

R63-40

## OBSERVATIONS ON THE TANNING ACTION OF SYNTHETIC POLYPHENOLS\*

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### ABSTRACT

Nonswelling alkaline solutions in the pH range of 8.5–9.5, first used by the authors to explore tanning characteristics of aldehydes, have now been used in a study of the tanning action of binuclear phenol derivatives of low molecular weight. These compounds are of importance because of their use by other workers to demonstrate their theories of the mechanism involved in the vegetable tanning process.

Nonswelling alkaline solutions can be used to advantage to dissolve compounds sparingly soluble in the acid pH range. In addition, these same solutions are especially well suited to tanning trials in the absence of air.

The results of the described work support the theory that polyphenols linked by a carbon atom tan by the formation of hydrogen bonds between the collagen chains. This reaction is independent of the presence or absence of oxygen in the air. Phenols fused together as in naphthalenediols, on the other hand, have no tanning properties in the absence of air. However, one of them—the 2,6 homolog—produces leather when used for tanning in the presence of air. The explanation offered by the authors is that the 2,6 homolog undergoes oxidation and polymerization, forming compounds which tan because of their quinoid nature.



### INTRODUCTION

A number of authors have investigated the affinity of model substances to collagen in order to gain new insights into the nature of the tanning action of natural or synthetic tannins (1–5). These compounds most often consist of two or more phenol rings that are either attached to a central carbon atom or fused together as in naphthalenediols.

\*Presented at the Fifty-eighth Annual Meeting of the American Leather Chemists Association at the Grand Hotel, Mackinac Island, Michigan, June 17–20 1962.

The authors working in this field did not publish adequate experimental evidence for a faithful duplication of their efforts by others. This is true especially of Mikhailov (4), who studied the tanning potency of three naphthalenediols and of 2,2',4,4'-tetrahydroxydiphenylmethane. Mikhailov found that the 2,6-naphthalenediol is superior in tanning potency to the other two examined by him, i.e., the 1,5 and 1,7 homologs, and that, as one would expect, excellent leather is obtained by tanning with 2,2',4,4'-tetrahydroxydiphenylmethane (methylenediresorcinol in *Chemical Abstracts*). Since this compound is easily prepared from resorcinol and formaldehyde (6), it comes as a surprise that Mikhailov was the first to report on its tanning ability. A related compound, however, was examined by Tu and Lollar (2), i.e., 2,4-dihydroxybenzhydrol which is prepared from resorcinol and benzaldehyde (7). Tu and Lollar, testing this compound in solvent systems, found it to have excellent tanning properties.

Attempts have been made in the past to synthesize the so-called *beta*-resorcylalcohol,  $C_6H_3(OH)_2 \cdot CH_2OH$ , which does not carry a benzene side chain as the benzhydrol does, and should also have tanning potency, but it has been shown that this compound does not exist (8).

The explanations given for the tanning effect of some of the compounds did not seem fully convincing to the present author following the suggestion of Endres (9) that oxygen is indispensable for the tanning action of piceatannol, one of the components of spruce bast; a tannage results from oxidation to a monomolecular quinone compound or to quinoid condensation products. It seemed plausible that the presence of oxygen could also account for the tanning ability of 2,6-naphthalenediol and possibly might have an influence upon the tanning ability of dihydroxybenzhydrol and of tetrahydroxydiphenylmethane, two compounds characterized by either one or two resorcinol substitutions.

#### EXPERIMENTAL

Experiments designed to test this possibility were conducted in aqueous solutions of sodium carbonate and bicarbonate of the same strength (at least 1.0 normal) as in tanning trials with various aldehydes (10) and with a pH range of 8.5 to 9.5. The advantages of these solutions are that (a) they render hydroxy compounds soluble and (b) they prevent any swelling of the hide.

All experiments were carried out using cattlehide grain splits weighing between 30 and 120 g. per experiment. The pieces used were equilibrated in the alkaline solutions before they came in contact with the organic compounds, as was done in the previous work. The primary criterion for measuring the progress of tanning was the rise in the shrinkage temperature ( $T_s$ ). A second indication of tanning action was the degree of tannage found in

the air-dry pieces after completion of each tanning experiment. The degree of tannage was determined as in vegetable leather.

Finally, instead of being appraised subjectively by feel, the air-dry leathers were tested for stiffness by method 4211 of the Federal Specification KK-L-311, using the Timius Olsen Stiffness Tester (1" wide specimens mounted with the grain up, using a 0.5" span and a 1-lb. or 2-lb. load at a 20° angle). The measurements were used to calculate the relative stiffness factor as required by the method.

**Tanning in absence of air.**—Delimed hide pieces weighing 30–50 g. were first alkalinized by tumbling in a 1-gallon jar with a small volume of a solution containing  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  in molar ratios varying between 3:2 and 3:1. Afterwards they were transferred together with the solution to a 200-ml. jar which was filled to the brim with saturated sodium bicarbonate solution, requiring about 160–170 ml. of this solution. The chemical was added in powder form, the jar was closed and tumbled 5–6 hours per day until the  $T_s$  remained stable, usually 3–4 days, then the pH was gradually lowered by additions of sulfuric acid. When the pH of the solution remained stable between 3.5 and 5.0, the hide pieces were freed of salts and other water-soluble matter by three changes of water in 1-gallon jars.

