hydrolysate was extracted continuously overnight with chloroform, with the addition of lead carbonate to the chloroform solution. The chloroform extract was filtered, evaporated, and the sirup distilled, to yield 13.2 mg. (90%), $[\alpha]^{24}D$ +83° (in chloroform, c 0.66).

1,6-Anhydro-2,3-di-*o*-methyl-4-*o*-*p*-tolylsulfonyl-β-L-idopyranose (X).—A solution of 30 mg. of IX and 72 mg. of *p*-toluenesulfonyl chloride in 0.3 ml. of dry pyridine and 0.1 ml. of alcohol-free chloroform was stored at room temperature for 3 days. The excess acid chloride was decomposed with water, and the product was taken up in 5 ml. of chloroform. The solution was washed successively with ice-cold N sulfuric acid, water, sodium bicarbonate solution, and water, then dried over potassium carbonate. Evaporation of the filtered solution gave a sirup, which was dissolved in benzene and chromatographed on 2.5 g. of silica gel. Crystalline material (40 mg.) was obtained as a single peak eluted with a mixture of benzene and ether (1:1). Recrystallization from a mixture of ether and pentane gave 25 mg. (45%) of rectangular plates, m.p. 69–69.5°, $[\alpha]^{21}D$ +27° (in chloroform, c 2.23).

Anal. Calcd. for $C_{15}H_{20}O_7S$: C, 52.32; H, 5.86; S, 9.30. Found: C, 52.31; H, 5.76; S, 9.33.

1,6-Anhydro-2,3-di-*o*-methyl-4-*o*-*p*-phenylazobenzoyl-β-L-idopyranose (XI).—A solution of 28 mg. of sirupy IX and 56 mg. of *p*-phenylazobenzoyl chloride in 1 ml. of dry pyridine was heated at 100° for 14 hr. in a sealed tube. After cooling at 0°, the excess of acid chloride was decomposed by addition of one drop of water and the mixture was kept for 0.5 hr. at room temperature. It was evaporated to dryness by codistillation with toluene, and the crystalline residue was dissolved in ethanol-free chloroform and passed through a column (7 cm. × 2 cm. diameter) of neutral alumina, activity Brockman III. Elution with 100 ml. of chloroform gave 32 mg. (55%) of orange sirup which was recrystallized from a mixture of benzene and pentane as clusters of plates, m.p. 108–109°, $[\alpha]^{21}D$ −76° (in chloroform, c 0.65).

Anal. Calcd. for $C_{21}H_{22}N_2O_6$: C, 63.31; H, 5.57; N, 7.03; OCH_3, 15.58. Found: C, 63.20; H, 5.60; N, 7.00; OCH_3, 15.74.

1,6-Anhydro-2,3,4-tri-*o*-methyl-β-L-idopyranose (XII).—A solution of 200 mg. of 1,6-anhydro-β-L-idopyranose[4] in 1 ml. of water at 70° was vigorously stirred and, at 10-min. intervals, ten additions of 1 ml. of 30% aqueous sodium hydroxide and 0.35 ml. of dimethyl sulfate were made. Then the temperature of the stirred suspension was maintained at 100° for 1 hr. The cooled mixture was diluted with an equal volume of water and passed through a column (7 cm. × 1.7 cm. diameter) containing a mixture of Norit A and Celite (2:1). The column was washed with 350 ml. of water when the effluent was sulfate-free. The column was then washed with 80 ml. of acetone. The acetone solution was evaporated to dryness and the residue, dissolved in a mixture of hexane and benzene 4:1, was chromatographed on 10 g. of silicic acid. Elution with a mixture of benzene and ether 1:1 gave crystalline fractions which were recrystallized from a mixture of ether and pentane to give 114 mg. (42%) of stout prisms, m.p. 39–40°, $[\alpha]^{19}D$ +88° (in chloroform, c 1.0).

Anal. Calcd. for $C_9H_{17}O_5$: C, 52.93; H, 7.90; OCH_3, 45.60. Found: C, 52.85; H, 7.85; OCH_3, 45.68.

Elution with acetone gave an additional 49 mg. of sirup, which was not further investigated.

