tion of 3,9-dimethyl-1,2-benzanthracene, and it offers promise of being capable of wide application and modification. Two variations of the new method, however, were applied without success to the problem at hand, steric hindrance again proving to be an obstacle in essential stages of the synthesis.

In the course of the work, practical methods were developed for preparing the 1,8-methylbromo, methylchloro, chlorobromo, bromoiodo, and dibromo derivatives of naphthalene, and 1-methyl-4-bromonaphthalene.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASSACHUSETTS

RECEIVED NOVEMBER 4, 1938

[CONTRIBUTION FROM THE SQUIBB INSTITUTE FOR MEDICAL RESEARCH, DIVISION OF ORGANIC CHEMISTRY]

Brassicasterol. I. Empirical Formula and Hydrogenation

BY ERHARD FERNHOLZ AND HOMER E. STAVELY

Brassicasterol is a phytosterol first isolated from rapeseed oil by Windaus and Welsch[1] and has since received little attention. Schmid and Waschkav[2] reported a crystallographic examination of the tetrabromide of brassicasteryl acetate and found it to be similar to the corresponding derivative of stigmasterol.

The brassicasterol reported by Windaus and Welsch[1] was isolated from a technical waste by-product of rapeseed oil refining. We thought it possible that the sterol had not originally been present in the raw oil, but had resulted from isomerization of stigmasterol in the presence of the concentrated sulfuric acid used in the refining process. In order to remove this uncertainty in the present investigation, we have used an unrefined rapeseed oil of Japanese origin.[3] However, the brassicasterol isolated by us had practically the same physical constants as those given by Windaus and Welsch.[1] Brassicasterol is, therefore, very similar to, but not identical with stigmasterol.

From analyses of the tetrabromide acetate and propionate Windaus and Welsch[1] gave an empirical formula $C_{28}H_{46}O$ for brassicasterol. Experience has shown that combustions of bromides do not give analyses sufficiently accurate to distinguish between homologs. Dinitrobenzoates[4] give more reliable data for this purpose, even though the analytical differences between homologs are smaller. Analytical results of brassicasteryl dinitrobenzoate and brassicastyl dinitrobenzoate indicate an empirical formula $C_{29}H_{48}O$ for brassicasterol, identical with that of stigmasterol.

(1) Windaus and Welsch, *Ber.*, **42**, 612 (1909).
(2) Schmid and Waschkav, *Monatsh.*, **48**, 139 (1927).
(3) Courtesy of Welch, Holme and Clark.
(4) Windaus, Von Werder and Oeshaider, *Ber.*, **65**, 1006 (1932).

Catalytic hydrogenation of brassicasterol gave a saturated sterol not identical with stigmasterol, as shown in Table I. Hence the difference between

TABLE I

Substance	M. p., °C.	$[\alpha]^{25}D$
Stigmastanol	137	+25
Stigmastyl acetate	131	+15
Stigmastyl *m*-dinitrobenzoate	215	+13
Brassicastanol	142	+24
Brassicastyl acetate	143	+15
Brassicastyl *m*-dinitrobenzoate	202	+14

stigmasterol and brassicasterol does not lie in the position of a double bond, but in the carbon skeleton.

Brassicastanol is also different from ostreastanol.[5]

Experimental

Isolation of Brassicasterol.—Unrefined rapeseed oil (6.8 kg.) was saponified with methanolic potassium hydroxide and the unsaponifiable matter extracted with ether, giving 20.4 g. of crude crystalline sterol after crystallization from ethanol. It was acetylated with acetic anhydride and brominated according to the method of Windaus and Welsch.[1] The yield of tetrabromide was much less than that reported by these authors; 1.1 g. of pure tetrabromide was obtained; m. p. 205° (dec.). The bromination mixture had to be kept for several days for complete precipitation of the tetrabromide.

Debromination yielded an acetate whose m. p. could not be raised above 152° (Windaus and Welsch[1] reported 157–159°); $[\alpha]^{22}D$ −65° (20.0 mg. in 2.06 cc. chloroform, $\alpha^{26}D$ −0.63, 1-dm. tube) (not previously reported).

By saponification brassicasterol was obtained; m. p. 146°; $[\alpha]^{22}D$ −61° (Windaus and Welsch reported m. p. 148°, $[\alpha]D$ −64°).

Brassicasteryl *m*-Dinitrobenzoate.—Brassicasterol (0.45 g.) and an excess of *m*-dinitrobenzoyl chloride in pyridine were heated on a steam-bath. The ester was recrystallized from benzene by addition of ethanol giving rhombic plates,

(5) Bergmann, *J. Biol. Chem.*, **104**, 553 (1934).

m. p. 219°, $[\alpha]^{25}D$ −28° (18.7 mg. in 2.0 cc. chloroform, $\alpha^{25}D$ −0.26, 1-dm. tube). *Anal.* Calcd. for $C_{35}H_{48}O_6N_2$: C, 70.92; H, 8.16. Calcd. for $C_{36}H_{50}O_6N_2$: C, 71.25; H, 8.30. Found: C, 71.24, 71.15; H, 8.24, 8.28.[6]

Hydrogenation of Brassicasterol.—Brassicasterol (0.13 g.) in ethanol was hydrogenated at atmospheric pressure in the presence of 0.1 g. of palladium black for twenty-four hours. The crystalline residue left on evaporation of the ethanol gave a faint Liebermann color test. Upon recrystallization from ethanol the test was negative. The colorless leaflets contained solvent of crystallization, m. p. 142°, $[\alpha]^{25}D$ +23.6 (22.1 mg. in 2.0 cc. chloroform, $\alpha^{25}D$ +0.26, 1-dm. tube). The carbon values were about 2% low due to unremovable solvent of crystallization.