**Tanning in presence of air.**—The hide pieces used were prepared in the same manner as for the tanning trials in absence of air. The volume in the tanning liquor was maintained at 100–200 % of the weight of the hide pieces. An open jar was used for agitation so that air had free access to the liquor and hide pieces. After several days the pH of the liquor was lowered by additions of sulfuric acid, and after reaching a pH near 5.0 the hide pieces were removed and washed as described above.

**Other tests in presence of air.**—In additional tests where air was *not* excluded, the hide pieces, prepared in the same manner as before, were tanned in tumbling jars in which the ratio of liquor to air volume was very large, as it is usually in tannery drums. The jars were frequently opened either for adding the tanning compounds or for gradually lowering the liquor pH to near 5.0 by addition of sulfuric acid. The tanning compounds used here were 2,6 naphthalenediol as well as three other naphthalenediols as shown in Table I, together with other data on these tanning trials.

One more test was performed with 1,5-naphthalenediol, using it for tanning in a very dilute caustic soda solution. This was the method used by Li (1) on this diol.

TABLE I  
TANNING WITH NAPHTHALENEDIOLS IN TUMBLING JARS

(0.2 moles /100 g. hide substance in solutions  
measuring 60% of the volume of the wet hide)

Position of Hydroxyls	1,5	2,6	1,4	2,3
Molar Ratio of Na <sub>2</sub> CO <sub>3</sub> to NaHCO <sub>3</sub>	3:1	3:1	3:2	3:2
Normality of Solution at Equilibrium with Hide	1.27	1.27	1.45	1.45
T <sub>s</sub> at End of Alkaline Phase	75	83	69	72

### RESULTS AND DISCUSSION

The results obtained by tanning first in the absence and then in presence of air are presented in Table II.

TABLE II  
TANNAGE IN ABSENCE AND PRESENCE OF AIR

	Without Air			With Air			Used per 100 g. Hide Substance Moles g.	
	T <sub>s</sub> (°C.)	Degree of Tannage	Relative Stiffness Factor	T <sub>s</sub> (°C.)	Degree of Tannage	Relative Stiffness Factor		
2,6-Naphthalenediol	66	2.5	*	80	18	17	0.2	32
Methylenediresorcinol	94	59	1.6	84	47	4.0	0.3	70
2,4-dihydroxybenzhydrol	68	16	43	74	28	40	0.3	65

\*Too high for the scope of the instrument.

The difference between tanning in the absence and in the presence of air in the case of 2,4-naphthalenediol is impressive. There can be no doubt that with oxygen present a full, though rather firm, leather is obtained. The color of this leather is slate grey.

Smaller differences in T<sub>s</sub> between tanning in the presence and in the absence of air were observed with methylenediresorcinol and dihydroxybenzhydrol. Moreover, only the latter tanned better in the presence of air. The methylenediresorcinol tanned better in the absence of air. It also was a better tanning agent when the T<sub>s</sub> obtainable by both compounds and the softness of the resulting leather were used as yardsticks. All T<sub>s</sub> figures decreased 5°–8°C. after accelerated aging (4 months at 38°–39°C. and 95% R.H.). A comparison with the T<sub>s</sub> figures observed by others reveals that Mikhailov (4) obtained 92° as against our 94° for methylenediresorcinol and

that Tu and Lollar (2) by a solvent tannage obtained 98° for the dihydroxybenzhydrol. Nayudamma and his coworkers (5), on the other hand, reported a  $T_s$  of 84° for methylenediresorcinol. The color of the leather was brownish except for the methylenediresorcinol leather tanned in the absence of air, which was pinkish.

Actually, because dihydroxybenzhydrol has a lower number of phenolic hydroxyl groups than methylenediresorcinol, one should expect that it has a lower  $T_s$  and gives a stiffer, less satisfactory leather. Why oxygen should have the opposite effect on both compounds is more difficult to understand. However, it may be connected with the rate of oxidation and polymerization which seems to be higher for the benzhydrol derivative. These changes, which manifest themselves in the rapid darkening of the yellow compound, may increase its tanning ability, originally based on only two phenolic hydroxyls. The methylenediresorcinol, by contrast, already has four phenolic hydroxyls and does not gain any more tanning power by oxidation. In fact, Mikhailov (4) has shown, and our own experiments have confirmed, that the corresponding pyrogallol derivative of methane is less of a tanning agent, raising the  $T_s$  of hide to only 83° although it has 50% more hydroxyl groups than methylenediresorcinol.

The other tests described above with four different naphthalenediols confirmed that the 2,6 diol is the only useful tanning compound. The three other diols yielded hard and bony products.

A comparison of their shrinkage temperatures is given in Table III.