Thiocarbonyls. IX. The Use of Thin Layer Chromatography in the Separation of the Isomeric Trithiofluorobenzaldehydes[1]

E. CAMPAIGNE AND M. GEORGIADIS[2]

Contribution No. 1103 from the Chemistry Laboratories of Indiana University, Bloomington, Indiana

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Thin layer chromatography was found to be very successful in the separation and purification of the α- and β-isomers of trimers of *o*-, *m*-, and *p*-fluorothiobenzaldehydes. By the use of this method pure samples of each isomer may be obtained from small quantities of crude mixture, and purity of samples may be checked. The conformation of the isomers was established by nuclear magnetic resonance, and it was possible to determine the ratio of isomers in crude product by n.m.r. spectra of samples dissolved in the minimum required solvent. Contrary to previous claims, it was found that the α-(*cis–trans*) isomer is always formed to a higher degree than the β-(all *cis* equatorial) isomer, which is consistent with a reasonable mechanism proposed for trimer formation.

The products usually obtained by treating aldehydes with hydrogen sulfide in the presence of an acid catalyst, usually hydrogen chloride, are trimers of the thioaldehydes. This general area has been the subject of several reviews.[3,4] Some forty or more different aromatic aldehydes have been converted to trithianes, but never more than two isomers have been obtained and for some only one trithiane could be prepared.[3,5,6] Studies based on dipole moments of substituted (and unsubstituted) trithiobenzaldehydes indicate that the α-isomer has the *cis,trans*-2,4-6-triaryl-1,3,5-trithiane structure, having one axial and two equatorial phenyl groups on a chair trithiane ring, while the β form has the all equatorial *cis,cis*-2,4,6-triaryl-1,3,5-trithiane orientation.[7]

Traditionally, the higher melting, less soluble product was assigned the β-configuration.[3] Consequently repeated recrystallizations gave product rich in the β-isomer, and the mother liquor was enriched in this way in the α-isomer. This repeated recrystallization or selective extraction of one isomer was the reported technique of separation of trithianes.[3,8] Although the above seems reasonable, in practice the separation was a tedious task. The α- and β-isomers form eutectics,[8] which may confuse the structure assignment on the basis of melting point. During the procedure of recrystallization, there is a danger that the more soluble isomer will be lost, and even if tedious work or luck yields the α-isomer this may not be 100% pure. The assignment of the structure on the basis of melting points may be erroneous in cases where the melting points are close together or, as in tri-(*m*-fluorothio-

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(1) This work was supported by a grant, no. G-9855, from the National Science Foundation to Indiana University. For paper no. VIII of this series see E. Campaigne and B. E. Edwards, *J. Org. Chem.*, **27**, 3760 (1962).

(2) Taken from a thesis to be submitted by M. G. in partial fulfillment of the requirements for the degree, Doctor of Philosophy.

(3) E. Campaigne, *Chem. Rev.*, **39**, 1 (1946).

(4) A. Schoenberg and A. Wagner, in Houben-Weyl, "Methoden der Organische Chemi," George Thieme Verlag, Stuttgart, 1955, Vierte Auflage, Band IX.

(5) E. Campaigne and W. M. Budde, *Proc. Indiana Acad. Sci.*, **58**, 111 (1948).

(6) J. A. Stanfield and L. B. Reynolds, Jr., *J. Am. Chem. Soc.*, **74**, 2878 (1952).

(7) K. Hayasaki, *J. Chem. Soc.. Japan, Pure Chem. Sect.*, **74**, 386 (1953); *Chem. Abstr.*, **48**, 11e (1954); *J. Chem. Soc. Japan*, **76**, 284 (1955); *Chem. Abstr.*, **50**, 11,749b (1956).

(8) G. F. Suyver, *Rec. trav. Chim.*, **24**, 377 (1905).

benzaldehyde), where the all *cis* or β-isomer actually melts lower.

Because of the above reasons it was thought that the elegant technique of thin layer chromatography (t.l.c.)[9] might be more suitable for the separation of isomeric forms of the unknown trimers of *o*-, *m*-, and *p*-fluorothiobenzaldehydes, and n.m.r. spectroscopy could be employed for the rigorous assignments of structure of the isomeric forms.[10] Thin layer chromatography was used in two ways. First it was employed to find the solvent system for column chromatography using several "open" columns, that is plates covered with silica gel G, and secondly to assay the fractions coming from a preparative column.

