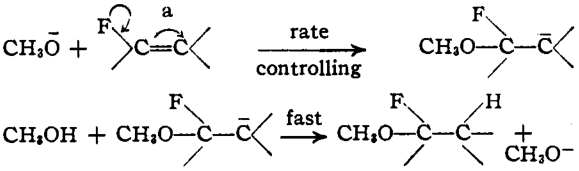
Trichlorofluoroethylene was also observed to react readily but with some loss of halogen acid, while tetrachloroethylene did not react at 0°.

The physical properties and analytical data for the three ethers obtained pure are summarized in Table I. All three ethers were saturated to permanganate solution. They yielded fluoride ion in large amount when heated with alcoholic potash along with trace amounts of chloride ion from the chlorine containing compounds. The structures assigned are consistent with the above observation, and the presence of $-CF_2-$groupings alpha to oxygen explained the observed stability toward the sodium methylate reagent.

The mechanism of addition is postulated as follows



The role of fluorine relative to chlorine in promoting addition of nucleophilic type reagents and effecting the orientation of addition is considered to be due to its greater tendency to enter into resonance with the double bond so as to predispose the system to polar activation of the type indicated above (arrow *a*). There is also considerable reason to believe that fluorine is capable of electron release relative to chlorine as an activation mechanism.[7] The general electron withdrawal (inductive effect) by the halogens on the double bond favors the development of acceptor activity by activation in marked contrast to the exclusively nucleophilic reactivity shown by simple ethylenic hydrocarbons.

TABLE I

	CH_3OCF_2-CHF_2	CH_3OF_2-CHClF	$CH_3OCF_2CHCl_2$
F. p., °C.	−107	−92[a]	− 35
B. p., °C.	+ 36.5	+70.6	+105
$n^{20}D$	<1.3	1.3340	1.3861
d^{20}_4	1.2939	1.3636	1.4262
*MR*D		22.46	27.18
ARE[b]		1.01	0.97
% C calcd.	27.3	24.3	21.8
% C found	27.4	24.4	21.9
% H calcd.	3.03		2.42
% H found	3.11		2.51
Mol. wt. calcd.	132	148.5	164.9
Mol. wt. found	135	149	167

[a] A second crystalline form m. p. −109° was also indicated. [b] Calculated using atomic refractivities listed by Gilman.[6]

ITHACA, N. Y. RECEIVED APRIL 30, 1947

---

[6] Gilman, "Organic Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1938, p. 1739.

[7] See for example Watson, "Modern Theories of Organic Chemistry," 2nd ed., Oxford University Press, London, 1941, p. 101.

Occurrence of Pectic Materials in Wood

BY W. W. PIGMAN, E. ANDERSON AND R. L. LEAF, JR.

Hardwoods contain small amounts (usually less than 0.5%) of materials that yield furfural and carbon dioxide when distilled with 12% hydrochloric acid.[1,2] After hydrolysis of a hemicellulose fraction of beechwood O'Dwyer[1] isolated a cinchonine salt similar to that reported for D-galacturonic acid. Anderson has isolated fractions from hardwoods and softwoods that have specific rotations and solubility characteristics similar to fruit pectins.[2] By hydrolysis of the material in the presence of bromine he produced mucic acid. This evidence proves qualitatively the presence of galacturonic acid in the original wood, which on the basis of O'Dwyer's identification is apparently the D-isomer.

In order to demonstrate more conclusively the presence of pectic materials[3] in a typical wood, it was decided to isolate galacturonic acid n ithe form of the difficultly soluble sodium calcium D-galacturonate[4] after enzymic hydrolysis[5] of wood pectic material. To give some quantitative aspects to the procedure the results were compared with those obtained with citrus pectic acid under the same conditions. Unfortunately for the quantitative aspects, the yields are greatly affected by the purity of the pectic material.[6]

Pectic material isolated from the inner bark of black spruce, in which it occurs in fairly large amounts (10%),[7] was treated with a commercial enzyme preparation. Crystalline sodium calcium galacturonate was isolated in a yield of 28% of the theoretical. Citrus pectic acid under the same conditions gave a yield of 53%. The product had the same calcium analysis and specific rotation as described by Isbell and Frush.[4] On oxidation with bromine under slightly acid conditions it gave mucic acid in a yield of 64% of the theoretical.

On the basis of this work there is no doubt that D-galacturonic acid occurs in the inner bark of the black spruce in a polymerized form. Since enzymic reactions are generally very specific, it is likely that the polymerized form is structurally similar to citrus pectic acid and that wood pectins are closely related to citrus pectins.

