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ACKNOWLEDGMENTS AND ADDRESSES

Received February 6, 1969, from the *Department of Pharmaceutics, School of Pharmacy, State University of New York at Buffalo, NY 14214*

Accepted for publication March 3, 1969.

Presented to Basic Pharmaceutics Section, APHA Academy of Pharmaceutical Sciences, Montreal meeting, May 1969.

This investigation was supported by a National Cancer Institute grant No. CA-10104. The author is indebted to the SUNY/B Computing Center (partially supported by N.S.F. grant GP-7318 and P.H.S. grant PO7FR0012605) for computing services; to Mrs. Phyllis Sackman for her technical assistance; to Dr. C. K. Johnson for making his ORTEP program available; to Professor K. N. Trueblood for his thermal analysis routine; and to Prof. Philip Coppens for a number of interesting discussions.

Nuclear Magnetic Resonance and Rheological Studies on the Thixotropic Properties of Montmorillonite-Water Systems

ARTHUR H. KIBBE and OSCAR E. ARAUJO

Abstract □ Several proposed mechanisms of the thixotropic behavior of montmorillonite-water systems were evaluated. The effects of temperature, reshearing, concentration, and storage time on these systems were studied by means of NMR and rheological measurements. The specific parameters used were the change in line width of the NMR spectrum and the static yield values obtained from the rheograms. The results indicate clear agreement with the theory that the colloidal particles upon contact adhere to form a spacious matrix resembling a house of cards.

Keyphrases □ Montmorillonite-water systems—rheology □ Thixotropic behavior—montmorillonite-water systems □ Stability—montmorillonite-water systems □ NMR spectroscopy—analysis

Montmorillonite-water systems have long been under study by physical chemists and more recently by the pharmaceutical industry because of their unique thixotropic behavior.

Hause and Reed (1) found that as little as 0.05% bentonite was sufficient to stop gas bubbles from rising to the surface.

Norton and Johnson (2) studied the properties of monodispersed clay-water systems and calculated the thickness of the water film, finding it to be approximately two molecules thick.

Freundlich (3), von Engelhardt (4), and Hause (5) assume that there are long-range electrical forces which permit the individual particles to act over distances of the order of 10^3 Å. This would be similar to the type of structure found in a magnet where all the free electrons of the iron are lined up in the same direction.

Usher (6), Kuhn (7), and Hofmann (8) prefer a mechanical picture of thixotropy in which the particles touch one another, adhere on contact, and build up a spacious matrix resembling a house of cards.

Macy (9), McBain (10), and Grim and Cuthbert (11) explain the rheological mechanism of montmorillonite mixtures by assuming that the aqueous layer which surrounds the clay particle becomes rigid as if it had crystallized into ice.

Williamson (12) reviewed the physical relationship between clay and water systems and concluded that the "ice" theory is the least satisfactory explanation for the rigidity of the water film on clay.

The strength of thixotropic gels increases with decreasing particle size. Brownian molecular motion is nonexistent in truly thixotropic systems and the particles which have ceased to move seem to be clearly separated from each other by water (12).

In 1945 Ewing (13) felt that bentonite had become of such importance in pharmaceutical preparations that he

sought to elucidate its physical properties and make corrections to the USP monograph.

The effect of processing on the rheology of clays was studied by Simon *et al.* (14). They found that increasing the operating pressure of the colloid mill used in the preparation resulted in an increase in thixotropic index while changing the speed had little effect.

Levy suggested that four rheological parameters were useful in defining thixotropic systems: dynamic and static yield values, as well as plastic viscosity and thixotropic area (15). He also studied the kinetics of the buildup time for various clay systems and found that recovery time could be expressed in terms of torque and time between shearing (16).

