

0° with a hydrocarbon solution of 3,5-dinitrobenzoyl chloride.

The yield of ester is affected rather critically by the temperature, the nature and concentration of the alkali, and to a lesser extent by the catalytic effect of sodium acetate. Preliminary experiments showed that it was necessary to dissolve the solid dinitrobenzoyl chloride in an inert solvent so as to keep it in a liquid phase during the course of the reaction. When ether is used for this purpose the melting points of the esters, with the exception of ethyl, are consistently low. This is true even when extreme care is taken to remove all alcohol from the ether and therefore must be due to cleavage of the ether. Benzene is satisfactory except for its high melting point and this is easily lowered by the addition of dry ligroin.

Although the yield of ethyl ester is greater at 0° than at room temperature, it is not necessary to employ the difficultly-maintained lower temperatures. The yield of ethyl ester is four times as great when formed in the presence of 5% sodium hydroxide as it is when a similar concentration of sodium carbonate is used, and weaker bases such as sodium bicarbonate give negligible yields of the ester. Increasing the concentration of sodium hydroxide in the reaction mixture at 0° increased the yield of ethyl ester as shown in Fig. 1. It is impractical to use concentrations of sodium hydroxide in excess of 20% because the reaction mixture becomes semi-solid and difficult to handle.

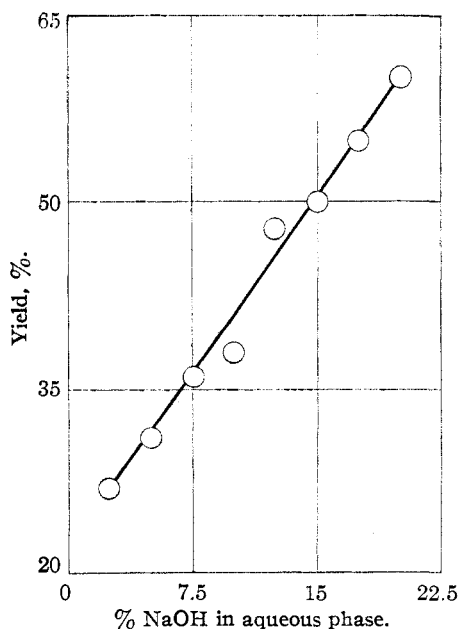


Fig. 1.

**Reagent.**—To 25 g. of 3,5-dinitrobenzoyl chloride is added 50 ml. of dry sulfuric acid-washed ligroin and the resulting solution is then diluted to 250 ml. with dry benzene.

**Procedure.**—One-half gram of sodium acetate crystals is dissolved in 10 ml. of a 5% aqueous solution of the alcohol, then 10 ml. of 40% sodium hydroxide is added and the solution cooled to 0°. Five ml. of the solution of 3,5-dinitrobenzoyl chloride in benzene–ligroin is then added and the mixture alternately shaken and placed in an ice-bath for one-half hour. The mixture is then transferred to a separatory funnel and extracted with 30 ml. of ether. The ether solution is washed with an equal volume of water, then 5% hydrochloric acid, and again with water. Evaporation of the solvent yields the crude derivative as recorded in Table I.

TABLE I

Alcohol	SUMMARY OF RESULTS			
	Crude ester, g.	Yield, %	M. p. of crude ester, °C.	M. p. in lit., <sup>a</sup> °C.
Methyl	0.09 <sup>b</sup>	17	94–96	107
Ethyl	.27	52	90–91	93
<i>n</i> -Propyl	.37	67	72–73	74
Isopropyl	.10	18	117–118	122
<i>n</i> -Butyl	.37	64	62–63	64
<i>s</i> -Butyl	.06	10	72–73	75
Isobutyl	.30	52	83–84	86
<i>t</i> -Butyl	.01	1		142
Allyl	.22	42	40–41	48

<sup>a</sup> Shriner and Fuson, "Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 2nd Ed., 1940, p. 185. <sup>b</sup> Obtained only after three successive additions and shakings with the acid chloride solution.

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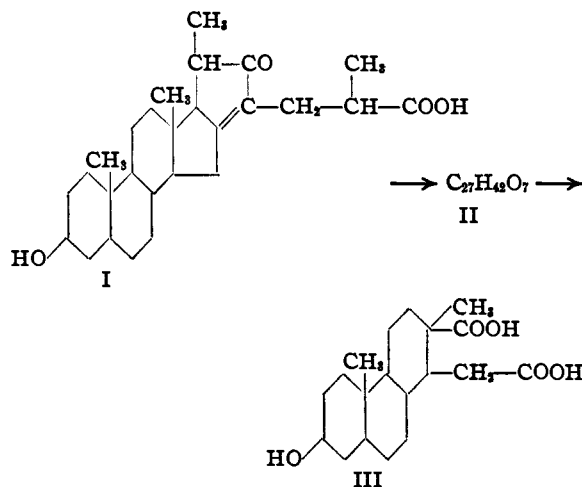
### Sterols. CXXVI. Sapogenins. LII. The Structure of the Side Chain of Sarsasapogenin. The Identification of the Acid Obtained by the Haloform Reaction on the Dibasic Acid from the Potassium Permanganate Oxidation of Anhydrosarsasapogenic Acid

