entities (Ag), separable by chromatography in Partridge mixture and by electrophoresis in borate, pH 10. One of the products migrated like N-acetylglucosamine and reacted likewise in the Morgan–Elson test. The other product was again subjected to hydrolysis and analysis and was found to contain only alanine and muramic acid.

When the chromatographically immobile portion of the lysozyme lysate was subjected to brief, mild treatment with acid, there appeared several small reducing fragments, among them glucosamine and N-acetylglucosamine, as well as an additional reducing and ninhydrin-negative entity. Hydrolysis of this material liberated glucosamine and alanine in the ratio of approximately 2:1.

We cannot, at this time, decide what the detailed structures of the fragments are, and which, if any, of the conceivable structures may occur in the native cell wall. However, we feel that the observations presented give new knowledge about the association, with one another, of streptococcal cell wall constituents.

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ARYL FLUOROALKYL ETHERS AND SULFIDES: EVIDENCE FOR SULFUR *d*-ORBITAL INTERACTION

Sir:

We wish to report a new general method for the synthesis of aryl perfluoroalkyl ethers, the results of quantitative measurements demonstrating that fluoroalkoxy groups may be considered as halogen-like and that sulfur d-orbital interaction is significant when sulfur is bonded to the strongly electron-withdrawing fluoroalkyl group.

Aryl trifluoromethyl ethers have been synthesized by the reaction of hydrogen fluoride or antimony fluorides with aryl trichloromethyl ethers[1] which were prepared by chlorination of the anisoles or phenyl esters of chlorothiocarbonic acid. It now has been found that the reaction of sulfur tetrafluoride[2] (hydrogen fluoride catalyst) with aryl fluorocarbonates[3] and perfluoroalkyl esters[4] provides a general, direct synthesis of aryl perfluoroalkyl ethers.[5] For the preparation of aryl trifluoromethyl ethers, a convenient procedure is to react the phenols with carbonyl fluoride[3,6] in a Hastelloy autoclave at 100°. Without isolation of the fluorocarbonate, the sulfur tetrafluoride then is added and the reaction mixture heated for several hours at 150–175°. The hydrogen fluoride by-product from the carbonyl fluoride reaction serves as catalyst for the reaction. For phenol and *m*- and *p*-nitrophenol, the yield of the ether is 60 to 80% over-all for the two steps. The reaction is general for substituted phenols including hydroquinone and resorcinol, provided that the substituents or the aromatic ring do not react with hydrogen fluoride or sulfur tetrafluoride.

$$\mathrm{ArO\overset{O}{\overset{\|}{C}}X + SF_4 \xrightarrow{HF} ArOCF_2X \ (\text{where } X = F \text{ or } R_f)}$$

The ionization constants of the trifluoromethoxy- and trifluoromethylthio-anilinium ions and benzoic acids[7,8] have been determined by standard literature methods[9,10,11] and are reported in Table I. The calculated σ-parameters are given in Table II and compared with those of several other substituents. The inductive and resonance contributions of the groups can be evaluated from σ_I and σ_R-parameters calculated according to Taft and Lewis.[12] From these results it can be seen that the OCF_3 group is very much like Cl, in that it withdraws electrons inductively but supplies them by resonance. Over-all it is a slightly stronger deactivating group than the halogens.[13]

TABLE I

IONIZATION CONSTANTS

Substituent X	Ionization constants ($-\log h$) (25°) of $XC_6H_4CO_2H$ in 50% ethanol	Ionization constants ($-\log h$) (25°) of $XC_6H_4NH_3^+$ in water
m-OCF_3	5.14	3.25
p-OCF_3	5.19	3.82
m-SCF_3	5.13	3.30
p-SCF_3	4.98	2.78

The SCF_3 group has a σ_m value similar to that of the OCF_3 group, but unexpectedly has a more positive σ_p value with an added positive increment of 0.13 for the σ_p from ionization of anilium ions over the benzoic acids. This result is indicative of a +R group. Recently Beishline[14] reanalyzed the ionization constant data for the SCH_3, $SCOCH_3$ and SCN groups on the basis of Taft's σ_R param-

(1) (a) British Patent 765,527 (1957). (b) L. M. Yagupolsky and V. I. Troitskaya, *J. Gen. Chem.*, USSR (English Trans.), **27**, 518 (1957). (c) N. N. Iarovenko and A. S. Vasileva, *J. Gen. Chem.*, USSR (English Trans.), **28**, 2539 (1958).

(2) (a) C. W. Tullock, F. S. Fawcett, W. C. Smith and D. D. Coffman, *J. Am. Chem. Soc.*, **82**, 539 (1960). (b) W. R. Hasek, W. C. Smith and V. A. Engelhardt, *ibid.*, **82**, 543 (1960).