The structure of all clay minerals consists essentially of mica-like layer lattices in which the ultimate building units are SiO_4 and AlO_6 and MgO_6 groups as shown in Fig. 1 (17). All clay minerals have in common that they are infinitely extended networks, only in two dimensions. Thus, these minerals consist of stacks of sheets. Due to the high surface energy of structures like this and due to the structure itself, clays have unique rheological properties (17, 18), which led to the selection of bentonite-water systems as models for this investigation. A new approach was proposed to elucidate the mechanism and structure of these thixotropic mixtures. It was believed that by means of a NMR spectrometer the degree of water mobility could be determined. These findings coupled with rheological studies using static yield value as a measure of thixotropy would serve as a basis for differentiating among the foregoing proposed mechanisms of thixotropic behavior.

In this investigation the only hydrogens are those associated with the water; thus, any change in the motion of the water about the clay will be reflected by a change in the line width of the NMR spectrograph.

It is known that water has a very sharp peak and ice a very broad peak. If, as is the case in montmorillonite-water systems, some hydrogens are attached strongly to a lattice structure while others are free to move about in a random manner, then the line width will be thinner than pure ice and thicker than pure water (19-21).

EXPERIMENTAL

Preparation of Samples—The montmorillonite used in this study was bentonite USP.¹

Suspensions in a concentration range of 6 to 14% w/w bentonite were prepared using preserved distilled water containing 0.2% benzoic acid. The proper quantity of preserved water was measured and heated to 90°. The previously weighed bentonite was then spread on the surface and allowed to hydrate while the slurry cooled. After the mixture had reached room temperature, it was transferred to a blender² connected to a rheostat.³ All samples were blended for 30 sec. at a rheostat setting of 50. The suspensions were then placed in a beaker and stirred gently to allow all the air bubbles to escape.

The samples were transferred to the appropriate NMR tubes and to specially modified containers constructed to accommodate the star-shaped rotor used in the rheological studies. They were then placed in the proper constant-temperature baths.

Rheological Measurements—The rotary viscometer⁴ used in this study for all viscosity measurements employs a strain gauge on the

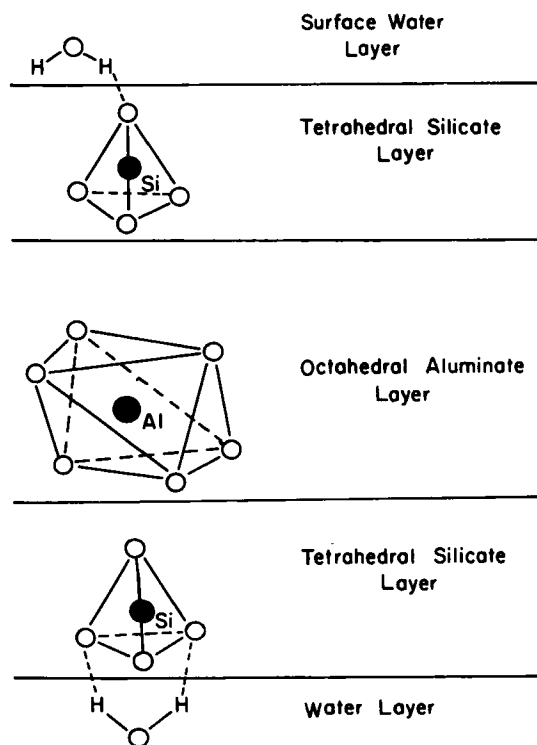


Figure 1—Basic structure of a single bentonite-water platelet.

rotor and measures the force necessary to maintain a set rate of shear. By use of a specially designed star-shaped rotor the instrument produces reliable thixotropic data. This rotor does not disturb the sample when introduced and, therefore, is ideal for use with thixotropic systems. The rotary viscometer was employed in conjunction with a variable range recorder.⁵ The readings on the chart paper were calibrated to coincide with those on the "S" scale of the rotary viscometer. Values off the "S" scale are directly proportional to the shearing stress in dynes/cm.² at the surface of the rotor. The dual measuring head was employed to allow greater range of viscosity measurements.