Trithianes are hydrophobic substances of rather low polarity soluble in several organic solvents. Therefore nonpolar organic solvents were tested using t.l.c and their polarity was varied by addition of a small amount of a second solvent. In general good solvent systems for the separation of aromatic trithianes can be obtained by mixing cyclohexane with a portion of *one* of the following: (a) diethyl ether, dioxane, acetone, 1,2-dimethoxyethane or (b) benzene, toluene, xylene, thiophene, etc. Class A, that is oxygen containing solvents, give high R_f values and good separation. Class B, that is aromatic solvents, give low or very low R_f values and are preferred when multistage or repeated chromatography on the same plate is desirable. A superior solvent system in many cases for the separation of aromatic trithianes seems to be 5–10% diethyl ether in cyclohexane. The chromatograms can be developed as brown spots by spraying with a mixture of 0.1 *M* copper acetate and 0.1 *M* silver nitrate in 3–4 *M* alcoholic ammonia, after heating for half an hour at 100–120°. Although the chromatograms of trithiobenzaldehydes can be developed differently, the above spray can be used for the detection of a variety of organic sulfur compounds in t.l.c. and it has been used extensively in these laboratories. If the chromatograms are kept for a day or two after development, the background color becomes gray but the spots remain brown and faint spots indicating impurities or byproducts become more apparent.

Since the R_f values depend on the surface offered by the molecule and its dipole moment, it was reasonably expected the α-isomer would migrate faster. The all-equatorial arrangement of the β-isomer offers more surface and has higher dipole moment.[7] It should therefore have the lower migration rate. In the quantitative separation of the isomeric trithiofluorobenzaldehydes (which was achieved on a silicic acid column using the solvent system which gave the best separation with the t.l.c. technique) it was expected that the α-isomer would be eluted first. This expectation was confirmed by n.m.r. spectroscopy (see Table III).

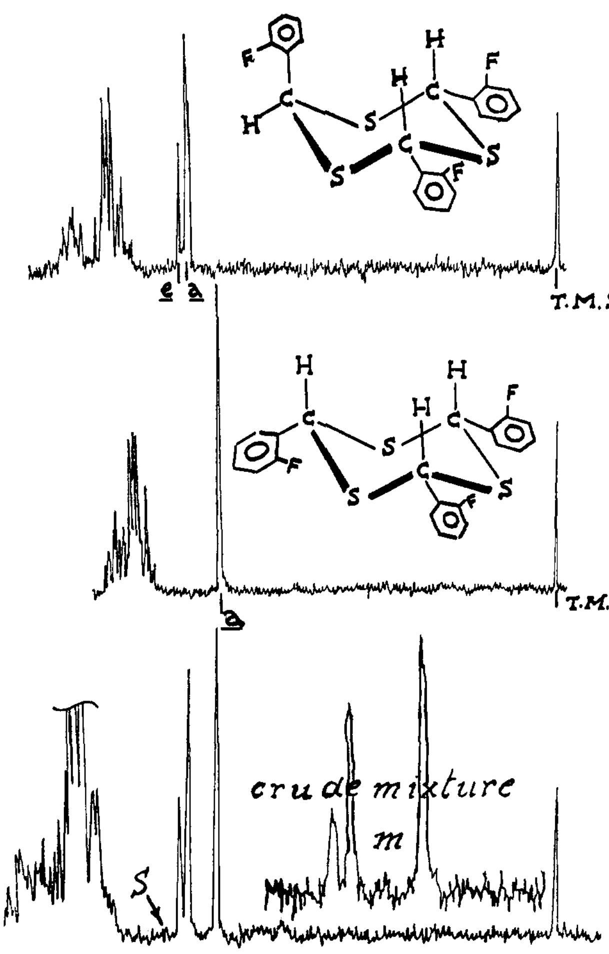

Fig. 1.—N.m.r. spectra of pure and crude tri(*o*-fluorothiobenzaldehydes): s, saturated solution; m, minimum amount of solvent.

