100-ml. portions of ether. Removal of the ether left 4.5 g. of red solid which was crystallized twice from water to yield 0.8 g. of the hydrate of *o*-benzoylbenzoic acid, m. p. 93–94°. Its identity was confirmed by conversion to anthraquinone.

Summary

1. It has been shown that the dimer of α-phenylacrylonitrile possesses a structure similar to that of Fittig's isatropic acids and is probably a substituted tetralin.

2. Several hydrolysis products of the dimer of α-phenylacrylonitrile are described.

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[CONTRIBUTION FROM THE MULTIPLE FELLOWSHIP OF THE CORN PRODUCTS REFINING COMPANY, MELLON INSTITUTE]

Sitosterols from Corn Gluten

BY DOROTHY M. RATHMANN AND LOUISE R. MORROW

Anderson and co-workers[1] found that the "sitosterols from corn" are a complex mixture containing sitostanols and a small amount of stigmasterol in addition to α-, β- and γ-sitosterols, and that relatively more sitostanol was obtained from the endosperm than from the germ. In the commercial isolation of zein from corn gluten,[2] one stage consists in extraction of an alkaline isopropyl alcohol solution with hexane to remove the lipids. The resulting extract contains at least 95% of the oil originally present in the gluten. After washing the extract with water and evaporating off the hexane there is obtained a dark red-brown oil, known as "xanthophyll oil," about 11% of which consists of nonsaponifiables. The crude phytosterols are isolated in a yield of 8% (based on the oil), as a cream-colored solid having a sitosterol content of at least 85%. A typical batch of this sterol mixture constituted the starting material for the present investigation.

Removal of the non-steroid contaminants and some degree of fractionation (Table I) was achieved by recrystallization of the acetates which were then hydrolyzed. Further fractionation was obtained by the adsorption analysis of the *i*-sitosteryl methyl ethers. Although adsorption has been employed[3] as a means of freeing the *i*-steryl methyl ethers from unreacted sterols, there seems to have been no investigation of the method as a means of analyzing phytosterol mixtures.

In order to obtain data on the probable behavior of the ethers of the sitosterols during adsorption, *i*-cholesteryl methyl ether and cholesteryl methyl ether were prepared by the method of Stoll[4] and chromatographed. The results indicated that the recovery of both types of ethers would be high and that the *i*-steryl methyl ether would be less strongly adsorbed than the corresponding steryl methyl ether.

Chromatography of the ethers derived from the sitosterol fractions is summarized in Table II from which it is apparent that the sitosterol fraction of highest negative specific rotation yielded primarily *i*-γ-sitosteryl methyl ether (I). Intermediate fractions yielded a complex mixture of *i*-sitosteryl methyl ethers (II) and sitosteryl methyl ether (III). The sterol fraction of lowest specific rotation yielded principally episitostanol (IVA) and sitostene (V) which may have been derived from sitostanol in the course of preparing the methyl ethers.

On the basis of this preliminary investigation, it is concluded that γ- and β-sitosterols are the major components of the phytosterols from xanthophyll oil, that stigmasterol is absent, and that the content of sitostanol is much lower than was found by Anderson in corn gluten. Many small fractions have not been fully characterized. Speculations regarding the possible occurrence of the α-sitosterols are consequently not warranted.

Experimental

With the exception of the crude sitosterols, samples were dried over phosphorus pentoxide for several hours at 60° and 2 mm. pressure before being analyzed.

Specific rotations were determined at room temperature (25 ± 2°) for a chloroform solution of the compound in a 2-dm. tube, using sodium light. The concentration was 2.0 ± 0.2 g. per 100 ml. of solution. Barton and Cox[5] reported that, in the range used in the present work, the specific rotations of various sterol derivatives were independent of temperature and concentration. Consequently these data are not listed for each compound.

Carbon-hydrogen analyses were conducted by G. L. Stragand, Microchemical Laboratory, University of Pittsburgh. The infrared spectra were obtained and interpreted by R. B. Hannan, Jr., Department of Research in Chemical Physics, Mellon Institute.

