COMMUNICATIONS TO THE EDITOR

THE STRUCTURE OF CELLULOSE ETHERS OBTAINED BY THE METHYLATION OF CELLULOSE MATERIALS DISPERSED IN QUATERNARY AMMONIUM BASES

Sir:

The methylation of cellulosic materials dispersed in certain quaternary ammonium bases has been reported[1] to proceed as a homogeneous molecular cellulose reaction. The structure of the apparently homogeneous water-soluble methylcellulose prepared in this manner was thought to be similar to the water-soluble methylcellulose obtained by Traube, Piwonka and Funk[2] on methylating a cellulose–copper hydroxide–sodium hydroxide complex. However, since no chemical evidence was presented to substantiate this conclusion, researches on the structure of these partially methylated cellulosic materials have been undertaken in this Laboratory.

The methylation of both wood pulp and ash-free viscose rayon dispersed in 1.8 N dimethyldibenzylammonium hydroxide with dimethyl sulfate, according to the procedure of Bock,[1] yields methylated cellulosic materials containing 12 to 16% methoxyl, corresponding to 0.7 to 0.9 methyl group to each $C_6H_{10}O_5$ unit of cellulose. Acetylation of this material with acetic anhydride in pyridine solution, followed by methyl alcoholysis at 125° in the presence of 1% dry hydrogen chloride gave a mixture of partially methylated methylglucosides and α- and β-methylglucosides. The latter crystalline constituents were isolated from the mixture in yields of 30–35%, which after purification was found to be largely α-methylglucoside, m. p. 164–165°; sp. rot. +157.8° (H_2O). The sirupy constituents representing 65–70% of the total alcoholysis mixture, after acetylation with acetic anhydride in pyridine solution, were subjected to distillation under high vacuum. The following fractions were obtained:

Fraction	B. p., 0.1 mm.	% OCH₃	% Yield[a]
I	130–140°	29.5	25–30
II	140–150°	22.5	20–25
III	160–175°	19.5	5–10

[a] Yield based on original weight of acetylated product.

(1) L. H. Bock. *Ind. Eng. Chem.*, **29**, 985 (1937).

(2) W. Traube, R. Piwonka and A. Funk, *Ber.*, **69**, 1483 (1936).

Evidence that Fraction I contained traces of trimethylmonoacetyl methylglucoside (OCH₃, 44.6%) mixed with the predominating dimethyldiacetyl methylglucoside (OCH₃, 30.4%) was shown by the fact that further fractional distillation yielded a fraction (b. p. 130–140°) with a methoxyl content of 31.7%. Fraction II yielded a small amount of crystalline 2-methyltriacetyl α-methylglucoside (OCH₃, 18.5%) with melting point 120–121°, remaining constant when mixed with an authentic specimen.[3] Fraction III yielded crystalline 2-methyltriacetyl α-methylglucoside (m. p. 120–121°), tetraacetyl β-methylglucoside (m. p. 104–105°) and a sirupy product presumably dimethyldiacetyl methylglucoside.

Acetolysis of the methylated wood pulp and viscose rayon (OCH₃, 13.5%) in a manner similar to that described by Lieser[4] gave a 5% yield of cellobiose octaacetate (m. p. 224–225°; sp. rot., +41.5° ($CHCl_3$)).

These experiments confirm the assumption of Bock[1] that the "water-soluble" methylated cellulosic materials obtained by use of the quaternary ammonium bases are very similar in structure to those obtained by Traube, Piwonka and Funk.[2] The results indicate, however, that methylation proceeds by diffusion of dimethyl sulfate into a particle structure, from which it follows that the cellulose component of these materials is not molecularly dispersed in quaternary ammonium bases but rather is dispersed as particles. Slit ultramicroscopic observations[5] of cellulosic materials dispersed in quaternary ammonium bases and of the methylated product dispersed in water verify the above conclusion by showing the presence of microscopic particles approximately 1 μ in diameter.

This work is being extended to other partially methylated cellulosic materials.

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(3) W. N. Haworth, E. L. Hirst and E. G. Teece, *J. Chem. Soc.*, 2858 (1931).

(4) Th. Lieser, *Ann.*, **483**, 132 (1930).

(5) *Cf.* J. Compton, THIS JOURNAL, **60**, 1807 (1938).