The n.m.r. spectroscopic technique was used not only for the rigorous assignment of structure to the isolated isomeric forms but also for the determination of the ratio of α- and β-forms in the crude mixtures before separation. Recently[10] the n.m.r. spectra of 1,3,5-trithianes have been discussed in detail. In the case of the trithiofluorobenzaldehydes using carbon disulfide as solvent, the results are unambiguous. The spectrum of α-isomers exhibits two peaks (Fig. 1, 2, and 3) in a ratio 2:1 in contrast to the single peak for axial hydrogen of the all *cis* substituted β-isomer. The single peak of the β-isomers is shifted upfield and never stands between the a and e peak of the α-isomers. This different order in chemical shift between the α- and β-isomers of the trithiofluorobenzaldehydes in carbon disulfide as solvent is in accord with the chemical shift of the trithiobenzaldehydes.[11]

If saturated solutions are used, n.m.r. shows the relative solubility and as expected tri(*m*-fluorothiobenzaldehyde) was observed to be more soluble than the *para* isomer, but the *ortho* isomer was the most soluble (compare Fig. 1, 2, and 3). In the quantitative determination of the ratio of α- and β-isomers in the crude material by n.m.r., the use of saturated solutions may lead to errors, since the solubility of the α- and β-isomers may differ. The minimum amount of solvent necessary to dissolve the sample completely should be used in each case. In the case of tri(*m*-fluorothiobenzaldehyde) the β-isomer, which melts lower than the α-isomer, is almost as soluble in carbon disulfide. The figures show n.m.r. spectra of the crude material of both saturated solution and minimum amount of solvent. As expected, the ratio of α- to β-isomer is 2:1 for trimers of both *p*- and *m*-fluorothiobenzaldehyde, but is more nearly 1:1 in the *ortho* case. It is now ap-

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[9] E. Stahl, *Angew. Chem.*, **73**, 646 (1961).

[10] E. Campaigne, B. E. Edwards, and N. F. Chamberlain, *J. Org. Chem.*, **27**, 135 (1962).

[11] E. Campaigne, B. E. Edwards, and N. F. Chamberlain, *ibid.*, **27**, 4718 (1962).

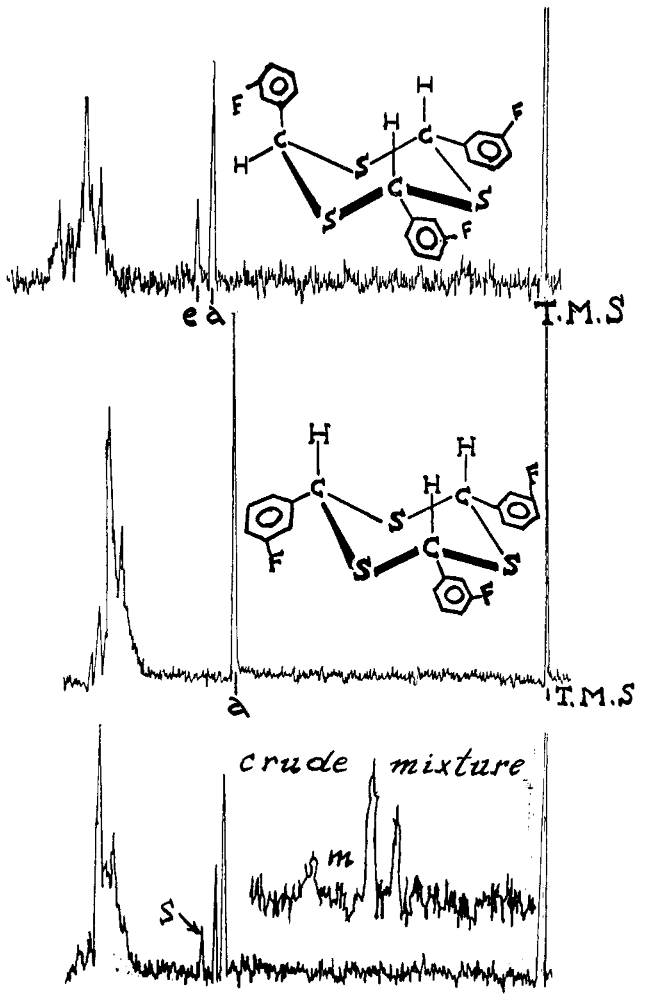


Fig. 2.—N.m.r. spectra of pure and crude tri(*m*-fluorothiobenzaldehydes): s, saturated solution; m, minimum amount of solvent.

parent that assignment of structure on the basis of melting point may be in error, and reinvestigation of previous reports (*cf.* ref. 5 and 6) will be required. The n.m.r. data, R_f values, and other physical properties are listed in Tables I, II, and III.

