was added a warm solution of 40 g. of mercuric chloride in 100 ml. of dry benzyl alcohol. The heating and stirring were continued for 4.5 hr. The mixture was then cooled to room temperature, filtered, washed with aqueous potassium iodide solution and water, dried with anhydrous magnesium sulfate and evaporated to a sirup at 1 mm. pressure. The residue was extracted several times with petroleum ether (b.p. 30–60°). When the extract was concentrated to 100 ml., the material crystallized as fine needles, and was recrystallized from ethanol–water; yield 6.5 g., m.p. 61–63° depressed to 54–60° when mixed with starting material of m.p. 61–62°, $[\alpha]^{25}D$ +25° (*c* 1.5, acetone).

Anal. Calcd. for $C_{27}H_{34}O_8S$: C, 62.54; H, 6.60; S, 6.18. Found: C, 62.56; H, 6.28; S, 6.02.

3,4,5-Tri-*O*-acetyl-2-*S*-ethyl-2-thio-D-xylose(lyxose) Dimethyl Acetal (IV).—Sirupy 3,4,5-tri-*O*-benzoyl-2-*S*-ethyl-2-thio-D-xylose(lyxose) diethyl dithioacetal (II, 20 g.) was demercaptalated by the procedure described above for the preparation of 3,4,5-tri-*O*-acetyl-2-*S*-ethyl-2-thio-D-xylose(lyxose) dibenzyl acetal using methanol instead of benzyl alcohol to produce sirupy 3,4,5-tri-*O*-benzoyl-2-*S*-ethyl-2-thio-D-xylose(lyxose) dimethyl acetal (III); yield 16 g. This sirup (III, 16 g.) was dissolved in 50 ml. of ethanol containing 50 mg. of sodium methoxide. After standing for 48 hr. in the refrigerator, the ethanol was evaporated under reduced pressure, the residue was extracted with ether, the extracts filtered and again evaporated to a sirup. The sirup was dissolved in water and washed with petroleum ether (b.p. 30–60°). The petroleum ether was washed several times with water. The combined aqueous solutions were evaporated under reduced pressure to a sirup; yield 6 g. A portion of the sirup (1 g.) was distilled at 0.05 mm. and 100° bath temperature. The distilled, sirupy 2-*S*-ethyl-2-thio-D-xylose(lyxose) dimethyl acetal (V, 250 mg., see below) was dissolved in 3 ml. of dry pyridine and treated with 450 mg. of acetic anhydride. After standing for 48 hr. it was mixed with 10 ml. of cold water, extracted with ether, dried with anhydrous sodium sulfate and evaporated to a sirup which crystallized (IV) upon addition of petroleum ether (b.p. 30–60°); yield 200 mg., m.p. 58–59°, $[\alpha]^{20}D$ +43° (*c* 2, chloroform).

Anal. Calcd. for $C_{15}H_{26}O_8S$: C, 49.16; H, 7.15; S, 8.75. Found: C, 49.43; H, 7.19; S, 8.71.

In subsequent preparations the crystalline material was obtained by acetylation of undistilled V.

3,4,5-Tri-*O*-acetyl-2-*S*-ethyl-2-thio-D-xylose(lyxose) dimethyl acetal (IV) can also be obtained (68% yield) from 3,4,5-tri-*O*-acetyl-2-*S*-ethyl-2-thio-D-xylose(lyxose) diethyl dithioacetal (VII) by substituting methanol for benzyl alcohol in the procedure described above for preparing the corresponding dibenzyl acetal VIII.

2-*S*-Ethyl-2-thio-D-xylose(lyxose) Dimethyl Acetal (V).—3,4,5-Tri-*O*-acetyl-2-*S*-ethyl-2-thio-D-xylose(lyxose) dimethyl acetal (crystalline IV, 5 g.) was dissolved in 50 ml. of absolute ethanol containing 150 mg. of sodium methoxide and allowed to stand at room temperature for 24 hr. The sodium ion was removed by stirring with an excess of cation exchange resin (Amberlite IR-120)[9] and the solution was evaporated under reduced pressure to a sirup. The sirup was extracted with ether, the extract evaporated to a sirup and distilled at 0.05 mm. and a bath temperature of 100°; yield 1.1 g. (V), $[\alpha]^{20}D$ +38° (*c* 1, chloroform).

Anal. Calcd. for $C_9H_{20}O_5S$: C, 44.94; H, 8.39; S, 13.34. Found: C, 45.25; H, 8.40; S, 13.36.