THE RELATIVELY INERT OXYGEN ATOM OF DI-GOXIGENIN, SARMENTOGENIN AND THE STEROID COMPOUNDS OF THE ADRENAL CORTEX

Sir:

We have recently described [THIS JOURNAL, **60**, 1493, 2566 (1938)] a series of etio-cholanic acids and esters with oxygen atoms at C-3 and C-12. Steiger and Reichstein [Helv. Chim. Acta, **21**, 828 (1938)] have prepared from digoxigenin a similar series of acids which were thought to have oxygen atoms at C-3 and C-11. Since the 3,x-diketo-4-etio-cholenic acids derived from digoxigenin and from corticosterone proved to be different, they considered it doubtful that an oxygen atom occupied C-11 in the acids derived from digoxigenin. Through the courtesy of Professor Reichstein we have been able to compare directly the methyl diketo-etio-cholanates and the methyl diketo-4-etio-cholenates from the two sources. The results given in the table show that the properties of the esters from the two sources are identical. We conclude that Reichstein's acids are identical with those derived from desoxycholic acid and that the inert oxygen atom of digoxigenin, which was assigned to C-11 by Tschesche and Bohle [Ber. **69**, 793 (1936)], is actually at C-12.

	Acid or ester	From digoxigenin M. p., °C.	$[\alpha]^{19}D$	From desoxycholic acid M. p., °C.	$[\alpha]^{25}D$
1	Methyl diketo-etio-cholanate	171-172[a]	138.3 ± 2	169-170[a]	142 ± 3
2	Methyl diketo-4-etio-cholanate	236-238[b]	185 ± 2	236-238[b]	190 ± 6
3	Diketo-etio-cholanic acid	170		178	
4	Dihydroxy-etio-cholanic acid	280-286		283-286	
5	Methyl dihydroxy-etio-cholanate	180-183		145-146	

[a] Mixtures melted at 169-170°.
[b] Mixtures melted at 236-237°.

The other comparisons of the table are less satisfactory since the specific rotations of these compounds of Reichstein were not known and specimens were not available for mixed melting point determinations. The melting points of the diketo-etio-cholanic acids are in reasonable agreement, since we have found, as has Reichstein, that the acid is very difficult to purify. The methyl dihydroxy-etio-cholanates appear to be different since the melting point of our ester was sharp and could not be raised by distillation or recrystallization. Accepting this difference, epimerism at C-12 is indicated since the configuration of both esters at C-3 is α (no precipitation with digitonin).

This difference is not certain, however, since the corresponding acids melt at the same point.

It has been generally accepted since the work of Tschesche and Bohle [Ber. **69**, 2497 (1936)] that digoxigenin and sarmentogenin differ only in the configuration at C-9. Inasmuch as some of the adrenal steroids contain an oxygen atom which corresponds in almost all respects with the inert oxygen atom of sarmentogenin, it has been assumed [Marker, THIS JOURNAL, **60**, 1725 (1938)] that they had a configuration at C-9 like that of sarmentogenin which was supposed to have a cis linkage of rings B and C instead of the normal or trans linkage. Marker [THIS JOURNAL, **60**, 1061 (1938)] has made the same assumption for his urane compounds. There is now no need to assume such a configuration at C-9 for sarmentogenin to explain its difference from digoxigenin, although such a possibility is by no means excluded. Consequently, such an assumption for the adrenal compounds has no basis. Indeed, all the evidence [Reichstein, Helv. Chim. Acta, **19**, 402 (1936); **20**, 978 (1937); **21**, 161 (1938)] points to a normal steroid skeleton with an oxygen atom at C-11.

DEPARTMENT OF BIOCHEMISTRY   H. L. MASON
THE MAYO FOUNDATION   W. M. HOEHN
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ABSENCE OF COMBINED FATTY ACID IN CEREAL STARCHES

Sir:

The common cereal starches contain fatty material which cannot be extracted by solvents such as petroleum ether, ethyl ether or carbon tetrachloride. From this behavior, T. C. Taylor and his co-workers assumed that the fatty acid must be present as an ester of the carbohydrate substance. His later work indicated that the α-amylose fraction of the starch was characterized by—and owed its insolubility to—this esterification with fatty acid.

Recent investigations in these Laboratories show that the fatty acids in corn, wheat and rice starches can be removed completely by Soxhlet extraction with certain water-miscible fat solvents, particularly methanol, the cellosolves, and 80% dioxane. The de-fatted starch retains its characteristic granule structure and optical birefringence, and gelatinizes in hot water to give a paste of normal high viscosity. By treatment

with alcoholic oleic acid, such de-fatted starch can be reimpregnated with fatty acid, and this added fat cannot be extracted by hydrocarbon type solvents.

