FIG. 4

incident. Thus by the interpolation method of Fig. 3 both the temperature and composition of points on the boundary curves may be found. By this method the points given in Table II have been located.

COMPOSITION IN WEIGHT, PER CENTS			FREEZING POINTS, DEGREES	
MNT	DNT	TNT	Primary	Secondary
60	30	10	31.55	22.55
60	10	30	34.15	28.6
55	35	10	27.85	22.9
55	25	20	28.95	16.85
55	10	35	30.65	29.3
50	30	20	24.8	17.9
50	25	25	25.1	18.7
50	10	40	31.65	29.2
45	45	10	25.6	23.2
45	10	45	36.05	28.95
40	50	10	29.4	23.0
40	40	20	22.65	18.6
40	30	30	18.0	17.6
40	25	35	24.9	20.6
35	50	15	30.1	17.75
35	45	20	25.5	17.75
35	40	25	21.8	16.85
35	30	35	24.55	19.1
35	25	40	30.65	22.25
25	50	25	34.25	24.6
25	45	30	29.85	24.1
25	35	40	31.5	22.85
25	30	45	37.95	36.9
10	60	30	46.8	37.95
10	55	35	43.85	39.15
10	45	45	40.05	38.35
10	40	50	44.25	

COMPOSITION IN WEIGHT, PER CENTS			FREEZING TEMPERATURE	
MNT	DNT	TNT	DEGREES	
48.5	41.5	10	23.4	
43.5	36.5	20	18.95	
52.5	10	37.5	29.35	
44	25	31	20.8	
41	30	29	17.8	
10	46.7	43.3	39.2	
25	39.8	35.2	25.4	
35	35.2	29.8	17.5	

These points fall exactly on smooth curves which approximate to straight lines, the boundary curves being drawn to scale in Figs. 4 and 5. From the data of Tables I and II, and from the data for the binary systems in the third paper of this series, Figs. 4 and 5 have been constructed. Fig. 4 shows the isothermals for the primary freezing points, and Fig. 5 shows the isothermals for the secondary freezing points, the latter isothermals being of course straight lines from the vertices of the triangle. The composition of the eutectic mixture is 39 per cent MNT, 33.5 per cent DNT, and 27.5 per cent TNT and the eutectic temperature is 16.7°.

FIG. 5

With the above tabulated data it is possible to identify any unknown mixture of these three components. First, the primary and the secondary freezing points should be determined, and then the identity of the solid phases should be established. The methods of finding freezing points have already been given. For the identification of the solid phases an indirect method is proposed rather than the doubtful method of trying to isolate the freezing component free from the melt. The following consideration demonstrated how this indirect identification may be made. Take any mixture, say B of Fig. 1. The addition of component X to the mixture raises the primary freezing point, and the addition of either Y or Z to the mixture lowers the primary freezing point. The first phase to separate is therefore that one which, when added to the unknown mixture, raises the primary freezing point. Similarly it may also be shown that the second phase to separate is that one of Y or Z whose addition to the unknown mixture raises the secondary freezing point. We are thus able to locate the unknown in one of the six triangles of Fig. 1: XMF, XNF, YMF, YOF, ZOF, or ZNF. Reference to Figs. 4 and 5 locates the point from the temperatures of primary and of secondary freezing.

SUMMARY

In this paper we have shown how to identify any unknown mixture of the three nitrotoluenes, MNT, DNT, and TNT, from a study of the ternary system of these components.

UNIVERSITY OF NORTH CAROLINA
CHAPEL HILL, N. C.

PARACYMENE. III—PREPARATION OF 2-CHLORO-5,6-DINITROCYMENE

By H. A. LUBS AND R. C. YOUNG

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This compound was first prepared by von Gerichten¹ in 1878, who, however, simply described it as a dinitrochlorocymene melting from 108° to 109°, and

¹ Ber., 11 (1878), 1091.

made no attempt to determine the orientation of the various groups. Moreover, von Gerichten's description of its method of preparation is very meager, no mention being made of the amount of acids, time, or temperature necessary for nitration. Neither does he state the yield obtainable. Fileta and Crosa,¹ ten years later, prepared the same compound, but neither did they determine the positions of the various groups. They mention the fact that besides the solid dinitrochlor compound melting from 109° to 110°, there is also produced a liquid isomer. Their evidence in support of this statement is solely that an analysis of the liquid indicated it to be a dinitrochlor compound.