Experimental

The pectic acid was made by direct extraction with 5%

---

[1] M. H. O'Dwyer, *Biochem. J.*, **20**, 656 (1926); I. A. Preece, *Biochem. J.*, **25**, 1304 (1931).

[2] E. Anderson, *J. Biol. Chem.*, **165**, 233 (1946), and earlier papers.

[3] In the present sense a pectic material is one which, on hydrolysis, yields a substantial amount of D-galacturonic acid.

[4] H. S. Isbell and H. L. Frush, *J. Research Natl. Bur. Standards*, **32**, 77 (1944); R. Pasternack and P. P. Regna, U. S. patent 2,338,534 (1944).

[5] H. H. Mottern and H. L. Cole, THIS JOURNAL, **61**, 2701 (1939); W. W. Pigman, *J. Research Natl. Bur. Standards*, **25**, 301 (1940).

[6] H. S. Isbell and H. L. Frush, *J. Research Natl. Bur. Standards*, **32**, 90 (1944).

[7] E. Anderson and W. W. Pigman, *Science*, **105**, 601 (1947).

ammonium hydroxide of the inner bark of the black spruce (*Picea mariana* B. S. P.) and of holocellulose from the inner bark.[7] It was precipitated as calcium pectate. By treatment with hydrochloric acid the calcium pectate was converted to an impure pectic acid with $[\alpha]^{20}_{\text{D}}$ +80° (3% NaOH) and containing 66.5% uronic anhydride (on an oven-dry basis).

A control experiment using commercial pectic acid[8] containing 77% uronic anhydride gave sodium calcium galacturonate in 53% of the theoretical yield.

The hydrolyses were carried out according to the directions of Isbell and Frush[6] except that: (1) an aqueous dispersion of pectic acid was treated with sodium bicarbonate until the *p*H was 3.8; (2) the hydrolysis time was twelve days at 38°; 12 g. of pectic substance (oven-dried) was used.

From 13 g. of wood pectic material (containing 11% moisture) 3.1 g. of sodium calcium D-galacturonate $[NaCa(C_6H_9O_7)_3 \cdot 6H_2O]$ was obtained; this yield is 28% of the theoretical value. The equilibrium specific rotation in 0.1 *N* nitric acid was $[\alpha]^{20}_{\text{D}}$ +43.4 (*c*, 2%), whereas Isbell and Frush reported $[\alpha]^{20}_{\text{D}}$ +44.0. The product contained 5.26% calcium; this value compares with 5.35% calculated for the above formula.

When 0.601 g. of the above product was dissolved in dilute hydrochloric acid and treated with bromine for four hours at room temperature 0.257 g. of insoluble material separated. A further crop of 0.066 g. was obtained from the mother liquor. The melting point of the material was 208–210° (dec.). Upon the basis of the insolubility and melting point the material must be mucic acid. The yield was 64% of the theoretical value.

---

[8] California Fruit Grower Exchange, Ontario, Cal.

INSTITUTE OF PAPER CHEMISTRY
APPLETON, WISCONSIN
UNIVERSITY OF ARIZONA
TUCSON, ARIZONA

RECEIVED SEPTEMBER 12, 1947

Trimethylhalosilane Preparations[1]

BY B. O. PRAY,[2] L. H. SOMMER, G. M. GOLDBERG, G. T. KERR, P. A. DI GIORGIO[3] AND F. C. WHITMORE

Previously reported preparations of trimethylfluorosilane have utilized the reaction of trimethylchlorosilane with zinc fluoride,[4] and with antimony trifluoride in the presence of antimony pentachloride.[5]

We have found that trimethylfluorosilane can be prepared directly in about 80% yield by the addition of ammonium fluoride to a solution prepared from hexamethyldisiloxane and concentrated sulfuric acid.[6]

$$(CH_3)_3SiOSi(CH_3)_3 \xrightarrow[H_2SO_4]{NH_4F} 2(CH_3)_3SiF$$

A similar procedure, using ammonium chloride, constitutes an excellent method for the preparation of trimethylchlorosilane in good yield (85%) and high purity. This method for trimethylchlorosilane gives better yields and is more convenient than that involving reaction of methylmagnesium halide with silicon tetrachloride.[7] The latter forms an azeotrope with trimethylchlorosilane[8] and careful fractionation is required to effect separation from dimethyldichlorosilane and methyltrichlorosilane which are also formed.[7] The present method gives only trimethylchlorosilane. Thus, hexamethyldisiloxane is a convenient starting material for three of the trimethylhalosilanes.[9]