Brassicastyl Acetate.—The acetate, prepared by refluxing with acetic anhydride for thirty minutes, was recrystallized from ethanol as colorless leaflets, m. p. 143°, $[\alpha]^{25}D$ +14.5° (18.0 mg. in 2.0 cc. chloroform, $\alpha^{25}D$ +0.13, 1-dm. tube). *Anal.* Calcd. for $C_{31}H_{54}O_2$: C, 81.16; H, 11.86. Found: C, 81.12; H, 11.82.

(6) Analyses reported in this paper were carried out by Mr. J. F. Alicino, Fordham University.

Brassicastyl *m*-Dinitrobenzoate.—To a solution of brassicastanol in dry pyridine was added an excess of *m*-dinitrobenzoyl chloride and the solution was heated on the steam-bath for one hour. Water was added, the precipitate filtered, and recrystallized from benzene–ethanol: colorless leaflets, m. p. 202°, $[\alpha]^{25}D$ +13.9° (15.8 mg. in 2.0 cc. benzene, $\alpha^{25}D$ +0.11, 1-dm. tube). *Anal.* Calcd. for $C_{35}H_{52}O_6N_2$: C, 70.43; H, 8.78. Calcd. for $C_{36}H_{54}O_6N_2$: C, 70.79; H, 8.91. Found: C, 71.00, 71.07; H, 8.75, 8.77.

Summary

Brassicasterol has been isolated from unrefined rapeseed oil. The empirical formula $C_{29}H_{48}O$ is more probable than the formula $C_{28}H_{46}O$ given in the literature.

Catalytic hydrogenation of brassicasterol yields a saturated sterol different from its isomer stigmastanol.

NEW BRUNSWICK, N. J. RECEIVED NOVEMBER 23, 1938

[CONTRIBUTION FROM THE UNITED STATES DEPARTMENT OF AGRICULTURE, BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE]

Replacement of the Diazo Group by the Acetoxy Group. II. The Preparation of *m*-Bromophenyl and *m*-Iodophenyl Acetates

BY L. E. SMITH AND H. L. HALLER

In the course of a study of the relative toxicity of the isomeric halogenated phenols to goldfish, the results of which will be reported elsewhere, it was necessary to prepare *m*-bromophenol and *m*-iodophenol. The procedures recorded for their preparation were tried,[1,2] but the resulting compounds were difficult to purify and the yields were low.

Recently it has been shown that *m*-chlorophenyldiazonium borofluoride interacts with acetic acid to give *m*-chlorophenyl acetate[3] in good yield. As the acetate can be hydrolyzed readily to the free phenol, the reactions provide a useful method of preparing phenols.

It now has been found that the *m*-bromophenyldiazonium and *m*-iodophenyldiazonium borofluorides also react with acetic acid to give the corresponding acetates, from which the free phenols are obtained on saponification. They have been identified as their phenoxyacetic acid derivatives. No rearrangement of the acetates with the formation of hydroxy methyl ketones has been observed.[4]

(1) Diels and Bunzl, *Ber.*, **38**, 1486 (1905).

(2) Ullmann, *Ann.*, **332**, 38 (1904).

(3) For previous article see Haller and Schaffer, THIS JOURNAL, **55**, 4954 (1933).

(4) Smith and Haller, *ibid.*, **56**, 237 (1934).

Experimental

***m*-Bromophenyldiazonium Borofluoride.**—This compound was obtained in the usual manner by treating a solution of *m*-bromophenyldiazonium chloride with a 40% solution of hydrofluoroboric acid. The yield was 94.5%. The product melted at 145°.[5]

***m*-Bromophenyl Acetate.**—Fifty-one and two-tenths grams of *m*-bromodiazonium borofluoride was heated cautiously with 200 cc. of glacial acetic acid under reflux until the evolution of nitrogen ceased. Then the solution was refluxed for five minutes, concentrated under reduced pressure, and diluted with water. The oil that separated was extracted with ether, and the ether solution was washed with sodium bicarbonate solution and then with water and dried over anhydrous sodium sulfate. The remaining oil was distilled under reduced pressure. It boiled at 95–96°, (2 mm.); yield 19.3 g.

Anal.[6] Calcd. for $C_8H_7BrO_2$: C, 44.65; H, 3.25. Found: C, 43.99, 43.92; H, 3.20, 3.19.

***m*-Bromophenol.**—Nineteen grams of *m*-bromophenyl acetate in 100 cc. of ethyl alcohol and 65 cc. of 10% aqueous potassium hydroxide was refluxed for one hour. The solution was then concentrated under reduced pressure, made acid with dilute sulfuric acid, and extracted with ether. The ether solution was extracted with sodium bicarbonate solution, washed with water, dried over anhy-

(5) All melting points are uncorrected.

(6) Analyses were made by F. Acree, Jr., of the Division of Insecticide Investigations.