(3) H. J. Emeleus and J. F. Wood, *J. Chem. Soc.*, 2183 (1948).

(4) R. F. Clark and J. H. Simons, *J. Am. Chem. Soc.*, **75**, 6305 (1953); M. Green, *Chem. and Ind.*, 435 (1961).

(5) All new compounds have been characterized by analysis and spectral properties.

(6) M. W. Farlow, E. H. Man and C. W. Tullock, *Inorganic Syntheses*, **6**, 155 (1960).

(7) The aryl trifluoromethyl sulfides have been prepared by fluoride replacement in aryl trichloromethyl sulfides [see L. M. Yagupolsky and M. S. Marenets, *J. Gen. Chem.* USSR (English Trans.), **22**, 2273 (1952)]. The reaction of aryl Grignard reagents with trifluoromethylsulfenyl chloride is an improved route to this class of sulfide and will be described in a future publication (see W. A. Sheppard, Abstracts of American Chemical Society Meeting, Chicago, Illinois, September, 1961, p. 7-M.

(8) The aryl perfluoroalkyl ethers and sulfides have been shown to have stability comparable to benzotrifluoride and the perfluoroalkoxy and perfluoroalkylthio groups are inert to normal chemical transformations involving the aromatic residue. Thus, the anilines and benzoic acids were prepared by catalytic reduction of the nitro derivatives and oxidation of the tolyl compounds. Both the trifluoromethoxy and trifluoromethylthio groups have been shown to be *o,p*-directing to electrophilic aromatic substitution.

(9) A. Bryson, *J. Am. Chem. Soc.*, **82**, 4858 (1960).

(10) J. D. Roberts, R. L. Webb and E. A. McElhill, *ibid.*, **72**, 408 (1950).

(11) A preliminary communication of p*K*a measurements on the above benzoic acids was recently reported by L. M. Yagupolsky and L. M. Yagupolskaya, *Proc. Acad. Sci.* (English Trans. from *Doklady Akad. Nauk SSSR*), **134**, 1207 (1960)) and values are essentially in agreement with those reported in Table I. The only discussion of these results was the comment that the SCF_3 and OCF_3 groups were like halogens.

(12) R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, **81**, 5343 (1959).

(13) The designation "super-halogen" has been suggested to describe this behavior of the perfluoroalkoxy groups.

(14) R. R. Beishline, *J. Org. Chem.*, **26**, 2533 (1961).

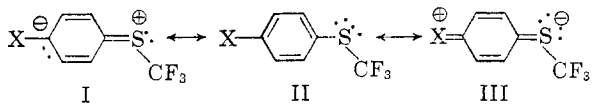
TABLE II

σ-PARAMETERS

	From ionization of: $XC_6H_4CO_2H$		$XC_6H_4NH_3^+$		$XC_6H_4CO_2H$[b]			
	OCF_3	SCF_3	OCF_3	SCF_3	Cl	OCH_3	SCH_3	$SCCH_3$ (O)
σ_m	+0.39	+0.40	+0.47	+0.46	+0.37	+0.11	+0.14	+0.37
σ_p	+0.35	+0.51	+0.28	+0.64	+0.23	−0.27	−0.01	+0.42
σ_I[a]	+0.51	+0.31	+0.50	+0.40	+0.47	+0.21	+0.22	+0.32
σ_R[a]	−0.13	+0.17	−0.23	+0.22	−0.25	−0.47	−0.24	+0.10

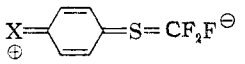
[a] Calculated using equations 1, 6 and 3 with appropriate α and ρ_I values from Table II, Reference 12. [b] Values are from H. H. Jaffee, *Chem. Rev.*, **53**, 222 (1953); F. G. Bordwell and P. J. Barton, *J. Am. Chem. Soc.*, **78**, 854 (1956); F. G. Bordwell and G. C. Cooper, *J. Am. Chem. Soc.*, **74**, 1058 (1952).

eters and presented arguments for expansion of the valence shell of the sulfur in the $SCOCH_3$ and SCN groups.[15] The σ_R parameters for the SCF_3 group are considerably larger positive values and provide much more striking evidence for large contributions of form III.



I II III

The contribution of resonance form I must be minor, but becomes significant in the transition state for substitution of the ring by an electrophilic reagent since the orientation[8] is ortho-para and not meta. For a SCH_3 group, resonance form I must make the major contribution rather than form III. Contribution from resonance form IV, involving fluoride ion "no-bond" structures, is considered unlikely on



IV

the basis of comparison with resonance effects for the CF_3 and SF_5 groups.[16]

Observations in support of the above discusssion also have been made for the OCF_2CF_3, OCF_2CF_2H and SCF_2CF_2H groups and will be presented in detail in a future publication.

