Precipitated by Mayer's reagent, of which about 16.9 cc. were required, a white flocculent mercury salt was obtained which yielded 0.2255 gram of alkaloid equivalent to 0.52 per cent.

The leaf of *D. glaucum* when assayed by this method yielded but one crop of *d*-mannitol that weighed 0.18 gram and melted at about 160°. Recrystallization from 95% of alcohol raised the melting point to 165°. The yield is therefore 0.36%. The determination of crude alkaloid in 43 grams of the plant showed that ether extracted 0.1608 gram that required 1.87 cc. 0.1 *N* sulfuric acid, after which chloroform extracted 0.0388 gram requiring 0.51 cc. 0.1 *N* sulfuric acid. These were purified in the usual manner and there was obtained 0.1358 gram, equivalent to 0.32%. The resin precipitated weighed 0.9802 gram or 2.28%.

An analysis of the ash of the leaves of *D. geyeri* by Mr. Fred V. Skinner gave the following results:

CO_2	22.40	22.38
Sand	1.13	1.13
Carbon	0.33	0.33
SiO_2 (soluble)	11.88	11.72
$Fe_2O_3 + Al_2O_3$	5.36	5.28
CaO	24.49	24.34
MgO	0.05	0.05
K_2O	22.42	22.39
Na_2O	1.88	1.93
P_2O_5	1.26	1.44
SO_3	3.26	3.38
Cl	0.42	0.42
H_2O	3.36	3.36
Summation	98.24	98.15

LARAMIE, WYOMING.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

ETHYL CYANOTARTRONATE AND ITS REACTIONS WITH AMINES.

BY RICHARD SYDNEY CURTISS AND LLOYD F. NICKELL.

Received April 26, 1913.

For some time the senior author and his co-workers have been interested in the reactions of the oxomalonic esters with substances having dissociable hydrogen, such as alcohols, amines, and halogen acids.[1] In continuation of this work we have tried the action of prussic acid on ethyl oxomalonate, and have studied the action of the cyanhydrin thus formed with different types of amines.

Ethyl oxomalonate, $O = C : (COOC_2H_5)_2$, is a greenish yellow oil which reacts vigorously with water, hence the reaction between it and

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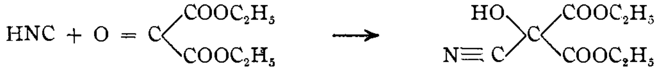
[1] Curtiss and Spencer, THIS JOURNAL, **31**, 1053; Curtiss, Hill and Lewis, *Ibid.*, **33**, 400; Curtiss and Strachan, *Ibid.*, **33**, 396.

prussic acid must be carried out under anhydrous conditions. Pinner and Bischoff[1] tried the reaction of anhydrous prussic acid on chloral, which is an analogue of ethyl oxomalonate, but noted no action. We have found, however, that anhydrous prussic acid completely discharges the color of ethyl oxomalonate, showing that a reaction occurs.[2]

This action is as follows:



$$HNC + O = C\begin{cases}COOC_2H_5\\COOC_2H_5\end{cases} \longrightarrow \begin{matrix}HO\\N\equiv C\end{matrix}\!\!>\!C\begin{cases}COOC_2H_5\\COOC_2H_5\end{cases}$$

The product of this reaction, ethyl cyanotartronate, reacts vigorously with ammonia, and with primary and secondary aliphatic amines to form very unstable addition compounds. Tertiary aliphatic amines, and aromatic amines react very slowly, if at all. Owing to the marked instability of all of these products only those formed by the action of benzyl, diethyl, and dipropyl amines have been successfully analyzed and characterized.

Experimental.

Preparation of Ethyl Cyanotartronate.—Anhydrous prussic acid was prepared according to the method of Wade and Panting,[3] passed over phosphorus pentoxide, and condensed in a tube containing 5.73 grams of ethyl oxomalonate, until a volume equal to that of the oxomalonate had condensed. The two substances were then mixed by shaking, kept thoroughly protected from atmospheric moisture by phosphorus pentoxide and allowed to stand at 30° for twenty-four hours. The green color of the oxomalonate slowly faded, and at the end of that time had been completely discharged, indicating complete reaction. Later experiments showed that the speed of this reaction is greatly influenced by small changes in temperature. At 20° seventy-two hours are necessary for complete action, while at 15° the green color of the oxomalonate is not discharged on standing for a week.

When the reaction was complete the substance was allowed to stand in an evacuated desiccator over sulfuric acid and solid sodium hydroxide to remove the excess of prussic acid. The contents of the tube were then diluted with six volumes of ether and allowed to stand in an evacuated desiccator, as before, until the ether was evaporated. This was repeated twice, after which no odor of prussic acid could be detected. This method of purification was used because distillation dissociates the substance into its original constituents. Upon weighing, 0.89 gram of prussic acid was found to have combined. The results of several such experiments are given on the following page:

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[1] *Ann.*, **179**, pp. 74–100.