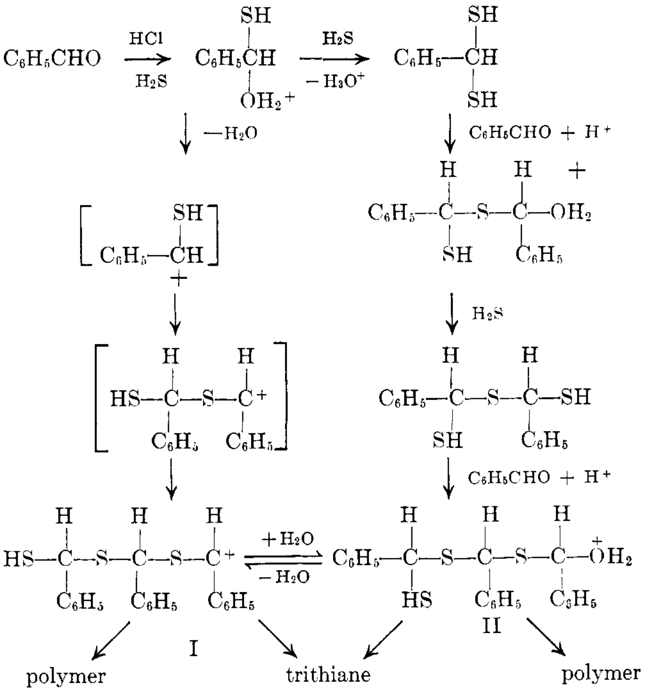
TABLE I

N.M.R. SPECTRA OF TRITHIOFLUOROBENZALDEHYDES

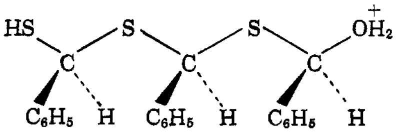
Fig.	Compound	Isomer	H^a Type	c.p.s. (tetramethylsilane)	δ p.p.m. (tetramethylsilane)	τ
1	*o*-Fluoro-	α	a	358.9	5.981	4.018
			e	363.9	6.066	3.934
		β	a	340.9	5.682	4.318
2	*m*-Fluoro-	α	a	319	5.317	4.683
			e	332	5.533	4.467
		β	a	313	5.217	4.783
3	*p*-Fluoro-	α	a	319	5.317	4.683
			e	334	5.567	4.433
		β	a	309	5.150	4.850

[a] a = axial, e = equatorial; tetramethylsilane was used as internal standard, CS_2 solvent

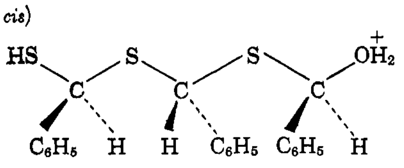
Although the mechanism of trithiane formation is complicated[12] it is probable that the formation of the so called α-isomer is stereochemically and statistically favored even though the β-isomer is thermodynamically the more stable isomer. The formation of the trithiane ring most likely takes place after a linear trimer is formed. At the moment of ring closure the substituent at carbon C-1 and C-2 may be either *cis* or *trans*. If we assume that the third carbon atom is a carbonium ion (I), then at the moment of ring closure the phenyl group at C-3 can enter either an equatorial or axial position, forming either β- or α-isomer, if the C-1, C-2 carbons are *cis* substituted. If carbons C-1, C-2 are *trans* substituted, then the phenyl group of the carbonium ion C-3 enters at ring closure only in an equatorial position forming exclusively the α-isomer. Since it is equally probable that the substituents at C-1, C-2 are either *cis* or *trans*, it is reasonable that the α-isomer is always the major product.



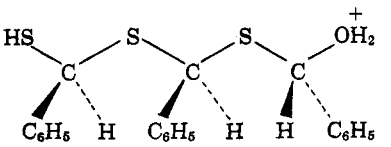
If we assume that the ring closure occurs by backside displacement of a protonated hydroxyl group (II), again the formation of the α-isomer is favored. Intermediate II can have the following configurations:



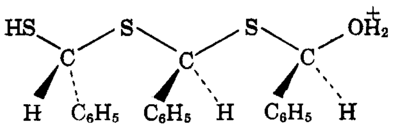
IIa. (*cis-cis*)



IIb. (*trans-trans*)



IIc. (*cis-trans*)



IId. (*trans-cis*)

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[12] E. Campaigne in "Organic Sulfur Compounds," N. Kharasch, ed., Pergamon Press, 1961, Chap. 14, p. 141.

