

containing tartaric acid. The red variety was converted into the black variety by heating at 115°.

X-Ray powder photographs were taken at room temperature using CuK and FeK radiation. The above red product, and a sample of the red sulfide from Kahlbaum, both gave photographs showing absolutely no evidence of a crystalline nature. The black variety prepared above gave a pattern identical with that of stibnite, both as to position and intensity of the lines, indicating that there could be little if any amorphous material in the product.

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Sulfonic Acid Esters of 4,4'-Dihydroxydiphenyl

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In connection with some other work in progress in this Laboratory a number of aryl sulfonic acid esters of 4,4'-dihydroxydiphenyl have been prepared. The method of preparation used was the same as that previously reported¹ except that the phenol (5 g.) was treated with 2.1 molecular proportions of the necessary acid chloride. The crystalline products were colorless except in the case of the *m*-nitrobenzenesulfonate, which was obtained as tan flakes. Of the esters, the benzene- and the *o*-nitrobenzenesulfonyl derivatives are best suited for use as derivatives for the identification of the phenol, for they are the ones most readily purified. The experimental results are summarized in Table I.

TABLE I
SULFONIC ACID ESTERS OF 4,4'-DIHYDROXYDIPHENYL

Sulfonyl chloride used	Solvent	Yield, ^a %	M. p., °C.	Formula	Analyses, %	
					Calcd.	Found
Benzene	<i>n</i> -PrOH	89	148	C ₂₄ H ₁₈ O ₆ S ₂	S, 13.73	13.97
<i>p</i> -Toluene	<i>n</i> -PrOH	Quant.	187-188 ^b	C ₂₆ H ₂₂ O ₆ S ₂		
<i>o</i> -Nitrobenzene	Gl. AcOH	Quant.	191-192	C ₂₄ H ₁₆ O ₁₀ N ₂ S ₂	S, 11.51	11.93
<i>m</i> -Nitrobenzene	Cyclohexanol	Quant.	216-217	C ₂₄ H ₁₆ O ₁₀ N ₂ S ₂	S, 11.51	11.51
<i>p</i> -Nitrobenzene	1,4-Dioxane	87	231	C ₂₄ H ₁₆ O ₁₀ N ₂ S ₂	S, 11.51	11.44
<i>p</i> -Bromobenzene	^c	Quant.	201-202	C ₂₄ H ₁₆ O ₆ Br ₂ S ₂	Br, 25.64	25.98

^a Crude product. ^b This compound was prepared by Gilman, Beaber and Myers [THIS JOURNAL, 47, 2047 (1925)] by treating the phenol with the acid chloride in the presence of potassium hydroxide. Benzene was used for crystallization and a product melting at 189-190° was obtained in 21.2% yield. ^c The compound was first dissolved in acetone and then precipitated by the addition of water; it was purified by crystallization from cyclohexanol and finally by washing with ethanol.

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(1) Hazlet, THIS JOURNAL, 59, 287 (1937).

Sterols. LXVII. Sarsasapogenin Derivatives. Bromo Compounds

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In a preceding paper¹ of this series the reaction of sarsasapogenin acetate with bromine to yield a monobromo derivative of the composition C₂₉-H₄₅O₄Br was described. We have made several additional observations which are of interest concerning the nature of the bromo compounds.

The great ease of bromination of sarsasapogenin and its derivatives is exemplified by the fact that sarsasapogenone reacts with one mole of bromine to give a compound which is identical with the compound formed when bromosarsasapogenin is oxidized at 25° with chromic anhydride.

The bromo compounds are peculiar in that they appear to be unaffected by boiling with pyridine or by treatment with pyridine and silver nitrate in the cold. The bromine is, however, easily eliminated by other reactions. Catalytic hydrogenation of bromosarsasapogenin acetate in hot acetic acid followed by hydrolysis gave a rather poor yield of dihydrosarsasapogenin.¹ Treatment of bromosarsasapogenin acetate with sodium and amyl alcohol gave a good yield of sarsasapogenin. Similar results were obtained with sodium and ethanol. Treatment of bromosarsasapogenin acetate with zinc dust and acetic acid gave sarsasapogenin acetate. Attempts to hydrolyze the bromo compounds with potassium acetate were unsuccessful, non-crystalline mixtures being obtained. Bromosarsasapogenin, upon Clemmensen reduction in alcohol solution with amalgamated zinc, gave a good yield of tetrahydrosarsasapogenin.

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(1) Marker and Rohrmann, *ibid.*, 61, 846 (1939).