(9) A product of the Rohm and Haas Co., Philadelphia, Pa.

COLUMBUS 10, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

The Controlled Thermal Decomposition of Cellulose Nitrate. VII. Carbonyl Compounds[1,2]

BY M. L. WOLFROM AND G. P. ARSENAULT

RECEIVED OCTOBER 15, 1959

An investigation of the carbonyl compounds formed from the ignition of cellulose nitrate was made. Isolated as the 2,4-dinitrophenylhydrazine derivatives were acetone, acetaldehyde, formaldehyde, methylglyoxal, glyoxal, mesoxaldehyde and hydroxypyruvaldehyde. A gas chromatographic study of the cellulose nitrate (cast from ethyl acetate) ignition products demonstrated the presence therein of acetaldehyde, acetone, acrolein, ethyl acetate, hydrogen cyanide and a new, unidentified substance which is not a carbonyl compound. Ethanol is not a product of ignition of cellulose nitrate. The origin of the compounds isolated is discussed.

The controlled thermal decomposition of cellulose nitrate has been under investigation in this Laboratory.[2–5] Thus, the liquid mixture of cellulose nitrate ignition products has been reported to contain carbonyl compounds, among which formaldehyde, glyoxal and two oxidation stages of glycerose (glyceraldehyde) or dihydroxyacetone (without carbon fragmentation) were isolated.[4] The latter two compounds were present in small amounts only and, at all pressures investigated, the total carbonyl content of the liquid mixture of cellulose nitrate ignition products was larger than the sum of the amounts of carbonyl which could be ascribed to the presence of formaldehyde and glyoxal in the liquid mixture.[6] In the work herein reported, a more thorough investigation was made of the carbonyl compounds present in the liquid mixture of ignition products.

Cellulose nitrate containing 12.6% N was ignited[4] at 75 mm. pressure. A large fraction (74%) of the total carbonyl content of the aqueous solution (product I, Fig. 1) of the resulting liquid mixture of ignition products was accounted for by the presence therein of formaldehyde and glyoxal (Table I). Product I was frozen and sublimed three times at low temperature, under freeze-drying conditions. The sublimates were numbered in the order in which they were obtained (products II–IV, Fig. 1) and the residue of the repeatedly sublimed product I was dissolved in water (product V, Fig.

(1) This work was supported by the United States Army Ordnance Department under contracts (DA-33-019-ord-727, -1476 and -2042; supervising agency, The Ballistic Research Laboratories, Aberdeen Proving Ground, Md.) with The Ohio State University Research Foundation (Projects 496, 591 and 679).

(2) Previous communication: M. L. Wolfrom, K. S. Ennor and A. Chaney, THIS JOURNAL, **81**, 3469 (1959).

(3) M. L. Wolfrom, J. H. Frazer, L. P. Kuhn, E. E. Dickey, S. M. Olin, D. O. Hoffman, R. S. Bower, A. Chaney, Eloise Carpenter and P. McWain, *ibid.*, **77**, 6573 (1955).

(4) M. L. Wolfrom, J. H. Frazer, L. P. Kuhn, E. E. Dickey, S. M. Olin, R. S. Bower, G. G. Maher, J. D. Murdock, A. Chaney and Eloise Carpenter, *ibid.*, **78**, 4595 (1956).

(5) M. L. Wolfrom, A. Chaney and P. McWain, *ibid.*, **80**, 946 (1958).

(6) Reference 4, Fig. 5.

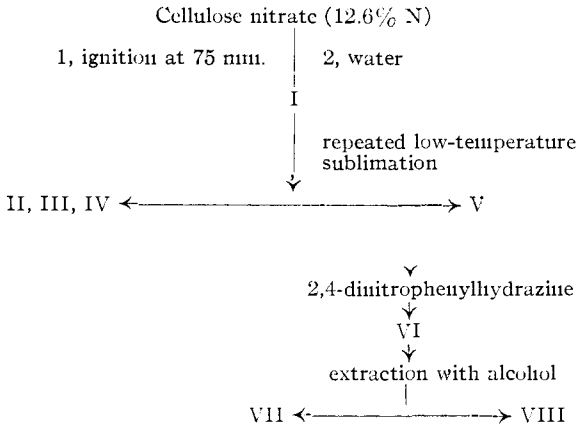

Fig. 1.—Product relationships.

