ANALYSES

Salt	In, % Calcd.	In, % Found		C, % Calcd.	C, % Found		H, % Calcd.	H, % Found		Cl, % Calcd.	Cl, % Found	
$(C_2H_5COO)_2InOH$	41.31	41.40	41.48	25.91	25.72	25.80	3.99	3.93	4.02			
n-$(C_3H_7COO)_2InOH$	37.54	37.67	37.62	31.38	31.32	31.20	4.94	4.76	4.84			
$(CCl_3COO)_2InOH$	25.12	24.96	25.03	10.51	10.61	10.56	0.22	0.25	0.29	46.60	46.63	46.38
$(C_6H_5COO)_2InOH$	30.71	30.71	30.48	44.94	44.82	44.75	2.94	2.91	3.01			
o-$(C_8H_8COO)_2InOH$	28.56	28.62	28.42	47.77	47.62	47.71	3.76	3.72	3.67			
m-$(C_8H_8COO)_2InOH$	28.56	28.63	28.52	47.77	47.70	47.83	3.76	3.65	3.60			
p-$(C_8H_8COO)_2InOH$	28.56	28.41	28.39	47.77	47.70	47.86	3.76	3.71	3.80			

the salt from an acid indium sulfate solution by means of a solution of sodium benzoate and washing the precipitate with alcohol and ether; yield quantitative.

The ortho, meta and para toluates were each prepared by adding indium hydroxide to a slight excess over the theoretical quantity of the melted acid and the mixture kept in the melted state until all the hydroxide was dissolved. After being cooled, the excess acid was removed by boiling the melt in water, filtering off the salt and washing it with alcohol and ether; yield quantitative.

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d-Ribose from the Croton Bean

BY JOSEPH R. SPIES WITH NATHAN L. DRAKE

Cherbuliez and Bernhard[1] have recently isolated from the croton bean, *Croton tiglium* (L), a new glycoside, which they identified as 2-hydroxy-6-amino-purine-*d*-riboside, and which they proposed to call a "crotonoside." They did not, however, succeed in crystallizing the sugar residue obtained by hydrolysis.

The accumulation of a quantity of this material has afforded us an opportunity to examine it. We have succeeded in crystallizing the sugar residue and have conclusively established its identity as *d*-ribose, thus confirming the findings of these workers.

Experimental

Isolation of the Crotonoside.—The glycoside was extracted from the ground unshelled beans with methanol and isolated as described by Cherbuliez and Bernhard.[1] From 125 kg. of beans was obtained 345.0 g. of crude product which contained about 25% of pure crotonoside (0.07%). When recrystallized to constant melting point and dried in the Abderhalden at 110°, it decomposed at 245–247°. (All melting points were taken with standardized Anschütz thermometers.)

Anal. Calcd. for $C_{10}H_{13}O_5N_5$: C, 42.37; H, 4.59; N, 24.73. Found: C, 42.01; H, 4.47; N, 24.56.[2]

Crystallization of *d*-Ribose.—The crotonoside was hydrolyzed and the ribose isolated as described by Cherbuliez and Bernhard.[1] The sirup obtained was dried in a vacuum over phosphorus pentoxide, and when nucleated with an authentic specimen of *d*-ribose it slowly crystallized.[3] Recrystallization three times from absolute ethanol and once from dry isopropanol gave a product that melted constantly at 83–87° with previous softening at 80°. The melt, however, was cloudy; $[\alpha]^{20-25}\mathrm{D}$ $-17.5°$ (c = 5.00 g./100 ml.); (Levene and Jacobs, 85°, $[\alpha]^{20}\mathrm{D}$ $-19.2°$)[4] (Phelps, Isbell and Pigman, 87°, $[\alpha]^{1}\mathrm{D}$ $-23.7°$.)[5]

Tetraacetate.—The tetraacetate (tetraacetylribose) was prepared as described by Levene and Tipson,[6] who give 110° as the melting point and $[\alpha]^{24}\mathrm{D}$ $-52.0°$ and $[\alpha]^{25}\mathrm{D}$ $-54.3°$ in chloroform. The present writers' product was recrystallized to constant melting point from ethanol; m. p. 108–109°; in chloroform $[\alpha]^{24}\mathrm{D}$ $-54.1°$ (c, 6.52 g./100 ml.).

Anal. Calcd. for $C_{13}H_{18}O_9$: C, 49.06; H, 5.66. Found: C, 49.33; H, 5.88.

Phenylosazone.—The phenylosazone was recrystallized to constant melting point from 40% ethanol; m. p. 165–165.5° (Levene and LaForge, 166°).[7]

***p*-Bromophenylhydrazone.**—The *p*-bromophenylhydrazone was prepared as described by Cherbuliez and Bernhard.[1] It was recrystallized to constant melting point from an absolute ethanol–ether solution; m. p. 164° (Ekenstein and Blanksma,[8] 164°) (Levene and Jacobs,[9] 170°).

