

Hydroxybenzenesulfonyl Fluorides and Their Plant Desiccation Activity

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A series of hydroxybenzenesulfonyl fluorides and derivatives thereof was synthesized and evaluated as fast plant desiccants. Their activity was compared with the plant response of some hydroxybenzenesulfonyl chlorides and other related benzenesulfonyl compounds, and with some structurally

unrelated commercial products. Structure-activity relationship is discussed. 3-Chloro-4-hydroxybenzenesulfonyl fluoride, 3,5-dichloro-4-hydroxybenzenesulfonyl fluoride, and 3,6-dichloro-4-hydroxybenzenesulfonyl fluoride caused considerable desiccation in 1 to 5 days in field tests.

There are some scattered references (Hall, 1966; McCoy *et al.*, 1954; Steinkopf, 1927, 1930) on the preparation of fluorosulfonated phenols, but their effects on plants have not been studied to any extent. The primary objective of this paper is to report the desiccation and defoliation properties of these compounds, especially the fast desiccation achieved in both greenhouse and field tests.

The fluorosulfonated phenols studied by us can be divided into two major subclasses, A and B, and are supplemented by a third subclass, C. The latter contains miscellaneous products (XLIV to LIV), including several of the starting materials—i.e., products lacking the fluorosulfonyl group. Subclass C also includes a related sulfone, and phenols which are chlorosulfonated, sulfonated, or amidosulfonated. Subclass A (I, XIII to XV, XXV, XXVI, and XXVIII to XLIII) comprises structures containing a free phenolic OH-group. They are fluorosulfonated in *o*- or *p*-position to the hydroxyl and contain, in addition, one or two substituents in the benzene ring, usually chlorine, but also methyl, amino, nitro, fluorosulfonyl, and carboxyl groups as well as fluorine. Substitution on the phenolic hydroxyl of the products of subclass A resulted in structures which are included in subclass B (II to XII, XVI to XXIV, and XXVII). These structures were designed to provide various rates of hydrolysis (within the plant) to the free phenols of subclass A. Thus, if the free hydroxyl is taking part in the mechanism of fast desiccation, alone or in combination with the fluorosulfonyl group or with other groups of the molecule, the authors hoped to achieve both a total fast desiccation and defoliation by translocation of the derivative before it had been hydrolyzed to the free phenol and had caused "freezing" of the leaves to the stem. The hydrogen of the phenolic hydroxyl was replaced by carbamyl, carboxy, methanesulfonyl, sulfamyl, and other moieties such as $-\text{CH}_2\text{CO}_2\text{Et}$, Ac, COCCl_3 , and COCH_2Cl , some of which form part of the molecule of many well known products causing plant response.

The structure-activity relationship of these three subclasses of compounds, both between and within the subclasses, was an important object of this study.

PRODUCTS

With the exception of I, XIV, XVI, XXXVII, XXXVIII, XL, XLI, XLVIII, L to LIII, and LV to LVII the materials screened in the six-crop, the bean, and the greenhouse-tree

tests were thoroughly purified and analyzed prior to screening. The melting and boiling points, yields, analytical results, and recrystallization solvents, for all but the purchased compounds L to LIII and LV to LVII, are given in Tables I and II. Product LIV is *p*-chlorobenzenesulfonyl fluoride; LV to LVII are listed in the section on field testing. Products I, XXXVII, XXXVIII, XL, XLI, and XLVIII were prepared according to literature references (Armstrong, 1875; Steinkopf, 1927, 1931) and their melting and boiling points checked with those reported in the literature. Compounds L to LIII and LV to LVII are commercially available and were screened without additional purification. The field tests in Florida and Arkansas were carried out with technical grade materials having an assay of at least 93 to 95%.

Most structures of subclass A—i.e., I, XIII to XV, XXV, XXVI, XXVIII to XXXII, and XXXV to XLIII, as well as II—were prepared by fluorosulfonation of the respective phenols in excess of fluorosulfonic acid without any solvent. For larger sample preparation, however, the use of solvents such as CHCl_3 , CCl_4 , and others can be advantageous. Two examples of the general fluorosulfonation procedure (for compounds XV and XXXVI), as well as the preparation of the bis(fluorosulfonated) product (XXXV), the nitro compound (XXXIII), and its reduction product (XXXIV) are given in the experimental section.