1). The results of quantitative assays performed on products I–V are shown in Table I. Thus, it has been demonstrated that repeated sublimation of product I has the effect of removing formaldehyde from this product, whereas glyoxal remains in the sublimation residue (product V, Fig. 1). The reason for using, in our work, a more dilute product I (50 ml. per g. of cellulose nitrate ignited) than in previous work (20 ml. per g. of cellulose nitrate ignited)[4] is now apparent (Table I, footnote *g*) since the higher dilution favored the removal, by sublimation, of formaldehyde from product I.

TABLE I

FRACTIONATION OF THE AQUEOUS SOLUTION OF THE LIQUID MIXTURE OF CELLULOSE NITRATE IGNITION PRODUCTS BY LOW-TEMPERATURE SUBLIMATION

	Yield,[a] mmoles/mmole ignited[b]			
Product[c]	Formaldehyde[d]	Glyoxal[e]	Total carbonyl content[d]	Unidentified carbonyl content[f]
I	0.255	0.255	1.04	0.275
II	.188[g]	.002	...	...
III	.025	.002	...	...
IV	.008	None	...	...
V	.012	0.222	0.599	0.143
Sum (II-V)	0.233	0.226	...	...

[a] The formaldehyde, glyoxal and total carbonyl analyses were carried out on the products immediately after the products were obtained, with the exception of product I, which was analyzed prior to subliming. [b] See footnote 7. [c] See Experimental portion for preparation. [d] The formaldehyde and total carbonyl assays have been described in ref. 4. [e] The glyoxal assay has been described in ref. 5. [f] Calculated by subtracting from the total carbonyl content of a product the amount of formaldehyde and twice the amount of glyoxal present in the same product. [g] Separate experiments showed that *ca.* 50% less formaldehyde is found in product II when a more concentrated (5-fold; 10 ml. per g. of cellulose nitrate ignited) product I is sublimed.

An examination of Table I (last column) shows that there is a difference of 0.132 mmole of carbonyl per mmole of cellulose nitrate ignited[7] between the unidentified carbonyl content of product I and that of product V. This difference may be largely due to aging processes, since Wolfrom, Chaney and McWain[8] have reported that the total carbonyl content of product I decreased by 0.07 mmole per mmole of cellulose nitrate ignited[7] during the first 72 hours after ignition. In addition, a part of this difference may be caused by the removal of volatile carbonyl compounds other than formaldehyde, on subliming product I. The presence in product I of such volatile carbonyl compounds is not in doubt since acetone, acetaldehyde and acrolein were isolated in the course of our work.

The reaction of product V with 2,4-dinitrophenylhydrazine afforded a precipitate (product VI, Fig. 1) which was expected to contain a large proportion of glyoxal bis-(2,4-dinitrophenylhydrazone) since glyoxal accounted for 74% of the total carbonyl content of product V (Table I). Since bis-(2,4-dinitrophenylhydrazones) are highly insoluble substances, product VI was fractionated by extraction with ethanol (96%) into an alcohol-insoluble fraction (product VII, Fig. 1), and an alcohol-soluble fraction (product VIII, Fig. 1) obtained in 7.8% (of VI) yield.

Silicic acid column chromatography was employed to separate product VIII into six zones. From the materials in these zones were obtained, by further separation and purification processes, the 2,4-dinitrophenylhydrazones of acetone, acetaldehyde and formaldehyde, the bis-(2,4-dinitrophenylhydrazones) of methylglyoxal, glyoxal and hydroxypyruvaldehyde, mesoxaldehyde tris-(2,4-dinitrophenylhydrazone), and 2,4-dinitroaniline. Other substances were also present and they are believed to be 2,4-dinitrophenylhydrazine derivatives of polymeric nature.

Product VII was recrystallized twice from nitrobenzene to afford glyoxal bis-(2,4-dinitrophenylhydrazone) in 22% (of VII) yield. The low yield of glyoxal bis-(2,4-dinitrophenylhydrazone) was expected because the mother liquor of the first recrystallization was pitch black, indicating that product VII contained a considerable amount of tars. Tars and polymeric materials were consistently obtained in large amounts when product I or a fraction thereof was treated with 2,4-dinitrophenylhydrazine. This fact was particularly evident when the reaction was heated, even for very brief (5 min.) periods of time in which case the precipitate obtained was brown to black.