Hence, it appears that free fatty acid is distributed throughout the starch granule as an extraneous impurity. To explain selective extraction, it is suggested that only those fat solvents bearing hydrophilic groups can penetrate into the granule, hydrocarbon types merely washing the surface. This investigation is being continued, and final results will be reported in detail at an early date.

CORN PRODUCTS REFINING COMPANY
EDGEWATER, N. J.　　　　　THOMAS JOHN SCHOCH
　　　　RECEIVED SEPTEMBER 23, 1938

PANTOTHENIC AND NICOTINIC ACIDS AS GROWTH FACTORS FOR LACTIC ACID BACTERIA

Sir:

In a previous publication the preparation of highly active concentrates (1 unit in 0.5 γ) of an essential growth factor for lactic acid bacteria has been described [Snell, Strong and Peterson, *Biochem. J.*, **31**, 1789 (1937)]. Considerable difficulty has been encountered in attempts to further purify this factor, and a long series of fractionation procedures resulted in only about a two-fold increase in activity (1 unit in 0.20 γ).

Recently, information became available [R. J. Williams, papers presented before the American Chemical Society at Milwaukee, Wisconsin, Sept. 5–9, 1938, and private communications] which revealed a striking similarity between the properties of the above growth factor and pantothenic acid [Williams, *et al.*, THIS JOURNAL, **55**, 2912 (1933)]. Both are water-soluble, nitrogenous, organic, hydroxy acids, easily destroyed by aqueous acids or alkalies, but relatively resistant to the action of light, nitrous acid, bromine, and mild oxidizing agents. Through the kindness of Dr. R. J. Williams it has now been possible to subject two samples of pantothenic acid to our bacterial test. One preparation, A, contained approximately 40%, and the other, B, 83% calcium pantothenate. The following results were obtained on *Lactobacillus casei* as the test organism:

Supplement	γ Added per 10 cc. medium				Cc. 0.1 N acid produced per 10 cc. medium			
	a	b	c	d	a	b	c	d
Sample A	0.0	0.05	0.1	0.5	0.5	1.4	3.5	7.0
Sample B	.0	.02	.05	.3	.5	1.3	3.3	7.8

These and other tests indicated that sample A contained one unit in approximately 0.13 γ, and that B possessed about twice this activity.

Sample B was further tested on *Bacillus lactis acidi*, *Lactobacillus arabinosus*, *Lactobacillus pentosus*, *Lactobacillus delbrückii*, *Bacillus brassicae*, *Streptococcus lactis*, *Leuconostoc mesenteroides*, and *Propionibacterium pentosaceum*, and proved to be highly active for each organism. All of these organisms had previously been shown to require the growth factor. It appears certain that the active substance in our concentrates is identical with pantothenic acid, and that our best preparation contained approximately 26% pantothenic acid.

In addition to pantothenic acid some lactic acid bacteria seem to require nicotinic acid as well. Six species tested were found to grow very poorly or not at all in an acid-hydrolyzed casein medium containing both riboflavin and pantothenic acid. When small amounts of nicotinic acid were added to this medium, a marked improvement in growth and acid production occurred in some cases.

Organism	γ Nicotinic acid added per 10 cc. medium				Cc. 0.1 N acid produced per 10 cc. medium			
	a	b	c	d	a	b	c	d
L. casei	0.0	0.1	0.3	0.5	2.2	4.1	5.4	6.6
L. arabinosus	.0	.1	.3	.5	1.7	4.7	...	5.2

From the above data it appears that nicotinic acid is also an essential growth factor for at least two species of lactic acid bacteria.

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MADISON, WISCONSIN
　　　　RECEIVED SEPTEMBER 24, 1938

ORIENTATION OF HIGH MOLECULAR WEIGHT LINEAR POLYMERS IN UNSTRETCHED FILMS

Sir:

Recent electron diffraction studies by Storks[1] furnish definite evidence that unstretched films of polyethylene sebacate consist of relatively small crystallites which are oriented with their long axes approximately in the plane of the film, and with limited rotation around this axis, "probably due in part to the presence of carbonyl groups along the chain." Further, Storks points out that such films will probably show a preferred orientation until the film thickness exceeds the average chain length; only beyond this point do high molecular weight linear polymers exhibit truly amorphous Debye–Scherrer ring patterns.