Fluorosulfonation of 2,3-dichlorophenol at 40° to 45° C. gave isomers XXVIII and XXIX which were separated by fractional recrystallization from CCl_4 . Similarly, fluorosulfonation of 3-methyl-2-nitrophenol gave isomers XLII and XLIII. The structures of subclass B—i.e., III to XII, XVI to XXIV, and XXVII—were obtained by the reaction of the fluorosulfonated phenols (I, XV, and XXVI, respectively), with the appropriate reagent to achieve substitution on the phenolic hydroxyl. The reaction solvents are listed in Table I. The preparation of III to XII, XVI, XXIII, and XXVII is described in the experimental section. The 3,5-dichloro derivatives (XVII to XXII and XXIV) were obtained by the procedures used for their 3-chloro analogs (III, V to IX, and XII), starting with the phenol (XV) instead of I.

Structures XLIV to XLVI of subclass C (Table II) were prepared by a procedure exemplified by the description of the synthesis of XLVI in the experimental section. There also are described the syntheses of XLVII, XLIX, and LIV. Compound XLIX was obtained as a by-product of XXXVI.

TESTING PROCEDURES

The testing program comprised three phases: (A) primary screening, (B) greenhouse-tree test, and (C) field tests. The primary screening included a six-species test and a separate

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Table I. Hydroxybenzenesulfonyl Fluorides

