

bonyl group, and at 6.46  $\mu$  (asym. stretching) and 7.32  $\mu$  (sym. stretching) for the nitro group.

#### EXPERIMENTAL

*5,9-Dinitro-2,12-tridecanedione.* To 0.05 mole (8.10 g.) of 1,5-dinitropentane,<sup>9</sup> 50 ml. of 90% aqueous ethanol, eight drops of 13% methanolic sodium hydroxide, and 0.12 mole (9.90 g.) of 85% methyl vinyl ketone were added with stirring. The reaction mixture was gradually heated and kept at 50  $\pm$  2°, with continuous stirring, for 20 hr., after which it was cooled and acidified to a pH of four with *N* hydrochloric acid. The acidified reaction mixture was chilled and the solid that separated out was collected by filtration. The crude product, m.p. 61–72°, weighed 5.15 g. Crude yield, 34%. Careful recrystallization from ethyl acetate gave pure *5,9-dinitro-2,12-tridecanedione*, m.p. 77.5–78.5°, representing 73% by weight of the crude taken for purification. Refined yield, 25%.

*Anal.* Calcd. for C<sub>13</sub>H<sub>22</sub>N<sub>2</sub>O<sub>6</sub>: C, 51.64; H, 7.34; N, 9.21. Found: C, 51.80, 51.88; H, 7.35, 7.50; N, 9.57, 9.63.

The *disemicarbazone* of the refined product was prepared. The derivative melted at 180.0–180.5° (dec.), after one recrystallization from aqueous tetrahydrofuran.

*Anal.* Calcd. for C<sub>15</sub>H<sub>28</sub>N<sub>4</sub>O<sub>6</sub>: C, 43.26; H, 6.78; N, 26.91. Found: C, 43.48, 43.30; H, 6.84, 7.03; N, 26.70, 26.79.

*2,5,9,12-Tridecanetetrone* (II). A solution of 2.7 g. (approximately 27 mmoles) of sulfuric acid in ten ml. of water was cooled down to 0–5° with an ice bath. The solution of the disodium salt, previously prepared by allowing a mixture of 0.9 g. (3 mmoles) of *5,9-dinitro-2,12-tridecanedione*, 20 ml. of methanol, 10 ml. of water, and 9.0 ml. of 2*N* methanolic sodium hydroxide (approximately 18 mmoles of sodium hydroxide) to stand 1.5 hr., was added to the acid solution, with stirring, over a 15-min. period. The mixture was chilled and filtered to give the first crop of solid, which was 0.6 g. of sodium sulfate. The liquor was evaporated, rechilled, and filtered to yield a second crop of solid, which was the crude product weighing 0.2 g. (28%). Recrystallization from aqueous ethanol gave *2,5,9,12-tridecanetetrone*, m.p. 106–107° (dec.). The compound was unstable to light and air at room temperature.

*Anal.* Calcd. for C<sub>13</sub>H<sub>20</sub>O<sub>4</sub>: C, 64.98; H, 8.39. Found: C, 64.95, 65.02; H, 8.43, 8.46.

*Reaction of II with semicarbazide.* By following the procedure of Shriner, Fuson, and Curtin<sup>10</sup> and employing 0.5 g. of II, 0.1 g. of a solid was obtained which after several recrystallizations from aq. ethanol melted at 211–214° (dec.).

*Anal.* Calcd. for C<sub>17</sub>H<sub>32</sub>N<sub>12</sub>O<sub>4</sub> (tetrasemicarbazone): N, 35.88; for C<sub>15</sub>H<sub>26</sub>N<sub>6</sub>O<sub>4</sub> (disemicarbazone): N, 23.71. Found: N, 26.50, 26.71.

*Reaction of II with 2,4-dinitrophenylhydrazine.* The procedure of Shriner, Fuson, and Curtin<sup>10</sup> was followed. The reaction mixture was filtered and the solid, after several recrystallizations from aq. ethanol melted at 125.5–126.5°. It was identified as the semicarbazone of acetone. A mixed melting point determination with an authentic sample gave no depression.

The above filtrate deposited on cooling a solid which was unreacted II.

*5,9-Dibromo-5,9-dinitro-2,12-tridecanedione.* A solution consisting of 1.8 g. (6 mmoles) of *5,9-dinitro-2,12-tridecanedione*, 60 ml. of methanol, 10 ml. of water, and 6.0 ml. of 2*N* methanolic sodium hydroxide (approximately 12 mmoles of sodium hydroxide) was cooled to 3° with an ice bath. Then 9.0 g. of bromine was added with stirring, and

the mixture was removed from the ice bath and allowed to stand for 5 min. The excess bromine and some solvent were stripped off and the mixture was chilled and filtered to give 1.7 g. (61%) of *5,9-dibromo-5,9-dinitro-2,12-tridecanedione*, m.p. 65.5–66.5°. Recrystallization from carbon tetrachloride gave a refined product, m.p. 65.5–66.0°.