Table II

Properties of Trithiofluorobenzaldehydes

	ortho		*meta*		*para*	
	α	β	α	β	α	β
Crude yield, %[a]	96		84		98	
Ratio of isomers						
by n.m.r.[a]	55	45[b]	66	33	66	33
by column chromatography[c]			47[d]	25[d]	64[e]	30[e]
Anal. Calcd. for $C_{21}H_{15}F_3S_3$	Found		Found		Found	
C, 59.97	59.66	60.04	59.95	59.99	60.04	59.84
H, 3.60	3.74	3.58	3.54	3.71	3.71	3.65
S, 22.87	22.77	23.12	23.18	22.75	22.69	22.86
Mol. wt.,[f] 420.53	422	428	426	426	426	420[g]
Melting points,[h] °C.	109–110	173.5–174	173–173.5	166–166.5	183–184	221–222

[a] The products show two spots + polymers in t.l.c. [b] In repeated runs the ratios of α:β were 57:43 and 50:50. [c] See Experimental for material balance. [d] Each isomer was not very pure, after two recrystallizations α 39%, β 15%, and each isomer showed one spot in t.l.c. [e] Each pure sample showed one spot in t.l.c. [f] Mol. wt. determined by "Mechrolab" vapor pressure osmometer. [g] Mol. wt. by cryoscopic method (solvent bromoform). [h] All melting points are corrected.

Table III

R_f Values of Trithiofluorobenzaldehydes in T.l.c.

	α	β	% Ether in cyclohexane
Trithiobenzaldehyde	0.405	0.14	5
m-Fluoro-	.383	.11	5
	.495	.14	6
	.657	.2	7
p-Fluoro-	.44	.04	6
	.68	.067	8
o-Fluoro-	.47	.41	10
	.212	.14	*a*
	.335	.27	*b*

[a] 10% benzene. [b] 5% acetone.

Ring closure of IIa leads to the α-isomer, since inversion at C-3 gives the *cis–trans* configuration to the ring. IIb likewise forms α-isomer, since inversion at C-3 gives the *trans–cis* ring configuration. IIc will therefore yield β-isomer (*cis–cis* ring) while IId must again form α-isomer (*trans–cis* ring). Thus three of the four possible linear trimers will form α-isomer on ring closure. Formation of trithiane rings by this mechanism may be sterically hindered in some cases (*cf.* IIb) so that polymer formation is favored, and the relative proportions of α- and β-isomers altered. This may explain the altered ratio in the *o*-fluorobenzaldehyde case (Table II). This mechanism is favored by the following: (1) it is most unlikely that three molecules collide simultaneously to form the trithiane ring; (2) ketones are known to form monomeric thiones and *gem*-dithiols, which are probably intermediates in the formation of cyclic trimers and polymers[12]; (3) contrary to previous reports,[3] the ratio of yields of the conformational isomers, α and β, are in accord with this mechanism.

