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.

SCHOOL OF CHEMISTRY
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Sulfonic Acid Esters of 4,4′-Dihydroxydiphenyl

BY STEWART E. HAZLET

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 reported[1] 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	*n*-PrOH	89	148	$C_{24}H_{18}O_6S_2$	S, 13.73	13.97
p-Toluene	*n*-PrOH	Quant.	187–188[b]	$C_{26}H_{22}O_6S_2$		
o-Nitrobenzene	Gl. AcOH	Quant.	191–192	$C_{24}H_{16}O_{10}N_2S_2$	S, 11.51	11.93
m-Nitrobenzene	Cyclohexanol	Quant.	216–217	$C_{24}H_{16}O_{10}N_2S_2$	S, 11.51	11.51
p-Nitrobenzene	1,4-Dioxane	87	231	$C_{24}H_{16}O_{10}N_2S_2$	S, 11.51	11.44
p-Bromobenzene	[c]	Quant.	201–202	$C_{24}H_{16}O_6Br_2S_2$	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

BY RUSSELL E. MARKER AND EWALD ROHRMANN

In a preceding paper[1] of this series the reaction of sarsasapogenin acetate with bromine to yield a monobromo derivative of the composition $C_{29}H_{45}O_4Br$ 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.

We wish to thank Parke, Davis and Company for their generous support and assistance in the various phases of this work.

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

Experimental Part

Bromosarsasapogenin.—A solution of 820 mg. of sarsasapogenin in 50 cc. of glacial acetic acid was cooled to 20°. Two drops of 48% hydrobromic acid was added and 2.1 cc. of 1.05 *M* bromine in acetic acid solution run in dropwise. The bromine was taken up readily with the liberation of hydrogen bromide. The mixture was poured into water and the precipitated solid collected and washed with water. The residue was crystallized from aqueous acetone to give white needles which began to decompose at about 125°.

Anal. Calcd. for $C_{27}H_{43}O_3Br$: C, 65.4; H, 8.8. Found: C, 65.1; H, 8.8.

In carrying out the bromination of sarsasapogenin derivative on a somewhat larger scale (5–10 g.) the reaction mixture often became deep blue in color.

Bromosarsasapogenone from Bromosarsasapogenin.—To a solution of 100 mg. of bromosarsasapogenin in 50 cc. of glacial acetic acid was added 300 mg. of chromic anhydride in 10 cc. of 80% acetic acid. After standing at room temperature for forty minutes the mixture was poured into water, the precipitated material was extracted with ether and the ethereal extract washed with sodium carbonate solution and water. The ether was evaporated on the steam-bath and the residue crystallized from acetone to give pale tan crystals, m. p. 191° dec. This gave no depression with a sample of bromosarsasapogenone prepared by the direct bromination of sarsasapogenone.

Anal. Calcd. for $C_{27}H_{41}O_3Br$: C, 65.7; H, 8.4. Found: C, 65.3; H, 8.3.

Bromination of Sarsasapogenone.—Sarsasapogenone was treated with bromine as described in the preceding experiments. The material was crystallized from acetone to give white crystals, m. p. 190° dec. The material evidently was contaminated with some of the dibromo compound as is shown by the analysis. The material gave no depression with the product obtained in the preceding experiment.

Anal. Calcd. for $C_{27}H_{41}O_3Br$: C, 65.7; H, 8.4. Found: C, 65.1; H, 8.0.

Reduction of Bromosarsasapogenin Acetate. (a) **With Zinc and Acetic Acid.**—To a solution of 500 mg. of bromosarsasapogenin acetate in 50 cc. of glacial acetic acid heated on the steam-bath was added with shaking 3 g. of zinc dust in small portions over a period of twenty minutes. White crystals had separated out at the end of this time. The mixture was poured into water and extracted with ether. The ethereal extract was washed first with sodium carbonate solution and then with water. Evaporation of the ethereal solution gave a crystalline residue which was crystallized from acetone to give white needles, m. p. 142°; yield 250 mg. This gave no depression with an authentic sample of sarsasapogenin acetate. The mother liquors yielded some unchanged bromosarsasapogenin acetate.

(b) **With Sodium and Amyl Alcohol.**—To a boiling solution of 700 mg. of bromosarsasapogenin acetate in 50 cc. of *n*-amyl alcohol was added 2.5 g. of sodium in small pieces over a period of two hours. The mixture was cooled and shaken first with an excess of dilute hydrochloric acid and then with water. The amyl alcohol was evaporated on the steam-bath and the residue, after treatment with Norite, was crystallized from acetone to give white needles of sarsasapogenin, m. p. 197°, which gave no depression with an authentic sample.

Similar results were obtained with sodium and absolute ethanol.

(c) **By Catalytic Hydrogenation.**—A mixture of 1 g. of bromosarsasapogenin acetate, 0.5 g. of Adams catalyst, and 80 cc. of glacial acetic acid was shaken with hydrogen at 3 atmospheres and 70° for eight hours. The mixture was filtered and the filtrate evaporated *in vacuo*. The oily residue was diluted with water and the mixture extracted with ether. The ethereal solution was washed with water and the ether evaporated. The residue would not crystallize; it was refluxed for fifteen minutes with an excess of alcoholic potassium hydroxide, poured into water and extracted with ether. The ethereal extract was washed with water and the ether evaporated on the steam-bath. The residue was crystallized from ether–pentane to give white needles, m. p. 163°. This gave no depression with a sample of dihydrosarsasapogenin. The yield was rather poor and the mother liquors contained brominated products.

Anal. Calcd. for $C_{27}H_{46}O_3$: C, 77.4; H, 11.1. Found: C, 77.3; H, 11.2.

(d) **By Clemmensen Reduction.**—Reduction of 500 mg. of the bromoacetate by the Clemmensen method, as described in a previous paper for sarsasapogenin acetate gave a product which crystallized from acetone as compact white crystals, m. p. 191°; yield 375 mg. This gave no depression with an authentic sample of tetrahydrosarsasapogenin, m. p. 193°.

(e) **Treatment with Pyridine.**—Treatment of bromosarsasapogenin acetate with boiling pyridine for twelve hours did not remove the bromine. Treatment with pyridine and silver nitrate at 25° for twenty-four hours was likewise without effect on the substance.

Dibromosarsasapogenone.—To a solution of 7 g. of sarsasapogenone in 350 cc. of glacial acetic acid was added 5 drops of 48% hydrobromic acid and 33.8 cc. of 1.05 *M* bromine in glacial acetic acid was slowly run in over a period of forty minutes at room temperature. The solution became intensely blue and much hydrogen bromide was liberated. The solution was poured into 2 liters of water and the precipitate collected and washed with water. The dried material was crystallized from acetone–ethyl acetate to give small compact white crystals, m. p. 190° dec.

Anal. Calcd. for $C_{27}H_{40}O_3Br_2$: C, 56.7; H, 7.1. Found: C, 57.2; H, 7.3.

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Sterols. LXVIII. Highly Branched Aliphatic Esters of Estrone and α-Estrodiol

BY RUSSELL E. MARKER AND EWALD ROHRMANN

The trimethylacetates and the *t*-butylacetates of estrone and α-estrodiol were prepared by the