No.	R	R'	M.P. °C. (B.P. °C./ Mm.)	Yield, %	Analyses, %				Solvent	
					C	H	Cl	S	Reactn.	Recryst.
I	4-OH	3-Cl	80-82	43	Not analyzed, lit. ^a m.p. 83-84°				FSO ₃ H	^b
II	4-OMe	3-Cl	55-56	12	c. 37.40	2.18	15.77	14.25	FSO ₃ H	C ₆ H ₁₄
III	4-OSO ₂ Me	3-Cl	52-54	64	f. 37.44	2.85	16.07	14.22	PhH	^c
IV	4-OSO ₂ NMe ₂	3-Cl	101-02	58	c. 29.12	2.09	12.28	22.20	MeCN	^c
V	4-OAc	3-Cl	58-59	65	f. 29.76	2.19	11.90	22.28	PhH	^e
VI	4-OC(O)CH ₂ Cl	3-Cl	67-68	60	c. 30.24	2.85	11.16	4.41 ^d	PhH	CCl ₄
VII	4-OC(O)CCL ₃	3-Cl	76-78	43	f. 30.41	2.93	11.48	4.65 ^d	PhH	CCl ₄
VIII	4-OC(O)OEt	3-Cl	(107-10/ 0.03)	83	c. 38.03	2.39	...	12.69	PhH	CCl ₄
IX	4-OC(O)NHEt	3-Cl	97-98	85	f. 38.21	2.49	...	12.63	PhH	CCl ₄
X	4-OC(O)NEt ₂	3-Cl	55-57	64	c. 33.46	1.75	24.70	...	PhH	CCl ₄
XI	4-OC(O)NHPh	3-Cl	103-04	64	f. 33.82	1.84	24.15	...	PhH	CCl ₄
XII	4-OC(O)NH C ₆ H ₄ Cl _(meta)	3-Cl	105-07	82	c. 26.99	0.85	...	9.01	PhH	CCl ₄
XIII	2-OH	4-Cl	69-75	24	f. 27.24	1.07	...	8.79	PhH	...
XIV	2-OH	5-Cl	69-73	90	c. 38.24	2.85	6.72 ^f	11.34	PhH	...
XV	4-OH	3,5-Cl ₂	90.5-91.5	62	f. 38.89	3.13	6.51 ^f	11.16
XVI	4-OMe	3,5-Cl ₂	43-45	85	c. 38.37	3.22	6.75 ^f	4.24 ^d	PhH	^g
XVII	4-OSO ₂ Me	3,5-Cl ₂	84-86	56	f. 38.60	3.54	6.94 ^f	5.73 ^d	PhH	^g
XVIII	4-OAc	3,5-Cl ₂	100-01.5	65	c. 42.65	3.58	6.13 ^f	4.52 ^d	PhH	^g
XIX	4-OC(O)CH ₂ Cl	3,5-Cl ₂	91-93	54	f. 42.47	4.27	5.70 ^f	4.48 ^d	...	CCl ₄
XX	4-OC(O)CCL ₃	3,5-Cl ₂	96-98	85	c. 47.35	2.75	10.75	4.24 ^d	...	CCl ₄
XXI	4-OC(O)OEt	3,5-Cl ₂	70-72	79	f. 47.35	3.12	10.71	4.40 ^d	...	^b
XXII	4-OC(O)NHEt	3,5-Cl ₂	127.5-28.5	68	c.	3.84 ^d	...	^b
XXIII	4-OCH ₂ CO ₂ Et	3,5-Cl ₂	150-55/0.5	43	f.	3.84 ^d	...	^b
XXIV	4-OC(O)NH C ₆ H ₄ Cl _(meta)	3,5-Cl ₂	92.5-93.5	58	c. 34.20	2.09	9.03 ^f	15.21	FSO ₃ H	...
XXV	2-OH	3,5-Cl ₂	71-72	53	f. 34.52	2.05	8.7 ^f	15.25	FSO ₃ H	^h
XXVI	4-OH	2,5-Cl ₂	86-88	71	c. 34.20	2.09	...	15.21	FSO ₃ H	^h
XXVII	4-OCH ₂ CO ₂ Et	2,5-Cl ₂	84-85	27	f. 33.29	2.53	...	14.22	FSO ₃ H	CCl ₄
XXVIII	4-OH	2,3-Cl ₂	135-37	40	c. 29.40	1.22	...	13.05	FSO ₃ H	CCl ₄
XXIX	2-OH	3,4-Cl ₂	91-97	10	f. 29.00	1.36	...	13.05	FSO ₃ H	CCl ₄
XXX	4-OH	3-Cl-6-Me	87-88.5	44	c. 32.44	1.94	27.37	12.37	EtOEt	^h
XXXI	2-OH	5-Cl-4-Me	72-73	13	f. 33.09	2.16	27.02	12.22	PhMe	CCl ₄
XXXII	2-OH	5-Cl-3-Me	34-35	23	c. 26.01	1.56	...	19.84	PhH	CCl ₄
XXXIII	4-OH	3-Cl-5-NO ₂	82-83.5	56	f. 26.31	1.69	...	19.92	PhH	CCl ₄
XXXIV	4-OH	3-Cl-5-NH ₂	115-18	89	c. 33.47	1.76	24.70	...	PhH	CCl ₄
XXXV	4-OH	3-Cl-5-SO ₂ F	98-99	27	f. 33.78	1.93	24.33	...	PhH	CCl ₄
					c. 29.88	1.25	33.08	...	PhH	ⁱ
					f. 29.70	1.52	33.11	...	PhH	C ₆ H ₁₄
					c. 24.58	0.51	45.45	...	PhH	C ₆ H ₁₄
					f. 25.58 ^h	0.81 ^e	44.73 ^h	...	PhH	C ₆ H ₁₄
					c. 34.07	2.21	PhH	C ₆ H ₁₄
					f. 34.68	2.48	CCl ₄
					c. 34.19	2.54	22.43	4.43 ^d	...	CCl ₄
					f. 34.02	2.57	22.01	4.55 ^d	...	CCl ₄
					c. 36.27	2.74	5.74 ^f	...	EtOH	...
					f. 36.49	3.17	6.04 ^f	ⁱ
					c. 39.16	1.77	26.68	3.51 ^d	...	ⁱ
					f. 39.34	1.90	26.46	3.64 ^d	...	ⁱ
					c. 29.40	1.22	28.95	13.05	FSO ₃ H	CCl ₄
					f. 29.58	1.46	28.29	12.81	FSO ₃ H	CCl ₄
					c. 29.40	1.22	28.95	13.05	FSO ₃ H	CCl ₄
					f. 29.57	1.57	29.37	12.98	C ₆ H ₄ Me ₂	^k
					c. 36.27	2.74	...	9.67	FSO ₃ H	^l
					f. 36.58	3.04	...	9.79	FSO ₃ H	^l
					c. 29.40	1.22	7.75 ^f	...	FSO ₃ H	^l
					f. 29.69	1.41	7.61 ^f	...	FSO ₃ H	^l
					c. 29.40	1.22	7.75 ^f	...	FSO ₃ H	^l
					f. 29.65	1.40	7.71 ^f	...	FSO ₃ H	^l
					c. 37.40	2.68	8.46 ^f	...	FSO ₃ H	C ₆ H ₁₄
					f. 37.60	2.85	8.69 ^f	...	FSO ₃ H	C ₆ H ₁₄
					c. 37.40	2.68	...	14.25	FSO ₃ H	C ₆ H ₁₄
					f. 37.70	2.77	...	13.97	FSO ₃ H	C ₆ H ₁₄
					c. 37.40	2.68	...	14.25	FSO ₃ H	C ₆ H ₁₄
					f. 37.62	2.97	...	14.39	FSO ₃ H	C ₆ H ₁₄
					c. 28.11	1.18	...	5.48 ^d	H ₂ SO ₄ / HNO ₃	^m
					f. 28.35	1.40	...	5.65 ^d	EtOH	...
					c. 31.94	2.23	8.42 ^f	6.21 ^d	EtOH	...
					f. 32.25	2.45	8.50 ^f	5.49 ^d	FSO ₃ H	...
					c. 24.64	1.03	12.14	21.90	FSO ₃ H	...
					f. 24.83	1.18	12.14	21.94	FSO ₃ H	...

