TABLE I

PREPARATION DETAILS AND ANALYSES

Product	Starting compound	Yield G.	Yield %	M. p. or b. p. °C.	M. p. or b. p. Mm.	Physical form, color	Analysis Calcd.	Analysis Found
o-$CH_3C_6H_4SeH$	*o*-$CH_3C_6H_4Br$	85.5	35	41	99	25	Colorless		
m-$CH_3C_6H_4SeH$	*m*-$CH_3C_6H_4Br$	85.5	40	47	89	16	liquid		
o-$CH_3C_6H_4SeO_2H$	*o*-$CH_3C_6H_4SeH$	4.0	3.3	72	123–125		White needles	C 41.38	C 41.03
									H 3.91
m-$CH_3C_6H_4SeO_2H$	*m*-$CH_3C_6H_4SeH$	7.0	5.7	96	118–119		White needles or plates	H 3.94	C 41.46
									H 4.07

The compounds are colorless liquids when absolutely pure, but rapidly turn yellow on contact with the air. Direct analyses were found to be impracticable because their acid nature renders the Parr bomb method inapplicable and their instability and toxic properties make handling for carbon and hydrogen determinations difficult. For identification, they were converted to the acids $CH_3C_6H_4SeO_2H$[2] by dissolving in nitric acid and these compounds analyzed for carbon and hydrogen. This does not distinguish them from the ditolyl diselenides, which would behave in the same way, but the boiling points were much too low for them to have been diselenides. The copper salts were also prepared by standard means.[3] They were blue crystalline solids without m. p.

(2) Pyman, *J. Chem. Soc.*, [1] **115**, 166 (1919).

(3) Stoecker and Krafft, *Ber.*, **39**, 2200 (1906).

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Note on the Preparation of *d*-Galacturonic Acid

BY IRA A. MANVILLE, FRANCIS J. REITHEL AND PAUL M. YAMADA

In a recent article[1] there was described a method for the enzymic preparation of *d*-galacturonic acid from polygalacturonic acid. We have had the pre-publication privilege of using this method for preparing the *d*-galacturonic acid necessary for our work on its nutritional significance. It was found in our laboratory that the method, though far superior to former methods in many respects, gave varying yields. Although this in no way detracted from the excellence of the method, it posed the question as to what factors should be considered in improving the yield.

First of all we tried different pectins. Of these, there seemed to be considerable variation even between "batches." Most satisfactory in our work was General Food's Certo Apple Pectin RX 1 or 2. California Fruit Exchange Citrus Pectin, Sample B-6712, also gave good results. We are not prepared to explain why these are better, but simply state the result of empirical observations and call attention to the importance of this detail.

Secondly, we found that in the preparation of pectic (polygalacturonic) acid, it was quite necessary for the best yield to remove the last trace of the calcium chloride which we used for controlling the swelling of the pectin. This was accomplished as follows. After swelling the pectin in alcohol and calcium chloride, adding sodium hydroxide, acidifying and washing (until no precipitate resulted upon the addition of sodium oxalate or five volumes of alcohol), the resultant pectic acid was suspended again in a volume of water equivalent to that of the alcohol. About half as much sodium hydroxide was added as before. It was then acidified and washed again. The pectic acid obtained has no contamination with pectin or calcium chloride. That the concentration of calcium chloride affects enzymic action is shown by the fact that addition of calcium chloride to the enzyme–pectic acid mixture will inhibit the action of the enzyme.

Thirdly, we found that of those preparations tried, only Röhm and Haas Pectinase 46 AP seemed to yield satisfactory results. This is the enzyme contained in the preparation used by Mottern and Cole.

Several other minor points should be mentioned. After enzyme action is complete, we find it advantageous to add the sulfuric acid before filtration. Further, it is often wise to work up the sludge from the alcohol precipitation by treating it with small amounts of sulfuric acid and carrying it on in the same manner as the original material.

By carefully observing all these points in technique, we have been able to obtain yields as high as 36% of the theoretical and have had no difficulty in obtaining a very pure product which, after recrystallization in the β-form from boiling absolute alcohol, has a melting point of 160°.

The purpose of this note is to aid those using

(1) Mottern and Cole, THIS JOURNAL, **61**, 2701 (1939).

Mottern and Cole's method for the first time in obtaining the best results possible. Full acknowledgment is made to Mottern and Cole for their kindness in letting us use their method and for supplying us with goodly quantities of *d*-galacturonic acid.