In the present work, trimethylbromosilane[9] and trimethyliodosilane have been prepared by fission of the phenyl–silicon bond in phenyltrimethylsilane with bromine and iodine, respectively.[10]

$$C_6H_5Si(CH_3)_3 \xrightarrow{X_2} C_6H_5X + (CH_3)_3SiX$$

The above synthesis of trimethyliodosilane completes the series of trimethylhalosilanes. Trimethyliodosilane is a colorless liquid which fumes vigorously in moist air and acquires an iodine color on standing.

Experimental

Hexamethyldisiloxane from Ethyl Orthosilicate.[11]—Ethyl orthosilicate, 8.7 moles, was added with vigorous stirring during thirty minutes to 28 moles of methylmagnesium bromide in 12 liters of ether while keeping the reaction mixture at 10°. Stirring and cooling were continued for one hour followed by refluxing for two hours. Ether and product were then distilled. After removal of the ether, the product was dissolved in 700 cc. of concentrated sulfuric acid, and the resulting solution was added to ice. Fractionation of the upper layer, after washing and drying, gave 380 g. (2.35 moles) of hexamethyldisiloxane, b. p. 99–100°, n^{20}_{D} 1.3771, 54% yield.

Trimethylfluorosilane.—Ammonium fluoride, 24.2 g. (0.7 mole) was added from a dropping bottle to a stirred ice-cold solution of 32.4 g. (0.2 mole) of hexamethyldisiloxane in 60 cc. of concentrated sulfuric acid during one hour. Warming gave 31 g. of distillate of clear colorless liquid. Fractionation gave 3.2 g., b. p. 15.4°, and 27.8 g., b. p. 15.8° at 734 mm., of pure trimethylfluorosilane.

Anal. Calcd. for C_3H_9SiF: F, 20.6. Found: F, 20.3, 20.4.

A molecular weight determination by the vapor density method gave mol. wt. 92 (calcd. 94).

Trimethylchlorosilane.—Dry powdered ammonium chloride, 321 g. (6 moles), was added during three hours with vigorous stirring to a solution prepared from 324 g. (2 moles) of hexamethyldisiloxane and 1000 g. of concentrated sulfuric acid. During the addition the flask was cooled in an ice-bath. Upon completion of the addition, *the upper layer was separated as quickly as possible.* Fractional distillation gave 369 g. (3.4 moles) of trimethylchlorosilane, b. p. 58° (734 mm.), n^{20}_{D} 1.3884, d^{20} 0.8581, a yield of 85%.

Trimethylbromosilane.—Using the method of Bygden,[12] phenyltrimethylsilane, b. p. 168 (734 mm.), n^{20}_{D} 1.4900, was prepared in 72% yield by the reaction of phenyltrichlorosilane with methylmagnesium bromide. Liquid bromine, 162 g. (1 mole), was added with stirring to 150 g. (1 mole) of phenyltrimethylsilane in a flask cooled with cold tap-water, and the reaction mixture was heated on the steam-bath for one hour. Fractional distillation gave

---

[1] Paper XI in a series on organsilicon compounds; paper X, THIS JOURNAL, **69**, 2108 (1947).

[2] Present address: Pittsburgh Plate Glass Co., Barberton, Ohio.

[3] Present address: General Electric Research Laboratory, Schenectady, N. Y.

[4] Newkirk, THIS JOURNAL, **68**, 2736 (1946).

[5] Booth and Suttle, *ibid.*, **68**, 2658 (1946).

[6] *Cf.* Flood, *ibid.*, **55**, 1735 (1933).

[7] Gilliam and Sauer, *ibid.*, **66**, 1793 (1944).

[8] Sauer, U. S. Patent 2,381,139, *C. A.*, **39**, 4890 (1945).

[9] The preparation of trimethylbromosilane from hexamethyldisiloxane has been reported by Gilliam, Meals and Sauer, THIS JOURNAL, 1161 (1946).

[10] Grüttner and Cauer, *Ber.*, **51**, 1289 (1918), have reported a similar fission of *p*-di-(triethylsilyl)-benzene with bromine.

[11] *Cf.* Daudt, U. S. Patent 2,386,441; *C. A.*, **40**, 1866 (1946).

[12] Bygden, *Ber.*, **40**, 2274 (1907).