.5	Degree of Tan. %	40% Acetone Washables	Degree of Tannage %
1.9	56.2	4.3	51.9	6.0	48.6	25	15.0

TABLE XXI.

Physical Characteristics of 2,4-dihydroxybenzhydrol Leather

No. Sample	Tensile Strength lb./sq. in.	Stitch Tear lb./in.	% Stretch	Shrinkage Temp. °C.	Leather Character
7	3,470	716	32.5	91	Very good
8	3,306	676	31.2	97	Very good
9	3,220	759	27.6	Boiling	Good
10	3,180	415	26.0	96	Good

TABLE XXII.

Aqueous Acetone (40%) Reversibility of 2,4-dihydroxybenzhydrol Leather

A Modified Wilson-Kern Procedure

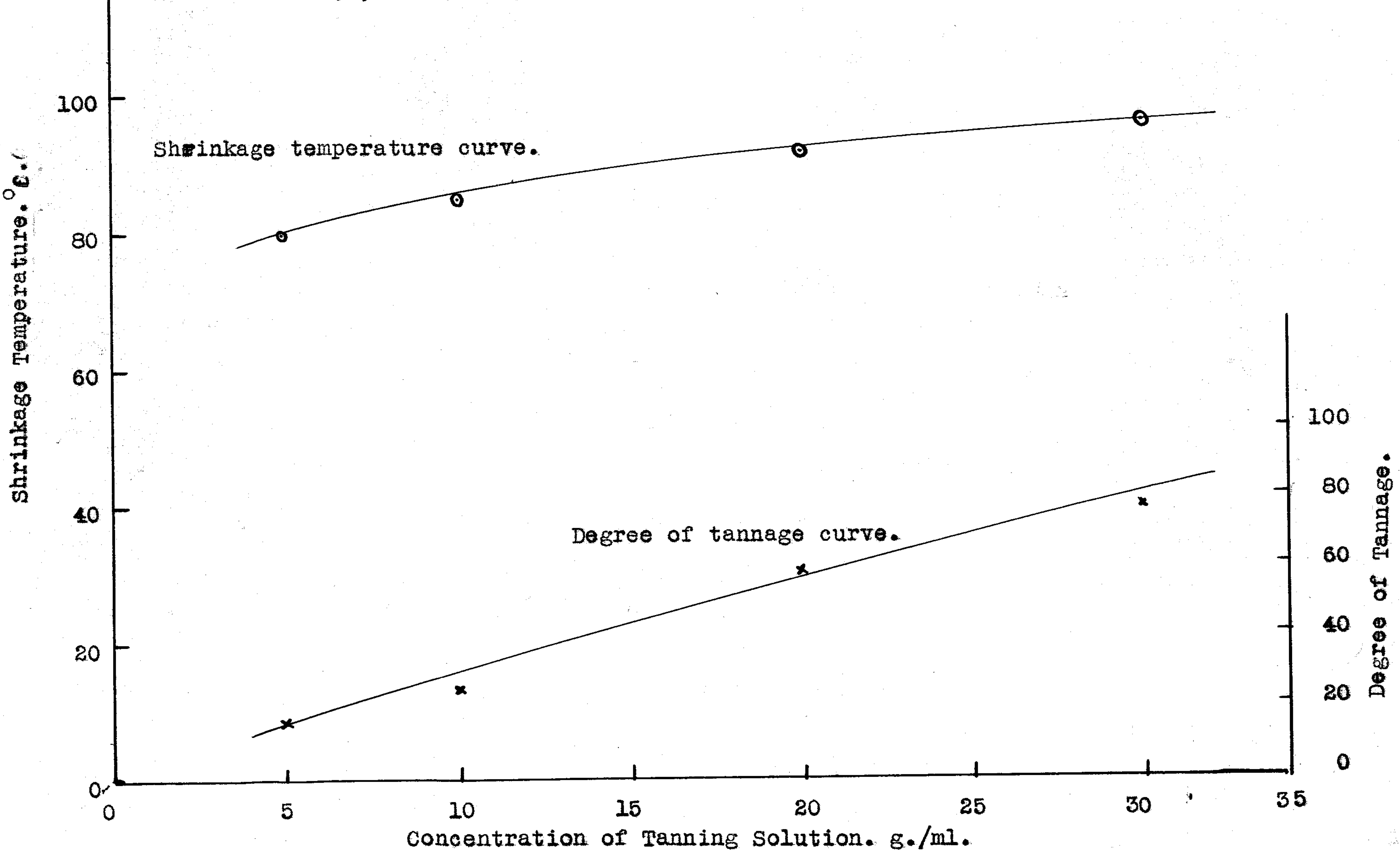
Time of Wash Hours	Degree of Tannage	Washable %
0	59.5	0
24	25.0	21
72	19.0	25
144	16.0	27

TABLE XXIII.