*Anal.* Calcd. for C<sub>13</sub>H<sub>20</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>6</sub>: C, 33.93; H, 4.38; N, 6.09; Br, 34.74. Found: C, 33.81, 33.72; H, 4.18, 4.25; N, 6.00, 6.26; Br, 34.51, 34.69.

R. B. WETHERILL LABORATORY OF CHEMISTRY  
PURDUE UNIVERSITY  
WEST LAFAYETTE, IND.

### Alkali-Resistant Hemicellulose in Luffa Cellulose<sup>1</sup>

CHEN-CHUAN TU<sup>2</sup>

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This work was undertaken to investigate the relationship of the alkali-resistant hemicellulose and cellulose in the skeletal substance of the dishcloth gourd (*Luffa cylindrica*). In 1927<sup>3</sup> its constituents were reported to be cellulose, lignin, hemicellulose, and small amounts of mannan and galactan. An analysis of its constituents is shown in Table I.

TABLE I

ANALYSIS OF LUFFA CONSTITUENTS	
alpha-Cellulose	62.8%
Pentosan	19.5%
Lignin	12.1%
Uronic anhydride	6.7%

Table II indicates that alcohol extraction, delignification with chlorine dioxide (sodium chlorite in acid solution), and alkali extraction were found to be a proper sequence of procedures for cellulose evaluation. The skeletal structure of the gourd was completely disintegrated by using the above sequence. The completion of disintegration was observed by the changes in the physical state of the gourd upon chemical treatment. When the other sequences in Table II were used, disintegration was incomplete. If the disintegration is incomplete, some hemicellulose originally trapped in the cellulose would not be separated. There appears to be some alcohol-soluble compound serving as a cementing agent to bind cellulose and hemicellulose together to a certain extent. It is possible that the alcohol-soluble constituent might be affected by the chemical treatments, particularly chlorine dioxide or alkali, so as to become less soluble in alcohol, rendering

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(2) Present address: Experiment Station, Hawaiian Sugar Planters' Association, Honolulu 14, T. H., U.S.A.

(3) S. Masuda, *Cellulose Industry*, **3**, 321 (1927).

(9) H. Feuer and G. Leston, *Org. Syntheses*, **34**, 39 (1954).

(10) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, John Wiley and Sons, Inc., New York, New York, 1956, p. 218.

the disintegration incomplete. Likewise, if delignification is incomplete, disintegration would also be incomplete.

TABLE II

METHODS OF CELLULOSE PREPARATION	
Sequence of Treatment	
1. Alcohol, ClO <sub>2</sub> , KOH (10%)	Skeletal structure completely disintegrated
2. Alcohol, KOH, ClO <sub>2</sub>	Skeletal structure collapsed or deformed, but not completely disintegrated
3. KOH, alcohol, ClO <sub>2</sub>	
4. KOH, ClO <sub>2</sub> , alcohol	
5. ClO <sub>2</sub> , alcohol, KOH	
6. ClO <sub>2</sub> , KOH, alcohol	

The cellulose, prepared as described above, still contained a small amount of alkali-resistant hemicellulose. The alkali-soluble hemicellulose was identified as xylan by paper chromatography after it was hydrolyzed with acid in the usual manner.

A small amount of alkali-resistant xylan in cellulose may be explained as a result of similar solubility in alkali of some higher degree of polymerization (D.P.) alkali-resistant xylan and of the lower D.P. fractions of cellulose. If this assumption is correct, it may be possible to remove the region of overlapping D.P. by a proper choice of solvent. Cupriethylenediamine was selected. Table III indicates that when about 30% of the material had been dissolved in a proper concentration of cupriethylenediamine solution, no detectable amount of xylan remained. Also, in Figure 1a<sup>4</sup> based on the summative and integral viscosity curves of Figure 1, the area