Glyoxal bis-(2,4-dinitrophenylhydrazone) was by no means the only component, aside from tars, of product VII. The chromatographic properties of product VII indicated that it also contained the bis-(2,4-dinitrophenylhydrazone) of methylglyoxal and hydroxypyruvaldehyde, and mesoxaldehyde tris-(2,4-dinitrophenylhydrazone). Since these derivatives are quite insoluble in alcohol, it is reasonable that they should be present in product VII.

Although derivatives of substances containing three carbon atoms—triose phenylosazone, mesoxaldehyde bis-(phenylhydrazone), methylglyoxal bis-(2,4-dinitrophenylhydrazone), mesoxaldehyde tris-(2,4-dinitrophenylhydrazone) and hydroxypyruvaldehyde bis-(2,4-dinitrophenylhydrazone) (in addition to acetone and acrolein)—have been detected, the facile interconversion of the parent substances under hydrazone-forming conditions[9-11] effectively

(7) The nmoles of cellulose nitrate was calculated by division of the grams decomposed by the sum of the millimolecular weight of one anhydro-D-glucose unit (0.162) and the increase in millimolecular weight caused by the nitrate ester groups (0.045 times the degree of substitution).

(8) Reference 5, Table I.

(9) M. L. Wolfrom and G. P. Arsenault, *J. Org. Chem.*, in press.

conceals the real origins of these products. Possibly only one or two fragments containing three carbon atoms are formed by cleavage of the anhydro rings of the cellulose nitrate and these are subsequently converted, during isolation, to these various derivatives.

Our isolation of minute amounts of acetaldehyde and acetone as their 2,4-dinitrophenylhydrazones from the liquid mixture arising from the ignition of cellulose nitrate suggested that the ignition products might contain other organic compounds which could be isolated by these techniques only with great difficulty. Hence, a search by gas–liquid partition chromatography was initiated since this mode of separation provides a rapid method of analysis for the freshly prepared liquid mixture of cellulose nitrate ignition products.

A typical gas–liquid partition chromatogram for the decomposition products of 12.6% N cellulose nitrate is shown in Fig. 2. Collection of the various components at the appropriate times permitted their examination by infrared absorption techniques which in conjunction with the observed retention times, determined for known substances, resulted in the identification of acetaldehyde, acetone, acrolein, ethyl acetate and hydrogen cyanide. A number of known[4] components of the mixture of decomposition products—formaldehyde, α-dicarbonyl compounds and acids—are permanently retained by the polyethylene glycol column employed in this work.[12]

Although attempts were made to remove the last traces of ethyl acetate casting solvent from the cellulose nitrate sheets by extraction with hot water,[13] it is apparent that this effort was not completely successful. In view of the known[14] difficulties encountered in removing organic solvents from cellulose nitrate, this result is not unexpected. Comparison of the area of the ethyl acetate zone with the areas resulting from known samples indicated that a minimum 0.01 mmole of ethyl acetate had been retained by each mmole of cellulose nitrate ignited.

The component responsible for the zone which succeeded ethyl acetate from the column (Fig. 2) exhibited only one major infrared absorption band at 10.5 μ and has not been identified. The last zone, in addition to hydrogen cyanide,[2,4] appeared to be contaminated with an unidentified carbonyl compound which absorbed at 5.8 μ.

The absence of zones following the hydrogen cyanide zone indicated that ethanol was not present in the mixture of cellulose nitrate ignition products. It is suggested that the traces of ethanol, which have been detected in previous work,[4] arose from the slow acid hydrolysis of the ethyl acetate. Alternatively the ethanol may have been completely pyrolyzed[15] or oxidized by nitrogen dioxide to acetaldehyde and its degradation products.