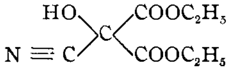
[2] Cf. Curtiss and Spencer, THIS JOURNAL, **31**, 1054.

[3] *J. Chem. Soc.*, **1898**, p. 255.

Wt. of ethyl oxomalonate. Grams.	Wt. HNC. Grams.	1 mol. HNC. Grams.
5.72	0.89	0.88
9.11	1.42	1.41
8.77	1.23	1.25

The product, a colorless oil, was analyzed.

Calculated for:



$$\begin{array}{r} HO \\ N \equiv C \end{array} > C < \begin{array}{l} COOC_2H_5 \\ COOC_2H_5 \end{array}$$

C, 47.76 ; H, 5.47; N, 6.96.
Found: C, 47.82, 48.28; H, 5.74; N, 7.09, 6.99.

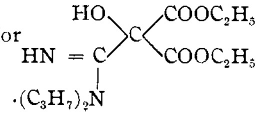
Molecular weight determinations were made according to the Beckmann freezing-point method, by solution in benzene. The results were as follows:

Wt. of C_6H_6. Grams.	Wt. of ethyl cyanotartronate. Gram.	ΔTF.	M found.	M theory.
15.13	0.6491	0.89°	243	201
15.40	0.5610	0.78°	234	...

Ethyl cyanotartronate is a colorless oil having the consistency of concentrated sulfuric acid. Its specific gravity is 1.16 at 30°/30°. Upon long standing it gradually assumes a yellow amber color, but produces no odor of prussic acid. Although it cannot be distilled, owing to dissociation into ethyl oxomalonate and prussic acid, it can be heated to 90° before any noticeable dissociation occurs. It is easily soluble in ether, benzene, alcohol, acetone, chloroform, and ethylacetate, but is insoluble in ligroin and in water. It dissolves in alkaline solutions giving a deep yellow color. A solution of the oil in absolute ether when treated with metallic sodium gives only a slight evolution of hydrogen, but in an hour and a half a mass of deliquescent, unstable, white crystals comes out of the solution.

Action of Dipropyl Amine on Ethyl Cyanotartronate.—1.76 grams of ethyl cyanotartronate were dissolved in 2 cc. of dry ether, and a solution of 0.88 gram (1 mol) of dipropyl amine in 5 cc. of ether was added drop by drop, the flask in which the reaction was taking place being kept at —17°. In a few seconds white crystals separated out. These were quickly filtered, washed on the filter with cold, dry ether, and dried at 10° in a vacuum desiccator over calcium chloride. After three hours the melting point was taken, and the substance analyzed. The melting point was 72.5°–73°. The analyses gave the following results:

Calculated for



$$\begin{array}{r} HO \\ HN = \underset{\underset{(C_3H_7)_2N}{|}}{C} \end{array} > C < \begin{array}{l} COOC_2H_5 \\ COOC_2H_5 \end{array}$$

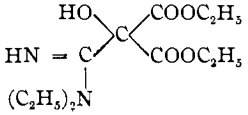
C, 55.62 ; H, 8.67 ; N, 9.27.
Found: C, 55.45, 54.97; H, 8.70, 8.77; N, 9.14, 9.25.

The dipropylamine addition product of ethyl cyanotartronate is easily soluble in benzene, chloroform, acetone, acetic ether, and methyl alcohol; fairly soluble in water, ethyl alcohol, ether, and carbon tetrachloride; and slightly soluble in carbon bisulfide and ligroin. If kept at 10° in a desiccator, this substance is stable for several days, but if exposed to the air or kept at 25° it decomposes in a few hours to a reddish brown tar.

If dipropylamine is added to ethyl cyanotartronate drop by drop, a vigorous reaction with evolution of much heat occurs. The resulting product is similar to the product formed when the addition product decomposes as described above.

Action of Diethylamine on Ethyl Cyanotartronate.—To 1.6 grams of ethyl cyanotartronate dissolved in 4 cc. of dry ether, and kept at —17°, 1 cc. (in excess of 1 mol) of diethylamine was slowly added from a dropping funnel. A white precipitate formed instantly. The ether was filtered off, the precipitate washed on the filter with cold ether, and dried an hour over calcium chloride in a vacuum desiccator kept at 10°. The melting point was taken and the substance analyzed. The compound melted at 56°. The analyses were as follows:

Calculated for



C, 52.52; H, 8.08; N, 10.20.
Found: C, 52.19; H, 8.16; N, 10.04, 10.14.

This product is very soluble in benzene, water, methyl alcohol, acetone and acetic acid; readily soluble in ethyl acetate; fairly soluble in carbon tetrachloride; and slightly soluble in ligroin and in ether. Like the dipropyl amine addition product it decomposes quickly to a red tar when exposed to the atmosphere or kept at room temperature.