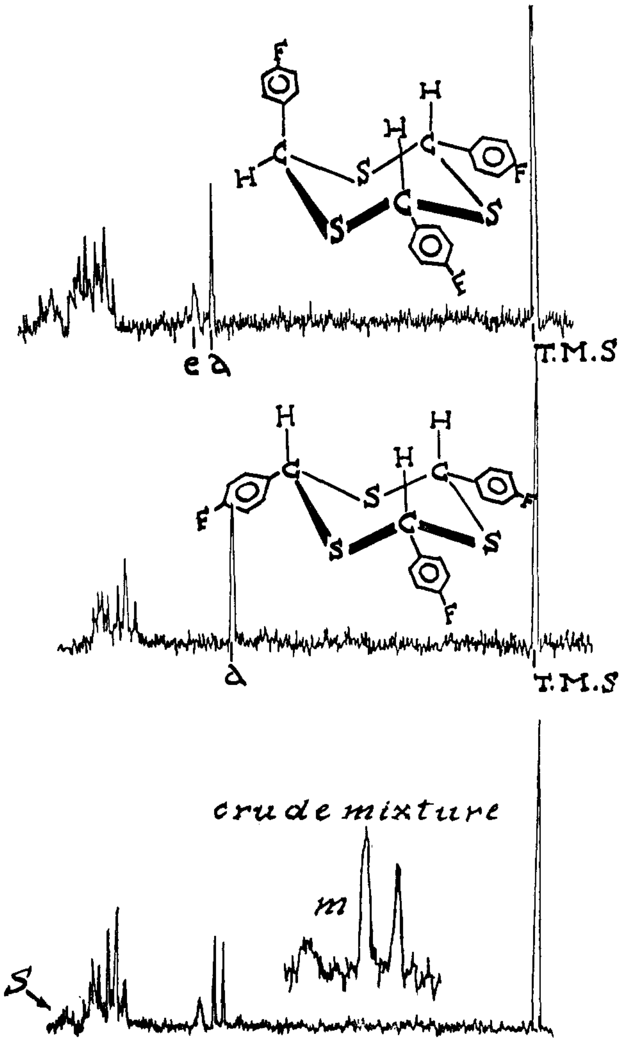

Fig. 3.—N.m.r. spectra of pure and crude tri(*p*-fluorothiobenzaldehydes): s, saturated solution; m, minimum amount of solvent.

Experimental

The n.m.r. spectra were obtained on a Varian Associates high-resolution n.m.r. spectrometer, Model V4300B, at Indiana University[13] with the help of Mr. Clause. Peak positions were determined relative to internal tetramethylsilane by the side band technique. Samples were run as saturated solutions and in minimum amounts of solvents at room temperature.

Preparation of Crude Trithiobenzaldehydes.—Five grams of *p*-fluorobenzaldehyde (Pierce Chemical Co., Rockford, Ill.), dissolved in 50 ml. of ethyl acetate, was maintained 0 ± 2° and dry hydrogen chloride was bubbled into the solution until saturation was reached. Hydrogen sulfide was then bubbled slowly into the solution with continuous stirring for 5 hr. The mixture was allowed to stand overnight at refrigerator temperature, the solid product collected and washed with cold ethyl acetate. The filtrate was evaporated under a stream of nitrogen to a small

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[13] We are indebted to the National Institute of Health for a grant to Indiana University for the purchase of the instrument.

volume, and additional hydrogen sulfide and hydrogen chloride passed through the filtrate to precipitate a second crop. After filtration, air was drawn through the solid for a period, and the sintered glass funnel of dried solid stored in an evacuated desicator to remove excess hydrogen chloride and hydrogen sulfide. In this way, 5.5 g. (98%) of crude tri(*p*-fluorothiobenzaldehyde) was obtained. Similar treatment of 5.0 g. of *m*-fluorobenzaldehyde (Pierce) gave 4.7 g. (84%) of crude product. Starting with 6 g. of *o*-fluorobenzaldehyde (Pierce), in 50 ml. of absolute ethanol, the yield was 6.05 g. (96%).

Thin Layer Chromatography.—A Desaga apparatus and silicic acid according to Stahl (Merk silica gel G) were used for the thin layer chromatography. A non-adjustable t.l.c. applicator was used for applying standard layers of 250 μ. As solvents for the separation of the trimers of *m*- and *p*-fluorothiobenzaldehydes 5–8% diethyl ether in cyclohexane were used and the R_f values are listed in Table III. Freshly made solvent mixtures were allowed to travel the premarked distance of 10 cm. on the plates. The spots were developed by spraying the chromatograms with a mixture of 0.1 *M* copper acetate and 0.1 *M* silver nitrate in 3 *M* alcoholic ammonia. Brown spots appeared after heating at 100–120° for 20 min. to half an hour. The spray was prepared as follows: 1.7 g. of silver nitrate and 1.8 g. of copper acetate were dissolved in 20 ml. of concentrated ammonia, then absolute ethanol was added and the volume made up to 100 ml. The solution was filtered and kept in a brown bottle. Copies of the chromatograms can be taken by tracing as well as by photography or Xerography.

Separation of α- and β-Isomers by Column Chromatography.—One hundred grams of silicic acid (160 mesh) was dried and activated by heating overnight, then, after cooling, put in a beaker and mixed with 6% diethyl ether in cyclohexane. The resulting slurry was transferred to the column and excess solvent allowed to drain. One gram of crude trithiofluorobenzaldehyde was dissolved in ether and then mixed with a very small amount of silicic acid. This mixture was stirred well, left to dry at room temperature, and transferred as a dry powder to the top of the column. The material was covered with a thin band of silicic acid and sand at the very top. The column was developed with 6–7% diethyl ether in cyclohexane as solvent under pressure. The 10-ml. fractions which were collected by an automatic fraction collector were subjected to thin layer chromatography. In this way, the progress of the separation was traced. Fractions containing only α- or only β-isomer were combined and crystallized from a benzene–cyclohexane mixture. Analytical samples were crystallized from absolute ethanol. Fractions containing both α- and β-isomers were combined and rechromatographed. The results obtained from column chromatography are shown in Table IV. Other physical properties and analyses are listed in Table II.