(15) The expansion of the sulfur outer shell was recently reviewed by G. Cilento, *Chem. Rev.*, **60**, 147 (1960).

(16) W. A. Sheppard, publication in preparation.

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NUCLEOTIDE AND OLIGONUCLEOTIDE COMPOSITIONS OF THE ALANINE-, VALINE-, AND TYROSINE-ACCEPTOR "SOLUBLE" RIBONUCLEIC ACIDS OF YEAST

Sir:

The alanine-, valine-, and tyrosine-acceptor "soluble" ribonucleic acids (RNAs) of yeast recently have been purified by countercurrent distribution.[1] Table I gives the results of analyses of the nucleotide compositions of the three purified RNAs. The alanine RNA, in comparison with the other two, has a very low content of adenylic acid (Ap) and a high content of guanylic acid (Gp), and possibly contains less pseudouridylic acid (PsUp). The valine and tyrosine RNAs differ little in nucleotide composition.[2]

(1) J. Apgar, R. W. Holley and S. H. Merrill, *J. Biol. Chem.*, in press. (For a recent review of the role of "soluble" RNA in protein synthesis see P. Berg, *Ann. Rev. Biochem.*, **30**, 293 (1961)).

The analyses in Table I are consistent with the formulas for the purified RNAs.[3]

Alanine RNA: $pGp[(Ap)_{10}(Cp)_{25}(Gp)_{23}(Up)_{17}(P_sUp)_3]A$
Valine RNA: $pGp[(Ap)_{16}(Cp)_{22}(Gp)_{24}(Up)_{16}(P_sUp)_4]A$
Tyrosine RNA: $pGp[(Ap)_{19}(Cp)_{22}(Gp)_{25}(Up)_{14}(P_sUp)_4]A$

As indicated in Table I, the partition coefficients of the valine and tyrosine RNAs in the countercurrent distribution solvent system differ by a factor of 20 although these two RNAs differ little in nucleotide composition. Presumably the different partition coefficients are a result of differences in nucleotide sequence. To obtain information on nucleotide sequences, pancreatic ribonuclease digests of the three purified RNAs were chromatographed on DEAE-Sephadex.[4] The results of the analyses are shown in Fig. 1. In the chromatographic patterns, the mononucleotides, cytidylic acid (peak at fraction 37) and uridylic acid (peak at fraction 50), are followed by dinucleotides and higher oligonucleotides. The peak at

TABLE I

NUCLEOTIDE COMPOSITIONS OF PURIFIED ALANINE-, VALINE- AND TYROSINE-ACCEPTOR RIBONUCLEIC ACIDS OF YEAST[a]

Nucleotide	RNA, Mole %: Alanine	Valine	Tyrosine
Ap[b]	12.1	19.1	21.7
Cp	29.9	27.5	26.7
Gp	33.7	29.5	30.2
Up	20.8	19.0	17.1
PsUp	3.7	4.9	4.4
Partition coefficient[c]	0.12	0.21	4.2

[a] Alkaline hydrolysates of 1 mg. of the RNAs were chromatographed on Dowex 1 columns 0.2 × 15 cm. according to the procedure of W. E. Cohn and E. Volkin, *Nature*, **167**, 483 (1951). The values given are averages of three or more determinations, and are not corrected for the terminal nucleoside and nucleoside diphosphates. [b] The abbreviations used are: Ap, adenylic acid; Cp, cytidylic acid; Gp, guanylic acid; Up, uridylic acid; and PsUp, pseudouridylic acid. [c] Partition coefficients of the purified RNAs in a countercurrent distribution solvent system composed of phosphate buffer, formamide and 2-propanol (see ref. 1).

(2) Previous analyses of fractions across the countercurrent distribution pattern indicated little change in nucleotide composition except at the end of the pattern, where the alanine RNA is found.

(3) The formulas assume terminal guanosine diphosphate (M. F. Singer and G. L. Cantoni, *Biochim. et Biophys. Acta*, **39**, 182 (1960)) and terminal adenosine (H. G. Zachau, G. Acs and F. Lipmann, *Proc. Natl. Acad. Sci.*, **44**, 885 (1958)) although these have not yet been established for the purified RNAs.

(4) The procedure used was a modification of that of M. Staehelin, E. A. Peterson and H. A. Sober, *Arch. Biochem. Biophys.*, **85**, 289 (1959). The use of DEAE-Sephadex (Pharmacia Fine Chemicals, Rochester, Minn.) in place of DEAE-cellulose is strongly recommended.