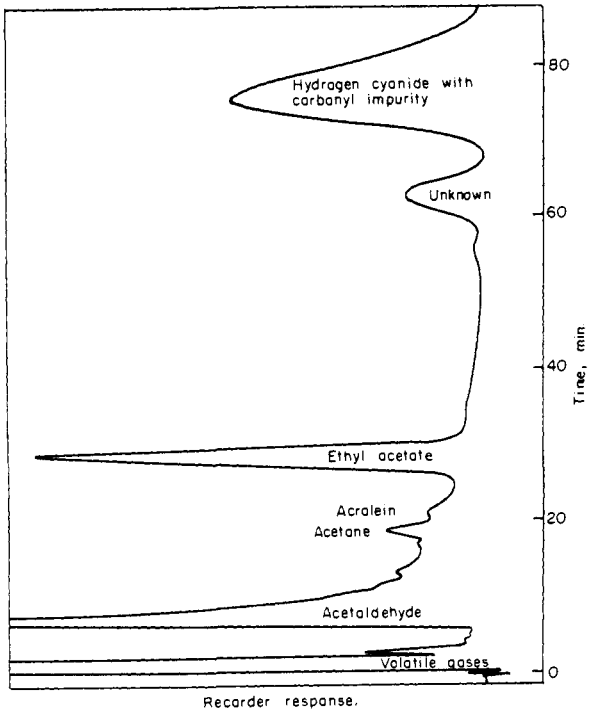

Fig. 2.—Gas-liquid partition chromatogram of the separation of the liquid mixture of cellulose nitrate ignition products.

Although acetaldehyde, acetone and acrolein were not detected in the previous work,[2–5] the more sensitive gas chromatographic technique has shown these substances to be present among the ignition products of cellulose nitrate. The role of the ethyl acetate-casting solvent[2,4] in the formation of these components cannot be evaluated without further study. Carbon–carbon bond formation[2] such as that found[16] to occur during the cool-flame combustion of methane may also play a role.

We have thus made an extensive investigation of the carbonyl compounds present in the cellulose nitrate ignition products in an attempt to explain the difference between the total carbonyl content of the ignition products and the sum of the amounts of carbonyl which can be ascribed to the presence of formaldehyde and glyoxal in the ignition products.[2,5,6] A few monocarbonyl compounds were found but only in small amounts. The small amounts of the α,β-dicarbonyl compounds which have now been found were probably included in the quantitative assay for glyoxal since all α,β-dicarbonyl compounds are oxidizable by hydrogen peroxide at *p*H 7.[2,17] Thus, a complete accounting for the high total carbonyl content and the low carbon recovery[2] (90%) has not been achieved.

Experimental[18]

Preparation and Ignition of Cellulose Nitrate.—The cellulose nitrate[19] employed was blended propellant type contain-

(10) C. L. Bernier and W. L. Evans, THIS JOURNAL, **60**, 1381 (1938).

(11) H. Reich and Barbara K. Samuels, *J. Org. Chem.*, **21**, 68 (1956).

(12) Private communication from Messrs. H. R. Menapace and V. G. Wiley of this department.

(13) Private communication from Dr. L. P. Kuhn, Ballistic Research Laboratories, Aberdeen Proving Gound, Md.

(14) F. D. Miles, "Cellulose Nitrate," Interscience Publishers, Inc., New York, N. Y., 1955, pp. 203-205.

(15) C. D. Hurd, "The Pyrolysis of Carbon Compounds," The Chemical Catalog Co. (Reinhold Publ. Corp.), New York, N. Y., 1929, p. 149.

(16) E. W. Malmberg, THIS JOURNAL, **76**, 980 (1954).

(17) T. E. Friedemann, *J. Biol. Chem.*, **73**, 331 (1927).

(18) All melting points were taken on a Kofler micro hot-stage and are corrected. The infrared spectra were obtained with a Perkin-Elmer spectrophotometer, model 21.

(19) Obtained from the Hercules Powder Co., Wilmington, Del.

ing 12.6% N. Cast sheets of cellulose nitrate were prepared as described previously,[3] employing ethyl acetate exclusively as the casting solvent. No attempt was made to remove the last residual traces of solvent from these sheets, except for the sheets used in the gas–liquid partition chromatographic study. The latter sheets, cut into 2 × 10 cm. strips, were submerged in hot water (90°) for 48 hr. The water was removed by decantation and the strips were dried to constant weight under reduced pressure over phosphorus pentoxide. The strips obtained in this manner were considered to be essentially free of removable ethyl acetate.[13]

The ignition of cellulose nitrate was carried out at 75 mm. pressure in the manner described earlier.[4] The condensate obtained on ignition was processed as described previously[4] except that a much higher dilution with water was used, the final volume of the condensate aqueous solution (product I, Fig. 1) being 50 ml. per g. of cellulose nitrate ignited.

Fractionation of the Condensate by Low-temperature Sublimation.—Freshly prepared product I (2 liters) was allowed to stand at room temperature for 36 hr., frozen, and sublimed under freeze-drying conditions, yielding an aqueous sublimate (product II, Fig. 1) and a non-volatile residue. The residue was dissolved in 2 liters of water, allowed to stand at room temperature for 36 hr. and sublimed. Thus, a sublimate (product III, Fig. 1) was obtained, and the corresponding residue was processed as in the case of the first non-volatile residue, affording a sublimate (product IV, Fig. 1) and still another residue which was dissolved in 200 ml. of water (product V, Fig. 1). The results of quantitative assays carried out on products I–V are recorded in Table I.

