

**$\beta$ -Sitoseryl Glucoside Tetrabenzoate.**—A 3.0-g. portion of the  $\beta$ -sitoseryl glucoside was dissolved in 35 ml. of pyridine and 25 ml. of benzoyl chloride was added. The mixture was heated at 100° for about 30 minutes with occasional stirring and then poured into water. When the precipitate had settled, the aqueous solution was decanted and the residue was dissolved in ether. The ethereal solution was washed with dilute sodium carbonate and then with water. After evaporation of the ether, the residue was twice recrystallized from ethanol. The yield was 4.2 g. The m.p. was 201°,  $[\alpha]^{25D}$  15.9° (chloroform, 1.3095 g./100 ml., 2-dm.).

*Anal.* Calcd. for  $C_{63}H_{76}O_{10}$ : C, 76.21; H, 7.71;  $C_6H_5CO$ , 42.33. Found: C, 75.93, 75.77; H, 7.68, 7.69;  $C_6H_5CO$ , 41.45, 41.63.

**Hydrolysis of the  $\beta$ -Sitoseryl Glucoside.**—A 2.1692-g. sample of the  $\beta$ -sitoseryl glucoside was hydrolyzed by the method of Thornton, *et al.*<sup>6</sup> The glucoside was refluxed for 22 hours with 100 ml. of absolute ethanol and 1 ml. of concentrated sulfuric acid, solution gradually taking place as the reaction progressed. The bulk of the ethanol was distilled off under reduced pressure and the residue was diluted with water and extracted with several portions of ether. The ethereal solution was washed with water and the washings added to the main solution which was then further acidified with 1 ml. of concentrated sulfuric acid and refluxed for five hours to hydrolyze any ethyl glucoside. The aqueous solution was cooled and made to 200 ml. volume. This solution was used in establishing the identity of the sugar.

**Identification of Glucose from Glucoside.**—A Shaffer-Hartmann titration of an aliquot representing 0.2169 g. of the original glucoside showed it to contain 0.0661 g. of reducing sugar, calculated as glucose, or 97.6% of the theoretical amount. A specific rotation based on this concentration gave a value of +52.4°, accepted value, +52.2°.

A portion of the hydrolysate was oxidized to saccharic acid and was converted to the characteristic boat-like crystals of its potassium acid salt as directed in Morrow and Sandstrom.<sup>7</sup>

When adjusted to 0.2 molar concentration, the hydrolysate was indistinguishable from a known glucose solution in time of osazone formation and microscopic appearance of the osazone.

**$\beta$ -Sitosterol Component of the Glucoside.**—The washed ether extract of the hydrolysis mixture from 2.1692 g. of the glucoside was evaporated and dried in a tared flask and found to weigh 1.503 g. (98%). This crude sterol was found to be 84.4% precipitable with digitonin (conversion factor, 0.257). Another sample of the crude sterol was recrystallized from ethanol and chromatographed over asbestos paper, developing with 1% ethanol in petroleum ether. Streaking with concentrated sulfuric acid showed only one component. Another sample of the crude sterols, acetylated and then brominated in an ether-glacial acetic acid mixture, showed no insoluble tetrabromides after 48 hours at 0–5°, hence the presence of a doubly-unsaturated sterol is unlikely.

For purification and preparation of derivatives, 61.0 g. of crude sterol glucoside was hydrolyzed as before and the sterols recrystallized from ethanol, petroleum ether and acetone until all that could be crystallized melted between 135 and 138° and weighed 35.1 g. (80%). Repeated recrystallizations from acetone failed to raise the m.p. above 137–138°;  $[\alpha]^{25D}$  –38.2° (chloroform, 5.0693 g./100 ml., 2-dm. tube).

*Anal.* Calcd. for  $C_{26}H_{50}O$ : C, 83.98; H, 12.16. Found: C, 84.28, 84.23; H, 12.00, 12.11.

**$\beta$ -Sitosterol Acetate.**—This was prepared in the usual way, m.p. 125–126°,  $[\alpha]^{25D}$  –40.3° (chloroform, 1.6824 g./100 ml., 2-dm. tube).

*Anal.* Calcd. for  $C_{28}H_{52}O_2$ : C, 81.52; H, 11.48. Found: C, 81.53, 81.69; H, 11.33, 11.34.

Saponification of the acetate regenerated the  $\beta$ -sitosterol unchanged.

**$\beta$ -Sitosterol Benzoate.**—This compound was prepared by heating  $\beta$ -sitosterol with benzoyl chloride and pyridine.

(6) M. H. Thornton, H. R. Kraybill and J. H. Mitchell, *THIS JOURNAL*, **62**, 2006 (1940).

(7) C. A. Morrow and W. M. Sandstrom, "Biochemical Laboratory Methods," John Wiley and Sons, Inc., New York, N. Y., 1935, pp. 165–166.

After purification the benzoate melted at 147–148°. The  $[\alpha]^{25D}$  was –13.6° (chloroform, 2.0760 g./100 ml., 2-dm. tube).