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Sterols. LXXIV. Acetic Acid Derivatives of Estrone and α-Estradiol

BY RUSSELL E. MARKER AND EWALD ROHRMANN

Estratriene-1,3,5-one-17-oxyacetic acid-3 was first prepared by Ercoli and Mamoli[1] by treatment of estrone in aqueous potassium hydroxide solution with chloroacetic acid. In the present work the 3-oxyacetic acid derivatives of estratriene-1,3,5-one-17-ol-3 and of estratriene-1,3,5-diol-17(α),3 were prepared by the reaction of these substances with ethyl chloroacetate in the presence of an excess of an ethanolic solution of sodium ethylate. Estratriene-1,3,5-one-17-ol-3 was also caused to react in a similar way with α-chloropropionic acid to yield estratriene-1,3,5-one-17-oxymethylacetic acid-3. The acidic substances were characterized further by the formation of the methyl esters.

We wish to thank Parke, Davis and Company for their generous support and assistance rendered during the course of this work.

Experimental Part

Estratriene-1,3,5-one-17-oxyacetic Acid-3.—To a boiling solution of 1 g. of estrone in 40 cc. of absolute ethanol was added 3.5 cc. of ethyl chloroacetate and a solution of 600 mg. of sodium in 20 cc. of ethanol. The mixture was refluxed on the steam-bath for fourteen hours after which 2 g. of potassium hydroxide was added and the refluxing continued for one hour. The mixture was diluted with water and the clear solution acidified with hydrochloric acid. The white solid was taken up in ether and the ethereal solution washed with water and 5% sodium carbonate solution. Evaporation of the ether yielded approximately 150 mg. of unreacted estrone.

The sodium carbonate washing was acidified with hydrochloric acid and the white solid taken up in ether. Evaporation of the ether gave a product which crystallized from aqueous acetone as small white plates, m. p. 209–211°; yield, 750 mg.

Anal. Calcd. for $C_{20}H_{24}O_4$: C, 73.2; H, 7.4. Found: C, 73.5; H, 7.5.

When the reaction was carried out using equivalent amounts of sodium and ethyl chloroacetate, only a poor yield of the acid was obtained.

A solution of 50 mg. of the acid in 10 cc. of 80% ethanol was refluxed for one hour with 75 mg. of hydroxylamine hydrochloride and 100 mg. of sodium acetate. The product was crystallized from 80% ethanol to give white crystals of the **oxime**, m. p. 230–232° dec.

Anal. Calcd. for $C_{20}H_{25}O_4N$: C, 69.9; H, 7.3. Found: C, 70.0; H, 7.4.

The **methyl ester** was prepared by treating 150 mg. of the acid in ether–methanol solution with an excess of an ethereal solution of diazomethane. The product was crystallized from aqueous acetone as white crystals, m. p. 130–132°.

Anal. Calcd. for $C_{21}H_{26}O_4$: C, 73.6; H, 7.7. Found: C, 73.5; H, 7.8.

Estratriene-1,3,5-ol-17(α)-oxyacetic Acid-3.—This was prepared from estratriene-1,3,5-diol-3,17(α) as described for estratriene-1,3,5-one-17-oxyacetic acid-3. The product was crystallized from aqueous acetone to give white crystals, m. p. 182–184°.

Anal. Calcd. for $C_{20}H_{26}O_4$: C, 72.7; H, 7.9. Found: C, 72.6; H, 7.9.

Treatment of the acid in ether–methanol solution with diazomethane yielded the **methyl ester** which crystallized as white crystals from ether–pentane, m. p. 94–96°.

Anal. Calcd. for $C_{21}H_{28}O_4$: C, 73.2; H, 8.2. Found: C, 73.3; H, 8.1.

Estratriene-1,3,5-one-17-oxymethylacetic Acid-3.—This was prepared from estrone and α-chloropropionic acid as described for the preparation of estratriene-1,3,5-one-17-oxyacetic acid-3 except that about three times as much sodium was used. The product was crystallized from aqueous acetone as white crystals, m. p. 195–198°.

Anal. Calcd. for $C_{21}H_{26}O_4$: C, 73.6; H, 7.7. Found: C, 73.3; H, 7.7.

Treatment of the acid in methanol–ether solution with diazomethane yielded the **methyl ester** which crystallized from aqueous acetone as small white crystals, m. p. 137–139°.

Anal. Calcd. for $C_{22}H_{28}O_4$: C, 73.9; H, 7.9. Found: C, 74.1; H, 7.9.

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(1) Ercoli and Mamoli, *Gazz. chim. ital.*, **68**, 142 (1938).

Identification of Propionic Acid in the Presence of Acetic and Butyric Acids

BY LOUIS MUSICANT AND FRANK J. KASZUBA

Pure propionic acid may be tested for readily in a number of ways, namely, as a derivative of *p*-toluidine,[1] benzylisothiourea[2] and the like; by the formation of 2-ethylbenzimidazole[3]; by its reac-

(1) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley & Sons, Inc., New York, N. Y., pp. 95, 144.
(2) S. Veibel and H. Lillelund, *Bull. soc. chim.*, [5] **5**, 1153 (1938).
(3) W. O. Pool, H. J. Harwood and A. W. Ralston, THIS JOURNAL, **59**, 178 (1937).