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[1] Cherbuliez and Bernhard, *Helv. Chim. Acta*, **15**, 464 (1932).

[2] The authors are indebted to Mr. H. M. Duvall of the University of Maryland for the micro Kjeldahl determination.

[3] The writers are indebted to Mr. F. P. Phelps, of the Bureau of Standards of the U. S. Dept. of Commerce, for this material.

[4] Levene and Jacobs, *Ber.*, **42**, 2469, 2474 (1909).

[5] Phelps, Isbell and Pigman, THIS JOURNAL, **56**, 747 (1934).

[6] Levene and Tipson, *J. Biol. Chem.*, **92**, 109 (1931).

[7] Levene and LaForge, *ibid.*, **20**, 429 (1915).

[8] Ekenstein and Blanksma, *Chem. Weekblad*, **10**, 664 (1913).

[9] Levene and Jacobs, *Ber.*, **42**, 2703 (1909).

BUREAU OF ENTOMOLOGY
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The Decomposition of Acetylphthalimide

BY CHARLES D. HURD, MALCOLM F. DULL AND
J. W. WILLIAMS

It was reported earlier[1] that acetylphthalimide decomposed at 240–325° into phthalimide, acetic

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[1] Hurd and Dull, THIS JOURNAL, **54**, 2437 (1932).

acid, ketene dimer and traces of ketene. The statement regarding ketene dimer should be withdrawn for it has not been possible to obtain this substance from acetylphthalimide in subsequent experimentation. The volatile products found were acetic acid, acetic anhydride, acetone and a small quantity of ketene.

This aligns acetylphthalimide with propionyl-, *n*-butyryl- and caproylphthalimides (all $C_6H_4(CO)_2N—COCH_2R$), all of which give rise on pyrolysis to phthalimide, the acid RCH_2COOH or its anhydride, and the ketone $(RCH_2)_2CO$. In contrast, isobutyryl- and diphenylacetylphthalimides (both $C_6H_4(CO)_2N—COCHR_2$) pyrolyze satisfactorily to ketenes, $R_2C{=}C{=}O$.

For a time it was considered that the non-production of ketene dimer from acetylphthalimide (dried as before by the toluene distillation method) was due to moisture. The same results were produced, however, on acetylphthalimide which was dried in a desiccator over phosphorus pentoxide for ten months.

Ethyl acetate was found to be an excellent solvent from which to crystallize acetylphthalimide. After such a purification it was dried thoroughly as mentioned above and 50 g. of it subjected to pyrolysis. In the 6 g. of distillate which was collected during two hours there was found 1.0 g. of acetone (b. p. 56–60°, soluble in water and identified by converting to dibenzylideneacetone of m. p. 111–112°), 1.1 g. of acetic anhydride (analyzed by the method of Whitford[2] with oxalic acid and pyridine), and 3.4 g. of acetic acid. The total acidity (acetic acid + anhydride) was 4.5 g. The distillate reacted with aniline to produce acetanilide, m. p. 112–113°. If acetoacetanilide was present also its quantity was too small for identification. Evidence for ketene was found by condensing the liquid products at 0° and passing the vapors into aniline. The yield of acetanilide was 0.4–0.5 g.

The above experiment was representative of several which were performed. Variations included the manner of drying, the size of the run (up to 108 g.) and the manner of heating (free flame or salt-bath so that the temperature within the flask ascended gradually from 220 to 325°). The results were essentially the same in all.

Summary.—The volatile products from the pyrolysis of acetylphthalimide are acetic acid, acetic anhydride, acetone and a small quantity of ketene. No significant amount of ketene dimer was produced.

[2] Whitford, THIS JOURNAL, **47**, 2939 (1925).

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COMMUNICATIONS TO THE EDITOR

COPPER SULFIDE-WATER CONTACT ANGLES

Sir:

Evidence has been obtained in this Laboratory which indicates that the presence of an adsorbed air film is the most probable cause of the contact angle of water with copper sulfide. Wark [Wark and Cox, *Am. Inst. Min. Met. Eng.*, Tech. Pub., No. 461 (1932)] has shown that a copper sulfide surface that has been ground under water exhibits no contact angle with water. If such a polished surface is exposed to air the contact angle with water assumes a definite value.

If a copper sulfide, covellite, surface is ground under water, such a surface has a zero contact angle with water; exposed to air this surface gives a definite contact angle with water. However, when such a specimen is put into a vessel in contact with water and the water is completely removed by evaporation at reduced pressure, the specimen being finally subjected to gentle warming while the container is evacuated, it is found that the surface again exhibits a zero contact angle with water. Further, when the water is again removed from the copper sulfide and air let into the vessel, the contact angle with water is again developed. Preliminary experiments with copper xanthate indicate a similar characteristic behavior.