

The Chemistry of Furfuryl Alcohol Resins

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Synopsis

Furfuryl alcohol resins contain a broad spectrum of compounds. The distribution of these compounds in a given resin varies with the manufacturing conditions. A resin containing a high proportion of low molecular weight constituents has been prepared and separated into fractions. Twelve compounds were separated from the resin; four of these are new compounds. The lower molecular weight constituents can be arranged into four major classes: polyfurfuryl alcohols, polyfurfuryl furans, methyl-substituted polyfurfuryl furans, and polyfurfuryl ethers.

INTRODUCTION

Catalyzed furfuryl alcohol polymerizes, yielding a complex liquid mixture of polyfurfuryl compounds which eventually condense into a solid product that is chemically inert.¹ The polymerization is generally carried out by using acid catalysts (mineral acids, strong organic acids, acyl halides, and Lewis acids); however, amines and γ -alumina have also been used to promote the condensation.¹⁻³

Several of the intermediate compounds formed during the initial stages of the acid-catalyzed polymerization of furfuryl alcohol have been identified. The first constituents to be isolated, difurylmethane and difurfuryl ether, were separated by Dinelli and his co-workers^{4,5} who also separated a five-ring compound, $C_{25}H_{22}O_5$, but did not positively identify it. Two additional components, 5-furfurylfurfuryl alcohol and 5-(5-furfurylfurfuryl)furfuryl alcohol, were obtained by Dunlop and Peters by distillation of a liquid resin.⁶ Water, formaldehyde, and levulinic acid are also produced during resinification. The composition of the liquid polymer and the mechanism of polymerization have also been studied by Hachihama and Shono.⁷⁻¹³ Takano examined the products from the initial stages of resinification and isolated two homologs of difurylmethane, 2,2'-methylenebis(5-furfurylfuran) and 2,5-bis(furfurylfurfuryl)furan.¹⁴⁻¹⁷ Conley and Metil proposed mechanisms for the oxidative degradation of the polymer by studying changes in the functional groups of the resin revealed by infrared spectroscopy.¹⁸ These workers also isolated a carbonyl compound, 5-hydroxy-3-pentenoic lactone, by fractionating a thermally condensed resin.

Although many resin constituents have been identified, none (with the exception of furfuryl alcohol) has been characterized by the newer instrumental methods of nuclear magnetic resonance spectroscopy and gel per-

meation chromatography. Infrared spectra have been reported for only a few of the compounds.

The resin constituents appear to fall into a few general classifications. A study of furfuryl alcohol resins was initiated in this laboratory to separate and characterize individual components which could be regarded as model compounds representing various fractions of the resins. In the course of this program, 12 compounds were isolated from furfuryl alcohol resins. These include a carbonyl compound (tentatively identified) and four other compounds which are reported here for the first time. Many of the individual constituents have been reported before; however, this is the first time that all of these compounds have been isolated from any given resin at one time. Infrared and NMR spectra and GPC elution volumes were obtained for all the compounds, and these data are included in this paper.

EXPERIMENTAL

Preparation of Resin

Furfuryl alcohol resins were prepared under conditions chosen to ensure that they were enriched in the lower molecular weight constituents and to avoid complications due to additives in commercial resins. A typical polymerization was carried out as follows. Eight hundred grams of furfuryl alcohol (Fisher Scientific, highest purity), 800 g water, and 1 ml sulfuric acid catalyst were heated on a steam bath for 35–45 min until two layers formed. The organic layer (575–600 ml) was separated and washed thoroughly (eight times) with equal volumes of water, yielding 350–450 ml low molecular weight resin.

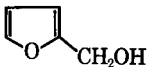
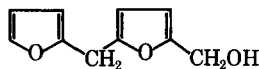
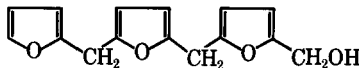
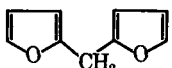
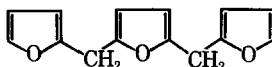
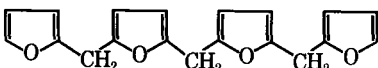
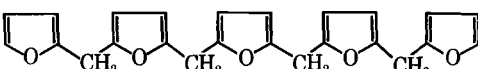
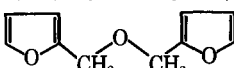
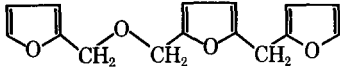
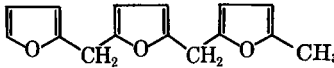
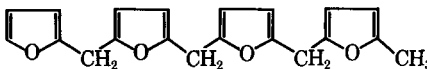
Fractionation of Resin

The resin was separated by distillation under nitrogen at 0.8 torr. Pressure in the distilling assembly (a standard distillation apparatus utilizing a Vigreux column and multiple receivers) was controlled automatically with a mercury manometer and solenoid valves. Fractions of 30–50 ml each were collected in the boiling ranges of (A) 25°–90°C, (B) 90°–110°C, (C) 110°–140°C, and (D) 145°C and up. Distillations were halted at the beginning of the thermosetting reaction.

