mained unchanged. The yield of pure α_2-sitosteryl *m*-dinitrobenzoate was only 0.4 g. An attempt to increase the yield by recrystallization of the material in the mother liquors was unsuccessful.

α_2-Sitosteryl *m*-dinitrobenzoate melted at 206°. It is much more soluble than α_1-sitosteryl *m*-dinitrobenzoate, and forms needles which are white with a yellowish tint. It gives a depression of the melting point when mixed with the α_1-*m*-dinitrobenzoate; $[\alpha]^{30}\text{D}$ +26.4° (24.2 mg. in 2 cc. of chloroform solution gave $\alpha^{30}\text{D}$ +0.32°).

Anal. Calcd. for $C_{37}H_{52}N_2O_6$: C, 71.57; H, 8.45; N, 4.51. Found: C, 71.70, 71.71; H, 8.24, 8.20; N, 4.81.

Titration with Perbenzoic Acid.—Twenty-four and two-tenths milligrams took up 1.38 mg. of oxygen on standing for four days at 0° with an excess of perbenzoic acid. This is equivalent to 2.26 atoms of oxygen. In another experiment 34.4 mg. took up 1.65 mg. of oxygen on standing for two days at 0°. This is equivalent to 1.82 atoms of oxygen. These values are not as good as in α_1-sitosteryl *m*-dinitrobenzoate. They do show, however, the presence of two double bonds.

α_2-Sitosterol.—The *m*-dinitrobenzoate described above was hydrolyzed on the water-bath with a 5% alcoholic solution of potassium hydroxide. The free sterol was recrystallized from alcohol and petroleum ether.

α_2-Sitosterol melts at 156°. It is soluble in the common solvents; $[\alpha]^{25}\text{D}$ +3.5° (22.6 mg. in 2 cc. of chloroform solution gave $\alpha^{25}\text{D}$ +0.04°).

Anal. Calcd. for $C_{30}H_{50}O$: C, 84.43; H, 11.82. Found: C, 84.40; H, 11.91.

α_2-Sitosteryl Benzoate.—α_2-Sitosterol was dissolved in pyridine and treated with benzoyl chloride. The solution was kept on the water-bath for one hour. The product was worked up in the usual manner. The benzoate was purified by recrystallization from a mixture of benzene and alcohol.

α_2-Sitosteryl benzoate is very soluble in benzene, and sparingly soluble in alcohol. It forms needles which melt at 164–166°. The melting point is not depressed by α_1-sitosteryl benzoate. $[\alpha]^{26}\text{D}$ +27.4° (25.6 mg. in 2 cc. chloroform solution gave $\alpha^{26}\text{D}$ +0.35°).

Anal. Calcd. for $C_{37}H_{54}O_2$: C, 83.71; H, 10.26. Found: C, 83.59, 83.39; H, 10.19, 10.32.

α_2-Sitosteryl Acetate.—α_2-Sitosterol was converted into its acetate by heating with acetic anhydride for one hour in a boiling water-bath. The acetate was recrystallized from alcohol. It forms small leaflets which melt at 124–126°. It is soluble in most solvents, but only sparingly soluble in methyl alcohol $[\alpha]^{27}\text{D}$ +16.5° (24.2 mg. in 2 cc. of chloroform solution gave $\alpha^{27}\text{D}$ + 0.20°).

Anal. Calcd. for $C_{32}H_{52}O_2$: C, 81.98; H, 11.19. Found: C, 81.75, 81.83; H, 11.07, 11.28.

We wish to express our thanks to Merck and Company, Inc., Rahway, N. J., for all the analyses in this article and for a grant-in-aid for this work.

Summary

Two new double unsaturated sterols have been isolated in a pure state from the most soluble fraction of the sitosterol complex obtained from wheat germ oil and formerly named by Anderson α-sitosterol.

The acetates, benzoates and *m*-dinitrobenzoates of these two sterols have been prepared and characterized.

α_1-Sitosterol is an isomer of stigmasterol.

α_2-Sitosterol is probably a homolog.

PRINCETON, N. J. RECEIVED OCTOBER 19, 1936

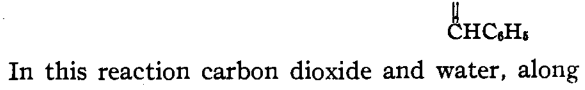
[CONTRIBUTION FROM THE PEDIATRIC RESEARCH LABORATORY OF THE JEWISH HOSPITAL OF BROOKLYN]

The Synthesis of Benzalphthalane

BY SAMUEL NATELSON AND AARON PEARL

In a recent paper[1] the relationship between benzalphthalide and certain naturally occurring materials was pointed out and a procedure for its conversion to compounds related to this series was demonstrated.