(1) Storks, THIS JOURNAL, **60**, 1753 (1938).

This work is in complete accord with a theory of partially oriented film structure proposed by us, which was advanced to explain qualitatively the results of film continuity studies.[2]

We have shown previously that the minimum coating weight of certain linear polymers on several metals varies essentially inversely as the average chain length.[2] If the chains made a 90° angle with the surface, a direct ratio of minimum coating weight to chain length would obviously be approximated. A system of oriented chains *parallel* to the surface would give a minimum coating weight independent of chain length. At any angle between zero and 90° which the chains make with the surface, a fixed chain length would give a coating weight directly related to the sine of the angle with the surface. Now, it is obvious from the work of Langmuir and others that a chain having only a single terminal polar anchoring group would tend to stand on end; with additional polar groups along the chain, the effective polarity gradient along the polymer would vary with the type and distribution of such groups. Assuming a relatively uniform distribution along the chain,[3,4] then the chain would incline at an

(2) Young, *et al.*, *Ind. Eng. Chem.*, **29**, 1277, 1280 (1937); **30**, 685 (1938). See also paper to appear shortly.
(3) Flory, THIS JOURNAL, **59**, 466 (1937).
(4) Marvel, *et al.*, *ibid.*, **60**, 280, 1045 (1938).

angle with the surface which was directly related to the polarity gradient. Finally, with uniform distribution of polar groups along the chain, the longer the chain the smaller would be this polarity gradient. Accordingly, the longer the chain the smaller would be the angle it makes with the surface and as a result, an increase in chain length would reduce the minimum coating weight. This was actually found by experiment.[2]

This line of reasoning had already led us to make electron diffraction studies, with inconclusive results. Storks' results obviously reopen this method of attack. They furnish independent confirmation of our theory of partial orientation in what are usually considered to be wholly amorphous films.

Unfortunately, our film continuity studies depend upon a specific method, namely, that of conductivity through discontinuous films. In the near future attempts will be made to get an independent check of this work by studying the diffusion of hydrogen through thin films on palladium and of helium through thin films on glass.

CONTRIBUTION FROM THE STONER-MUDGE,
INC., INDUSTRIAL FELLOWSHIP
MELLON INSTITUTE OF INDUSTRIAL RESEARCH
PITTSBURGH, PA., AND   G. H. YOUNG
THE PENNSYLVANIA STATE COLLEGE   W. K. SCHNEIDER
STATE COLLEGE, PA.   J. G. ASTON
                    RECEIVED AUGUST 13, 1938

NEW BOOKS

Catalysis from the Standpoint of Chemical Kinetics. By GEORG-MARIA SCHWAB, University of Munich. Translated from the First German Edition, with additions from the recent literature by the author, by HUGH S. TAYLOR, Princeton University, and R. SPENCE, Leeds University. D. Van Nostrand Company, Inc., 250 Fourth Ave., New York, N. Y., 1937. xi + 357 pp. 39 figs. 16 × 23.5 cm. Price, $4.25.

The German edition [reviewed in THIS JOURNAL, **54**, 3017 (1932)] of Dr. Schwab's "Katalyse," which appeared in 1931, ably filled the need for an ordered and condensed theoretical treatment of the whole field of catalysis, both homogeneous and heterogeneous. The present translation, delayed by "the difficult economic conditions in the world," closely adheres to the original arrangement and purpose, but has been brought up to date by the addition of new material to the extent of some 15%. The result is a book admirably suited to graduate courses in catalytic theory, and useful to the prospective investigator as an orientation into the many unsolved problems in this field.

The reader is assumed to be familiar with the principles of theoretical chemistry, including the kinetics of uncatalyzed reactions, and with elementary mathematics. The emphasis is on the significance of theories as applied to selected examples rather than on formal mathematical statements. The treatment of the various types of catalysis is organized on a systematic rather than historical basis. Experimental examples are frankly chosen for their value in illuminating general principles, and details are naturally minimized. The book is about equally divided between homogeneous catalysis (in gases and solutions) and heterogeneous catalysis (of gas reactions). Bio-catalysis is treated briefly; technical aspects of catalysis are excluded, as is also experimental technique.

Some idea of the current activity in catalytic investiga-