Unless otherwise stated, the **acetates** were prepared by refluxing the sterol with 10 volumes of acetic anhydride for thirty minutes. The **benzoates** were obtained from the reaction of 1 weight of sterol with 1 volume of benzoyl chloride in 10 volumes of anhydrous pyridine for twenty-four hours at room temperature. After being isolated in the usual fashion, these derivatives were recrystallized from ethyl acetate.

Properties of Sitosterols from Corn Gluten.—Crude sitosterols isolated from xanthophyll oil consisted of slightly tan crystals containing 85 to 90% sitosterols (digitonin-precipitable) and having total fatty acid contents as high as 6%, depending on the method of isolation. Melting points were in the range of 125 to 135°. Recrystallization of a mixture of two such preparations from ethyl acetate gave: crop A, 74% yield, m. p. 134–136°, $[\alpha]^{25}D$

(1) (a) Anderson and Moore, THIS JOURNAL, **45**, 1944 (1923); (b) Anderson, *ibid.*, **46**, 1450 (1924); (c) Anderson and Shriner, *ibid.*, **48**, 2976 (1926); (d) Anderson and Shriner, *J. Biol. Chem.*, **71**, 401 (1927); (e) Anderson, Nabenhauer and Shriner, *ibid.*, **71**, 389 (1927).

(2) Swallen, *Ind. Eng. Chem.*, **33**, 394 (1941).

(3) Fernholz and Ruigh, THIS JOURNAL, **62**, 3346 (1940).

(4) Stoll, *Z. physiol. Chem.*, **207**, 147 (1932).

(5) Barton and Cox, *J. Chem. Soc.*, 783 (1948).

TABLE I

PRELIMINARY FRACTIONATION OF CORN GLUTEN SITOSTEROLS

Acetate fractions			Sterol fractions[a]			Tosylate fractions[b]		
Yield, %[c]	$[\alpha]^{25}D$ ($CHCl_3$)[d]	M. p., °C.	Yield, %[e]	$[\alpha]^{25}D$ ($CHCl_3$)	M. p., °C.	Yield, %[f]	$[\alpha]^{25}D$ ($CHCl_3$)	M. p., °C.
5.3	−41	131–133	69	−36.5	137–138	77	−35.8	123–124
9.5	−40	130–133	69	−35.2	137–139	71	−36.9	125–127
4.4	−37	125–130	60	−32.4	136–137	70	−36.4	126–128
9.7	−33	118–125	70	−27.5	133–136	68	−29.1	126–131
10.9	−30	120–124	70	−23.8	133–135	..	....	.....
26.0	−28	121–124	67	−24.3	134–137	..	....	.....
11.5	−26	123–126	79	−19.5	135–137	35	−17.9	129–130
12.4	−25	120–126	68	−15.8	135	39	− 9.0	117–123
5.9	−22	126–127	62	−13.6	133–135	47	−10.5	112–124[g]
0.3	−13	107–117	21	−10.6	130–133	..	....	.....

[a] First crop from hydrolysis of acetate. [b] First crop after adsorption and recrystallization. [c] Based on sterol content of starting material. [d] Average values. [e] Based on theoretical yield from acetate fraction. [f] Based on theoretical yield from sterol fraction. [g] Decomposes.

−23.7°; crop B, 9.5%, m. p. 133–134°, $[\alpha]^{25}D$ −25.5°; and crop C, 4%, m. p. 129–132°, $[\alpha]^{25}D$ −30.6°.

Crop A contained 0.7% of volatiles, 1.3% of total fatty acid (as oleic) and had a sitosterol content of 95.8% by the digitonin method and 92.2% by the Liebermann-Burchard method. The bromine number was 415 as compared with 385 calculated for γ-sitosterol. An attempt to determine the sitostanol content directly by the method of Schoenheimer[6] gave an inconclusive result: the weight of sterol precipitated by digitonin after bromination was in excess of the amount equivalent to the digitonin added. A very low content of stigmasterol was indicated by the failure to isolate stigmasteryl acetate 22,23-dibromide from the products of the reaction of sodium iodide[7] with the crude bromositosteryl acetate (m. p. 109–115°, $[\alpha]^{25}D$ −29.6°).