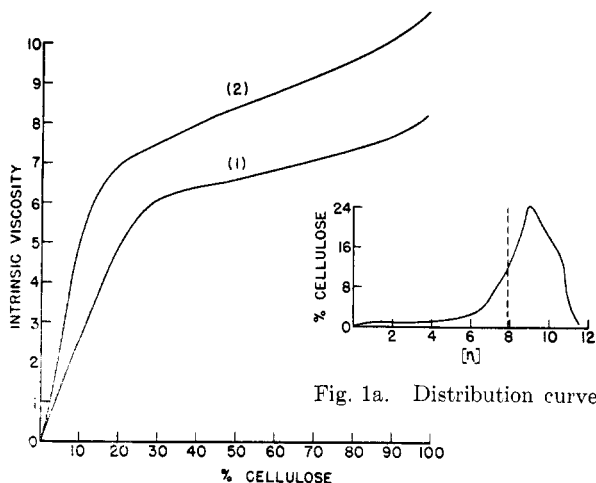


Fig. 1. Summative (1) and integral (2) curves

weights and consequent similar solubilities in alkali. It is unlikely that the alkali-resistant hemicellulose is chemically bound. This finding may be useful, in general, to support the view that the alkali-resistant hemicellulose in wood and other plant celluloses can also be explained by the overlapping of its D.P. with that of cellulose in the lower D.P. region.

## EXPERIMENTAL

*Preparation of cellulose and hemicellulose.* Twenty grams of the gourd was exhaustively extracted with 95% alcohol in a large Soxhlet extractor. After drying, the residue weighed 18.4 g. The alcohol-extracted gourd was delignified with sodium chlorite at pH 4 and 75° in the usual manner. The delignified gourd was deformed but its structure still re-

TABLE III  
FRACTIONATION DATA

No.	Cu(en) <sub>2</sub> Soln. M	Efflux Time (sec.)		Cellulose Dissolved, g./100 ml. (0.1 g. used)	Sugars Present after Hydrolysis				[η]
		Solv. t.	Soln. t <sub>1</sub>		Residue		Regenerated		
					Glucose	Xylose	Glucose	Xylose	
1	0.09	103.7	128.0	0.0220	99.50	0.50	—	—	5.7
2	0.15	111.0	136.2	0.0300	—	—	—	—	—
3	0.17	114.0	133.0	0.0275	Ca. 100.00	Undetectable	96.00	4.00	6.0
4	0.20	114.7	145.0	0.0397	Ca. 100.00	Undetectable	96.50	3.50	6.2
5	0.22	116.0	170.0	0.0594	Ca. 100.00	Undetectable	97.70	2.30	6.8
6	0.23	117.0	216.0	0.0900	—	—	—	—	7.9
7	0.24	117.5	224.0	0.0930	—	—	—	—	7.9
8	0.26	119.0	240.0	0.1052	—	—	—	—	8.2
9	Cellulose not treated with cupriethylenediamine solution				98.50	1.50	—	—	—

under the curve to the right of the dotted line indicates the region of xylan-free cellulose. In consequence, this work provides evidence that the presence of xylan hemicellulose in cellulose can be defined as a result of an overlapping of molecular

weights. The yield of holocellulose, *i.e.*, the weight of the delignified gourd, was 16.2 g. The holocellulose was extracted with 10% KOH under nitrogen overnight. At the beginning of the extraction, the gourd underwent disintegration. After the extraction was complete, the cellulose was separated and washed with 1% dilute acetic acid and water. The yield was 10.0 g. The solution was neutralized with 50% acetic acid and precipitation occurred. Alcohol was slowly added to the suspension until the alcohol concentration reached

(4) Wm. A. Mueller and L. N. Rogers, *Ind. Eng. Chem.*, **45**, 2522 (1953).

20%. On standing, the precipitated hemicellulose flocculated and was separated by centrifuging. The separated hemicellulose was treated with 95% alcohol, acetone, and ether in the usual manner. Two and five-tenths grams of dry, white hemicellulose, identified by hydrolysis and chromatography as 95% xylan, was obtained. The use of other sequences of reagents for the preparation of cellulose was not so successful as the one described above. The sequences of treatment and results are shown in Table II.

**Fractionation and characterization.** One-tenth gram of the cellulose obtained above was transferred into a 100-ml. centrifuge bottle to which 10 glass beads and a selected amount of water was added. The bottle was then stoppered with a serum-bottle rubber stopper.

The stopper was pierced with a syringe needle, to which, in addition to a cupriethylenediamine reservoir, nitrogen and vacuum lines with appropriate stopcocks were also connected. The air in the bottle was first evacuated and then replaced with purified nitrogen. The bottle was again evacuated and filled with cupriethylenediamine to make up 100 ml. and finally filled with nitrogen. The bottle was then shaken for 2 hr. and centrifuged. Ten milliliters of the supernatant solution was withdrawn with a syringe and transferred into an Ubbelohde viscometer in which the viscosity was determined. The transferring and the measurement of viscosity were conducted under nitrogen. The viscosities of the samples obtained with varied concentrations of cupriethylenediamine solution are shown in Table III. The residue was separated and washed with 1% acetic acid and water. Fifty milliliters of the supernatant solution was neutralized with 50% acetic acid. Precipitation occurred. The precipitate was centrifuged, separated, washed, and weighed. Thirty milligrams each of the residue and of the regenerated cellulose were hydrolyzed with sulfuric acid, chromatographed and analyzed for glucose and xylose.<sup>5</sup> The results are shown in Table III.