BY RUSSELL E. MARKER AND ANTHONY C. SHABICA

We have repeated the experiment of Fieser and Jacobsen<sup>1</sup> on the hypohalite oxidation of the dibasic acid (II)<sup>2</sup> obtained by the permanganate oxidation of anhydrosarsasapogenic acid (I).<sup>3</sup> We obtain an acid which corresponds with that of Fieser and Jacobsen.<sup>1</sup> We find, however, that it is the known 3( $\beta$ )-hydroxy-etio-bilanic acid (C<sub>19</sub>-H<sub>30</sub>O<sub>5</sub>) (III) and not the C<sub>25</sub> acid suggested by them. Although the analyses might fit either

- (1) Fieser and Jacobsen, *THIS JOURNAL*, **60**, 2753 (1938).
- (2) Marker and Rohrmann, *ibid.*, **61**, 2072 (1939).
- (3) Marker, Shabica and Turner, *ibid.*, **63**, 2274 (1941).

formula, the properties and mixed melting point determination definitely indicate acid III. It should be noted that the hypohalite oxidation is not a simple one. Two treatments are required.



We wish to thank Parke, Davis and Company for assistance.

### Experimental Part

**Haloform Reaction on the Dibasic Acid<sup>2</sup> Obtained from the Potassium Permanganate Oxidation of Anhydrosarsapogenoic Acid.**<sup>2</sup>—The dibasic acid was obtained according to the method described by Fieser and Jacobsen<sup>1</sup> by the oxidation of anhydrosarsapogenoic acid with potassium permanganate in alkali. It gave no silver mirror when heated with ammoniacal silver nitrate. This casts doubt on its being an alpha keto acid<sup>1</sup> and favors the  $\text{C}_{27}\text{H}_{48}\text{O}_7$  formula.<sup>2</sup>

To a solution of 1 g. of the dibasic acid in 15 cc. of dioxane was added 10 cc. of 10% sodium hydroxide solution and the mixture was treated at 60° with iodine-potassium iodide (200 g. of potassium iodide, 100 g. of iodine and 800 cc. of distilled water) until the color persisted for two minutes. No iodoform separated on dilution. The solution was acidified and the acids were filtered. They were dissolved in 15 cc. of 5% sodium hydroxide and heated with the potassium iodide-iodine solution on a steam-bath for five minutes. Water was added and the iodoform was filtered. The alkaline solution was acidified and the product was extracted with ether. The ethereal extract was washed well with water, sodium bisulfite solution and finally again with water. The ether was removed and the residue was treated in acetone with Norite. Upon standing with 50% acetone-water in a refrigerator overnight, a crystalline product separated. It was very soluble in acetone and only a small amount of material was obtained. It was crystallized from chloroform; m. p. 220–222°; yield about 50 mg. When mixed with an authentic sample of 3(β)-hydroxyetio-bilanic acid, there was no depression in melting point.

*Anal.* Calcd. for  $\text{C}_{19}\text{H}_{30}\text{O}_5$ : C, 67.4; H, 8.9; neut. equiv., 169.1. Found: C, 67.2; H, 8.9; neut. equiv., 174.2.

The residue after the evaporation of the above mother liquor was refluxed for thirty minutes with 20 cc. of acetic anhydride. The excess acetic anhydride was vacuum distilled and the residue was sublimed in a high vacuum at 185–190°. The sublimate crystallized from ether as flat prisms; m. p. 202–203.5°. When mixed with an authentic sample of the acetate of the anhydride of 3(β)-hydroxyetio-bilanic acid, m. p. 202–204°, there was no depression in melting point.

*Anal.* Calcd. for  $\text{C}_{21}\text{H}_{30}\text{O}_5$ : C, 69.6; H, 8.3. Found: C, 69.4; H, 8.3.

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### The Absorption Spectra of Para- and Diamagnetic Nickel Complexes

BY J. E. MILLS AND D. P. MELLOR

Attention has been drawn recently to what appears to be a correlation between the color and magnetic properties of nickel complexes.<sup>1</sup> Many paramagnetic nickel complexes are some shade of green or blue while diamagnetic complexes, as a rule, have colors ranging from bright red through reddish-brown to various shades of yellow. In the course of an extended survey of the magnetic properties of nickel complexes carried out in this Laboratory, it has become increasingly clear that little reliance can be placed on the above correlation. It has been shown, for example, that vermillion bis-1-hydroxy-acridine-nickel is paramagnetic ( $\mu = 3.2$  Bohr magnetons) and that green bis-formylcamphor-ethylenediamine-nickel is diamagnetic.

In order to determine what influence the magnetic condition of the nickel atom has on the absorption of light by its complexes, a systematic examination of the absorption spectra of para- and diamagnetic complexes in solution has been initiated. Wherever possible, a comparison has been made between the absorption spectrum of the metal-free and the metal-containing compound. Attention has so far been confined largely to complexes in which the nickel atom is linked to (a) two nitrogen and two oxygen atoms as in bis-salicylaldehyde nickel, or (b) to four oxygen atoms as in bis-acetylacetone-nickel. Complexes belonging to the latter group are always paramagnetic, while those belonging to the former may be either para- or diamagnetic. It was possible with these compounds to search for

(1) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 122; D. P. Mellor and D. P. Craig, *J. Proc. Roy. Soc. N. S. W.*, **74**, 475 (1940).