Further distillation of individual fractions was carried out on a Podbielniak mini-cal distillation system operated under nitrogen at 8.5 to 9.5 torr. This unit consists of a spinning band column with automatically controlled vacuum and reflux ratios.

Fraction A contained, primarily, unpolymerized furfuryl alcohol (I), difurylmethane (2,2'-methylenedifuran) (IV), and difurfuryl ether (2,2'-(oxydimethylene)difuran) (VIII). Chemical formulas and numerical designations are given in Table I. Furfuryl alcohol was removed by washing the sample thoroughly (ten times) with equal volumes of 1*N* sodium hydroxide, dissolving the washed sample in 50 ml diethyl ether, and drying

TABLE I. Furfuryl Alcohol Resin Components

No.	Compound	GCP peak Δ , ml
	Furfuryl alcohol	-17.0
I		
	5-Furfurylfurfuryl alcohol	4.5
II		
	5-(5-Furfurylfurfuryl) furfuryl alcohol	21.0
III		
	2,2'-Methylenedifuran	8.0
IV		
	2,5-Bis(5-furfuryl) furan ^a	24.0
V		
	2,2'-Methylenebis(5-furfurylfuran)	36.0
VI		
	2,5-Bis(5-furfurylfurfuryl)furan	46.0
VII		
	2,2'-(Oxydimethylene)difuran	13.5
VIII		
	5-Furfuryl-2,2'-(oxydimethylene)difuran ^a	29.0
IX		
	2-Methyl-5-(5-furfurylfurfuryl)furan ^a	29.0
X		
	2-Methyl-5-(5-furfurylfurfurylfurfuryl)furan ^a	41.0
XI		
XII	Carbonyl compound	24.5

^a New compounds.

over anhydrous magnesium sulfate. The diethyl ether was evaporated, and the residue was distilled, giving 5–10 ml compound IV and 2–3 ml VIII.

Fraction B was separated by extracting with 400-ml portions of petroleum ether. The solvent was evaporated, and the sample was tested for the presence of —OH by infrared analysis. When no —OH remained (10–12 extractions), the soluble portion was distilled, yielding 7–10 ml of 2,5-bis-(5-furfuryl)furan (V).

The impure fractions from the distillation of compound V were combined and chromatographed on alumina with petroleum ether. One of the elution fractions contained an ether which was purified further by GPC, giving several milliliters of 5-furfuryl-2,2'-(oxydimethylene)difuran (IX).

The pot residue from the distillation of compound V was eluted from an alumina column with petroleum ether, yielding about 2 ml of the carbonyl compound (XII).

Distillation of the petroleum ether-insoluble portion of fraction B yielded 12–15 ml 5-furfurylfurfuryl alcohol (II). An alternate method of separating II from fraction B is to esterify it with benzoyl chloride in pyridine¹⁹ and precipitate the ester from the whole fraction. The alcohol can then be reclaimed by saponification of the ester with sodium hydroxide.

Most of the major components of fraction C were more easily separated from fractions B or D. However, elution chromatography of the petroleum ether-soluble portion of fraction C led to the separation of milligram quantities of two solid components. One of these, 2,2'-methylenebis(5-furfurylfuran) (VI), can also be obtained in small quantities by elution of the petroleum ether-soluble portion of fraction D from alumina with petroleum ether. The other compound isolated from fraction C was 2,5-bis(5-furfurylfurfuryl)furan (VII).

Fraction D was extracted with 1-liter increments of boiling petroleum ether (12–14 times), leaving a small amount of brown residue. Repeated recrystallization of the extracted solid from 1-liter increments of petroleum ether (12–14 times) and distillation on the Podbielniak apparatus gave about 20 g 5-(5-furfurylfurfuryl)furfuryl alcohol (III).

In the course of this investigation, two methyl-substituted polyfurfuryl furans were identified in impure samples of other compounds. One of these, 2-methyl-5-(5-furfurylfurfuryl)furan (X), was obtained from fraction B as a mixture containing 15% to 20% compound V (calculated by GPC). A second methyl compound, 2-methyl-5-(5-furfurylfurfurylfurfuryl)furan (XI), was isolated from fraction C as a two-component mixture which contained approximately 65% compound VI (calculated from the nuclear magnetic resonance spectrum).