NMR Measurements—The clay samples were placed in 5-mm. tubes. Spectra were obtained with a dual-purpose NMR spectrometer⁶ recording the derivative of the absorption peak with use of 80 c.p.s. modulation. The input power was maintained several decibels below saturation levels. The temperature of the sample was controlled by a variable-temperature probe unit.⁷ The thermocouple near the sample was calibrated against the reading of a thermocouple inside an ice-water mixture at 0°.

Each line width reported corresponds to the mean of 10 spectral sweeps. All line widths are in cycles per second. These values are obtained by the use of an internal standard. A modulation of known frequency is added to the main signal. This creates a side band some distance away from the main peak which can be used to equate the cycles per second of the side band to distance on the chart paper. Thus, the number of cycles per second can be calculated per millimeter of chart paper. The line width can then be measured in millimeters and converted to cycles per second as shown in Fig. 2.

Temperature, Aging, and Concentration Studies—A study of the effect of temperature, aging, and concentration was undertaken using an incomplete split-plot design. A 1-kg. sample of a given concentration was prepared in the manner previously described, and distributed into three of the specially designed containers for the rheological studies and into three NMR tubes. The samples were then placed in three constant-temperature baths at 35, 41, and 54°. This procedure was repeated at different intervals of time, building up a series of different age samples in each bath. The samples were all removed simultaneously from the baths and readings taken on the NMR and a rotary viscometer.

¹ Fisher Scientific Co., Fair Lawn, N. J.

² Waring blender.

³ Powerstat, type 116, Superior Electric Co., Bristol, Conn.

⁴ Haake Rotovisco, instrument No. 67-369, Polyscience Corp., Evanston, Ill.

⁵ Model S.R., E. H. Sargent & Co., Birmingham, Ala.

⁶ Varian Associates.

⁷ Varian model V-4340.

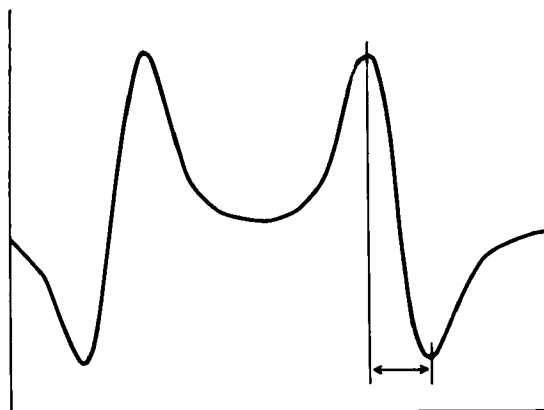


Figure 2—Typical NMR spectrogram illustrating line width measurements.

In order to study the effect of a wide range of concentration on the NMR line width, several 300-g. samples ranging from 8 to 15% w/w bentonite were prepared by the previously described method. A portion of each was placed in a NMR tube, stored at 54° for 2 weeks, and the NMR spectrographs run.

Repeated Shearing Studies—A 10% w/w bentonite sample was prepared in the manner previously described. It was distributed into 16 containers for viscosity measurements. The readings were taken on the rotary viscometer, and the containers emptied. The suspensions were recombined and subjected to uniform shearing after which they were again placed in the specially designed containers and measured on the rheometer.

NMR Low-Temperature Studies—A 15% w/w sample of bentonite was arbitrarily chosen for low-temperature NMR study. The temperature in the probe was controlled by passing nitrogen gas through liquid nitrogen and then into the probe. The temperature was lowered by increasing the rate of flow of the gas.

RESULTS AND DISCUSSION

In the introduction three prevalent theories on the nature and mechanism of thixotropy were discussed. *A priori* one would expect