Preparation and Fractionation of the Acetates.—A solution of equal weights of the crude sitosterols and acetic anhydride in 2 volumes of glacial acetic acid was refluxed for 5.5 hours and then allowed to stand overnight at room temperature. The yield of crude acetates was 95% (based on the sterol content of the starting material). The acetates were recrystallized once from ethylene dichloride containing ethyl alcohol and nine times from a 1:1 mixture of benzene and isopropyl alcohol, giving the fractions listed in Table I.

Hydrolysis of the Acetate Fractions.—A solution of 1 part by weight of the acetate in 5 to 6 volumes of 10% potassium hydroxide in 95% ethyl alcohol plus 1.5 volumes of benzene was refluxed under nitrogen for 2.5 hours. The sterols were isolated in the usual manner and were recrystallized from a 1:1 mixture of benzene–isopropyl alcohol. Some properties of the first crops of crystals are summarized in Table I for comparison with those of the acetate fractions from which they were obtained.

Preparation of the *p*-Toluenesulfonates.—The *p*-toluenesulfonate was prepared by the reaction of an equal weight of the sterol fraction and purified *p*-toluenesulfonyl chloride in 3 volumes of anhydrous pyridine for forty-three hours at room temperature. The product was usually isolated in 90% crude yield. The crude product was purified by adsorption on alumina from a hexane solution and some fractionation of the tosylates was simultaneously achieved. Properties of the first crops obtained by recrystallization from dry acetone are summarized in Table I. In agreement with the results of other workers, it was found that the conversion of a sterol to its tosylate does not have a marked effect on the specific rotation. Further recrystallizations yielded two distinctly different tosylates.

Sitostanyl *p*-Toluenesulfonate.—Recrystallization of the tosylate fraction of lowest specific rotation from ethyl acetate yielded a white powder, m. p. 146–148°, $[\alpha]^{25}D$ −0.5°. *Anal.* Calcd. for $C_{35}H_{53}O_3S$: C, 75.73; H, 10.24; S, 5.62. Found: C, 75.50; 75.72; H, 9.70, 9.76; S, 5.49. Although the melting point was lower than the decomposition point of 154–155° reported by Stoll[4] for sitostanyl tosylate, it agreed with that reported for stigmastanyl tosylate.[8] This tosylate fraction reacted with methanol containing potassium acetate to yield IVA and V.

Sitosteryl *p*-Toluenesulfonate.—Recrystallization of the tosylate fraction of highest specific rotation yielded colorless platelets, m. p. 123–124.5°, $[\alpha]^{25}D$ −34.3°. *Anal.* Calcd. for $C_{35}H_{56}O_3S$: C, 76.00; H, 9.92; S, 5.64. Found: C, 75.70; H, 9.71; S, 5.94. The specific rotation is in good agreement with the value, $[\alpha]^{25}D$ −36°, calculated for γ-sitosteryl tosylate by the method of Bernstein, *et al.*,[9] and differs markedly from $[\alpha]^{25}D$ −47° reported for stigmasteryl tosylate, m. p. 148–150°.[3] This tosylate fraction reacted with methanol containing potassium acetate to form I.

Preparation and Fractionation of the Methyl Ethers.—The *i*-sitosteryl methyl ether was prepared by refluxing a mixture of equal weights of the tosylate fraction and freshly fused potassium acetate in 50 volumes of methanol for twenty-four hours. About half of the methanol was distilled off before the reaction product was isolated by the addition of water and extraction with ether. The crude methyl ethers were obtained as oils in almost quantitative yields (based on the weights of the tosylate fractions).