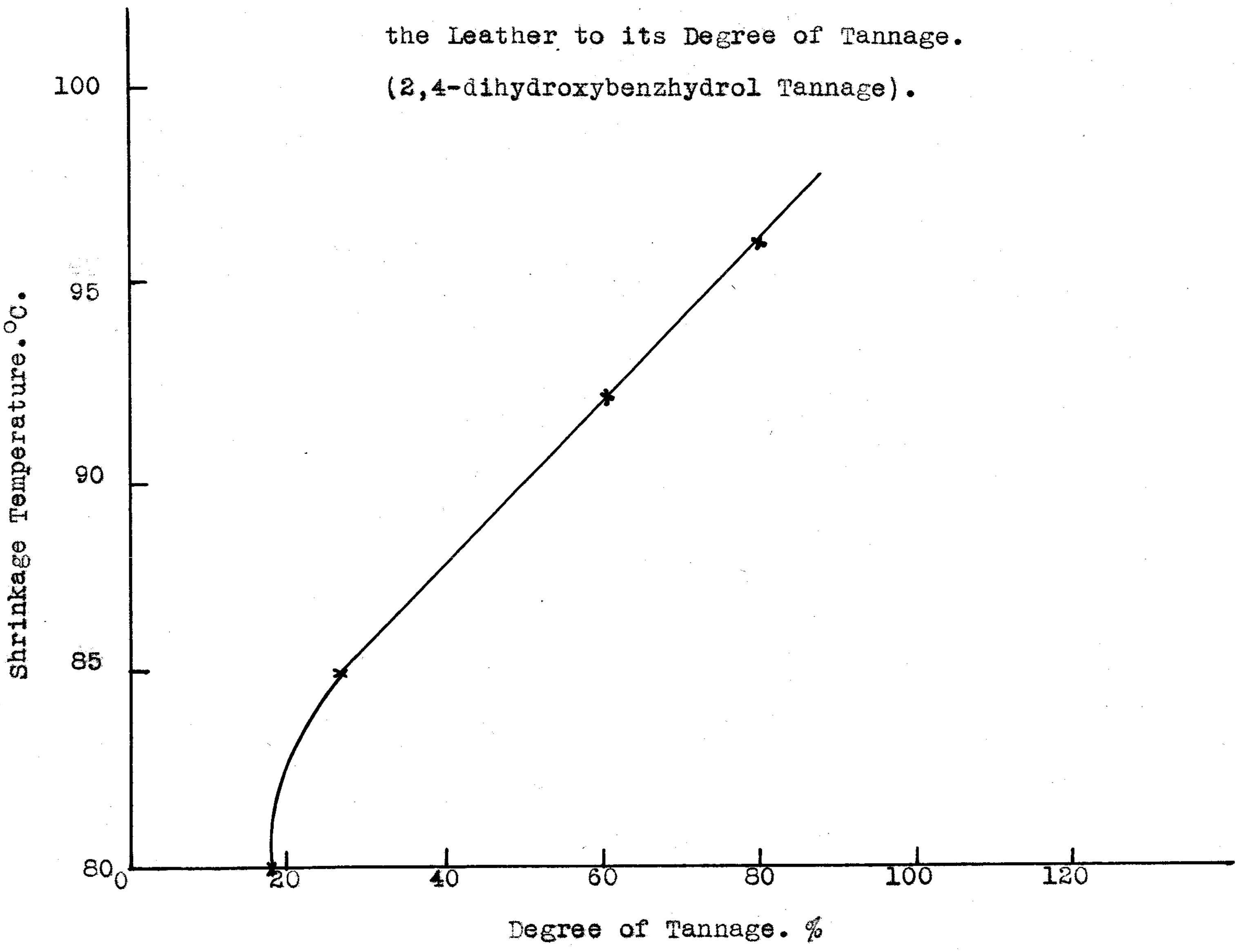
Tannage of Deaminized Calfskin Squares

Tanning Liquor	30% Quebracho in Acetone		10% 2,4-dihydroxybenzhydrol in Methanol	
Skin	Normal	Deaminized	Normal	Deaminized
Shrink. Temp. Ts. °C.	79.81	80.81	81.82	81.81
Degree of Tannage %	38.3	36.2	30.0	33.0
Leather Character	Very good	Very good	Very good	Very good