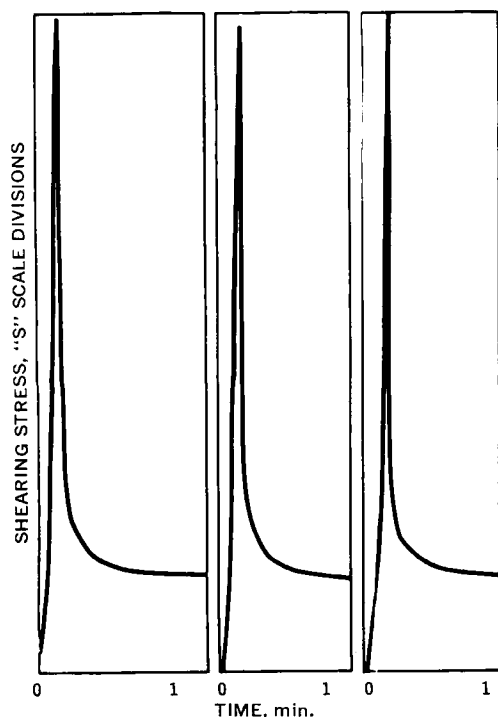


Figure 3—Typical rheogram of static yield value of bentonite-water samples measured on the rotary viscometer.

Table I—NMR and Viscosity Measurements of 6% w/w Bentonite Samples

| Time of Storage, days | Line Width, c.p.s.— | | | Static Yield Value, dynes/cm. ² | | |
|-----------------------|---------------------|-----|-----|--|------|------|
| | 35° | 41° | 54° | 35° | 41° | 54° |
| 1 | 149 | 152 | 148 | 58.6 | 53.6 | 75.3 |
| 2 | 155 | 149 | 149 | 65.3 | 67.0 | 56.9 |
| 3 | 147 | 152 | 149 | 67.9 | 79.5 | 61.9 |
| 6 | 145 | 151 | 148 | 70.3 | 82.0 | 75.3 |
| 8 | 146 | 152 | 149 | 69.5 | 54.4 | 82.1 |

the results to follow a given trend for any one theory. If the "ice" theory held true one would expect an increase in the line width with age, because the thixotropy would depend on the water structuring itself into a pseudocrystalline state. This type of structuring with time would tend to immobilize the water, curtailing the amount of free rotation the hydrogens are capable of exhibiting. Since restricting this motion causes a widening of the NMR spectrum line, a direct correlation would be established between this parameter and the age of the sample.

This theory could be extended to postulate that any other variable affecting thixotropy would also affect the line width. Since it will be shown that an increase of the temperature at which the sample is stored is directly proportional to the degree of thixotropy, temperature should also have a positive effect on the line width.

The theory advanced by Freundlich, von Engelhardt, and Hause proposes that the water, as a dipole, would orient itself in the direction of the existing electrostatic field. This would cause a weaker attraction than predicted by the "ice" theory even though more molecules would be involved in the resulting lattice. Since the water is restricted in its rotational motion due to the electrostatic attraction, the degree of thixotropy of the system would increase. The predicted effect of temperature, aging, and concentration on the line width would be the same as in the "ice" theory, but the expected degree of positive correlation would be different.

The matrix theory proposed by Usher, Kuhn, and Hofmann demands only that an initial adsorption of water occur to form hydrated platelets which gradually orient themselves relative to each other. This orientation can occur either edge to edge, side to side, or edge to side. The effect on the relative mobility of the water is negligible except for the initially adsorbed film. Thus, one would expect no correlation of temperature or aging with line width. Increasing concentration, however, would probably cause a widening of the NMR lines.

It was felt that the static yield value was the best rheological parameter to use in this study since it provides a very sensitive measure of thixotropic build-up. The static yield value is obtained, in dynes/cm.², by multiplying the maximum reading on the "S" scale by a constant obtained by calibrating the instrument with standard oils. A representative rheogram is shown in Fig. 3.

