and he has supplied us with specimens of pantothenic acid and calcium pantothenate in varying degrees of purity. With this material we have been able to test out this theory and to show that it well may be correct.

Using a control medium containing the products of complete acid hydrolysis of casein, lactic, pimelic and nicotinic acids and inorganic salts, but completely deficient in β-alanine, a series of media has been prepared in which increasing quantities of β-alanine were added to one set, pantothenic acid or calcium pantothenate to a second and the latter substance hydrolyzed by autoclaving with normal hydrochloric acid for thirty minutes at 15 lb. (1 atm.) to a third. The various media were autoclaved (*p*H 7.6) for ten minutes at 10 lb. (0.67 atm.) pressure. After inoculation with the strain of the diphtheria bacillus (Allen), and incubation for three days at 35°, the resulting bacterial growth was centrifuged down, washed and the bacterial nitrogen determined by a method already described, as a measure of bacterial growth [Mueller, *J. Bact.*, **29,** 383 (1935)]. The table shows the results obtained: A = β-alanine; B = Ca pantothenate (about 50%) stated to yield 16% β-alanine on hydrolysis; C = solution B after acid hydrolysis.

	γ added/10 cc. medium			Mg bacterial N/10 cc. medium		
	A	B	C	A	B	C
1 Control +	..	0.0	..	..	0.13	..
2 Control +	..	.31	..	..	.41	..
3 Control +	..	.62	..	..	.60	..
4 Control +	..	1.5	1.5	..	1.47	0.32
5 Control +	..	3.1	3.1	..	2.78	.16
6 Control +	1	6.2	6.2	0.39	3.67	.29
7 Control +	2.5	15.5	15.5	.24	4.70	2.05
8 Control +	5	31	31	6.12	5.35	5.76
9 Control +	10	62	62	6.78	6.60	lost[a]
10 Control +	20	125	..	7.30	7.06	..

[a] Heavy growth.

This and other similar experiments uniformly show a smooth, gradual increase in growth with the addition of pantothenic acid, whereas with β-alanine there is no definite increase over controls until a concentration of from about 2.5 γ per 10 cc. is used. At this point, initiation of growth is slow and irregular, possibly dependent on the size of the inoculum, (platinum loop of pellicle). At levels of 5, 10 and 20 γ concentration of β-alanine or its equivalent of panthothenic acid, growth is heavy and the amounts produced by the two materials are very nearly the same. Hydrolysis of pantothenic acid yields a solution with the properties of β-alanine, *i. e.*, no effect until the concentration of the latter in the hydrolytic products reaches 2.5 γ/10 cc. medium, whereas doubling this concentration regularly leads to heavy growth.

These facts tend to support the view that β-alanine must first be built up into some more complex material before it may be directly utilized by *C. Diphtheriae*, whereas with pantothenic acid no such preliminary synthesis is required.

It is interesting and significant that Snell, Brown and Peterson [THIS JOURNAL, **60,** 2825 (1938)] have shown recently that both pantothenic acid and nicotinic acid are apparently essential factors for growth of certain strains of the lactic acid bacteria. These organisms, unlike the diphtheria bacillus, seem to be unable to effect the synthesis of pantothenic acid from β-alanine, requiring the presence of the more complex material for satisfactory growth.

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RECEIVED NOVEMBER 23, 1938

PRESSURE–AREA RELATIONS FOR MONOMOLECULAR FILMS OF TRI-*p*-CRESYL PHOSPHATE AND RELATED COMPOUNDS

Sir:

Interesting differences in surface activity have been observed in a study of phosphorus-organic compounds closely related in structure. Monomolecular film properties of the three isomers of tricresyl phosphate (ortho, meta and para) are practically identical but quite unlike those of either tri-*p*-cresyl phosphite or tri-*p*-cresyl thiophosphate.

Pressure–area relations have been studied on a modified Cenco film-balance apparatus, using general techniques similar to those described by N. K. Adam[1] and Harkins, Ries and Carman.[2,3] The volatile solvent used for the Eastman compounds was twice-distilled benzene. Films were spread on distilled water.

Tri-*p*-cresyl phosphate forms well-behaved, compressible films, whereas the corresponding phosphite and thiophosphate show extremely poor film-forming properties. Films of the phosphite and thiophosphate require compression far beyond the minimum film area for monomolecular

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[1] N. K. Adam, "The Physics and Chemistry of Surfaces," Clarendon Press, Oxford, 1938.

[2] Harkins, Ries and Carman, THIS JOURNAL, **57**, 2224 (1935).

[3] Harkins, Carman and Ries, *J. Chem. Phys.*, **3**, 692 (1935).

thickness before an appreciable rise in pressure is observed. For example, at a pressure of only 1 dyne per cm., the tri-*p*-cresyl thiophosphate film thickness (62.9 Å.) is over five times as great as the maximum monomolecular thickness (11.6 Å.) of tri-*p*-cresyl phosphate.