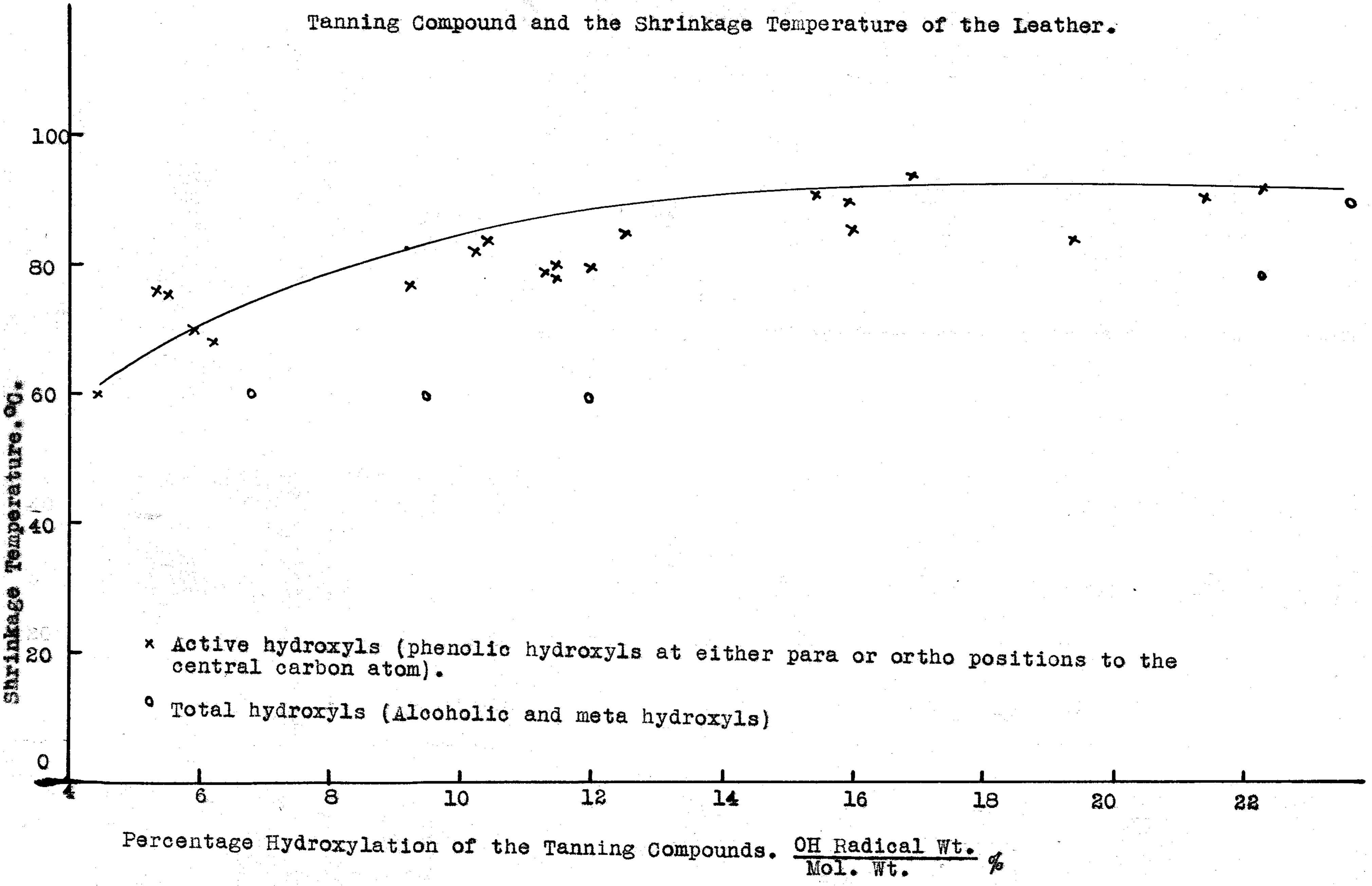
Curve 1. A Plot of the Relation of Shrinkage Temperature and Degree of Tannage to the Concentration of the Tanning Liquor. (2,4-dihydroxybenzhydrol tannage).