TABLE IV

YIELDS OF THE PRODUCTS FROM THE COLUMN

Tri(*m*-fluorothiobenzaldehyde)		
Alpha (α)	47% (crude)	0.47 g.
Beta (β)	25% (crude)	.25 g.
Red oil + impurities	6%	.06 g.
Yellow oil	6%	.06 g.
Tri(*p*-fluorothiobenzaldehyde)		
Alpha (α)	64% (crude)	.64 g.
Beta (β)	30% (crude)	.30 g.
α + β + impurities	6%	.06 g.

Preparation of Isomeric Tri(*o*-fluorothiobenzaldehydes) by Unidimentional Multipass Chromatography on Thick Plates. (Preparative T.l.c.).—Since the R_f values of the isomeric α- and β tri(*o*-fluorothiobenzaldehydes) were very close, preparative t.l.c. was applied instead of column chromatography. The regular applicator was modified to produce thick plates by placing ten narrow strips of plastic adhesive tape on each end of the applicator. In this way, silicic acid plates were produced to a thickness of from 1–2 mm. The crude material was dissolved in acetone and spotted in a linear narrow strip of 10 cm. at the origin. The technique of unidimentional multipass chromatography was applied. The progress of separation of the isomeric products can be followed by developing a portion of the plate with saturated solution of iodine in chloroform as brown strips or, by distilled water as distinct white strips, or the chromatograms can be read as strips of different transparency by placing an electric lamp behind the plate.

When the separation of the isomeric products was satisfactory, the strips of silicic acid containing the separate isomers were scraped off and collected in separate beakers. Each isomeric product was extracted by ether and hot benzene or acetone and transferred to centrifuge tube. After centrifugation, the clear solution was transferred to a clean centrifuge tube and evaporated under a stream of nitrogen. Each isomeric product was washed with a small amount of cyclohexane and recrystallized several times from ethanol. Evaporation, washing, recrystallization, and subsequent drying of the sample were done in the same centrifuge tube. During the recrystallization procedure, the purity of the isomers were checked by unidimentional multipass chromatograms which were developed by the described copper–silver sulfur-sensitive spray. Six to eight plates are sufficient to give enough material (about 60–80 mg.) of each isomer for n.m.r., molecular weight determination, and analysis. The material used for n.m.r. and molecular weight determination can be recovered. The physical properties of the tri(*o*-fluorothiobenzaldehydes) are listed in Table II.

Acknowledgment.—The authors wish to thank Professor Walter Meyer, of this department, for assistance in interpreting the n.m.r. spectra.

Evidence of a Biphenyl Group in Lignin[1]

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Received May 4, 1962

Studies of the ultraviolet spectra of lignin model compounds and enzymatic dehydrogenation of these substances indicate that biphenyl groups occupy an important rather than a minor role in coniferous lignin.

That coniferous lignin is a polymer of coniferyl alcohol and that the linkages occurring in dehydrodiconiferyl alcohol, in guaiacylglycerol-β-coniferyl ether, and in pinoresinol[3] are important contributors is now a widely accepted theory of lignin structure. Biphenyl groups, on the other hand, though they have been detected,[4] are generally assumed to occupy a minor role. Observations made during the past two years indicate a substantial number of such groups may be present.

Like coniferous lignin, I (Fig. 1), the simple model substance 4-propylguaiacol (II) has an ultraviolet absorption maximum at 280 mμ, but unlike that for lignin the curve falls abruptly to 0 at 300 mμ and nearly to 0 at 250 mμ before rising again, forming a deep

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[1] Presented at the 140th National Meeting of the American Chemical Society, Chicago, Ill., September, 1961.

[2] Maintained at Madison, Wis., in coöperation with the University of Wisconsin.

[3] K. Freudenberg, *Nature*, **183**, 1152 (1959).

[4] G. Aulin-Erdtman, *Svensk Papperstid.*, **55**, 745 (1952).