(Continued)

Table I. (Cont.)

No.	R	R'	M.P., °C. (B.P. °C./Mm.)	Yield, %	Analyses, %				Solvent	
					C	H	Cl	S	Reactn.	Recryst.
XXXVI	4-OH	3-F	70-71	16	c. 37.10 f. 36.84	2.06 2.21	...	16.49 16.58	FSO ₃ H	CCl ₄
XXXVII	4-OH	3-NO ₂	66-67.5	53	Not analyzed, lit. ⁿ m.p. 66.5-67°				FSO ₃ H	C ₆ H ₁₄
XXXVIII	4-OH	3-NH ₂	131-33	33	Not analyzed, lit. ⁿ m.p. 131-131.5°				FSO ₃ H	PhH
XXXIX	4-OH	3-CO ₂ H	179-82	14	c. ... f.	8.64 ^f 8.46 ^f	...	FSO ₃ H	PhH
XL	4-OH	3-Me	48-55 (128- 32/0.7)	5	Not analyzed, lit. ⁿ b.p. 169-170°/11 mm, m.p. 56°				FSO ₃ H	...
XLI	4-OH	H	74-76	11	Not analyzed lit. ⁿ m.p. 77				FSO ₃ H	...
XLII	4-OH	2-Me-3-NO ₂	127-29	26	c. 35.75 f. 35.80	2.76 2.85	8.08 ^f 7.98 ^f	5.96 ^d 6.00 ^d	FSO ₃ H	CCl ₄
XLIII	2-OH	4-Me-3-NO ₂	78-80	10	c. 35.75 f. 36.00	2.76 2.80	8.08 ^f 8.15 ^f	5.96 ^d 6.33 ^d	FSO ₃ H	C ₆ H ₁₄

^a Steinkopf, 1930. ^b Hexane-PhH (4:1). ^c 30% EtOH. ^d % N instead of % S. ^e Hexane-PhH (20:1). ^f % F instead of % Cl. ^g 80% EtOH. ^h Product could not be purified completely. ⁱ Petroleum ether (60-110°)—CCl₄ (3:1). ^j Hexane-PhH (1:1). ^k 95% EtOH. ^l Fractionally recrystallized from CCl₄. ^m 65% EtOH. ⁿ Steinkopf, 1927.

Table II. Other Chlorophenols and Derivatives

Product	R	R'	M.P., °C. (B.P. °C./Mm.)	Yield, %	Analyses, %				Solvent	
					C	H	Cl	S	Reactn.	Recryst.
XLIV	2-Cl	4-SO ₂ Cl	76-78	45	c. 31.75 f. 31.66	1.76 1.87	30.85 30.83	14.10 13.88	ClSO ₃ H	CCl ₄
XLV	4-Cl	2-SO ₂ Cl	37-38 (71-73/0.3)	20	c. 31.75 f. 31.54	1.76 1.90	30.85 30.74	14.10 13.87	ClSO ₃ H	...
XLVI	2,4-Cl ₂	6-SO ₂ Cl	82.5-85.5	59	c. 27.55 f. 27.63	1.15 1.32	40.67 40.99	12.26 12.39	ClSO ₃ H	CCl ₄
XLVII	2-Cl	4-SO ₂ NH ₂	196-99	86	c. 34.70 f. 35.17	2.91 3.28	6.74 ^a 6.55 ^a	15.44 15.38	NH ₄ OH	^b
XLVIII	2,6-Cl ₂	4-SO ₃ H ^r	>300	47	Not analyzed. ^d lit. ^e m.p. >300				H ₂ SO ₄	...
XLIX	3-F	4-SO ₂ X ^r	200-02	16	c. 50.35 f. 50.07	2.82 3.21	13.28 ^g 13.14 ^g	11.20 11.21	FSO ₃ H	^b
L	2-Cl	H			^h					
LI	2,4-Cl ₂	H			^h					
LII	2,5-Cl ₂	H			^h					
LIII	2,6-Cl ₂	H			^h					

^a % N instead of % Cl. ^b 25% EtOH. ^c Product crystallized with 1 mole of H₂O. ^d Calcd. N.E. 261, found N.E. 267. ^e Armstrong, 1875. ^f X = C₆H₃F_(m)(OH)_(n). ^g % F instead of % Cl. ^h Commercially available.

bean test. The latter was designed to disclose speed of activity and to supply leads for possible changes of product structures to be considered in the synthesis program. The data obtained from both sprayings were considered for the selection of compounds to be tested on trees in the greenhouse. This tree test was conducted on eight species of 2- to 3-year-old seedlings. The field test was carried out on turkey oak (*Quercus laevis*) in Florida and on a mixed forest in Arkansas. The criteria for selection of the products to be field-tested were the combined data of the primary screening and the greenhouse-tree test. The plant pots were placed in trays after treatment and watered from below to prevent washing off the sprayed chemicals.