Determination of Physical Properties

Exhaustive characterizations were performed only on new compounds. Other compounds were identified by comparison of physical properties with

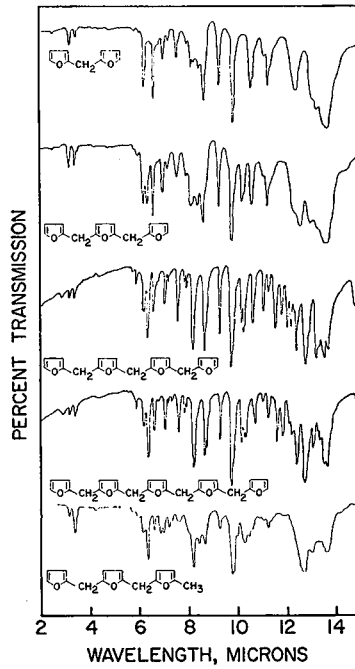


Fig. 1. Infrared spectra of furfuryl alcohol resin components.

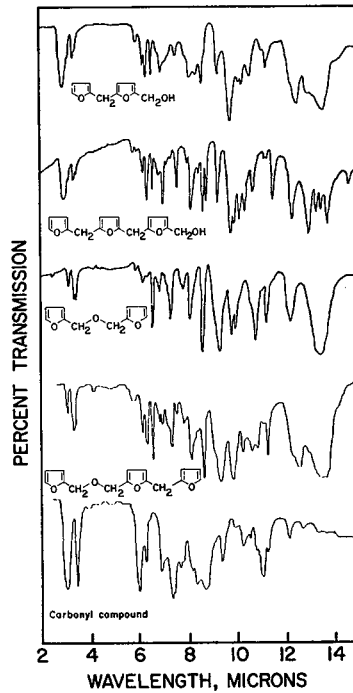


Fig. 2. Infrared spectra of furfuryl alcohol resin components.

published values and by analysis of infrared and nuclear magnetic resonance spectra.

Melting points were measured with a Köfler microscope hot stage. Boiling points were taken from the distillation data.

Infrared spectra were run on a Perkin-Elmer Model 221 spectrophotometer or a Perkin-Elmer Infracord. Spectra are presented for the various resin components in Figures 1 and 2.

A Mechrolab Model 301 vapor pressure osmometer was used to determine molecular weights in benzene solution.

Refractive indices were measured by using a Bausch and Lomb Abbe refractometer.

Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance spectra were taken with a Varian A-60 spectrometer. Samples of VII, IX, and XII were dissolved in deuterated chloroform; carbon tetrachloride was used as the solvent for the other samples. Tetramethylsilane was employed as the internal standard. Chemical shifts and relative intensities of the protons are listed in Table II.

Gel Permeation Chromatography

Gel permeation chromatograms were obtained through the use of a Waters Associate Model 200 chromatograph. This instrument was equipped with five 4-ft \times $3/8$ -in. Styragel columns having maximum permeabilities of 500, 60, 45, 45, and 45 Å. A 5 cm³ siphon was used to collect fractions. The detector employed was a differential refractometer. Toluene at 80°C was used as the eluent, with the sample flow rate maintained at 1 cm³/min. Initial experiments were performed with tetrahydrofuran and toluene at various temperatures to determine the optimum operating conditions. Sample concentrations varied from 0.2 wt-% to 6.0 wt-%. Injection times varied from 45 to 120 sec, depending on sample size. Refractometer response was linear, and resolution remained constant for the various sample sizes and injection times used.

Identification of Components

Known Compounds

2,2'-Methylenedifuran (IV). Isolated from fraction A by distillation: bp 65°C (9.0 torr) (lit. 62°–5°C (9 torr))¹²; n_D^{20} 1.5048 (lit. 1.5049).^{20,21}

2,2'-(Oxydimethylene)difuran (VIII). Isolated from fraction A by distillation: bp 103°–4°C (8.5 torr) (lit. 101°–2°C (2 torr)).²² Infrared analysis agrees with literature.²³

5-Furfurylfurfuryl Alcohol (II). Distilled from petroleum ether-insoluble portion of fraction B: bp 141°–3°C (9.0 torr) (lit. 131°–3°C (2.5 torr))⁶; n_D^{20} 1.5290 (lit. 1.5290).⁶ IR agrees with literature.²³

2,2'-Methylenebis(5-furfurylfuran) (VI). White solid separated by

liquid chromatography of petroleum ether-soluble portion of fraction C: mp 74°–5°C (lit. 73°–4°C).¹⁶