In addition to a solid compound melting from 108° to 109° we have isolated from the reaction product a substance which at first appeared to be an isomeric solid dinitrochlorocymene melting from 90° to 91°. Analyses showed that this supposedly dinitrochlorocymene was in reality a dinitrochlor compound but one containing a smaller amount of carbon and hydrogen than the corresponding cymene derivative.

A consideration of the constitutional formula of

2-chlorocymene, , indicates that there are three possible dinitro derivatives:

By reducing the dinitrochlor compound and determining whether the substance formed is an *o*-, *m*-, or *p*-diamine, the position of the various substituents can be established. Since there are a number of general reactions for the differentiation and characterization of the various diamines, the solution of this problem is a relatively simple matter. Our work proves that the compound described by von Gerichten is identical with Formula 1.

In addition to the two crystalline compounds there is also obtained a heavy liquid which, upon analysis, gives a nitrogen content corresponding quite closely to that of dinitrochlorocymene. We did not investigate this oil very extensively, but obtained evidence that it is composed partially at least of a mixture of the two compounds previously described.

EXPERIMENTAL WORK

The starting material used is *p*-cymene prepared by the purification of crude spruce "turpentine." This is chlorinated, nitrated, and the resulting dinitrochlor compounds reduced.

PREPARATION OF 2-CHLOROCYME—Chlorine is passed into *p*-cymene containing iron filings until slightly more than the theoretical gain in weight is obtained. The temperature is not allowed to rise

above 35°. The resulting product is washed with water, then with sodium carbonate solution, dried over calcium chloride, and fractionated *in vacuo*. Most of the material boils between 85° and 90° at 5 mm. pressure. This portion gives upon analysis practically the theoretical amount of chlorine for monochlorocymene. At atmospheric pressure practically all of this fraction boils between 215° and 218°. This material is used in the nitrations.

NITRATION OF 2-CHLOROCYME—It was found that an ordinary tin can was far superior to a glass vessel for the nitration because of the much greater heat conductivity of the former. A mixture of 140 g. of concentrated sulfuric acid and 194 g. of 25 per cent fuming sulfuric acid is cooled to 0° and 84 g. of 2-chlorocymene added slowly so as to prevent any considerable rise in temperature. To the same amount of concentrated and fuming sulfuric acid mixture are added 72 g. of fuming nitric acid. This mixed acid is then dropped into the well-agitated sulfuric acid chlorocymene mixture at a rate such that the temperature does not rise above 0°. At the end of the reaction, a solid collecting at the top of the acid mixture interferes with the stirring and tends to stall the motor. This solid is then mechanically separated and mixed with cracked ice. It is then washed with cold water, and with sodium carbonate solution, and filtered. By the filtration a portion of the adhering oil is also removed which weighs about 15 g. About 17 g. more of partially oily and solid material are obtained by pouring the acid mixture on cracked ice and extracting with ether. The ethereal solution is washed with water and sodium carbonate solution and the ether evaporated. The solid material which is mechanically removed from the acid mixture, after washing with water, sodium carbonate solution, and filtering, is washed with about 100 cc. of alcohol to free it further from oil and it is then recrystallized twice from about 200 cc. of alcohol. In this way about 30 g. of a slightly yellow crystalline product are obtained which melt at from 108° to 109°. Evaporation of the alcoholic mother liquors yields approximately 26 g. of material, hence the total weight of material isolated from 84 g. of chlorocymene amounts to about 88 g.

In one case there was obtained a small amount of material practically insoluble in alcohol, ether, and water, and infusible in a sulfuric acid bath. Though not identified, this compound appeared to be very similar to a chloroterephthalic acid. Such a compound could easily be formed from the oxidation of the methyl and isopropyl groups by nitric acid.

