[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH CAROLINA]

Chemical Constitution and the Tanning Effect. III. Polyhydroxybenzophenones[1]

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Previous communications from this laboratory have described the tanning properties of the gallic acid esters of certain sugars.[4,5] From an observation of the type compounds that the natural tannins are believed to be, as well as these synthetic materials, there seems to be in every case a pattern consisting of at least two benzene nuclei joined by some type of bridge, and having a sufficient number of water solubilizing groups to import to the compound a moderate degree of water solubility. This pattern may be only a part of the molecule in some cases, but it always appears to be present. Also of the fission products of all the natural tannins, the polyhydroxybenzenes and the polyhydroxybenzoic acids are the main constituents.

The present investigation describes the preparation of a series of polyhydroxybenzophenones which conform to the above molecular pattern, and evaluation of these materials as tannins. A literature investigation of known compounds of this series revealed the fact that 3',4',2,4,6-pentahydroxybenzophenone,[6] commonly known as maclurin, which was isolated from the wood of *Chlorophora tinctoria*, precipitates gelatin from solution, an indication that this polyhydroxy compound might have tanning properties. Therefore, this compound was included in the series which was prepared and tested. In no case, however, did these substances exhibit tanning properties as described in detail below.

Experimental

Preparation of Materials.—The methyl ethers of vanillin, catechol, resorcinol, hydroquinone, pyrogallol and phloroglucinol were prepared by the procedure described in "Organic Syntheses," Coll. Vol. II, p. 619. Veratroyl chloride was prepared by the action of thionyl chloride on veratric acid which was obtained by the oxidation of veratraldehyde. Anisoyl chloride was obtained from anisic acid by the action of thionyl chloride.

Synthesis of the Polyhydroxybenzophenones.—Method I, a Friedel–Crafts reaction between the methoxybenzoyl chloride and the methoxybenzene followed by demethylation, gave better yields in the first step but the demethylation was unsatisfactory when the number of hydroxyl groups exceeded three. Method II, a dehydration reaction between the hydroxybenzoic acid and the hydroxybenzene in the presence of zinc chloride,[7] was used when the acid chloride was not available or when Method I did not give good results.

A. **Method I.**—A solution of one-half mole of the methoxybenzoyl chloride and one-half mole of the methoxybenzene in dry carbon disulfide was added slowly to one mole of anhydrous aluminum chloride and 200 g. of dry carbon disulfide maintained at 15–20° and contained in a one-liter, three-necked flask equipped with stirrer, reflux condenser, dropping funnel and thermometer. The solution was allowed to warm up to room temperature and stirring was continued for three hours. The mixture was then let stand overnight, refluxed for three and one-half hours, cooled, poured onto ice and extracted with ether. The extract was washed with sodium carbonate solution and with water, then dried over calcium chloride. The product, isolated from the ether, was recrystallized from 50% alcohol.

The methoxybenzophenone was converted to the hydroxybenzophenone by heating with an equal weight of anhydrous aluminum chloride in anhydrous toluene for one hour at 120°. The mixture was poured into iced dilute hydrochloric acid and the toluene layer was washed with water. The hydroxybenzophenone was extracted with sodium carbonate solution and precipitated from this solution by the addition of carbon dioxide or dilute hydrochloric acid. The lower members were recrystallized from dilute ethanol, the higher members from very dilute hydrochloric acid. Over-all yields up to 65% were realized.

B. **Method II.**—Equal parts of the hydroxybenzoic acid and the hydroxybenzene were heated together with three parts of freshly fused and powdered zinc chloride for forty-five minutes at 125–140°. The reaction mass was taken up in dilute hydrochloric acid, filtered, the solid product washed thoroughly with sodium bicarbonate solution and finally crystallized from dilute ethanol or very dilute hydrochloric acid.

Tanning Procedure

The standard gelatin test was used as a preliminary indication of the tanning properties of these compounds. In all cases, the solutions resulting from the first crystallization of the hydroxy ketones caused gelatin precipitation, however these solutions always contained either aluminum or zinc salts, as well as other impurities. After a second crystallization, the resulting saturated solutions of the hydroxy ketones would in no case cause gelatin precipitation. Pure synthetic maclurin behaved as described above. It is probable that the sample of natural maclurin which was reported to have the property of precipitating gelatin contained some tannin material as an impurity, since the original source of maclurin is known to contain tannins also.

The standard procedure previously described[4] for conducting tannage tests could not be used since the polyhydroxybenzophenones were not soluble enough in 4% aqueous sodium chloride. The following modified procedure was therefore employed:

A standard size test piece of calfskin was dehydrated by agitation with several portions of absolute ethanol. It was then covered with three times its weight of absolute ethanol, treated with 25% of its weight of the pure material to be tested, and the whole agitated for twenty-four hours. A comparison was then made between the

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[1] Abstracted from a thesis presented by George B. Butler to The Graduate School of the University of North Carolina in partial fulfillment of the requirements for the Ph.D. degree, June, 1942.

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[4] Russell and Tebbens, THIS JOURNAL, **64**, 2274 (1942).

[5] Russell, Tebbens and Arey, *ibid.*, **65**, 1472 (1943).

[6] Haas and Hill, "An Introduction to the Chemistry of Plant Products," Longmans, Green and Co., London, 1928.

[7] Blueler and Perkin, *J. Chem. Soc.*, **109**, 541 (1916).