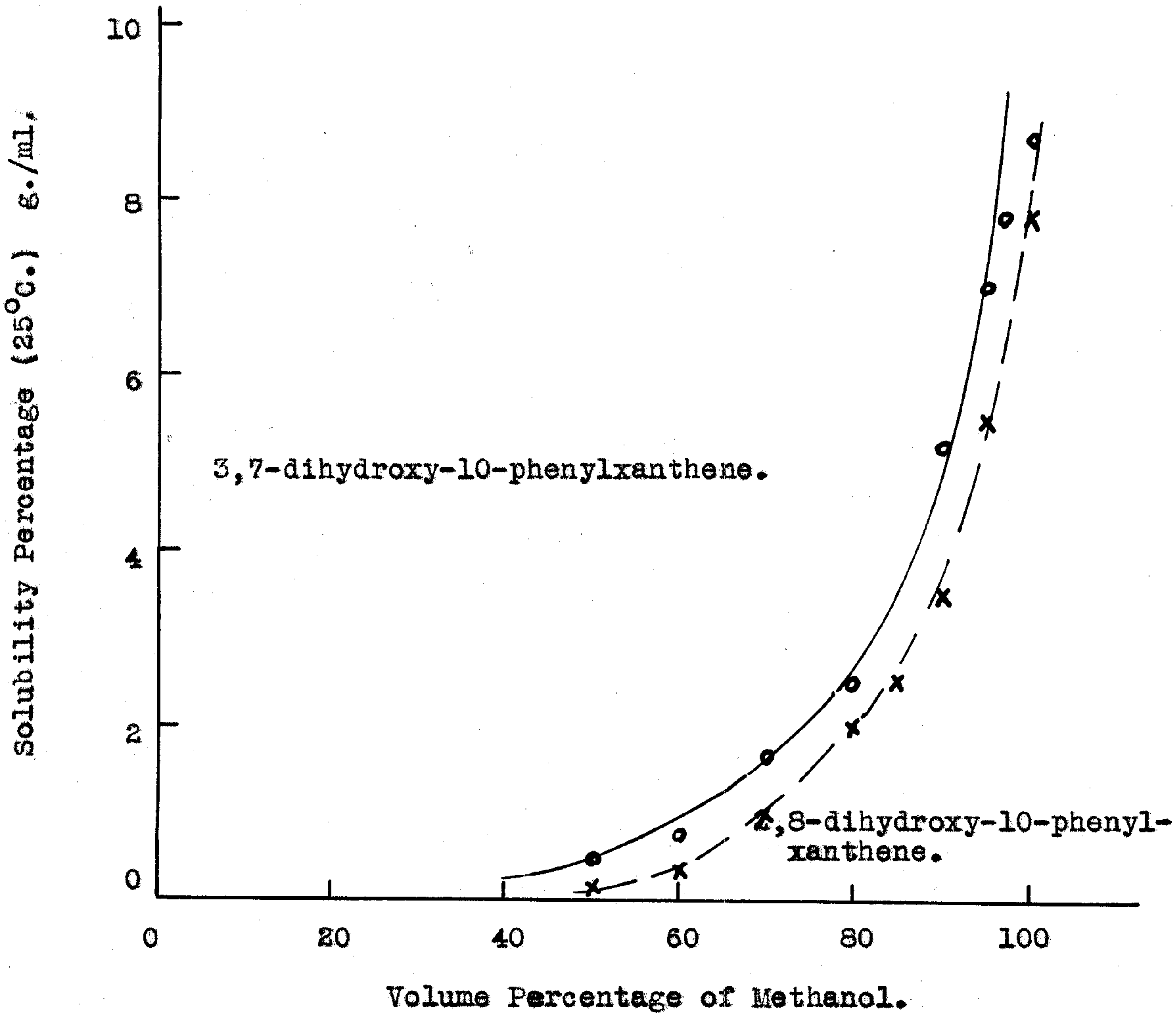
Curve 2. A Plot of the Relationship of Shrinkage Temperature of the Leather to its Degree of Tannage. (2,4-dihydroxybenzhydrol Tannage).