The dinitrochlor compound melting from 108° to 109° was analyzed for chlorine.

Calculated for $C_{10}H_{11}N_2ClO_4$, 13.7 per cent Cl. Found: 13.9, 13.8 per cent.

Optical properties of 2-chloro-5,6-dinitrocymene, m. p. 108°–109°, were determined by the immersion method under the microscope, using potassium-mercuric iodide liquids of known indices, as follows:¹

CRYSTALLIZATION—Plates and rods, probably belonging to the monoclinic system.

¹ Thanks are due to Edgar T. Wherry for the crystallographic work.

¹ *Gazz. chim. ital.*, 18 (1888), 296.

IN ORDINARY LIGHT—Colorless; in rods and plates, with irregular fracture.

REFRACTIVE INDICES (D)— $\alpha = 1.550$, $\beta = 1.645$, $\gamma = 1.660$, $s - \alpha = 0.110$; all ± 0.005 . Intermediate values are usually shown.

IN PARALLEL POLARIZED LIGHT—Extinction is often inclined, attaining a maximum angle of 30° . The double refraction is extreme, fourth order colors being frequently shown. Sign of elongation usually +.

IN CONVERGENT POLARIZED LIGHT—Biaxial, and partial interference figures often seen, the axial plane running lengthwise of the rods. The axial angle is fairly large, about $2E = 70^\circ$, and the sign —. The dispersion is strong, with $2Er < 2E_r$.

ISOLATION OF A SECOND DINITROCHLORO COMPOUND

When the liquid which was separated from the solid dinitrochlorocymene was allowed to stand in the ice box for several days, a small amount of crystals separated. Upon pouring off the supernatant oil, washing the crystals with cold alcohol and then recrystallizing from alcohol, yellowish needles with a melting point from 88° to 89° were obtained. In physical appearance they were very similar to the 2-Cl, 5,6-dinitrocymene. An ultimate analysis indicated its formula to be $C_7H_6N_2O_4Cl$ and not $C_{10}H_{12}N_2O_4Cl$ and hence there can be no doubt about these two compounds not being isomeric. It appears that during the nitration, a portion of the chlorocymene was oxidized to a compound poorer in carbon, and this compound subsequently nitrated. That such reaction can occur is indicated by the statement in Danish Patent No. 23,344, that *p*-nitrotoluene is produced by sulfonating *p*-cymene and then treating the product with nitric acid at a temperature from 40° to 60° .

This dinitrochloro compound can be reduced to a base melting from 115° to 116° , which from color reactions appears to have the amino groups in the meta position. Only a small amount of this base was isolated and hence it was not extensively investigated.

The following analyses¹ were obtained of the compound melting from 88° to 89° .

	SAMPLE 1 PER CENT	SAMPLE 2 PER CENT	AVERAGE PER CENT	THEORETICAL PER CENT FOR $C_7H_6N_2O_4Cl$
C.....	38.7	39.5	39.1	38.8
H.....	2.7	2.5	2.6	2.3
N.....	12.6	12.6	12.6	12.9
Cl.....	15.7	15.6	15.7	16.4

Crystallographic properties of the compound melting from 88° to 89° are as follows:

CRYSTALLIZATION—Needles, probably monoclinic.

IN ORDINARY LIGHT—Colorless; in needles or rods, with irregular fracture.

REFRACTIVE INDICES (D)— $\alpha = 1.640$, $\beta = 1.660$, $\gamma = 1.720$, $\gamma - \alpha = 0.080$; all ± 0.005 . Intermediate values are usually shown.

IN PARALLEL POLARIZED LIGHT—Extinction is inclined and may reach 40° . The double refraction is extremely strong, the colors being usually third order. The sign of elongation varies, but is more often —.

IN CONVERGENT POLARIZED LIGHT—Biaxial, the axial plane running crosswise, one optic axis often emerging in sight. The axial angle is large, about $2E = 120^\circ$, and the sign is +. The dispersion is strong, with $2Er > 2E_r$.

¹ The analyses for C, H, and N were made for us by L. J. Jenkins of the Nitrogen Laboratory of this Bureau, to whom we wish to acknowledge our thanks.