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INSTITUTE OF PAPER CHEMISTRY  
APPLETON, WIS.

(5) J. F. Saeman, W. E. Moore, R. L. Mitchell, and M. A. Millett, *Tappi*, **37**, 336 (1956); J. Pridham, *Anal. Chem.*, **28**, 1967 (1956).

### Structure of 2,1,3-Benzoselenadiazole and Its Derivatives. III.<sup>1</sup> Preparation and Absorption Spectra of 5-Styryl-4-nitro-2,1,3-benzoselenadiazoles<sup>2</sup>

EUGENE SAWICKI<sup>3</sup> AND ALBERT CARR<sup>4</sup>

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The nitration of 2,1,3-benzothiadiazole<sup>5</sup> and 2,1,3-benzoselenadiazole<sup>1</sup> (I) has been shown to

(1) Paper II: E. Sawicki and A. Carr, *J. Org. Chem.*, **22**, 507 (1957).

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(3) Present address: Robert A. Taft Sanitary Engineering Center, 4676 Columbia Parkway, Cincinnati 26, Ohio.

take place in the 4-position. The attack at this position is believed to be due to the greater electron density at the 4- and 7-positions of the dicationic salt of I as compared to the 5- and 6-positions.<sup>1</sup> Because of the ortho-para directing effect of the methyl group, the nitration of 5-methyl-2,1,3-benzoselenadiazole (II) could be expected in the 4-position. The following facts bear this out. The nitration of II gave a nitro derivative (III) whose

TABLE I  
ULTRAVIOLET-VISIBLE ABSORPTION SPECTRA OF SOME 2,1,3-BENZOSELENADIAZOLE DERIVATIVES

Substituted 2,1,3-Benzoselenadiazole	$\lambda_{\max}$ (log $\epsilon$ )			Solvent <sup>a</sup>
5-Nitro-	230 (3.71)	274 (4.02)	342 (4.21)	E
	224 (3.86)	274 (4.03)	348 (4.22)	A
4-Nitro-			400 <sup>b</sup> (3.2)	
		271 (3.57)	339 (4.19)	E
		275 (3.73)	370 (3.8) <sup>c</sup>	A
4-Nitro-5-methyl-			340 (4.16)	
			380 (3.7)	
			338 (4.27)	E
4-Nitro-5,7-dimethyl-		279 (3.61)	370 (3.3) <sup>c</sup>	A
			351 (4.22)	
			380 (3.7)	
5-Amino-	236 (4.25)	324 (3.94)	426 (3.80)	E
	265 (3.65)			
	236 (3.97)	333 (4.10)	459 (3.74)	Ac
	242 (4.14)	322 (4.00)	462 (3.28)	E
4-Amino-			329 (4.08)	
			336 (4.07)	
	231 (3.70)	333 (4.23)	370 (3.1) <sup>c</sup>	Ac
4-Amino-5-(and 7)-methyl-	238 (4.11)	323 (4.00)	466 (3.23)	E
			329 (4.04)	
			336 (4.05)	
5-Methyl-	232 (3.75)	330 (4.18)	370 (3.4) <sup>c</sup>	Ac
4-Nitro-5-styryl-	232 (3.70)	333 (4.24)	370 (3.3) <sup>c</sup>	E
		292 (4.33)	388 (4.32)	Ed
4-Nitro-5-(4'-methylstyryl)-		300 (4.26)	400 (4.23)	Ed
4-Nitro-5-(4'-chlorostyryl)-		295 (4.30)	382 (4.10)	Ed
4-Nitro-5-(3',4'-dimethoxystyryl)-	240 (4.22)	335 (4.22)	408 (3.79)	Ed
4-Nitro-5-(4'-dimethylamino-styryl)-		340 (4.38)	489 (4.32)	Ed

<sup>a</sup> E = 95% ethanol; A = 95% sulfuric acid; Ac = 50% alcoholic 1.2N HCl; Ed = 95% ethanol containing 0.2% dioxane. <sup>b</sup> Underlined values are shoulders. <sup>c</sup> Weak inflection.

(4) Taken in part from the dissertation to be submitted by Albert Carr in partial fulfillment of the requirements for the Doctor of Philosophy Degree at the University of Florida.

(5) L. Efros and R. Levit, *Zhur. Obshchei Khim.*, **23**, 1552 (1953); *Chem. Abstr.*, **48**, 12091 (1954).