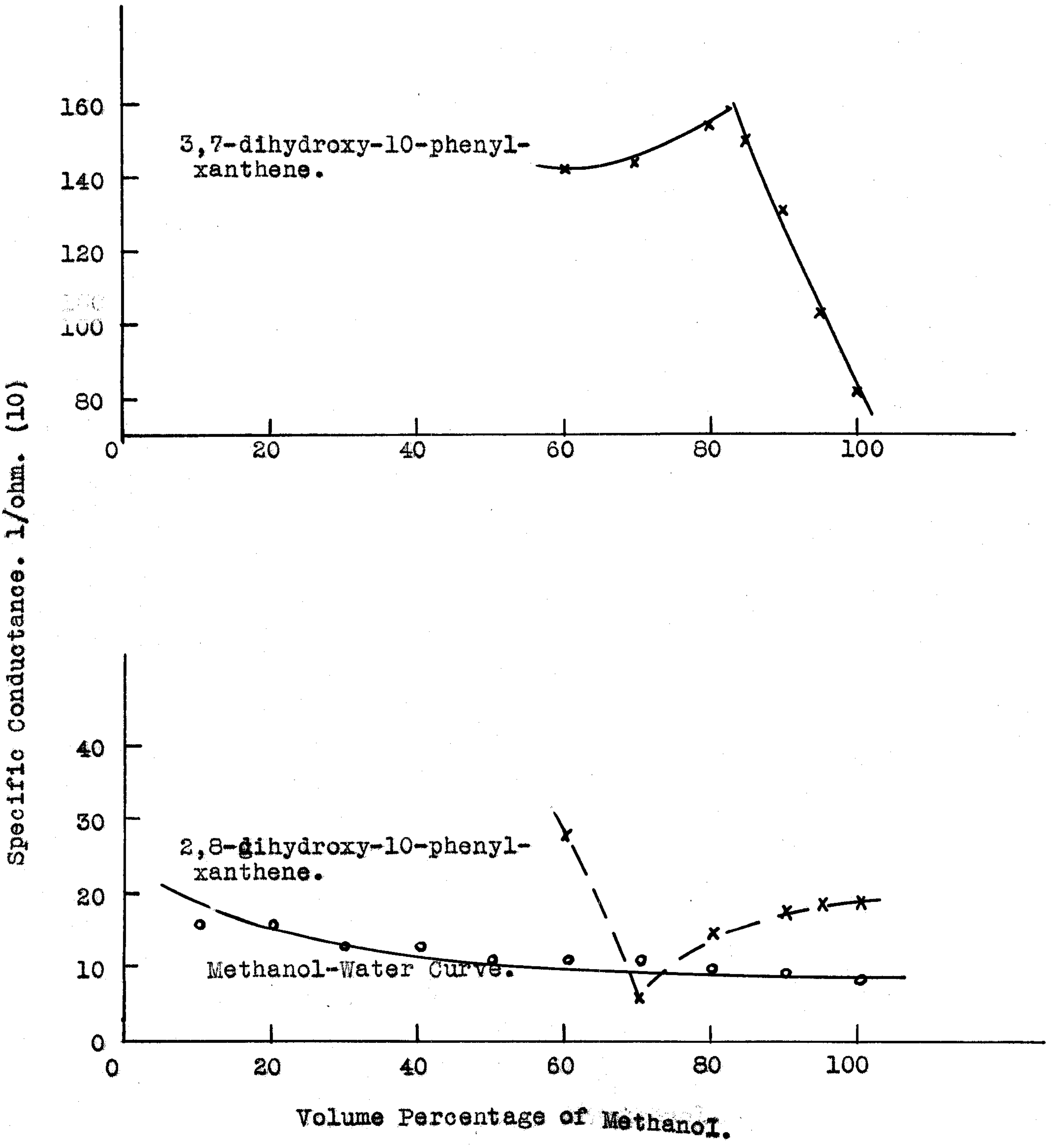
Curve 3. A Plot of the Relatioship between the Degree of Hydroxylation of the Tanning Compound and the Shrinkage Temperature of the Leather.