Primary Screening. SIX-SPECIES TEST. Seven-day-old plants of the following species were used: black Valentine bean (*Phaseolus vulgaris*), heavenly blue morning glory (*Convolvulus purpureus*), scarlet globe radish (*Raphanus sativus*), Lincoln soybean (*Glycine max*), Clinton oats (*Avena sativa*), and PI-9790 rice (*Oryza sativa*). These plants can be grown easily and uniformly in 1-quart plastic containers. The screening data obtained with them are easily reproducible. The broad-leaf species were thinned to two plants per pot prior to treatment. The two grasses—i.e., oats and rice—

were not thinned. Two pots of each species were used for each spraying. The candidate compounds were sprayed at the rates of 1.0 and 0.1 pound per acre. Samples used were 31- and 3-mg., respectively, dissolved in 12 ml. of acetone containing 0.5% Tween-20, and sprayed on an area of 0.33 sq. yard.

Observations were made after 1, 5, and 10 to 14 days and the optimum activity was used for the final rating. All plants were observed for extent of abscission, desiccation, kill, and various growth regulator effects. The following ratings were used: no effect (0%)—rating 1; slight effect (1 to 25%)—rating 2; moderate effect (26 to 75%)—rating 3; severe effect (76 to 100%)—rating 4. There could not be a rating higher than 4 for any one of the species even if the compound had "severe effect" in several of the responses. A chemical causing extreme effect on each of the six species received the rating 24. A chemical causing no effect on two species (2 × 1 = 2), slight effect on three (3 × 2 = 6), and severe effect on one (1 × 4 = 4) was rated 2 + 6 + 4 = 12. Table III lists the results of the primary six-species test.

BLACK VALENTINE BEAN TEST. The plants were thinned to one per 1-quart plastic container during the first week after planting and selected for uniformity prior to spraying. Each

Table III. Primary Screening Six-Species and Bean Tests

No.	6-Species Test Rating at Lb./Acre		Bean Test ^a , %/Days ^b					
	0.1	1.0	Desiccation, at Lb./Acre		Abscission, at Lb./Acre		Kill at Lb./Acre	
			1.0	10	1.0	10	10	
I	18	22	100/1	100/0.1	c	c	100/2	
II	8	18	20/14	100/1	50/21	c	0	
III	7	9	0	90/3	0	100/14	0	
IV	6	10	0	0	0	0	0	
V	16	21	100/1	100/1	90/14	c	100/2	
VI	10	22	80/2	100/0.1	75/14	c	100/3	
VII	14	21	80/3	100/1	50/21	c	100/2	
VIII	15	19	90/2	100/1	100/21	c	100/4	
IX	12	20	100/1	100/1	25/7	c	100/3	
X	8	10	0	0	0	0	0	
XI	9	20	5/3	100/2	0	c	100/14	
XII	16	21	100/1	100/0.15	100/14	50/21	0	
XIII	10	19	10/4	100/1	0	100/7	0	
XIV	9	19	5/2	100/1	0	100/14	0	
XV	16	24	100/1	100/1	100/14	c	100/7	
XVI	8	7	0	100/1	0	100/21	0	
XVII	7	8	0	10/7	0	50/21	0	
XVIII	11	19	5/14	100/1	87/21	c	100/14	
XIX	12	18	0	100/1	75/21	c	0	
XX	11	16	95/3	100/1	100/7	c	100/7	
XXI	14	19	80/14	100/1	37/21	100/14	0	
XXII	13	21	45/3	100/1	100/21	c	100/14	
XXIII	6	6	40/7	50/0.15	50/14	50/14	0	
XXIV	14	20	40/3	100/1	100/14	c	100/14	
XXV	11	21	0	75/1	12/21	100/7	0	
XXVI	18	24	100/0.2	100/0.2	100/21	c	0	
XXVII	7	8	0	0	0	0	0	
XXVIII	8	20	15/2	100/2	0	c	100/4	
XXIX	8	20	50/4	100/1	87/21	c	100/14	
XXX	13	16	95/4	100/0.15	50/14	c	100/14	
XXXI	13	18	5/3	100/1	0	c	0	
XXXII	6	16	15/3	100/0.15	25/21	c	0	
XXXIII	6	8	85/3	100/0.15	75/21	c	100/4	
XXXIV	6	6	0	10/3	0	50/4	0	
XXXV	8	11	10/4	100/1	0	100/14	0	
XXXVI	15	23	100/1	100/1	100/14	c	0	
XXXVII	6	10	15/1	100/0.15	0	c	100/7	
XXXVIII	6	6	0	10/3	0	50/4	0	
XXXIX	6	7	0	100/1	0	100/14	0	
XL	8	9	5/2	100/3	0	50/21	0	
XLI	6	7	10/1	100/0.15	0	c	100/4	
XLII	6	14	100/0.2	100/0.2	87/14	c	100/14	
XLIII	6	14	90/0.2	100/0.15	75/14	50/14	0	
XLIV	6	6	0	40/7	0	0	0	
XLV	6	7	0	50/4	0	50/14	0	
XLVI	8	9	0	90/7	0	50/14	0	
XLVII	9	9	0	0	0	0	0	
XLVIII	8	8	0	0	0	0	0	
XLIX	7	8	0	20/14	0	50/14	0	
L	6	6	0	10/14	0	0	0	
LI	6	6	0	50/14	0	50/14	0	
LII	6	6	0	0	0	0	0	
LIII	6	6	0	0	0	0	0	
LIV	7	9	0	0	0	0	0	