In an attempt to determine the ease with which the chlorine could be hydrolyzed from the nucleus an interesting color reaction was discovered, the nature of which we cannot explain. Upon heating about 20 mg. of the compound melting from 88° to 89° with several cc. of alcohol and adding a trace of solid sodium carbonate an intense blue color was developed in the alcoholic solution. This reaction was very useful to us in testing the various fractions for the presence of this compound since the blue coloration was not formed by the dinitrochlorocymene under identical conditions.

REDUCTION OF 2-CL, 5,6-DINITRO-*p*-CYMENE—After trying various reducing agents, the best procedure for the preparation of the diamino compound was found to be the following:

The dinitro compound is heated with water, and zinc dust and hydrochloric acid in small portions gradually added. A large excess of reagents is required. At the end of the reduction, especially if too large an excess of acid is avoided, the zinc chloride double compound with the diamino derivative precipitates out and can be filtered off. The double compound is then mixed with cracked ice and decomposed with strong ammonia water whereby practically all of the zinc goes into solution. The base is then separated from a small amount of zinc oxide by means of ether and the ethereal solution evaporated *in vacuo*. The product thus obtained can be recrystallized from ligroine in the form of rods or needles with a melting point from 67° to 68° . This compound was analyzed for nitrogen.

Calculated for $C_{10}H_{12}N_2Cl$, 14.1 per cent N. Found: 13.7, 13.5 per cent.

These slightly low results are possibly due to traces of ligroine which could be removed only with difficulty.

DETERMINATION OF THE ORIENTATION OF THE AMINO GROUPS IN 1-CL, 5,6-DIAMINO-*p*-CYMENE—By showing whether this compound is an *o*-, *p*-, or *m*-diamine the position of the various substituents is established. That this diamine is an ortho compound is evident from the following reactions:¹

1—An ethereal solution of the free base gives an intense blue color upon being shaken with a few drops of dilute ferric chloride solution. Such a blue color is given by 1,2-diaminonaphthalene and *o*-phenylenediamine but not by *m*- or *p*-phenylenediamine.

2—Upon boiling the free base with glacial acetic acid, evaporating the acetic acid, diluting with water and neutralizing, a yellowish precipitate is obtained which is soluble in hydrochloric acid.

3—The free base gives the phenanthrazine reaction which is characteristic of *o*-diamines. Upon adding a saturated solution of phenanthraquinone to an alcoholic solution of the free base and boiling, a yellowish precipitate which increases in amount upon cooling is obtained.

4—Upon condensing the free base with ammonium sulfocyanide and treating the product with alcoholic

¹ For a discussion of the reactions for the characterization of diamines and the literature pertaining thereto, see "Analyse und Konstitutionsermittlung organischer Verbindungen," Hans Meyer, Berlin (1909).

lead acetate, no lead sulfide is formed. This indicates that the diamine is not a meta or para compound.

5—The diamino compound does not give the Bismarck-Brown reaction characteristic of meta diamines.

6—This diamino compound does not give Lauth's reaction for *p*-diamines upon digesting in acid solution with hydrogen sulfide and ferric chloride.

SUMMARY

The nitration of 2-Cl-*p*-cymene does not proceed smoothly with the simple formation of dinitrochlorocymene. The principal product formed is 2-chloro-5,6-dinitro-*p*-cymene. Apparently an isomer is also formed which was not isolated.

Another dinitrochlor compound, with less carbon than that present in dinitrochlorocymene, is formed in small amount. The constitution has not been established.

A small amount of a compound of unknown constitution was also formed. This may be possibly a chloroterephthalic acid.

COLOR LABORATORY
U. S. BUREAU OF CHEMISTRY
WASHINGTON, D. C.