Tables I and II show the effect of temperature and aging on the line width of the NMR. Aging a bentonite sample over a period of 15 days has little effect on the line width, while it produces a large increase in the static yield value. Temperature also is shown to have an unusual effect on the static yield value of 10% w/w bentonite samples, as seen in Table II, increasing it to the point of making it impossible to read any sample over 1 week old. However, 6% w/w bentonite samples as shown in Table I, exhibited no observable effect due to temperature. Moreover, the line width measurements

Table II—NMR and Viscosity Measurements of 10% w/w Bentonite Samples

| Time of Storage, days | Line Width, c.p.s.— | | | Static Yield Value, dynes/cm. ² | | |
|-----------------------|---------------------|-----|-----|--|-------|----------------|
| | 35° | 41° | 54° | 35° | 41° | 54° |
| 1/4 | 139 | 139 | 139 | 606 | 638 | 901 |
| 1/2 | 143 | 143 | 140 | 917 | 1,015 | 1,408 |
| 1 | 143 | 141 | 138 | 1,015 | 1,063 | 1,637 |
| 3 | 144 | 142 | 139 | 1,965 | — | — ^a |
| 9 | 141 | 148 | 139 | — | — | — |
| 15 | 140 | 141 | 139 | — | — | — |

^a Samples too viscous to read on the rotary viscometer.

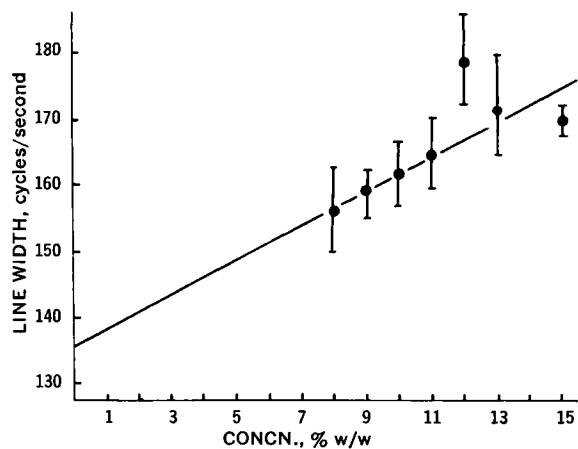


Figure 4—Effect of concentration on NMR line width of bentonite-water systems. Vertical bars represent \pm one standard deviation.

remained relatively constant throughout each of the aging and temperature studies.

Figure 4 shows that an increase in concentration causes a pronounced positive effect on the NMR line width measurements. The intercept of 134 c.p.s. is approximately equal to the line width that would be expected if the water were not bound to the platelets but was simply in contact with any solid surface.

Certain apparent discrepancies in the NMR data result from the fact that only those line widths measured on a given day can be compared.

The experimental evidence appears to point toward the matrix theory of thixotropic build-up. The lack of correlation of line width with temperature and aging as well as the positive effect of increased concentration on the line width are in agreement with this theory.

It might be argued that the other theories are the ones in action here, and that the NMR is not sensitive enough to truly measure what may be a very small change in the mobility of the water, but still enough to affect the static yield value.

A low temperature study was undertaken to test the validity of this argument. It was felt that as the temperature of the NMR probe and the sample was lowered near freezing a situation would be created in which the immobilization of the water in the manner predicted by the "ice" or "electrostatic" theory would be potentiated, and a widening of the NMR line would occur.

Table III indicates that as the temperature is lowered there is no effect on the line width until it drops below the freezing point of the 15% w/w bentonite water suspension, i.e., -5° . This fact lends credence to the matrix theory since the other two theories would predict line widening before the freezing point was reached.

Figure 5 indicates that the static yield values for the initial shearing of the 10% w/w bentonite-water samples are higher, at a given storage time, than those for samples that have been resheared. These results tend to further substantiate the validity of the matrix theory since they suggest that a realignment of the hydrated platelets occurs.

Table III—NMR Low Temperature Measurements of 15% w/w Bentonite Samples

| Temperature, $^{\circ}$ C | Line Width, c.p.s. |
|---------------------------|--------------------|
| 21 | 155.5 |
| 19 | 148.8 |
| 18 | 153.6 |
| 12 | 156.0 |
| 5 | 153.6 |
| 3 | 154.6 |
| -5 | 158.4 |
| -7 | 180.0 ^a |
| -8 | 177.6 ^a |
| -9 | 192.0 ^a |
| -10 | — ^b |

^a Result of one or two spectral sweeps while the suspension was freezing. ^b Sample was frozen and resultant line width too large to measure.