The crude product dissolved in 25 volumes of hexane was adsorbed on a column of alumina[10] which was then washed with hexane until no more material was eluted and then with hexane containing methanol to elute more strongly adsorbed compounds. The ratio of the weight of methyl ether to alumina in this preliminary adsorption was about 1:15. The eluate fractions were rechromatographed by a similar procedure, using an approximate weight ratio of the ether to alumina of 1:50, until the specific rotation was not significantly changed by readsorption.

The sole exception to this method of fractionation was the case of the product from the tosylate of low negative specific rotation. This consisted of a wax from which a crystalline mixture (IV) having $[\alpha]^{25}D$ +18° was obtained by slow cooling of a solution in hexane. The hexane mother liquor yielded only an oil which was finally chromatographed in the usual manner. Final results of the fractionations of the methyl ethers are summarized in Table II. The following fractions were identified:

I. ***i*-γ-Sitosteryl Methyl Ether.**—The oily methyl ether of $[\alpha]^{25}D$ +43 to 46° could not be crystallized from hexane, acetone or methanol, and the specific rotation could not be changed significantly by readsorption on

(6) Schoenheimer, *Z. physiol. Chem.*, **192**, 81 (1930).

(7) Fernholz and Stavely, THIS JOURNAL, **61**, 2956 (1939).

(8) Stoll, *Z. physiol. Chem.*, **246**, 1 (1937).

(9) Bernstein, Kauzmann and Wallis, *J. Org. Chem.*, **6**, 319 (1941).

(10) Alumina A541/2, especially prepared for chromatographic analysis, from the Fisher Scientific Company.

TABLE II

CHROMATOGRAPHY OF THE METHYL ETHERS OF SITOSTEROL FRACTIONS

Tosylate fraction $[\alpha]^{25}D$ ($CHCl_3$)[b]	First adsorption[a] Yield, %[c]	First adsorption[a] $[\alpha]^{25}D$ ($CHCl_3$)	Methyl ethers Second adsorption Eluant	Yield, %[d]	$[\alpha]^{25}D$ ($CHCl_3$)	Identity
−36	53	+43	Hexane	56	+44	I
	28	+37	Hexane	39	+43	I
			Hex–MeOH	3	−30	
−33	96	+31	Hexane	55	+42[e]	I
			Hexane	26	+30	
			Hex–MeOH	6	−33	
			Hex–MeOH	2	−30	
			Hex–MeOH	2	−15	
−28	89	+19	Hexane	42[f]	+46	I
			Hexane	9	+34	
			Hexane	3	+28	
			Hex–MeOH	15	−29	III
			Hex–MeOH	2	− 5	
			Hex–MeOH	2	+13	
−20	92	+25	Hexane	50	+39	II
			Hexane	17	+37	
			Hexane	8	+35	
			Hexane	3	+27	
			Hex–MeOH	11	−26	III
			Hex–MeOH	10	+ 3	
− 3	87	+ 9	.....	18	+18[g]	IV
			Hexane	58	+49	V
			Hexane	6	+37	
			Hex–MeOH	4	Negative	

[a] Hexane eluate. [b] Average values. [c] Based on theoretical yield from tosylate. [d] Recovery of ether adsorbed. [e] Readsorption: 91%, $[\alpha]^{25}D$ +44; 4%, $[\alpha]^{25}D$ negative. [f] Accidental loss responsible for low recovery. [g] Crystallized out before adsorption.

tive specific rotation which usually contaminates the γ-sitosterol isolated from plants and that the specific rotation of the benzoate is significantly higher than the value for β-sitosteryl benzoate. Since γ-sitosterol appears to be the primary hydrolysis product, ether I is tentatively identified as *i*-γ-sitosteryl methyl ether.

II. **Mixture Containing *i*-Sitosteryl Methyl Ether.**—This oily ether of $[\alpha]^{25}D$ +39 was hydrolyzed by the above method. Recrystallization of 52 g. of the product from hexane gave the following fractions:

(a) 12.9 g. of a **sitosterol** which after two recrystallizations from ethyl acetate had m. p. 132.5–134°, $[\alpha]^{25}D$ −33.3° and formed an **acetate**, m. p. 128–129°, $[\alpha]^{25}D$ −39.7° and **benzoate**, m. p. 143–144°, $[\alpha]^{25}D$ −13.7°. These properties were not changed significantly by further purification and appear to correspond to those of β-sitosterol (Table III).