Preparation and Fractionation of the 2,4-Dinitrophenylhydrazine Derivative of Product V.—Product V, arising from the ignition of 37.6 g. of cellulose nitrate, was added to a solution of 130 g. of 2,4-dinitrophenylhydrazine in 5.4 liters of 30% perchloric acid.[20] After 36 hr., the settled precipitate was removed by filtration and washed with water; yield 22.2 g. (product VI, Fig. 1).

Product VI (15 g.) was ground to a fine powder and covered with 4.5 liters of 96% ethanol. The suspension was stirred overnight and filtered, affording an alcohol-insoluble residue (product VII, Fig. 1) and a filtrate. The filtrate was evaporated to dryness under reduced pressure; yield 1.17 g. (7.8% of VI) (product VIII, Fig. 1).

Chromatographic Investigation of Product VIII.—Product VIII afforded six zones when chromatographed on silicic acid–Celite (5:1, 8% water) using benzene as the developer, according to the procedure of Wolfrom and Arsenault.[21] The zones were numbered from the bottom to the top of the column. Zones 1 and 2 moved off the column on development of the chromatogram and were collected separately by means of a fraction collector. After the column was extruded, zones 3–6 were eluted with ethanol. A total of 0.93 g. of product VIII was separated on nine columns (54 mm. diam. × 20 cm.). The yield of the material in each zone follows: zone 1, 0.2 g.; zone 2, 0.2 g.; zone 3, 0.1 g.; zone 4, 0.03 g.; zone 5, 0.04 g.; zone 6, 0.4 g.

Zone 1 material (0.2 g.) was sublimed at *ca.* 0.5 mm. pressure and 80°. Several recrystallizations of the sublimate from ethanol afforded a substance of m.p. 127–128°, undepressed on admixture with authentic acetone 2,4-dinitrophenylhydrazone. The identity of this substance with the acetone derivative was further demonstrated by comparing their infrared spectra.

The mother liquors from the recrystallizations of the sublimate of zone 1 material were combined and evaporated to dryness. The evaporation residue was separated into four zones when chromatographed on silicic acid–Celite (2:1) using 10% (volume) of ether in Skellysolve B (b.p. 65–69°) as the developer, according to the procedure of Malmberg.[16] Three zones remained on the column after full development, and they were numbered (1-A, 1-B and 1-C) from the bottom to the top of the column. After the column was extruded, these zones were eluted with ethanol. The material in the fourth zone, collected in the column effluent, weighed *ca.* 1 mg. and was not investigated.

Rechromatography of the material in zone 1-A afforded a substance which was fractionally sublimed at *ca.* 0.5 mm. pressure and 80°. The third (of four) fraction showed the m.p. 127–128° which was not depressed on admixture with authentic acetone 2,4-dinitrophenylhydrazone. Comparative chromatograms of the authentic acetone derivative and of the zone 1-A material further indicated their identity.

The total amount (*ca.* 5 mg.) of zone 1-B material was rechromatographed, and fractionally sublimed at *ca.* 0.5 mm. pressure and 80°. The mixed melting point of the seventh and last fraction, m.p. 161–165°, with authentic acetaldehyde 2,4-dinitrophenylhydrazone, m.p. 166–168°, was 162–167.5°. The identity of the zone 1-B material with the authentic acetaldehyde derivative was further demonstrated by comparison of their infrared spectra and by comparative chromatograms.

All of zone 1-C material (*ca.* 5 mg.) was rechromatographed and sublimed at *ca.* 0.5 mm. pressure and 80°. The sublimate, m.p. 166–167°, did not depress the melting point of authentic formaldehyde 2,4-dinitrophenylhydrazone. A comparison of the chromatographic properties and infrared spectra of zone 1-C material and of authentic formaldehyde 2,4-dinitrophenylhydrazone further demonstrated the identity of the two substances.

