TABLE I

SOLUBILITY OF SILICON TETRAFLUORIDE AT ROOM TEMPERATURE (27–33°) AND TOTAL PRESSURE OF 750–760 MM.

Solvent	G. SiF_4/100 cc. solvent	Wt. % of SiF_4 in soln.
Methyl alcohol, absolute	..	32.8
Methyl alcohol, 94% by wt.	..	39.0
Ethyl alcohol, absolute	57.2	36.4
Ethyl alcohol, 96.1% by wt.	60.8	37.8
Ethyl alcohol, 95% (U. S. P.)	61.4	38.1
Ethyl alcohol, 94.3% by wt.	61.5	38.1
Ethyl alcohol, 92.6% by wt.	63.4	38.8
Ethyl alcohol, 91.0% by wt.	63.9	39.0
Isopropyl alcohol, 98%	39.4	28.2
n-Butyl alcohol, 98% (U. S. P.)	30.4	23.4
Amyl alcohols (fusel oil)	20.9	17.3
Glycol, C. P.	..	26.2
Diethylene glycol, C. P.	..	17.6
Glycerol, C. P.	..	5.7
Acetone, C. P. anhyd.	3.2	3.1
Acetic acid (glacial)	1.1	1.1
Pyruvic acid, tech. (38–45%)	..	4.4

In addition to these quantitative data, it was found that silicon tetrafluoride is sparingly soluble in benzene and trichloroethylene, and insoluble in carbon tetrachloride at room temperature.

On the addition of 9% by weight of water to the saturated solution in 95% alcohol (U. S. P.), a gelatinous precipitate of hydrated silica was formed. However, when the original solution was subjected to vacuum distillation at room temperature, silicon tetrafluoride was evolved until a solution containing approximately 26.5% of the gas remained, which corresponds to a mole ratio of alcohol to silicon tetrafluoride of approximately 6:1. On adding an equal volume of water to the residual solution from the vacuum distillation, no precipitate formed, possibly because the silicon tetrafluoride had combined chemically with the ethyl alcohol. Subsequent addition of a soluble barium salt precipitated 95% of the fluorine as pure barium fluosilicate. This reaction offers a convenient method for preparing barium fluosilicate of high purity.

When saturated solutions in glycol were distilled in a vacuum at room temperature, 50 and 100°, the residual solutions contained fluorine equivalent to 26.2, 24.5, and 2.8% silicon tetrafluoride, respectively; on addition of water to them, a precipitate was formed in each case.

The above information is of interest in that such solutions in organic solvents may furnish the basis for the synthesis of organic fluorine compounds as well as a means of preparing pure fluorine salts. However, the authors do not plan to pursue the investigation further and, therefore, wish to relinquish the problem to others who may be interested in it.

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WILSON DAM, ALABAMA RECEIVED MAY 8, 1939

Occurrence of the Syringyl Radical in Plant Products

BY EINAR WEST, A. S. MACINNES, JOSEPH L. MCCARTHY AND HAROLD HIBBERT

It has now been shown that treatment of jute fiber, rye straw and corn stalks with a 2% solution of hydrogen chloride in anhydrous ethanol, according to the method described for the ethanolysis of spruce and maple woods,[1] gives rise to typical ethanolysis products, namely, ethanol lignin and a mixture of volatile oils. The yields of ethanol lignin and volatile oils are of the same order of magnitude as those obtained from spruce and maple woods. The presence of the syringyl radical has been established in the volatile oils from each of these fibers. Thus, following the procedures previously described,[2] α-ethoxypropiosyringone as the *p*-nitrobenzoate (m. p. 141–142°), syringoylacetaldehyde as the monosemicarbazone (m. p. 207–208°), and syringaldehyde as the 2,4-dinitrophenylhydrazone (m. p. 235–235.5°), were isolated. Mixed melting points with authentic specimens showed no depression.

These, and previous results with hard woods,[1,2] would seem to point to the presence of syringyl derivatives in the lignin constituents of all angiosperms, for example as indicated in corn and rye (monocotyledons) and in jute and maple (dicotyledons).

(1) Brickman, Pyle, McCarthy and Hibbert, THIS JOURNAL, **61**, 868 (1939).

(2) Hunter, Cramer and Hibbert, *ibid.*, **61**, 516 (1939); Pyle, Brickman and Hibbert, *ibid.*, **61**, 2198 (1939).

DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY
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Reaction of *p*-Fluorophenol with Benzene and Aluminum Chloride

BY ARTHUR W. WESTON[1] AND C. M. SUTER

Recently it was found[2] that in the deëthylation of *p*-fluorophenetole with aluminum chloride in benzene solution a by-product was obtained in

(1) Sharp and Dohme Post-Doctorate Fellow 1938–1939.

(2) Suter, Lawson and Smith, THIS JOURNAL, **61**, 163 (1939).

considerable amount. This was phenolic in nature and in an impure condition melted at 153–156°. It has now been determined that the same substance results from heating *p*-fluorophenol with benzene and aluminum chloride. When purified it melted at 163.5–164° and upon oxidation gave a high yield of benzoic acid. No depression of the melting point occurred when a sample of the unknown was mixed with *p*-hydroxybiphenyl. Hence

$$C_6H_6 + FC_6H_4OH \xrightarrow{AlCl_3} C_6H_5C_6H_4OH\ [+ HF]$$

p-fluorophenol must react as shown and the *p*-hydroxybiphenyl obtained in the deëthylation of *p*-fluorophenetole also results from this reaction.

Attempts to extend the reaction in various directions have been without success. Because aromatic fluorine may be under some conditions replaced by chlorine,[3] it seemed possible that *p*-chlorophenol was an intermediate in the reaction. However, *p*-chlorophenol showed no activity toward benzene in the presence of aluminum chloride. None of the corresponding hydroxybiphenyl was isolated when *p*-fluorophenol and aluminum chloride were heated with toluene or chlorobenzene.

By heating a mixture of 3 g. of *p*-fluorophenol, 7 ml. of benzene and 7 g. of aluminum chloride under reflux for two and one-half hours there was obtained about 1 g. of *p*-hydroxybiphenyl, m. p. 164°. The 51 g. obtained in the deëthylation of *p*-fluorophenetole[2] corresponds to 13% of the *p*-fluorophenol reacting with the benzene.

(3) Bacon and Gardiner, *J. Org. Chem.*, **3**, 281 (1938).

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COMMUNICATIONS TO THE EDITOR

SYNTHETIC AND NATURAL ANTIHEMORRHAGIC COMPOUNDS

Sir:

In our last communication [THIS JOURNAL, **61**, 1923 (1939)] the reported antihemorrhagic activity of 2-methyl-1,4-naphthoquinone was a minimum assay result. The total comparative activity of this compound is given in Table I. It is by no means as active as vitamin K [Ansbacher and Fernholz, *ibid.*, **61**, 1924 (1939)] or as low in activity as reported by Thayer, *et al.*, [*ibid.*, **61**, 1932 (1939)] and would seem to provide an effective, cheap, synthetic substitute for vitamin K. This compound, like phthiocol and others, is capable of maintaining the prothrombin level of chick blood at a normal value when sufficient is given.

We have purified or synthesized and tested a number of naphthoquinones and related compounds (Table I). Assays were conducted and results expressed as noted previously [*ibid.*, **61**, 1923 (1939)]. Entirely negative results were obtained with 1,4-benzoquinone, naphthalene, 1,4-naphthoquinone, anthraquinone, 1,2-dihydroxyanthraquinone, and hydrolapachol at levels of 100 mg. or more per kg. of diet. Thayer, *et al.*, [*ibid.*, **61**, 1932 (1939)] have reported some activity in 1,4-naphthoquinone. Fieser, *et al.*, [*ibid.*, **61**, 1925 (1939)] have indicated activity in lomatiol, lapachol and hydrolapachol. We have previously found lomatiol and lapachol to be inactive [*ibid.*, **61**, 1923 (1939)]. These other workers employ assay methods which require only twenty-four hours or less but which are, in our experience, likely to give misleading results.

TABLE I

ANTIHEMORRHAGIC ACTIVITY OF NAPTHOQUINONES

Substance	Level fed per kg. of diet, mg.	Activity in terms of cc. of ref. standard per g.[a]
2-Methyl-1,4-naphthoquinone	10	> 2400
2-Methyl-1,4-naphthoquinone	2.5	5150
2-Hydroxy-1,4-naphthoquinone	75	139
Phthiocol	20	287
Phthiocol ethyl ether	15	100
Phthiocol octadecyl ether	20	95
Phthiocol phytyl ether	20	< 50
Phthiocol monoacetate	15	420
Phthiocol triacetate	15	192
Alfalfa concentrate	0.5	>53600
Alfalfa concentrates[b]	0.2 to 0.3	63000

[a] Standard hexane extract of dried alfalfa representing 1 g. per cc. [b] From preliminary assays of alfalfa preparations (E. A. Doisy, P. Karrer).