TABLE I

Hydroxybenzophenone	Method of prepn.	M. p., °C.[a]	Empirical formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
3,4-Di-	I	132 (134)	$C_{13}H_{10}O_3$	...	..	...	..
4,4'-Di-	I	210 (210)	$C_{13}H_{10}O_3$	...	..	...	..
3,4,4'-Tri-	I	205	$C_{13}H_{10}O_4$	67.82	4.35	67.70	4.65
2,3,4-Tri-	I	118 (140)[b]	$C_{13}H_{10}O_4$	67.82	4.35	67.66	4.55
2,4,4'-Tri-	I	198 (200)	$C_{13}H_{10}O_4$	...	..	..	..
2',2,4-Tri-	II	138 (134)	$C_{13}H_{10}O_4$	...	..	...	..
2,4',5-Tri-	I	162	$C_{13}H_{10}O_4$	67.82	4.35	67.63	4.56
2',2,5-Tri-	II	98	$C_{13}H_{10}O_4$	67.82	4.35	67.70	4.39
2,3,4,4'-Tetra-	I	219	$C_{13}H_{10}O_5$	63.41	4.06	63.20	3.94
2,4,2',4'-Tetra-	II	180 (193)[c]	$C_{13}H_{10}O_5$	63.41	4.06	63.25	4.07
2,3,4,2',4'-Penta-	II	200 (168) (187)[d]	$C_{13}H_{10}O_6$	59.54	3.82	59.85	3.94
2',4',3,4,5-Penta-	II	253 (200)[e]	$C_{13}H_{10}O_6$	59.54	3.82	59.50	3.94
3',4',2,4,6-Penta-	I	220 (220)	$C_{13}H_{10}O_6$	...	..	...	..
2,3,4,3',4',5'-Hexa-	II	276 (273)	$C_{13}H_{10}O_7$	...	..	...	..
2,3,4,2',3',4'-Hexa-	II	240 (238)	$C_{13}H_{10}O_7$	...	..	...	..

[a] Melting points recorded in literature are enclosed in parentheses. [b] Reported to crystallize with one molecule of water of crystallization.[8] The monobenzoate of pyrogallol is also reported to have a melting point of 140°. [c] Reported to crystallize with 1.5 molecules of water of crystallization.[9] [d] Controversial melting points reported.[10] [e] Heilbron[11] lists this compound as having been reported by Korczynski and Nowakowski,[12] m. p. 242°. These authors reported 3',4',2,4,5-pentahydroxybenzophenone prepared by the Hoesch reaction between protocatechunitrile and 1,2,4-trihydroxybenzene, m. p. 242°.

test piece of skin and a similar piece of skin treated with mimosa tannin under the same conditions. While the piece of skin treated with mimosa tannin was converted to leather, in no case did the samples treated with the polyhydroxybenzophenones show any change. After thorough washing with cold water, and drying in air, these samples were converted to an inflexible, horn-like material characteristic of untreated skin. On storing samples of these test pieces in aqueous media, apparently normal putrefaction occurred.

The data concerning the polyhydroxybenzophenones are presented in tabular form.

Summary

Fifteen polyhydroxybenzophenones have been prepared and tested for tanning properties. None were found to have the property of converting hide to leather as judged by color, feel, texture, flexibility and fullness, even though one naturally occurring polyhydroxybenzophenone is reported in the literature to cause precipitation of gelatin, a preliminary test for tanning materials.

Four of these compounds have not previously been reported, while physical properties of four others reported in the literature are either controversial or fail to agree with those obtained in this investigation. Analyses are reported for these compounds.

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(8) Fischer and Rapaport, *Ber.*, **46**, 2393 (1913).

(9) Shoesmith and Haldane, *J. Chem. Soc.*, **125**, 113 (1924).

(10) Atkinson and Heilbron, *ibid.*, 2690 (1926).

(11) Heilbron, "Dictionary of Organic Compounds," Oxford University Press, New York, 1934.

(12) Korczynski and Nowakowski, *Bull. soc. chim.*, **43**, 335 (1928).

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

The Preparation of 4,5-Dimethylphenanthrene[1]

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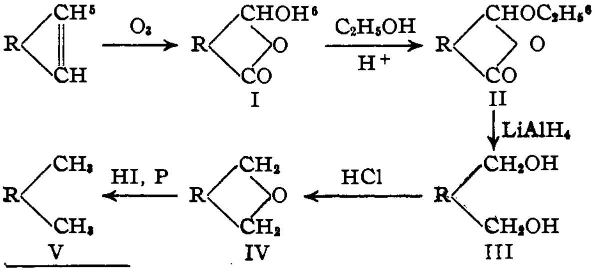
Considerable interest is associated with 4,5-dimethylphenanthrene (V) because of (1) its possible identity with the hydrocarbon,[3] $C_{16}H_{14}$, isolated from the dehydrogenation products of strophanthidin, and (2) its position as the parent hydrocarbon of compounds containing methyl groups in the so-called "impossible" positions.[4] In this paper we describe the preparation of V from pyrene by the steps outlined in the chart.



(1) The material herein presented is taken from the Ph.D. thesis of H. S. W., Ohio State University, December, 1948.

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(3) Lewis and Elderfield, *J. Org. Chem.*, **5**, 290 (1940); Jacobs and Fleck, *J. Biol. Chem.*, **97**, 57 (1932).

(4) See discussion in Newman, THIS JOURNAL, **62**, 2295 (1940), and Newman and Hussey, *ibid.*, **69**, 3023 (1947).

(5) R, $C_{14}H_8$, represents the phenanthrene nucleus carrying the substituents indicated in positions 4 and 5.

(6) Our reasons for preferring the cyclic structure for these compounds will be set forth in a forthcoming paper.