Since the hitherto unknown benzalphthalane offered promise of becoming a valuable intermediate in this field of research, its synthesis appeared desirable. An unsuccessful attempt was made to obtain this product by condensation of phthalide with phenylacetic acid as follows



In this reaction carbon dioxide and water, along with large yields of phthalide and toluene, were formed. Since phenylacetic acid under similar conditions does not evolve carbon dioxide, benzalphthalane was probably the initial reaction product but immediately hydrolyzed in accordance with the equation

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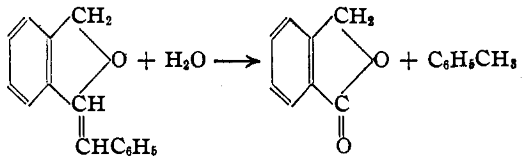
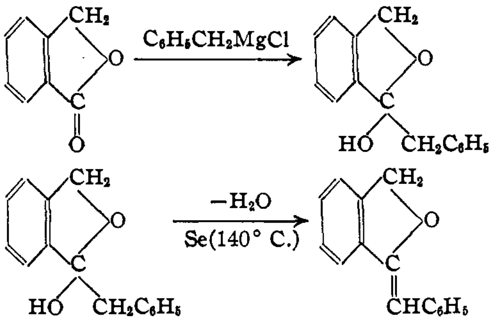
[1] Natelson and Gottfried, THIS JOURNAL, **58**, 1432 (1936).



However, a very satisfactory synthesis was effected by conversion of phthalide through a Grignard synthesis, employing benzylmagnesium chloride, to 1-benzyl-1-hydroxyphthalane, followed by dehydration of this product with the use of selenium.



Benzalphthalane is observed to be split readily, to yield phthalide, by numerous acidic or basic reagents, or even on exposure to air for several months. Because of this instability and the excellent results now obtained with derivatives of benzalphthalide, the application of the former in synthesis has been abandoned in favor of the latter.

Reaction between Phthalide and Phenylacetic Acid.—In four experiments 27 g. of phthalide, 27.5 g. of phenylacetic acid, 2 g. of freshly fused sodium acetate, and a pinch of pumice were heated in a sand-bath until the melt reached 140, 160, 180 and 230°, respectively. At 140° some water and carbon dioxide were evolved and at 180° all of the carbon dioxide was evolved. Even when a temperature of 230° was maintained for three hours, the reaction mixture, recrystallized from carbon bisulfide, yielded 25 g. of phthalide (m. p. 74.5°). (*Anal.* Calcd. for $C_8H_6O_2$: C, 71.64; H, 4.55. Found: C, 71.73; H, 4.61.) Distillation of the filtrate gave a fraction of b. p. 110° which was identified as toluene. In no case was benzalphthalane obtained.

In confirmation of the assumption that benzalphthalane is an intermediary product in the above reactions, it was found that phenylacetic acid either alone or admixed with fused sodium acetate does not evolve carbon dioxide when heated to 180°.

1-Benzyl-1-hydroxyphthalane.—An ether solution of benzylmagnesium chloride, prepared by dissolving 10 g. of magnesium in a solution of 60 g. of benzyl chloride in 300 cc. of anhydrous ether was added drop by drop with vigorous stirring to a cooled suspension of 52 g. of phthalide, prepared by the method of Russert,[2] in 200 cc. of anhydrous ether. As the Grignard reagent hits the phthalide suspension a vigorous reaction ensues and an orange color appears which disappears on stirring. After the addition was complete the reaction mixture was stirred for thirty minutes longer and then allowed to stand well corked overnight. Crushed ice and 380 cc. of 10% sulfuric acid were then added, the mixture was well shaken and the ether layer separated. The lower layer was again washed with ether and the combined ether washings were dried over anhydrous sodium sulfate and evaporated on a steam-bath. The oily residue crystallizes on stirring and cooling with alcohol and petroleum ether mixture and may be recrystallized from alcohol or from carbon bisulfide in long white needles; m. p. 137° yield 50 g.; insol. petroleum ether, sol. alcohol and carbon bisulfide.

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.64; H, 6.19. Found: C, 79.33; H, 6.44.

Benzalphthalane. Method 1.—Fifty grams of 1-benzyl-1-hydroxyphthalane is ground with 5 g. of selenium and heated on a sand-bath to 140°. The water given off is collected through a bent tube into a graduated cylinder. When the water ceases to come off, the material is allowed to cool and is recrystallized from alcohol, in which it is rather insoluble when cold. Benzalphthalane crystallizes as wedge-shaped golden crystals, m. p. 94°; yield 42 g.

Anal. Calcd. for $C_{15}H_{12}O$: C, 86.53; H, 5.77. Found: C, 86.33; H, 5.93.

Method 2.—To 50 g. of 1-benzyl-1-hydroxyphthalane was added 20 g. of cold concd. sulfuric acid. The mixture was shaken and then gently warmed to 40° for a few minutes. The mixture was allowed to come to room temperature and washed free of sulfuric acid with water and recrystallized from alcohol; m. p. 94°; yield 10–18 g.

Summary

1. Benzalphthalane is prepared by dehydration of 1-benzyl-1-hydroxyphthalane formed by the action of benzylmagnesium chloride on phthalide.

2. The reaction between phthalide and phenylacetic acid in the presence of sodium acetate is studied and a rationale proposed for the inability to obtain benzalphthalane from this reaction mixture.

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[2] Russert, *Ber.*, **46**, 1489 (1913).