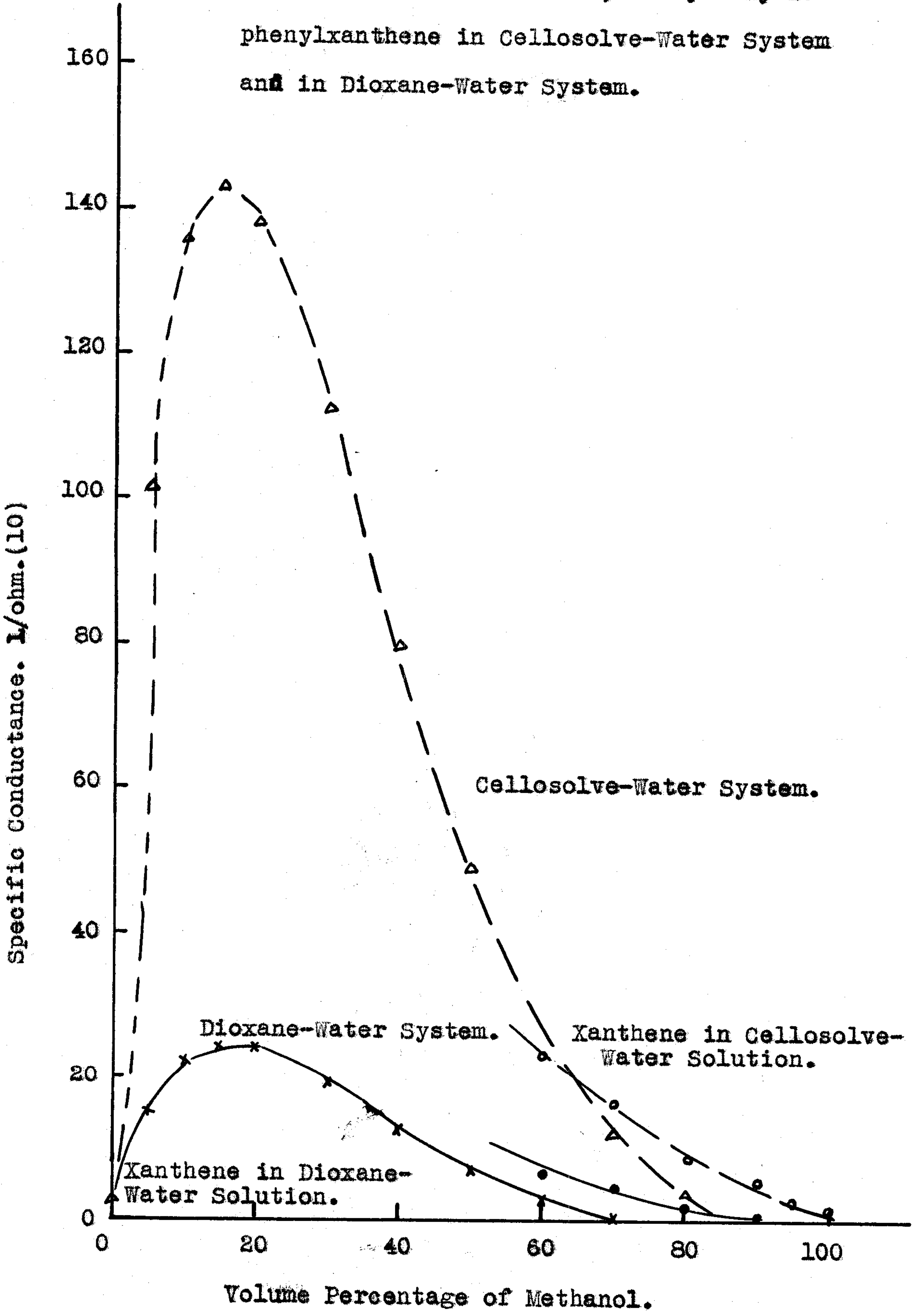
Curve 4. Solubility Curve of 3,7-dihydroxy-10-phenylxanthene and 2,8-dihydroxy-10-phenylxanthene in Different Methanol-Water Solutions.



Curve 5. Specific Conductance of Xanthenes in Methanol-Water System.



Curve 6. Specific Conductance of 3,7-dihydroxy-10-phenylxanthene in Cellosolve-Water System and in Dioxane-Water System.



Curve 7. Solubilities of 3,7-dihydroxy-10-phenylxanthene in Dioxane-Water System and in Cellosolve-Water System.