The material (0.2 g.) in zone 2 was rechromatographed, and sublimed at *ca.* 0.5 mm. pressure and 80°; yield of sublimate, 69 mg.; yield of sublimation residue, 68 mg. The sublimation residue was recrystallized five times from nitrobenzene to afford methylglyoxal bis-(2,4-dinitrophenylhydrazone) of m.p. 304–305° dec. which was not depressed on admixture with authentic material. The infrared spectra and the chromatographic properties of the recrystallized residue of sublimation and of methylglyoxal bis-(2,4-dinitrophenylhydrazone) were identical. The sublimate of zone 2 material was recrystallized twice from ethanol to afford 2,4-dinitroaniline, m.p. 178.5–180.0°, undepressed on admixture with authentic material. The identity of the recrystallized sublimate was further demonstrated by ultraviolet and visible absorption spectra and by infrared spectrum.

The material from zone 3 was rechromatographed and recrystallized three times from nitrobenzene to afford glyoxal bis-(2,4-dinitrophenylhydrazone) of m.p. (and mixed melting point with an authentic specimen) 336–338° dec. The infrared spectra and chromatographic properties of the recrystallized material and of authentic glyoxal bis-(2,4-dinitrophenylhydrazone) were identical.

Zone 4 material was chromatographed following the directions of Wolfrom and Arsenault.[21] Thus the material (32 mg.) was dissolved in 30 ml. of nitrobenzene–benzene (1:4 by volume) and adsorbed on a column (4.5 cm. diam. × 17 cm.) of silicic acid and Celite (5:1, 8% water). After development with 2.5 liters of benzene, the material showed a separation into three distinct zones. After extrusion of the column, the zones were eluted with acetone and the zone eluates, after evaporation, were rechromatographed on separate columns. The ultraviolet and visible spectra, the infrared spectra and the chromatographic properties of the three rechromatographed materials indicated that they may be 2,4-dinitrophenylhydrazine derivatives of polycarbonyl compounds of complex character.

Zone 5 material (40 mg.) was rechromatographed. The residue obtained by evaporation of the acetone eluate was extracted with 0.5 ml. of nitrobenzene and washed with ether; yield *ca.* 5 mg. This product was shown to be mesoxaldehyde tris-(2,4-dinitrophenylhydrazone) by comparison of its chromatographic properties, ultraviolet and visible absorption spectra, and infrared spectrum with those of authentic material.[9]

The material in zone 6 was black in appearance and contained much tar. This material (400 mg.) afforded several zones when chromatographed on silicic acid–Celite (5:1, 8% water) using 2% ether in benzene as the developer, according to the procedure of Wolfrom and Arsenault.[21] The lowest zone yielded material which, after two recrystallizations from nitrobenzene, gave 25 mg. of crystalline substance identified as hydroxypyruvaldehyde bis-(2,4-dinitrophenylhydrazone) by chromatographic properties, ultraviolet and visible absorption spectra, and infrared spectrum. The other more strongly adsorbed zones gave a blue-violet color by streaking with base on the extruded chromatogram; the color with alkali and the chromatographic properties indicated that these zones contained 2,4-dinitrophenylhydrazine derivatives of polycarbonyl compounds of complex character. No known derivative of 2,4-dinitrophenylhydrazine had identical properties.

(20) C. Neuberg, A. Grauer and B. V. Pisha, *Anal. Chim. Acta*, **7**, 238 (1952).

(21) M. L. Wolfrom and G. P. Arsenault, *Anal. Chem.*, in press.

Investigation of Product VII.—The chromatographic properties of product VII were compared with those of product VIII, following the procedure of Wolfrom and Arsenault.[21] With the exception of the absence of the equivalent of zones 1 and 4 in the chromatogram of product VII, the chromatographic properties of the two products were the same.

An amount (1 g.) of product VII was recrystallized twice from nitrobenzene to afford 222 mg. of glyoxal bis-(2,4-dinitrophenylhydrazone), m.p. 329–332° dec. undepressed on admixture with authentic material. The recrystallized material was further shown to be glyoxal bis-(2,4-dinitrophenylhydrazone) by infrared spectrum. The mother liquor from the first recrystallization was black, indicating that a large amount of tars was present in product VII.

Gas-Liquid Partition Chromatography of the Condensate.—The columns employed were packed with 40% polyethyleneglycol-400 on 30–60 mesh Firebrick C-22. The smaller column (5 mm. diam. by 1.2 m.) was operated at 30° using a helium flow of 50 ml. per min. while the larger column (13 mm. diam. by 4.9 m.) was operated at 80° with a nitrogen flow of 450 ml. per min. Both columns gave similar results. A typical chromatogram obtained on the small column is shown by Fig. 2; the larger column gave better resolution of the minor components. Freshly prepared red oil[4] found in the first spiral trap (Fig. 1[4]) was injected into the column with a hypodermic syringe inserted through a heated inlet. Considerable carbonization of the oil was noted.