^a All but XIV, XXV, and XXXI sprayed in form of water-suspension containing 0.5% of Tween-20; XIV, XXV and XXXI tested in acetone solutions. ^b Optimum ratings listed. ^c No defoliation, since all leaves were desiccated and "frozen" on stem.

had four fully developed leaves (two primary and two trifoliate) and was treated 14 days after planting. Four plants were used for 1.0 pound per acre and one plant for 10 pounds per acre. The formulation of the compounds is indicated in footnote ^a of Table III. Samples of 21 and 210 mg. for the lower and higher rate, respectively, dissolved in 10 ml. of acetone or suspended in 10 ml. of water, and containing 0.5% Tween-20 were sprayed over 0.22 sq. yard. Observations were made every hour during the first 5 hours and 1, 2, 3, 7, 14, and 21 days after treatment, looking for extent of desiccation, "freezing" of the leaves to the plant, abscission, and

killing effects. The optimum activity in per cent per day is recorded in Table III.

Greenhouse-Tree Test. This test was conducted on 2- to 3-year-old seedlings of the following eight species: eastern hemlock (*Tsuga canadensis*), Norway spruce (*Picea abies*), Chinese elm (*Ulmus parvifolia*), black locust (*Robina pseudo-acacia*), red maple (*Acer rubrum*), pin oak (*Quercus palustris*), California privet (*Ligustrum ovalifolium*), and Scotch pine (*Pinus sylvestris*).

The plants were field-grown, dug bare-root during the fall, and placed in cold storage until planting time. During

Table IV. Greenhouse-Tree Test

Activity, %/Day

Prod. No.	Rate, Lb./Acre	Hemlock		Spruce		Pine		Privet		Elm		Locust		Maple		Oak	
		Des.	Absc.	Des.	Absc.	Des.	Absc.	Des.	Absc.	Des.	Absc.	Des.	Absc.	Des.	Absc.	Des.	Absc.
I	5	90/7	20/2	50/1	0	90/7	0	90/7	0	20/1	0	90/3	0	90/1	60/21	90/7	40/21
	10	90/1	20/3	90/1	20/3	90/7	0	90/28	40/28	90/3	0	90/1	0	90/3	40/21	90/1	0
V	5	0	0	0	0	20/1	0	20/1	0	90/14	20/14	20/1	0	20/1	0
	10	0	0	0	0	20/1	0	50/14	0	50/1	0	50/1	20/28	50/28	0
VI	5	20/14	0	50/7	0	20/1	0	50/3	0	50/7	20/7	50/7	0	50/7	0
	10	20/3	0	50/1	0	20/1	0	90/1	0	90/1	40/3	90/1	0	90/1	0
VII	5	20/5	20/5	50/7	0	20/1	0	50/5	0	20/1	0	90/14	0	50/1	0	20/5	0
	10	50/5	20/5	20/5	0	50/5	0	90/7	20/28	90/7	0	90/5	0	90/7	0	90/1	0
XII	5	0	0	0	0	20/1	0	20/1	0	50/21	20/28	20/1	0	20/1	0
	10	20/14	20/28	20/1	0	20/1	0	20/1	0	90/1	40/7	90/1	0	20/1	0
XV	5	90/14	100/21	20/3	0	50/7	0	50/1	20/14	50/1	0	50/3	0	50/1	0
	10	100/14	100/14	90/7	0	90/3	0	90/7	20/14	90/1	40/3	90/1	20/14	90/1	0
XXII	5	50/3	0	90/3	0	20/1	0	50/3	20/7	90/3	40/7	90/3	0	90/7	0
	10	50/3	90/14	90/3	20/28	50/3	0	50/3	20/7	90/7	40/7	90/3	20/3	90/7	0
XXIV	5	20/3	20/28	90/3	0	50/7	20/28	50/3	0	90/3	40/3	50/3	40/28	50/3	0
	10	90/7	100/21	90/3	20/28	50/7	20/28	50/3	20/28	90/1	40/3	50/3	20/7	50/1	20/7
XXV	5	50/14	20/14	20/1	0	20/1	0	20/1	20/14	50/14	0	90/3	60/3	90/3	60/14	20/1	0
	10	90/3	20/14	90/3	0	50/1	0	50/7	20/14	90/3	20/14	90/3	40/3	90/1	20/14	90/1	20/14
XXVI	5	20/1	0	0	0	50/1	0	50/14	0	90/1	40/21	90/21	0	50/1	40/7
	10	20/1	0	20/1	0	50/1	0	90/14	0	90/1	40/14	90/1	40/21	90/1	40/7
XXXVI	5	0	0	0	0	20/1	0	20/1	0	20/1	0	20/1	0	20/1	0
	10	20/1	0	0	0	50/1	0	50/21	0	90/21	20/28	20/1	0	50/14	0
XLIII	5	50/3	0	20/7	0	20/1	0	50/1	0	50/1	0	50/1	0	50/7	0
	10	50/21	0	20/21	0	50/3	0	50/7	0	50/1	0	50/1	0	50/1	0	50/1	0