(b) An oil which after recrystallization from ethyl acetate gave 3.5 g. of a white powder, m. p. 115–117°, $[\alpha]^{25}D$ −12.1°. Only 59% of this material was precipitable with digitonin and the specific rotation continued to decrease on recrystallizations.

(c) 19.0 g. of a solid, m. p. 55–95°, $[\alpha]^{25}D$ −4.6°. Recrystallization from ethyl acetate yielded 2.5 g. of a white powder, m. p. 131–133°, $[\alpha]^{25}D$ −34.0°, similar to (a). The mother liquor was benzoylated and yielded 2.3 g. β(?)-sitosteryl benzoate, m. p. 139–141°, $[\alpha]^{25}D$ −14.2°. The remainder of the benzoylation product is an oil which is being further investigated.

(d) Oily material which has not been characterized.

Therefore, this ether fraction was a complex mixture which could not be adequately separated into its components by adsorption on alumina. A major component may be the *i*-β-sitosteryl methyl ether.

III. **Sitosteryl Methyl Ether.**—Recrystallization of III from ethanol in ethyl acetate yielded a white powder, m. p. 98–99°, $[\alpha]^{25}D$ −38.8°. *Anal.* Calcd. for $C_{30}H_{52}O$: C, 84.04; H, 12.23. Found: C, 84.13, 83.86; H, 11.89, 11.98.

TABLE III

SITOSTEROLS AND DERIVATIVES

	Sterol $[\alpha]D$ ($CHCl_3$)	Sterol M. p., °C.	Acetate $[\alpha]D$ ($CHCl_3$)	Acetate M. p., °C.	Benzoate $[\alpha]D$ ($CHCl_3$)	Benzoate M. p., °C.	Reference
Sitosterol from I	−36.2	134–135.5	−41.8	133–134	−16.1	140–142	
Sitosterol from II	−33.3	132.5–134	−39.7	128–129	−13.7	143–144	
Δ⁵-Poriferastenol	−37	139	−41.5	137	−16	141	11
γ-Sitosterol	−41 to −45	143–148	−45 to −48	143	−20	152	11
β-Sitosterol	−35.1	139–140	−39	127–128			12
	−36.0	140	−39.4	132	−13.5	146–147	12
	−36.6	136–137	−41.0	125–126	−13.8	146–147	13
22-Dihydrostigmasterol	−37	136.5–137.5			−13.5	146	14

alumina. This ether was hydrolyzed by refluxing with an equal weight of *p*-toluenesulfonic acid in 20 volumes of water and 180 volumes of acetone for two hours. One crystallization of the product from ethyl acetate gave a **sitosterol** in 62% yield, m. p. 131–133°, $[\alpha]^{25}D$ −35.1° which after adsorption on alumina and recrystallization from ethyl acetate had m. p. 134–135.5°, $[\alpha]^{25}D$ −36.2°. *Anal.* Calcd. for $C_{29}H_{50}O$: C, 83.99; H, 12.15. Found: C, 84.41, 84.27; H, 11.77, 11.89. The sterol took up 1.03 moles of bromine.

The **acetate** was obtained as a white powder, yield 77%, m. p. 131–134°, $[\alpha]^{25}D$ −41.1°, which after two recrystallizations had m. p. 133–134°, $[\alpha]^{25}D$ −41.8°.

The **benzoate** was obtained in 80% yield, m. p. 138–141°, $[\alpha]^{25}D$ −15.9° and after recrystallization had m. p. 140–142°, $[\alpha]^{25}D$ −16.1°.

Comparison of these data with those in the literature for purified sitosterols from various sources (Table III) shows that the properties are in agreement with those of Δ⁵-poriferastenol which Bergmann and Low[11] considered to be pure γ-sitosterol free from a phytosterol of more nega-

(11) Bergmann and Low, *J. Org. Chem.*, **12**, 67 (1947).

