and all attempts to convert this form into the metastable form were unsuccessful.

Experimental

In a 2-liter flask fitted with mercury-seal mechanical stirrer and reflux condenser, were placed 150 g. (0.8 mole) of *p*-chlorodiphenyl (Eastman Kodak Co. Techn.), 145 g. (0.8 mole) of *p*-benzophenone, and 525 cc. of anhydrous benzene. The mixture was heated until all of the solid had dissolved. Forty-five grams (0.2 mole) of sodium sand was then added, in small portions, through the top of the condenser, each portion being washed down with a little dry benzene. Just enough heat was applied to keep the reaction mixture refluxing gently. The time required for the addition of the sodium was two hours. The reaction mixture was then refluxed for two hours longer. After cooling, the unreacted sodium was destroyed by the addition of methanol. The mixture was then hydrolyzed with dilute hydrochloric acid, the benzene layer separated, and the carbinol isolated by removal of the benzene. After repeated recrystallization from ligroin (b. p. 90–120°) 180 g. of the carbinol was obtained, m. p. 135–136°; yield 67%.

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A Calcium Chloride Compound of α-*d*-Galactose[1]

BY RAYMOND M. HANN AND C. S. HUDSON

Although crystalline calcium chloride addition compounds of several aldose sugars have been obtained, one containing *d*-galactose as a component does not appear to have been described. The present note summarizes the experimental details leading to the isolation of α-*d*-galactose calcium chloride trihydrate.

Ten grams of α-*d*-galactose was dissolved in 16 cc. of water and 16 g. of calcium chloride dihydrate (2 moles) was added. Upon slowly concentrating the thin sirup in a desiccator, spontaneous crystallization occurred in seven months in a yield of 15 g. The substance may be recrystallized by solution in three parts of 90% alcohol containing 10% of calcium chloride dihydrate, separating in groups of clear colorless elongated prisms which melt at 129–130° (corr.). It must be preserved in a dry atmosphere to prevent deliquescence. Analysis and the course of mutarotation indicate that the compound is α-*d*-galactose calcium chloride trihydrate.

Anal. Calcd. for $C_6H_{12}O_6{\cdot}CaCl_2{\cdot}3H_2O$: Ca, 11.6; Cl, 20.5; galactose, 52.2. Found: Ca, 11.7; Cl, 20.4; galactose (by hypoiodite) 52.2.

MUTAROTATION OF α-*d*-GALACTOSE·$CaCl_2{\cdot}3H_2O$ IN WATER

Concentration 2.0173 g. in 25 cc. solution; tube length, 2 dm.; $T = 20 \pm 0.5°$.

Time after making soln., min.	$[\alpha]^{20}_D$	$[\alpha]^{20}_D$ based on galactose	$k_1 + k_2$	$k_1 + k_2$ pure galactose
2.7	+75.82°	+145.3°	....	....
3.8	74.65°	143.0°	0.0143	....
5.8	72.82°	139.5°	.0133	0.0127
7.8	71.43°	136.9°	.0121	.0117
8.9	70.57°	135.2°	.0121	.0118
10.9	69.28°	132.7°	.0116	.0107
14.1	67.67°	129.7°	.0108	.0105
25.0	62.42°	119.6°	.0101	.0096
38.4	57.92°	114.9°	.0094	.0092
48.0	56.13°	107.5°	.0094	.0089
73.0	50.19°	96.2°	.0092	.0086
∞	42.68°	81.8°	....	....

The extrapolated initial rotation of the galactose in each case was about +151° and the change in rate as mutarotation progressed was quite similar. The somewhat high equilibrium rotation, based on galactose, is probably due to the presence of calcium chloride.

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U. S. PUBLIC HEALTH SERVICE
WASHINGTON, D. C.
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[1] Publication authorized by the Surgeon General, U. S. Public Health Service.

Monolayers and Multilayers of Chlorophyll

BY IRVING LANGMUIR AND VINCENT J. SCHAEFER

Monolayers of chlorophyll[1] spread on a water surface from a benzene solution may be deposited in successive layers on a solid plate to form multilayers.

A benzene solution of chlorophyll illuminated by blue light shows red fluorescence. During the spreading of a drop of the solution on a water surface fluorescence disappears as soon as the benzene has evaporated.

Chlorophyll monolayers on water behave as two-dimensional liquids until subjected to a pressure of more than 20 dynes cm.$^{-1}$, when they become quite viscous. The *p*H of the water has apparently no effect on the viscosity below this pressure.