Table V. Desiccation Responses in Mixed Forest

Product	Rate, Lb./Acre	Days				
		1	5	10	30	60
		% Desiccation ^a				
I	3	32	42	54	42	32
XV	3	54	60	54	54	46
XXV	3	18	38	58	30	24
LV	6	0	32	62	46	...
LVII	26	2	46	60	72	78
I + LVII	3 + 26	35	42	48	75	75
XV + LVII	3 + 26	56	76	90	96	85
XXV + LVII	3 + 26	20	44	66	82	82

^a Calculated from visual observations made on extent of effect on 10 marked specimens of each of 20 species.

December and January the plants were potted individually in 1-quart plastic containers in a soil mixture and left in the greenhouse until the root systems were well established.

The formulation and spraying techniques were the same as those used in the six-species primary screening. The rates were equivalent to 5 and 10 pounds per acre—i.e., 155 and 310 mg. of product, respectively.

Observations for extent of abscission and desiccation effects were made 1, 3, 5, 7, 14, and 28 days after treatment. The optimum activity is reported in per cent per day in Table IV.

Field Tests. Four of the products—i.e., I, XV, XXV, and XXVI—were selected for the field testing. The least promising of these was XXV, which was included because of its similarity to one of the phenoxies used in the test. Three commercial products—i.e., sodium cacodylate (LV), isooctyl 4-amino-3, 5, 6-trichloropicolinate (LVI), and a 1-to-1 mixture (LVII) of the butyl esters of 2,4-D and 2,4,5-T—and their mixtures with I, XV, XXV, and XXVI were included in the test. The potentially most expensive product (XXVI) was used only in combination with LVII. The primary objective was to achieve fast desiccation, and observations were made 1, 5, and 10 as well as 30 and 60 days after treatment.

MIXED FOREST. Technical grade products I, XV, XXV, LV, and LVII and mixtures of LVII with I, XV, and XXV were sprayed with a commercial Bell sprayer-helicopter in 1.5-acre plots. The first three products and their mixtures with LVII were applied at 6 gallons per acre of a formulation in No. 2 fuel oil containing 3.3% (by volume) of acetone which was needed to dissolve I, XV, and XXV before adding the oil. The cacodylate (LV) was applied at 6 gallons per acre as an aqueous formulation. The liquid product (LVII) was used without any diluent at 3 gallons per acre. The results of this test are listed in Table V.

The mixed forest consisted of the following 20 species: white ash (*Fraxinus americana*), bitter nut hickory (*Carya cordiformis*), southern red oak (*Quercus falcata*), pin oak (*Quercus palustris*), post oak (*Quercus stellata*), water oak (*Quercus nigra*), blackjack oak (*Quercus marilandica*), hackberry (*Celtis occidentalis*), winged elm (*Ulmus alata*), American elm (*Ulmus americana*), hawthorne (*Crataegus spp*), sumac (*Rhus species*), sycamore (*Platanus occidentalis*), sweet gum (*Liquidambar styraciflua*), dogwood (*Cornus florida*), mulberry (*Morus nigra*), red maple (*Acer rubrum*), persimmon (*Diospyros virginiana*), honey locust (*Gleditsia triacanthos*), and osage orange (beau d'arc) (*Maclura pomifera*).