The infrared spectrum showed that this compound was an alkyl ether having an over-all spectrum very similar to that of cholesteryl methyl ether. III was not hydrolyzed by *p*-toluenesulfonic acid in aqueous dioxane and did not react with acetic anhydride. It took up 0.9 mole of bromine but the dibromide could not be crystallized. These properties are in fair agreement with those reported by Stoll[4] for sitosteryl methyl ether, m. p. 100°, $[\alpha]^{25}D$ −40.7°.

IVA. **Episitostanol.**—Recrystallization of IV from acetone gave two distinctly different compounds in approximately equal amounts. The less soluble, IVA, has been identified as episitostanol. The other, IVB, consisted of colorless plates, m. p. 128–131°, $[\alpha]^{25}D$ +8.6° and has not yet been identified.

The episitostanol (IVA) crystallized from ethyl acetate as silky needles, m. p. 200–201°, $[\alpha]^{25}D$ +24.5°. *Anal.* Calcd. for $C_{29}H_{52}O$: C, 83.58; H, 12.58. Found: C, 83.70, 83.51; H, 12.38, 12.26. It was not precipitated

(12) Dirscherl and Nahm, *Ann.*, **555**, 57 (1944).
(13) Wallis and Chakravorty, *J. Org. Chem.*, **2**, 335 (1937).
(14) Bernstein and Wallis, *ibid.*, **2**, 341 (1937).

by digitonin. The infrared spectrum revealed the presence of a free hydroxyl group and the probable absence of a double bond, but it otherwise exhibited a general appearance rather similar to the spectrum of cholesteryl methyl ether.

The **acetate** was obtained as silky, colorless needles, yield 68%, m. p. 78.5–80.5° (melt was slightly cloudy and had not cleared completely at 250°), $[\alpha]^{25}D$ +25.1°. *Anal.* Calcd. for $C_{31}H_{54}O_2$: C, 81.16; H, 11.87. Found: C, 81.06, 81.30; H, 11.66, 11.91.

The **benzoate** was obtained as shiny white platelets, yield 60%, m. p. 84–85.5° (melt was slightly cloudy but cleared completely by 140°), $[\alpha]^{25}D$ +24.3°. *Anal.* Calcd. for $C_{36}H_{56}O_2$: C, 83.03; H, 10.84. Found: C, 83.29, 83.28; H, 10.72, 10.51.

These properties correspond to those of episitostanols. Marker, *et al.*,[15] reported the preparation of epistigmastanol (epi-β-sitostanol), m. p. 204° and its acetate, m. p. 84°. Dalmer, *et al.*,[16] found the properties of epistigmastanol m. p. 200°, $[\alpha^{25}]D$ +25° (acetate, m. p. 85°, $[\alpha]^{25}D$ +27°) to be only slightly different from those of an episitostanol, m. p. 203°, $[\alpha]^{25}D$ +26° (acetate, m. p. 88°, $[\alpha]^{25}D$ +28°). In the absence of data on episitostanol no assignment of configuration to IVA is warranted.

V. **Δ²-Sitostene.**—Recrystallization of V from ethyl acetate gave shiny, white plates, m. p. 71–73°, $[\alpha]^{25}D$ +62.0°. *Anal.* Calcd for $C_{29}H_{50}$: C, 87.36; H, 12.64. Found: C, 87.21, 87.04; H, 12.34, 12.37. The infrared spectrum showed no bands characteristic of groups containing oxygen, but otherwise exhibited an over-all appearance similar to the spectrum of cholesteryl methyl ether. This hydrocarbon reacted with 0.98 mole of bromine. After two recrystallizations from benzene containing ethanol, the **dibromide** had m. p. 115–119°. In the reaction with the Liebermann-Burchard reagent, the hydrocarbon gave a purple color which rapidly changed to blue and then to a faint yellow-green.