*Anal.* Calcd. for  $C_{36}H_{54}O_2$ : C, 83.34; H, 10.49. Found: C, 83.36, 83.31; H, 10.49, 10.43.

Saponification of the benzoate regenerated the  $\beta$ -sitosterol unchanged.

**Acknowledgment.**—The author is indebted to O. W. Bissett of this Laboratory for the Shaffer-Hartmann sugar titration and to L. E. Brown of the Southern Regional Research Laboratory of this Bureau for the carbon and hydrogen analyses.

CITRUS PRODUCTS STATION  
BUREAU OF AGRICULTURE AND INDUSTRIAL CHEMISTRY  
WINTER HAVEN, FLORIDA RECEIVED JUNE 11, 1951

## The Standard Potentials of the Silver-Silver Chloride Electrode in Absolute Volts

BY D. F. SWINEHART

The standard potentials of the cell Pt-H<sub>2</sub>(g)/HCl(*m*)/AgCl-Ag have been accurately determined by Harned and Ehlers.<sup>1</sup> These constants are important for the determination of the thermodynamic properties of hydrochloric acid solutions and because they are used in the accurate determination of the ionization constants of weak acids and bases.

In 1948 the National Bureau of Standards officially changed from the international to the absolute system of electrical units.<sup>2</sup> All standard cells are now certified in absolute volts. It seems desirable to recalculate the results of Harned and Ehlers in the new units. The function  $2.30259 RT/F$  in international volts used by these investigators was evaluated from the constants listed by Lewis and Randall.<sup>3,4</sup> These values, however, due to a partial cancellation of errors, accidentally agree within one part in 10<sup>5</sup> with the presently accepted values of the function in absolute volts.

Therefore, their results have been recalculated in international volts using the values of  $2.30259 RT/F$  given in those units by Manov, Bates, Hamer and Acree.<sup>5</sup> This was done by calculating for a few points at the highest dilution values for the function which Harned and Ehlers used in extrapolating to  $m = 0$  to obtain  $E^\circ$ . This was done in the units used by them and again in international volts. The consistent small differences were then added to Harned and Ehlers' values for  $E^\circ$  to obtain  $E^\circ$  in international volts. This, in effect, uses their entire extrapolation procedure. These results are shown in the third column of Table I.

These results were fitted by least squares by the equation used by Harned and Ehlers yielding the result:  $E^\circ$  (international volts) =  $0.22247 - 6.4450 \times 10^{-4} (t - 25) - 3.276 \times 10^{-6} (t - 25)^2 + 8.99 \times 10^{-9} (t - 25)^3$ . Values of  $E^\circ$  calculated

(1) H. S. Harned and R. W. Ehlers, *THIS JOURNAL*, **55**, 2179 (1933).

(2) National Bureau of Standards Circular No. 475, 1949.

(3) G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923.

(4) H. S. Harned and D. D. Wright, *THIS JOURNAL*, **55**, 4849 (1933).

(5) G. G. Manov, R. G. Bates, W. J. Hamer and S. F. Acree, *ibid.*, **65**, 1765 (1943).

from this equation are shown in column four in Table I.

TABLE I  
STANDARD POTENTIALS OF THE CELL Pt-H<sub>2</sub>(g)/HCl(m)/AgCl-Ag

Temp., °C.	E° (obsd.) (Harned and Ehlers)	E° (obsd.) (int. volts)	E° (calcd.) (int. volts)	E° (calcd.) (abs. volts)	2.30259 RT/F (abs. volts)
0	0.23634	0.23641	0.23639	0.23647	0.054195
5	.23392	.23399	.23398	.23406	.055187
10	.23126	.23133	.23137	.23145	.056179
15	.22847	.22855	.22858	.22865	.057171
18	.....	.....	.22682	.22689	.057766
20	.22551	.22559	.22561	.22568	.058163
25	.22239	.22247	.22247	.22254	.059155
30	.21912	.21920	.21917	.21924	.060147
35	.21563	.21571	.21571	.21578	.061139
37	.....	.....	.21425	.21432	.061536
40	.21200	.21208	.21210	.21216	.062131
45	.20821	.20829	.20834	.20841	.063123
50	.20437	.20446	.20445	.20452	.064115
55	.20035	.20044	.20043	.20050	.065107
60	.19620	.19629	.19628	.19635	.066099

The constants of this equation were multiplied by the factor<sup>2</sup> 1.000330 yielding  $E^\circ$  in absolute volts:  $E^\circ$  (absolute volts) =  $0.22254 - 6.4471 \times 10^{-4}(t - 25) - 3.277 \times 10^{-6}(t - 25)^2 + 8.99 \times 10^{-9}(t - 25)^3$ . Values of  $E^\circ$  calculated from this equation are shown in column five in Table I. These results should be used in future calculations of the ionization constants of weak acids and bases.

For convenience, the values of the function  $2.30259 RT/F$  in absolute volts are shown in column six of Table I. These values were calculated using the constants listed by Bearden and Watts,<sup>6</sup>  $R = 8.3144$  abs. joules mole<sup>-1</sup> deg.<sup>-1</sup>,  $T_0 = 273.16^\circ\text{K}$ . and  $F = 96495.4$  abs. coulombs equiv.<sup>-1</sup>.