The absolute viscosities[2] of chlorophyll mono-

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[1] Made by Dr. A. Stoll of Basel and obtained from Dr. J. Franck of the Physics Department of Johns Hopkins University.

[2] Irving Langmuir and Vincent J. Schaefer, THIS JOURNAL, not yet published.

layers under various conditions are shown in Table I.

TABLE I

ABSOLUTE SURFACE VISCOSITY OF CHLOROPHYLL MONOLAYERS ON WATER

*p*H	F	μ_s
5.8	1.5	0.001
5.8	5	.001
5.8	7	.001
5.8	16	.305
3.0	9	.002
5.8	9	.002
10.0	9	.002
3.0	30	.242
5.8	30	7.8
10.0	30	40.7

Excellent multilayers (up to 600 layers) are easily built up as Y-films on glass or chromium, using a piston oil of tricresyl phosphate ($F = 9$ dynes cm.$^{-1}$) on distilled water. Built-up films of this type when measured by sodium light[3] give a thickness of 14.2 Å. using the value of the refractive index 1.64 as determined by Dr. Katharine B. Blodgett of this Laboratory. When higher piston oil pressures were used the monolayer was found to be easily compressible with $F = 16$. A-B hydrous films are formed with water separating the A- and B-monolayers, the thickness of the double layer being about 35 Å. When $F = 30$ the double layer shows a thickness of 59 Å. at *p*H 3.0 and 5.8 and 68 Å. at *p*H 10.0. By drying the successive layers, dehydrous multilayers can be built up.

A chlorophyll Y-multilayer is non-wettable by water, giving a contact angle of 80°, but is wettable and soluble in hydrocarbons such as hexadecane which becomes fluorescent when placed on the built-up film. A single layer of chlorophyll molecules will produce fluorescence in a drop of benzene placed in contact with it.

Monolayers of chlorophyll may be deposited on top of barium stearate multilayers as PRA, PRB or PRAB films. The A-monolayer and the B-monolayer both give a contact angle of 90° against water and the drop will flow over the surface when the slide is tilted about 25°. A PRAB film, however, shows a contact angle of only 70° with very great hysteresis when the slide is tilted.

Chlorophyll Y-films of thicknesses ranging from one to 600 layers were examined with a beam of blue light. No detection of fluorescence could be observed in any instance involving a built-up film. When a small amount of chlorophyll was dissolved in Petrolatum and a drop placed on a clean water surface, it showed distinct fluorescence but the small area to which the drop spread indicated that little of the chlorophyll had become adsorbed at the interface between the oil and the water. When enough was added to the oil to cause it to spread to a monolayer the fluorescence disappeared.

A minute amount of chlorophyll added to molten paraffin exhibits strong fluorescence. This property instantly disappeared upon the solidification of the paraffin. Chlorophyll mixed with heptadecanol and hexadecane and spread as monolayers on water or transferred to solids shows no fluorescence.

A monolayer of chlorophyll deposited on a substrate of pure barium stearate or egg albumin when immersed into benzene is completely dissolved, indicating the absence of strong adsorption forces between the substrate and the chlorophyll.

The absence of chlorophyll fluorescence when spread as a homogeneous or dispersed monolayer on water or when deposited as homogeneous or dispersed single or multi-layers on solids indicates that the fluorescent property of chlorophyll involves more than dispersion alone.

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The Ternary System Methyl Alcohol, Toluene and Water

BY L. S. MASON AND E. ROGER WASHBURN

In continuation of a series of earlier investigations of related binary and ternary systems[1] the solubility curve for the ternary system methyl alcohol, toluene and water at 25° has now been determined and the distribution of methyl alcohol between various proportions of water and toluene has been calculated. Incidentally, the refractive indices of various saturated solutions in this system have also been measured.

Materials.—Synthetically prepared methyl alcohol was desiccated over lime and fractionated from an all glass still. The relative density of the material used was d^{25}_{4} 0.78672 and the refractive index was n^{25}_{D} 1.32660.

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(3) Katharine B. Blodgett and Irving Langmuir, *Phys. Rev.*, **51**, 964 (1937).

(1) E. R. Washburn and others, THIS JOURNAL, 1931–1935; *J. Phys. Chem.*, 1936–1937; See *J. Phys. Chem.*, **41**, 457 (1937).