An interesting correlation between polar group structure and film properties is apparent when we consider the schematic diagrams in Fig. 1.

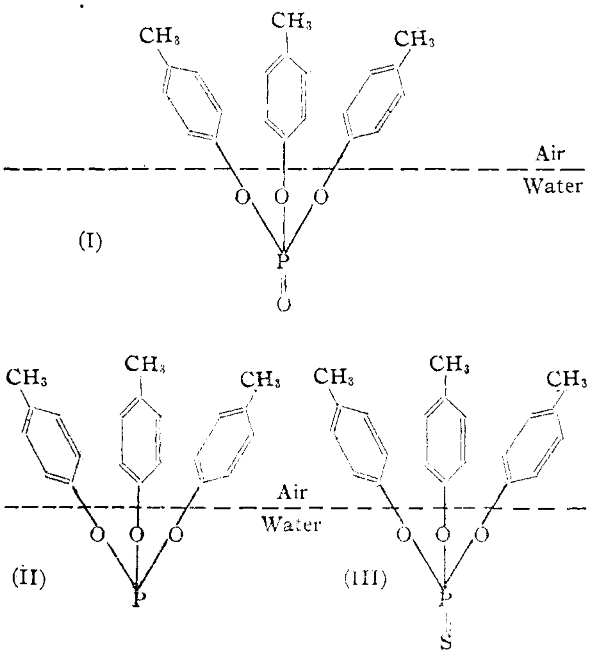

Fig. 1.—Schematic diagrams of molecular orientation at an air–water interface: (I) tri-*p*-cresyl phosphate; (II) tri-*p*-cresyl phosphite; (III) tri-*p*-cresyl thiophosphate. At expanded areas the rings are probably drawn close to the water.

The two poor film-forming compounds (II and III) differ from the tri-*p*-cresyl phosphate (I) in that they lack the P=O group. We must, therefore tentatively conclude that the important contribution to the polarity of the molecule is made by the P=O group as indicated by the superior film properties of tri-*p*-cresyl phosphate.

The most important pressure–area characteristics of a typical tri-*p*-cresyl phosphate film (27.9°) may be briefly summarized. The molecular area values at film pressures of zero (extrapolated), 5 and 8.76 dynes per cm. (the maximum) are, respectively, 99.4, 69.3 and 46.5 sq. Å. Using a density of 1.1284 g. per cc. the film thickness values at the same pressures are, respectively, 5.42, 7.78 and 11.6 Å. Partial overlapping of the molecules may perhaps account for the small areas in the final stages of the compression. The compressibility at $f = 0$, $[(a_0 - a_1)/a_0]/(f_1 - f_0)$ is 0.0607.

The above-mentioned compounds with each of the three rings attached directly to the polar group are much more compressible than the polycyclic compounds in which only one ring is attached to the principal polar group.[4] The molecular configurations of the latter type permit an approach toward vertical orientation and allow closer packing. It has been shown that films of horizontally oriented long chain molecules (polymers of ω-hydroxydecanoic acid) are much more compressible than those of vertically oriented molecules.[3] This present work indicates that perhaps the same general relationship applies to ring systems. The film compressibilities of a number of multiple ring compounds which are capable of vertical orientation range from one-sixth to about one-eighteenth that of tri-*p*-cresyl phosphate. In both types of orientation the films formed by ring compounds are, in general, more compressible than those composed of straight chain molecules. An increase in maximum film pressure with increasing vertical length of the ring system is also noted.

(4) Pressure–area relations for such a series of three-ring and five-ring compounds have been investigated and the data tabulated.[2,5]

(5) Harkins, Carman and Ries, THIS JOURNAL, **58**, 1377 (1936).

THE RESEARCH AND DEVELOPMENT DEPARTMENT
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RECEIVED NOVEMBER 17, 1938

THE STRUCTURE OF LUMISTEROL

Sir:

In a memoir entitled "Photochemical Interaction between Ketones and Alcohols," Weizmann, Bergmann and Hirshberg[1] in a discussion of the mechanism of ergosterol irradiation state that "at variance with the assumption of Spring[2] that this important reaction involves primarily epimerization at C_3, Windaus and Dimroth[3] were able to demonstrate that the secondary hydroxyl group at C_3 is actually not influenced by irradiation. . . ."

In the interest of accuracy it is necessary to note that in the paper cited I state that "the reactions of lumisterol, the primary photoisomeride of ergosterol, establish that it is a stereoisomer of the latter," no suggestion being made that it is the

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(1) Weizmann, Bergmann and Hirshberg, THIS JOURNAL, **60**, 1530 (1938).

(2) Spring, *Chemistry and Industry*, **55**, 837 (1936).

(3) Windaus and Dimroth, *Ber.*, **70**, 376 (1937); *cf.* Dimroth, *ibid.*, **69**, 1123 (1936).