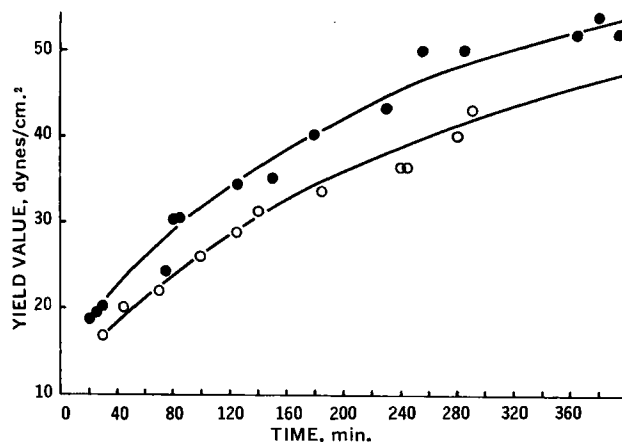


Figure 5—Effects of repeated shearing on 10% bentonite-water systems. Key: ●, initial samples; ○, resheared samples.

The bentonite can be said to be originally made up of deaggregated platelets which upon standing tend to orient themselves edge to edge producing an intricate matrix with small voids holding small amounts of water. This type of structure would exhibit a large yield value. After being repeatedly sheared these clay platelets would tend to line up and attach themselves to each other side to side forming stacks of montmorillonite which cannot immobilize water not already adsorbed on their surface. Upon standing a less intricate matrix would be formed with substantially larger voids. This type of structure would be less rigid and thus have a smaller yield value.

This type of orientation could also explain why certain low concentration samples which have been resheared appear to lose water to the surface upon standing. This is probably due to lower effective concentration of bentonite platelets which upon standing liberate water to the surface.

SUMMARY

This study was undertaken to elucidate the mechanism of thixotropy in montmorillonite suspensions.

The effect of temperature, aging, concentration, and reshearing on bentonite samples was evaluated. It was found that the static yield values increased with storage time, temperature, and concentration but decreased with repeated shearing. On the other hand, the NMR line width showed positive correlation only with concentration, but no apparent relationship with any of the other parameters.

The results appear to lend validity to the matrix theory as opposed to the "ice" or "electrostatic" theory of thixotropy.

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ACKNOWLEDGMENTS AND ADDRESSES

Received December 30, 1968, from the *Department of Pharmacy, College of Pharmacy, University of Florida, Gainesville, FL 32601*

Accepted for publication March 3, 1969.

The authors wish to express their appreciation to Dr. W. S. Brey, Jr., for his expert advice on the NMR studies.

Gas-Liquid Chromatographic Determination of Pantothenates and Panthenol

A. R. PROSSER and A. J. SHEPPARD

Abstract □ A procedure has been developed for the identification and quantitative determination of the pantothenates and panthenol by GLC. The pantothenate salts were converted to an ethyl ester by treatment with anhydrous ethanolic hydrogen chloride. The acetate derivatives of the pantothenic acid ethyl ester and panthenol were prepared by acetylation of the hydroxyl groups with a pyridine:acetic anhydride mixture. The excess reagents were removed and the oily residue was taken up in chloroform and injected on a 2.438-m. (8-ft.) × 4-mm. column packed with 2% neopentyl glycol sebacate (NPGSb). Trimethylsilyl and trifluoroacetate derivatives of the pantothenates and panthenol were also analyzed by gas chromatography. The procedure is very sensitive; as little as 0.25 mcg. can be detected. Structures of the acetate derivatives were confirmed by IR and NMR spectroscopy.

Keyphrases □ Panthenates, panthenol—separation, determination □ Derivatives—pantothenates, panthenol □ GLC—separation, analysis □ IR spectrophotometry—structure □ NMR spectroscopy—structure

A number of satisfactory methods are available for the identification and determination of the pantothenates and pantothenyl alcohol (panthenol) (1–7). However, previous reports (8–15) have shown that some of the water-soluble vitamins are amenable to GLC, thus suggesting that panthenol, pantothenic acid, and the pantothenic acid salts could also be determined by this technique.