2,5-Bis(5-furfurylfurfuryl)furan (VII). Yellow solid separated by liquid chromatography of petroleum ether-soluble portion of fraction C: mp 99°–101°C (lit. 94°–5°C).¹⁶

5-(5-Furfurylfurfuryl)furfuryl Alcohol (III). White solid extracted from fraction D with petroleum ether: mp 61°–2°C (lit. 62°–62.5°C)¹⁵; bp 192.5°–195°C (5.0 torr) (lit. 199°–202°C (3 torr)).⁶ IR agrees with published spectrum.²⁴

New Compounds

2,5-Bis(5-furfuryl)furan (V). Pale-yellow liquid which darkens rapidly on exposure to air. Distilled from petroleum ether-soluble portion of fraction B: bp 141°–6°C (8.5 torr); n_D^{20} 1.5324; n_D^{25} 1.5297. Molecular weight calculated 228, measured 227.

ANAL. Calcd for $C_{14}H_{12}O_3$: C, 73.67%; H, 5.30%; O, 21.03%. Found: C, 73.25%; H, 5.40%; O, 21.35%.

5-Furfuryl-2,2'-(oxydimethylene)difuran (IX). Yellow liquid which darkens on standing. Isolated by a combination of liquid and gel permeation chromatography from petroleum ether-soluble portion of fraction B: molecular weight calculated 258, measured 257.


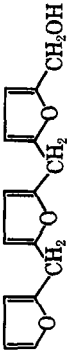
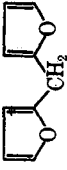

ANAL. Calcd for $C_{16}H_{14}O_4$: C, 69.76%; H, 5.46%; O, 24.78%. Found: C, 70.44%, H, 5.89%; O, 23.67%.

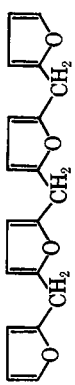
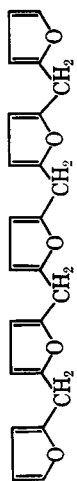
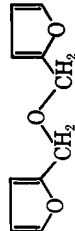
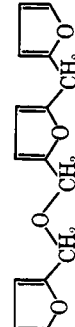
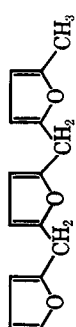
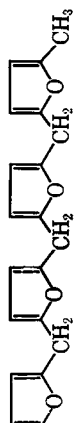
The sample used for chemical analysis had darkened, and the experimental values may be influenced by sample decomposition. No other data were obtained for this compound because it was difficult to purify.

Carbonyl Compound (XII). Very stable, yellow liquid which solidified on standing. This material was isolated by liquid chromatography of the pot residue from the distillation of the petroleum ether-soluble portion of fraction B and was not completely characterized. The NMR curve exhibits sharp, symmetrical peaks at 1.28, 2.21–2.35, and 3.17 ppm and a broad peak at 3.65 ppm, with relative intensities of 12, 2, 4, and 2, respectively. However, the melting range of 42–54°C indicates a lack of purity. The infrared spectrum shows the presence of carbonyl and hydroxyl groups and the absence of furan rings. The presence of a carbonyl group was verified by positive tests for ketones. The experimental molecular weight (188) and chemical analysis (C, 62.56%; H, 10.24%; O, 27.20%) suggest an empirical formula of $C_{10}H_{20}O_3$.

2-Methyl-5-(5-furfurylfurfuryl)furan (X). Identified in a mixture containing 15% to 20% V. The infrared spectrum of the mixture (Fig. 1) shows absorption due to compound V, but peaks attributed to X at 3.35, 6.35, 8.2, 9.8, and 12.7 μ were observed while the major peaks of V have become weak. Repeated GPC fractionations or preparative GPC would be necessary to separate the pure compound.

TABLE II
NMR Parameters for Furfuryl Alcohol Resin Components

Compound	Hydrogen type	δ , ppm	Relative intensity
	α -ring	7.20-7.23	1
	β -ring	5.86-6.22	4
	-CH ₂ O-	4.34	2
	-CH ₂ -	3.87	2
	-OH	4.12 (broad)	1
	α -ring	7.24-7.30	1
	β -ring	5.92-6.28	6
	-CH ₂ O-	4.40	2
	-CH ₂ -	3.89	4
	-OH	2.04-2.06	1
	α -ring	7.21-7.24	2
	β -ring	6.12-6.24	4
	-CH ₂ -	3.93	2
	α -ring	7.04-7.05	2
	β -ring	5.91-6.23	6
	-CH ₂ -	3.87	4