TABLE III  
HIGHEST SHRINKAGE TEMPERATURES (°C.) OBTAINED  
WITH NAPHTHALENEDIOLS IN PRESENCE OF AIR

Position of Hydroxyls	QM	Mikhailov (4)
1,4	69	—
1,5	72 and 74*	73
1,7	—	78
2,3	72	—
2,6	85†	90

\*In a re-run of Li's tannage

†In a grain split

The  $T_s$  of 90° as reported by Mikhailov is very high; the fact that it could not be reached in the present study supports the assumption that the tannage depends on oxidation products of the original diol. It must be remembered that 2,6-naphthalenediol is the reduced form of amphi-naphthoquinone, the only one of the four known quinones of naphthalene which is truly a quinone,

due to its high energy potential (11, 12). The conclusion then is that the hydroquinone or 2,6-diol is oxidized and possibly also polymerized in air, leading to a tannage of the same type as is obtained with benzoquinone.

Since the other diols showed little or no tanning action, it seemed unnecessary to provide information on the role of oxygen in their rather limited tanning ability. One may also ask whether amphi-naphthoquinone actually would give the same leather as the 2,6-diol, but the former was unobtainable and could not be tested.

To sum up, it is suggested that studies clarifying the influence of oxygen upon the tanning reaction have shed a new light on many tanning experiments conducted in the past. In the case of 2,6-naphthalenediol it was found that oxygen is responsible for its tanning ability, just as oxygen is necessary for the tanning action of picea-tannol, and for the same reason. Here, too, the tannage results from the oxidation to the quinone or to quinoid polymeric products.

Differences in tanning potency also exist between tanning in the presence or in the absence of air with synthetic polyphenols like methylenediresorcinol or dihydroxybenzhydrol. Tanning with these compounds is believed to mirror the vegetable tanning process; in both instances hydrogen bonds form between the aromatic tannin and the collagen molecule. This concept has been adopted by most workers in the field as a first approximation (13). Additional factors, principally the "trapping" of tannins inside the fine capillaries, contribute to the success of such a tannage. In the case of synthetic polyphenols it was demonstrated that the admission or exclusion of air also plays an important role. It is hoped that these observations on the role of oxygen will stimulate more experimental work and help us to understand more fully the mechanism of tanning with natural or synthetic polyphenols.

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Received July 16, 1962.

#### DISCUSSION

DR. WALLACE WINDUS (Eastern Regional Research Laboratory, Philadelphia, Pa.): Dr. Seligsberger's paper is an example of deductive reasoning from the known to the unknown, especially in reference to the 2,6-naphthalenediol.

I think it is gratifying to know more about the mechanisms of the reactions that take place in the production of leather. This knowledge may be theoretical at the time, but we always hope that, ultimately, it will lead to practical contributions. In any case it is a satisfaction in itself.

Some of the shrinkage temperatures in this work and in some of the earlier work are surprisingly high if we assume that the tanning mechanism is exclusively by hydrogen bonding. This bond is relatively weak, as exemplified by vegetable tanning. Perhaps some other factors are involved. Dr. Seligsberger suggested one possibility in the case of 2,4-dihydroxybenzhydrol—oxidation and polymerization—and this aspect may merit further attention.

Dr. Seligsberger and I have had some discussion as to who really deserves the credit for first describing the tanning action of the dimer, the 2,2', 4,4'-tetrahydroxydiphenylmethane. As Dr. Turley mentioned\*, Mr. Wolesenski of the National Bureau of Standards did very fine work in the middle twenties on the tanning action of a resorcinol-formaldehyde reaction product. He did not define its structure or attempt to determine any molecular weights.

I would like to ask Dr. Seligsberger if he feels that the earlier workers really had the dimer whereas Wolesenski may have had some other structure.

DR. SELIGSBERGER: By preparing the product described by Wolesenski, I received a solution which has tanning properties and gives leather with a shrinkage of about 84°C. However, the difference is that in following Wolesenski's directions for preparing the solution I used only a few drops of acid, but in preparing the methylenediresorcinol one has to use large excesses of acid, and the material precipitates out and has a white color. It is oxidized by air, forming a pinkish top layer over the powder, and is, as I found, almost insoluble in water on the acid pH side (about 1g/l at pH 3). As soon as one alkalinizes, the solubility goes up; so, obviously, here we have a different material from the one Wolesenski was using and which also has been used later on. The reason is that he boiled, and here boiling has to be avoided. Boiling, of course, condenses the resorcinol with the formaldehyde to give polymers.

\*JALCA, 57, 590 (1961).

DR. E. N. FILACHIONE (Eastern Regional Research Laboratory, Philadelphia, Pa.): Did you observe any effect at other pH values? I notice you used the strongly alkaline system. Would you get this same effect of air if you had some other pH values? You might expect this to work best in alkaline solutions, but I was just wondering about other pH ranges lower than the ones you investigated.

DR. SELIGSBERGER: I think that is a very good point. On the acid side tanning would be only possible in solvents, and I did not use any solvent tannage in the presence or absence of air. Maybe this should also be done to substantiate the work.

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*Reprinted from*  
THE JOURNAL *of the* AMERICAN LEATHER CHEMISTS ASSOCIATION  
Vol. LVIII, No. 1, January, 1963  
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