THE CARBOHYDRATES OF FRESH AND DEHYDRATED VEGETABLES

By K. GEORGE FALK

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The changes in enzyme action produced by dehydrating vegetables were described in a previous paper.¹ In this paper the results of the study of the content and distribution of carbohydrates in fresh and dehydrated vegetables are communicated. Carrots, potatoes, cabbage, and white turnips, fresh and dehydrated by the air-blast and vacuum processes, were analyzed for reducing sugars, dextrins and soluble starch, and insoluble starch (by difference after hydrolysis).

ple sugars (alcohol extraction) before and after hydrolysis, and reduction by dextrans and soluble starch (water extraction) after hydrolysis. The results were calculated as grams of cuprous oxide per gram of moisture-free substance (dried at 100°), and as percentages of total reducing power as evidenced by the weights of cuprous oxide. Fehling's solution was used for the determinations of the reducing powers.¹

The results obtained indicated that no change in the carbohydrate distribution as determined (such as a breakdown of the more complex to the simpler constituents during dehydration) was observable. Certain precautions, however, had to be taken in the analyses. In the alcohol extractions, treatment of the fresh vegetable, 20 to 30 g. with 200 cc. alcohol, included the water present in the vegetable. In order to prevent change, the fresh vegetable was not dried before the analysis. To parallel the conditions, with 3 to 4 g. of the dehydrated vegetable, 20 to 25 g. of water were added in the alcohol extraction. If this were not done, the more dilute alcohol with the fresh vegetable extracted more material than the more concentrated with the dehydrated. This was then shown by the increased water-extracted materials (dextrans and soluble starch) from the dehydrated substance, indicating erroneously a conversion of insoluble starch into dextrans and soluble starch.

Two complete series of results with carrots and potatoes are given in the table. The results in parentheses were obtained without the addition of water to the dehydrated vegetables in the alcohol extractions.

The alcohol-soluble sugars of the vacuum-dehydrated carrots shown in the table are apparently somewhat low, due to some unknown factor in the determination. In view of the possible experimental errors of sampling and extracting, these results, as well as the results of a number of other experiments, indicate no change in carbohydrate distribution as deter-

CUPROUS OXIDE PER GRAM SUBSTANCE

	Moisture Per cent	Total Reduction	—Alcohol Extract— Before Hydrolysis	After Hydrolysis	Water Extract After Hydrolysis	—Reducing Sugars— Before Hydrolysis Per cent of total	After Hydrolysis Per cent of Total	Dextrans + Sol. Starch Per cent of Total	Insol. Starch (by Diff.) Per cent of Total
CARROTS:									
Fresh.....	88.4	1.197	0.684	1.104	0.032	57.1	92.2	2.7	5.1
Air dehydrated.....	12.8	1.151	0.619 (0.562)	0.986 (1.039)	0.043 (0.085)	53.8	85.7	3.7	10.6
Vacuum dehydrated.....	12.5	1.171	0.567 (0.540)	0.869 (1.065)	0.049 (0.059)	48.5	74.2	4.2	21.6
POTATOES:									
Fresh.....	73.8	1.842	0.046	0.091	0.011	2.5	4.9	0.5	94.6
Air dehydrated.....	11.2	2.024	0.056 (0.045)	0.134 (0.079)	0.011 (0.063)	2.7	6.6	0.5	92.9
Vacuum dehydrated.....	13.7	2.020	0.058 (0.056)	0.106 (0.067)	0.010 (0.030)	2.9	5.2	0.5	94.3

Samples from the same vegetable, as uniform as possible, were used for each process. The separation of the reducing sugars and of dextrans and soluble starch was based upon the method of Street and Bailey,² which consisted in successively treating the vegetable with boiling 95 per cent alcohol and with cold water. The determinations made included total reducing power (after hydrolysis), reduction by sim-

mined. Cabbage and white turnips gave results similar to these, except for somewhat different amounts of the various constituents.

Thanks are due to Miss E. Blount, Mr. I. Neuwirth, and Mr. J. Gross for carrying out the large number of analyses required in this investigation.

HARRIMAN RESEARCH LABORATORY
ROOSEVELT HOSPITAL
NEW YORK CITY

¹ K. G. Falk, G. McGuire and E. Blount, *J. Biol. Chem.*, **33** (1919), 229.

² *THIS JOURNAL*, **7** (1915), 853.

¹ H. C. Sherman, "Methods of Organic Analysis," 2nd Ed., 1912, 74.