	α ring	7.23-7.30	2
	β ring	5.92-6.29	8
	-CH ₂ -	3.89-3.94	6
	α ring	7.22-7.38	2
	β ring	5.88-6.36	4
	-CH ₂ -	3.87-4.01	4
	α ring	7.31-7.35	2
	β ring	6.24-6.26	4
	-CH ₂ O-	4.38	4
	α ring	7.27-7.38	2
	β ring	5.98-6.30	6
	-CH ₂ O-	4.37-4.44	4
	-CH ₂ -	3.96	2
	CH ₃ -	2.17	
	CH ₃ -	2.21-2.27	

2-Methyl-5(5-furfurylfurfurylfurfuryl)furan (XI). Identified in a mixture containing 60% to 64% VI. GPC is not a satisfactory method of separating these compounds because they elute together; however, thin-layer chromatography experiments indicate that liquid chromatographic techniques should be applicable.

RESULTS AND DISCUSSION

In this investigation, as in previous ones, attempts to isolate the constituents of furfuryl alcohol resins have been successful only for the lower molecular weight components found in the distillable fraction of the resin. Twelve compounds were separated from an acid-catalyzed resin, and most of these fall into four general classifications: polyfurfuryl alcohols, polyfurfuryl furans, polyfurfuryl ethers, and methyl-substituted polyfurfuryl furans. The exception is compound XII, which is likely a cleavage-rearrangement product. All of the identified compounds have been characterized by infrared analysis, NMR, and GPC, and the results are reported in this paper, since these techniques had not previously been exploited. The NMR and GPC data are discussed separately below.

Among the newly identified compounds, the methyl-substituted polyfurfuryl furans are the most difficult to purify, and these compounds could not be separated from the unsubstituted parent compounds. Although the presence of the dimeric methyl compound would also be expected, this compound was not detected by GPC. The predicted elution is at a Δ of 15 ml, a value which is approximately the same as that for difurfuryl ether.

With the isolation and identification of the trimer (V), the poly furfuryl furan series is complete through the pentamer.

The identification of a second ether (IX) indicates that a series of polyfurfuryl ethers is also present in furfuryl alcohol resins.

Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance was very useful for identification of the unknown compounds isolated in this study. In the cases of IX and XI, initial identification of the compounds was made with NMR. The four-ring methyl compound (XI) was present in a mixture with the unsubstituted tetramer (VI). The concentration of XI, as determined by NMR, was 36% to 40%.

The chemical shifts and relative proton intensities for each compound identified are listed in Table II. Coupling constants were not calculated because in many cases samples were too small or of insufficient purity to obtain optimum NMR spectra. Ranges are reported for the chemical shifts when the spectra were of higher orders and could not be resolved. The chemical shifts were assigned by comparing experimental spectra with published spectra for furan and furfuryl alcohol.²⁵ The α -proton on the furan ring appears at 7.42 ppm in furan and furfuryl alcohol. The β -proton is located at 6.47 ppm in furan and at 6.33 ppm in furfuryl alcohol. There-

fore, the peak at 3.39 ppm in difurylmethane (IV) was assigned to the $-\text{CH}_2-$ protons. Likewise, the peak at 3.48 ppm for difurfuryl ether (VIII) was assigned to the $-\text{CH}_2\text{O}-$ protons, and the peak at ~ 2.2 ppm in the methyl compounds was assigned to the $-\text{CH}_3$ protons. The $-\text{CH}_2\text{O}-$ proton peak appears at 4.57 ppm in furfuryl alcohol. Since the chemical shift of $-\text{OH}$ peaks is known to change with temperature, the $-\text{OH}$ assignment was verified by heating the sample to 50° or 60°C and observing the shift in each case.

Relative intensities are not reported for the pentamer (VII) because the sample was too small for reliable integration. Only the chemical shifts for the $-\text{CH}_3$ peaks are listed for compounds X and XI because the samples were impure.

Gel Permeation Chromatography

Gel permeation chromatography was used extensively in our work, not only for separations but also to determine sample purity; samples which appear to be pure by other methods frequently contain sufficient impurities to show additional GPC peaks. The chromatograph was calibrated with the known compounds. Identification of new compounds was then verified from their positions on the calibration curves. In some cases, initial identification was made from the GPC curves and verified by other methods.

Positions of GPC peaks are reported in Table I. The peak positions are expressed as the difference (Δ) between the sample peak position and that of the dissolved nitrogen which appears in each chromatogram. The dissolved nitrogen provides a constant internal standard, and the Δ values are independent of any changes in instrumentation or column packings. Two samples, I and XII, peak in the opposite direction from all others because the refractive index of their solutions is lower than that of the reference.

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