This compound is not like the γ-sitostene (m. p. 73°, $[\alpha]^{25}D$ −59.3°) prepared by Bonstedt.[17] Comparison with the properties of the cholestenes as summarized by Fieser and Fieser[18] indicates that our hydrocarbon may be a sitostene having one double bond in ring A, probably between C2 and C3. The isolation of this sitostene and episitostanol from the same fraction is in agreement with the observations of Stoll[9] that the product of the reaction of epicholestanyl tosylate with methanol is Δ²-cholestene rather than epicholestanyl methyl ether.

(15) Marker, Lawson, Wittle and Oakwood, THIS JOURNAL, **59**, 2714 (1937).

(16) Dalmer, Werder, Honigmann and Heyns, *Ber.*, **68**, 1814 (1935).

(17) Bonstedt, *Z. physiol. Chem.*, **176**, 269 (1928).

(18) Fieser and Fieser, "Natural Products Related to Phenanthrene," 3rd Edition, Reinhold Publ. Corp., New York, N. Y., 1949, p. 249.

Chromatography of *i*-Cholesteryl Methyl Ether.—This ether was prepared in 92% yield by the method of Stoll[19] as a waxy white solid. A chromatogram of 14.8 g. of this product on alumina by the same method as was used for the sitosterol derivatives was as follows: **fraction A**, 9.6 g., $[\alpha]^{25}D$ +48°; **B**, 3.7 g., +32°; **C**, 0.7 g., −30°; **D**, 0.4 g., +14°. Rechromatographing A yielded A1, 6.4 g., +51.2°; A2, 2.9 g., +48.3°. A2 combined with B gave the chromatogram: 3.8 g., +50.5°; 0.9 g., +44.6°; 1.2 g., +6.2°.

Recrystallization of A1 from ethyl acetate gave white crystals, m. p. 78–79°, $[\alpha]^{25}D$ +54.5° as compared with m. p. 79°, $[\alpha]^{25}D$ +55° reported by Stoll for *i*-cholesteryl methyl ether. Hydrolysis with *p*-toluenesulfonic acid in aqueous acetone gave cholesterol in 80% yield. It therefore appeared that the products of the reaction of cholesteryl tosylate with methanol containing potassium acetate form a relatively simple chromatogram and that no material less strongly adsorbed than *i*-cholesteryl methyl ether was present.

Chromatography of Cholesteryl Methyl Ether.—This ether was prepared in a manner analogous to the preparation of the *i*-steryl methyl ethers with the exception that potassium acetate was omitted from the reaction mixture. A chromatogram of 14.7 g. of the crude product on alumina had the following sequence: **fraction A**, 8.7 g., $[\alpha]^{25}D$ −40.4°; **B**, 5.1 g., −39.9°; **C**, 0.7 g., −38.3°; **D**, 0.2 g., −38.9°.

Recrystallization of A and B from ethyl acetate yielded 12.8 g. of colorless needles, m. p. 82–83°, $[\alpha]^{25}D$ −42.7°, as compared with m. p. 84°, $[\alpha]^{25}D$ −46°, reported by Stoll.[4] This material could not be hydrolyzed by *p*-toluenesulfonic acid in aqueous acetone. It adsorbed more strongly on a column of alumina than did *i*-cholesteryl methyl ether and could be separated from the *i*-steryl ether by developing the chromatogram with hexane.

Summary

The sterols of the xanthophyll oil isolated from corn gluten are shown to be a mixture which probably contains γ- and β-sitosterols and sitostanols. The presence of other compounds, precipitable by digitonin and having a low specific rotation and high bromine number, was indicated.

The chromatography of crude *i*-sitosteryl methyl ethers on alumina is described.

A new sitostene and an episitostanol were isolated. These compounds were presumably derived from sitostanol during the reactions with *p*-toluenesulfonyl chloride and methanol.

PITTSBURGH 13, PENNSYLVANIA RECEIVED MARCH 25, 1950

(19) Stoll, *Z. physiol. Chem.*, **246**, 14 (1937).