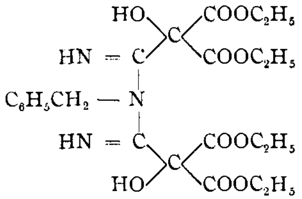
Molecular-weight determinations by the freezing-point method in nitrobenzene gave the following results:

Wt. of nitrobenzene. Grams.	Wt. of substance. Gram.	ΔT_F.	M found.	M theory.
23.08	0.5986	0.73°	252	274
27.52	0.8024	0.78°	264	...

Diethyl amine reacts with ethyl cyanotartronate at room temperature more vigorously than does dipropyl amine. A reddish decomposition product is the result.

·*Action of Benzyl Amine on Ethyl Cyanotartronate.*—To a solution of 1.39 grams of ethyl cyanotartronate in 2 cc. of dry ether a solution of 0.39 gram (0.5 mol) of benzylamine in 2 cc. of ether was slowly added. White crystals separated in fifteen seconds. These were filtered, washed with ether on the filter and dried in a vacuum desiccator over calcium chloride at 10° for two hours. The melting point was then taken and a sample analyzed. The melting point was 55–56°. The analyses gave the following results:

Calculated for:



C, 54.19 ; H, 6.13 ; N, 8.27.

Found: C, 54.47, 54.14; H, 5.98, 6.15; N, 8.20, 8.11.

The benzyl amine addition product of ethyl cyanotartronate is easily soluble in alcohol and ethyl acetate; extremely soluble in acetone, chloroform, methyl alcohol, nitrobenzene, and benzene; fairly soluble in xylene and ether; and slightly soluble in carbon bisulfide and ligroin.

When benzyl amine is added to ethyl cyanotartronate at room temperature a slow reaction with the development of some heat occurs. A thick pasty sirup is formed. The benzyl amine addition product decomposes to a tarry mass, as do the two already described, when kept at 25° or exposed to the air.

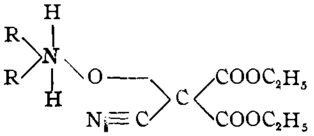
Action of Other Amines on Ethyl Cyanotartronate.—Isobutyl, ethyl, and ethyl benzyl amines give red tars at once and generate much heat when added directly to ethyl cyanotartronate at room temperature. Added at —17° thick sirups that cannot be purified were formed. The behavior of triethyl amine is entirely different. When added to ethyl cyanotartronate, triethyl amine produced no reaction at first. However, after five minutes a slight color appeared, and in half an hour a red tar had formed.

Aniline, the toluidines, ethyl aniline, isoamyl aniline, and methyl aniline were miscible with ethyl cyanotartronate, but no heat was evolved and no apparent action occurred on standing.

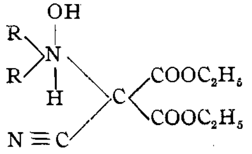
Ammonia gas added to an ethereal solution of ethyl cyanotartronate at —17° gave a white, crystallin precipitate. This product, however, was very unstable, decomposing in the air in five minutes to a red gum, and we did not succeed in obtaining analyses.

Structure of the Addition Products of Amines with Ethyl Cyanotartronate.—So far as the composition of the products are concerned which ethyl cyanotartronate forms with the secondary amines (dipropyl and diethyl amine) where a mol of the amine unites with a mol of the cyanotartronate, we might have any one of three possible structures:

(1) A salt, as:

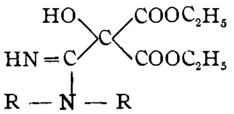


(2) A substituted ammonium hydroxide such as Stadnikoff[1] uses to explain the Strecker reaction:



or

(3) An amidine:



With benzyl amine, however, we have one molecule of the amine adding to two molecules of the cyanotartronate. Evidently this eliminates the possibility of a salt as in (1). In further support of this conclusion, we note that the action of triethyl amine is anomalous and that aromatic amines are evidently without action in spite of their basicity. In (2) a molecule of water must first split off before a second molecule of cyanotartronate could add. Analysis shows that water is not eliminated in this way. We are, therefore, led to conclude that the amidine structure in (3) is the correct one.

URBANA, ILL.

[CONTRIBUTION FROM THE TEXAS AGRICULTURAL EXPERIMENT STATION.]

PHYTIC ACID IN COTTONSEED MEAL AND WHEAT BRAN.

BY J. B. RATHER.[2]

Received April 19, 1913.

It has been shown by the writer[3] that the phosphorus compounds of cottonseed meal are nearly all organic in nature, and especially that cottonseed meal does not contain meta- or pyrophosphoric acid, as has been claimed.[4] The work here presented is a continuation of the study of the phosphorus compounds of cottonseed meal, together with an investigation of the acid-soluble phosphorus compounds of wheat bran.

[1] *Ber.*, 44, 40.

[2] Under the general direction of G. S. Fraps, chemist. Full details of this work may be found in Bulletin 156 of the Texas Experiment Station.

[3] Texas Exp. Sta., *Bull.* 146.

[4] Hardin, S. C. Exp. Sta., *Bull.* 8, new series; Crawford, *J. Pharm. Expt. Therapeutics*, 1, 51.