Unmodified polyhydroxy and carboxylic organic compounds, such as panthenol and pantothenic acid and its salts, are not volatile enough for direct GLC, and both have a tendency to decompose at high temperatures or are not soluble enough in the common organic solvents. However, these problems are easily overcome by converting the compounds to volatile derivatives such as acetates (AC), trimethylsilyl ethers (TMSE), or trifluoroacetates (TFA) for GLC analysis.

This paper describes the GLC determination of the acetate derivatives of pantothenic acid ethyl ester and panthenol. The acetyl derivatives (acetates) were chosen because of their relatively high degree of volatility and stability and their ease of preparation and cleanup. The ethyl ester of pantothenic acid was chosen rather than the methyl ester so that both derivatives would have

equal carbon numbers and molecular weights; thus the separation would be based on the arrangement of the constituents within the molecule. Other derivatives such as trimethylsilyl ether, trifluoroacetate, and propionate were investigated and are discussed.

EXPERIMENTAL

Instrumentation—A gas chromatograph¹ fitted with a high-temperature hydrogen-flame ionization detector (FID) and a β -argon ionization detector (AID) with a 56- μ c. ²²⁶Ra foil was used with a 5-mv., 2-sec., 27.94-cm. (11-in.) strip chart recorder.

Materials—The following were used: *d*-pantothenyl alcohol, *d*-pantothenic acid calcium salt, and *dl*-pantothenyl alcohol (Sigma Chemical Co., St. Louis, Mo.); *d*-pantothenic acid calcium salt, trifluoroacetic anhydride (TFAA), propionic anhydride, and valeric anhydride (Eastman Organic Chemicals, Distillation Products Industries, Rochester, N. Y.); *dl*-pantothenic acid (K & K Laboratories, Inc., Plain View, N. Y.); *d*-pantothenic acid sodium salt (Mann Research Laboratories, Div. of Becton Dickinson & Co., New York, N. Y.); bis(trimethylsilyl)acetamide (BSA) (Perco Supplies, San Gabriel, Calif.); bis(trimethylsilyl)trifluoroacetamide (BSTFA) (Supelco, Inc., Bellefonte, Pa.); trimethylchlorosilane (TMCS) and hexamethyldisilazane (HMDS) (Applied Science Laboratories, Inc., State College, Pa.); and chloroform, (Baker analyzed reagents/spectrophotometric, J. T. Baker Chemical Co. Phillipsburg, N. J.). All other solvents and reagents used were reagent grade and required no further purification.

Preparation of Derivatives—Esterification—The methyl and ethyl esters of pantothenic acid were prepared from calcium pantothenate and sodium pantothenate; the procedure of Stoffel *et al.* (16) was used for the preparation of the methanolic and ethanolic HCl solutions. In a typical experiment, 54.4 mg. of calcium pantothenate (or its equivalent of sodium pantothenate) and 5 ml. of 2.5% (w/w) ethanolic HCl were stirred in a small round-bottom flask with a stirring bar for 1.5 hr. at room temperature. The ethanolic HCl solution was removed by flash evaporation.

Acetylation—The pantothenic acid ethyl ester (ethyl pantothenate) and panthenol were converted to the acetate derivatives by treating each compound with a 1:1 mixture of acetic anhydride and pyridine.

Panthenol (50.0 mg.) and/or pantothenic acid ethyl ester (obtained from the above described esterification of 54.4 mg. of calcium pantothenate) was placed in a small round-bottom flask containing a stirring bar and 3 ml. each of acetic anhydride and pyridine were added. The reaction mixture was stirred for 1 hr. at room temperature. The acetylating reagents were removed by flash evaporation at 40–50°. If the reaction product was to be used for spectroscopic

¹ Model 5000 series, Barber-Colman, Rockford, Ill.