As the components emerged from the columns, they were collected in cold traps containing carbon disulfide. Acetaldehyde, ethyl acetate, acrolein and hyrogen cyanide were each identified by elution times and infrared absorption spectra in comparison with known samples. Acetone was identified only by comparison of elution times. Although the carrier gas flow was continued for 8 times the elution time of the last zone (Fig. 2), no further zones appeared.

Comparison of the areas of the zones ascribed to acetaldehyde, ethyl acetate and acrolein to the areas produced by known amounts of these substances indicated that 0.02, 0.01 and less than 0.001 mmole, respectively, had been obtained per mmole[7] of cellulose nitrate ignited.

The well-defined zone (unknown, Fig. 2) produced a strong single peak at 10.5 μ in the infrared absorption spectrum. The infrared spectrum of the hydrogen cyanide zone contained an absorption maximum at 5.8 μ which has not been explained.

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COLUMBUS 10, OHIO

[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY, MCGILL UNIVERSITY, AND THE WOOD CHEMISTRY DIVISION, PULP AND PAPER RESEARCH INSTITUTE OF CANADA]

The Constitution of a Glucomannan from White Spruce (Picea glauca)

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A glucomannan has been isolated from the wood of white spruce (*Picea glauca* (Moench) Voss) with its mannose component representing 82% of the mannose residues present in this species. The electrophoretically homogeneous polysaccharide contained only mannose and glucose residues in a ratio of 3:1. Partial acid hydrolysis yielded crystalline 4-*O*-*β*-D-mannopyranosyl-D-mannose, 4-*O*-*β*-D-mannopyranosyl-D-glucose, 4-*O*-*β*-D-glucopyranosyl-D-mannose, *O*-*β*-D-mannopyranosyl-(1 → 4)-*O*-*β*-D-mannopyranosyl-(1 → 4)-D-mannose and *O*-*β*-D-mannopyranosyl-(1 → 4)-*O*-*β*-D-mannopyranosyl-(1 → 4)-*O*-*β*-D-mannopyranosyl-(1 → 4)-D-mannose. Hydrolysis of the fully methylated polysaccharide gave 2,3,6-tri-*O*-methyl-D-mannose and 2,3,6-tri-*O*-methyl-D-glucose, in addition to traces of tetra-*O*-methylhexoses. The number-average degree of polymerization of the nitrated glucomannan was 107 and its weight-average value was 182. It is suggested that the glucomannan present in white spruce contains, on the average, slightly more than 100 D-mannose and D-glucose residues, linked together by (1 → 4)-*β*-glycosidic bonds. The composition of the partial hydrolyzate indicates the presence of very few contiguous glucose residues. The degree of branching of the polysaccharide has yet to be determined.

In the last few years, hemicelluloses composed of glucose and mannose residues have been isolated from several species of coniferous woods. These glucomannans have been shown to contain most, if not all, of the mannose residues occurring in these woods. The present study is concerned with the isolation and constitution of a glucomannan from the wood of white spruce, a species unusually rich in mannose residues.[1,2] The structures of a water-soluble arabogalactan[3] and two acidic oligosaccharides[4] isolated from the same wood have recently been reported.

Holocellulose, prepared from the extractive-free wood by the chlorite method,[5] was exhaustively extracted with 17.5% sodium hydroxide[6] containing 4% boric acid.[7] Fehling solution[8] was added to the extract and the precipitated copper complex was thoroughly washed with water and subsequently decomposed with acid. Addition of alcohol gave a crude polysaccharide in a yield of 12.7% of the original wood. After two more precipitations as the copper complex, the final product corresponded to 6.7% of the wood. The sugar composition of the polysaccharides[9] is presented in Table I. The crude polysaccharides apparently still contained minor quantities of galactose, arabinose and xylose residues in addition to small amounts of uronic acids which were not determined. In the final product all these sugars had disappeared except for a faint trace of xylose. The ratio of mannose to glucose remained essentially unchanged throughout and approximated 3:1, thus indicating the homogeneous nature of the product. When subjected to electrophoresis in a borate buffer,[10] the polysaccharide traveled as one compact spot on the glass paper, thus corroborating the above

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