DuMond and Cohen<sup>7</sup> list a slightly different value of the Faraday, 96519.4 abs. coulombs equiv.<sup>-1</sup> on the physical scale corresponding to 96493.1 abs. coulombs equiv.<sup>-1</sup> on the chemical scale. This value, differing from that of Bearden and Watts by 2 parts in 10<sup>6</sup>, would increase  $2.30259 RT/F$  by one digit in the fifth significant figure but this is within the limits of error of the above calculations.

(6) J. A. Bearden and H. M. Watts, *Phys. Rev.*, **81**, 73 (1951).

(7) J. W. M. DuMond and E. R. Cohen, *ibid.*, **82**, 555 (1951).

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF OREGON  
EUGENE, OREGON

RECEIVED JULY 18, 1951

### A New Synthesis of 4,6-Diamino-2,5-dichloropyrimidine

BY E. C. TAYLOR, JR.,<sup>1</sup> AND P. DRENCHKO

In the course of a program on synthetic pteridines, 4,6-diamino-2-chloropyrimidine was desired as a possible intermediate. Chlorination of 4,6-diamino-2-hydroxypyrimidine with phosphorus oxychloride was unsuccessful; no reaction took place and the starting material was recovered

(1) du Pont Postdoctoral Fellow in Chemistry, 1950-1951.

unchanged. Addition of phosphorus pentachloride to the phosphorus oxychloride reaction mixture resulted in the formation of a clear solution, but the product of the reaction proved to be 4,6-diamino-2,5-dichloropyrimidine and not 4,6-diamino-2-chloropyrimidine as expected. The compound was formed in 64% yield, as contrasted with a 12.2% yield by the only previously reported method involving the treatment of 2,4,5,6-tetrachloropyrimidine with ammonia.<sup>2</sup> Such anomalous introduction of halogen by phosphorus pentachloride has been observed previously in the pyrimidine series. Chlorination of 2-amino-4,6-dihydroxypyrimidine with phosphorus oxychloride and phosphorus pentachloride gives largely 2-amino-4,5,6-trichloropyrimidine and some 2-amino-4,6-dichloropyrimidine, and barbituric acid under the same conditions yields 2,4,5,6-tetrachloropyrimidine.<sup>3</sup> Likewise, 2-hydroxy-4-methylpyrimidine has been reported to yield a compound designated as 2:x:x:x-tetrachloro-4-methylpyrimidine upon treatment with the same reagents.<sup>3</sup> Thus it would appear to be a valid generalization that chlorination in the 5-position of a pyrimidine may readily occur if phosphorus pentachloride is employed.

#### Experimental

**4,6-Diamino-2,5-dichloropyrimidine.**—A mixture of 200 ml. of phosphorus oxychloride, 130 g. of phosphorus pentachloride and 20 g. of 4,6-diamino-2-hydroxypyrimidine<sup>4</sup> was heated under reflux for two hours, the excess phosphorus oxychloride removed by distillation under reduced pressure and the sirupy residue poured onto ice. The resulting acid solution was adjusted to pH 8 with sodium bicarbonate and the precipitate which formed was collected by filtration, washed thoroughly with water and dried. The crude product was then placed in a soxhlet cup and continuously extracted with acetone over a period of 20 hours. Removal of the acetone and crystallization of the residue from ether-petroleum ether gave 18.2 g. (64%) of white needles melting at 303-305°. The reported<sup>2</sup> melting point for 4,6-diamino-2,5-dichloropyrimidine is 302-304°.

*Anal.* Calcd. for C<sub>4</sub>H<sub>4</sub>N<sub>2</sub>Cl<sub>2</sub>: C, 26.8; H, 2.3; N, 31.3. Found: C, 27.1; H, 2.4; N, 31.1.

(2) S. J. Childress and R. L. McKee, *This Journal*, **72**, 4271 (1950).

(3) J. R. Marshall and J. Walker, *J. Chem. Soc.*, 1004 (1951).

(4) A. Bendich, J. F. Tinker and G. B. Brown, *This Journal*, **70**, 3109 (1948).

NOYES CHEMICAL LABORATORY  
UNIVERSITY OF ILLINOIS  
URBANA, ILLINOIS

RECEIVED OCTOBER 20, 1951

### Spallation Products from Cobalt and 240 Mev. Protons

BY GENEVIEVE WAGNER AND EDWIN O. WIIG

The nuclear reactions resulting when thin targets of pure cobalt (<sup>59</sup>Co) were bombarded with 240 Mev. protons in the 130-inch Rochester cyclotron have been studied. In order to observe the products of the reactions inert carriers were added to a solution of the target and fractions containing the radioisotopes were separated.

The gross decay curve of each chemically separated fraction was resolved to give the half-lives of the individual radioactive species. The specific nuclides shown in Table I were identified on this basis. Further verification was provided by testing for positive and negative β-particles whenever the