TURKEY OAK FOREST. Technical grade products XV, XXV, XXVI, LVI, and LVII and mixtures thereof were used at the rates indicated in Table VI. The application was made on 20 × 20 foot plots by a truck-mounted sprayer equipped with

Table VI. Desiccation Responses in Turkey Oak Forest

Product	Rate, Lb./Acre	Days			
		5	10	30	60
		% Desiccation ^a			
LVI	4	20	20	20	80
XV + LVI	6 + 4	60	80	80	80
XXV + LVI	6 + 4	80	80	80	80
XXVI + LVI	6 + 4	60	60	60	80
LVII	16	40	60	60	80
XV + LVII	6 + 16	100	100	100	100
XXV + LVII	6 + 16	20	40	40	80
XXVI + LVII	6 + 16	60	100	100	100

^a Calculated from visual observations on extent of desiccation of all specimens.

an elevated boom. There was an insignificant scattering of other species in the oak forest. The mixtures of XV, XXV, and XXVI with LVI and LVII were formulated in No. 2 fuel oil containing 2.5% by volume of xylene which was needed to dissolve XV, XXV, and XXVI prior to dilution with oil; LVI and LVII were also formulated in No. 2 fuel oil but without xylene. All formulations were sprayed at 20 gallons per acre. The results are listed in Table VI.

DISCUSSION OF RESULTS

Forty-three fluorosulfonated phenols with free (subclass A) or substituted (subclass B) phenolic hydroxyl group were tested in the primary six-crop and bean tests. Of these, six (IV, X, XVII, XXVII, XXXIV, and XXXVIII) were practically inert and an additional six (III, XVI, XXIII, XXXIX, XL, and XLI) affected the plants only moderately at the applied rates. The slight desiccation caused by XXIII was very fast—i.e., in the first 3 to 4 hours after spraying with 10 pounds per acre. Seven of these 12 products have their OH group blocked with moieties which would be removed by hydrolysis to yield the free phenols at relatively slower rate than the groups $-C(O)CH_2Cl_{3-x}$, $-C(O)NPh$, or $-C(O)-NHC_6H_5$. This group of seven structures should have included II which, indeed, exhibited very low activity at 0.1 pound per acre in the six-crop and at 1.0 pound per acre in the bean test and only moderate effect at the 1.0 pound per acre in the six-crop screening. Furthermore, of the two fast desiccating products (XXIII and XLI), the latter, which is a free phenol, was rated higher. There is strong evidence that the free phenolic hydroxyl is at least partly responsible for the activity. All of the 15 structures (I, V, VI, IX, XII, XV, XXVI, XXX, XXXII, XXXIII, XXXVI, XXXVII, and XLI to XLIII) causing complete and fast desiccation (within the first 5 hours at 10 pounds per acre or within the first 24 hours at 1.0 pound per acre) are either free phenols or can be easily hydrolyzed to the free phenols.

The lack of activity of the starting materials (L to LIII) is an indication of the necessity of the sulfonyl group in addition to the phenolic hydroxyl. The inertness of the sulfone (XLIX), the sulfonamide (XLVII), the sulfonic acid (XLVIII), and especially the sulfonyl chlorides (XLIV to XLVI) corresponding to I, XIV, and XXV, respectively, demonstrates the necessity and specificity of the fluorosulfonyl group.

These data combined with the lack of activity of LIV, which is dehydroxylated XIII, suggest that both a hydroxyl group, or a masked hydroxyl group, and a fluorosulfonyl moiety are required for the activity exhibited by this class of compounds. The simplest structures which meet this prerequisite are the three isomeric hydroxybenzenesulfonyl fluorides, of which the

p-isomer (XLI) was prepared and tested. It is a fast desiccant but has only moderate activity.

Apparently a ring substitution in XLI is needed for higher over-all activity and fast desiccation. This substituent can, by steric hindrance, or by inductive or resonance effect, determine the rate of hydrolysis or the rate of other reactivity of the fluorosulfonyl group and the reactivity or pK value of the phenolic or latent phenolic hydroxyl. These three effects, however, are very difficult to evaluate separately or in combination with each other.

The introduction of a nitro group in the *m*-position to SO_2F of XLI, resulting in XXXVII, seemed to improve the activity of XLI very little. The reduction of NO_2 to NH_2 (XXXVIII) or the introduction of CH_3 (XL) or $COOH$ (XXXIX) in the *m*-position to SO_2F of XLI lowered the activity. The introduction of halogen, however—i.e., Cl (I) and F (XXXVI)—in the same position considerably improved the over-all activity and the desiccation. Thus, a particular electronegativity of the substituent adjacent to the phenolic hydroxyl of ring-substituted *p*-hydroxybenzene-sulfonyl fluorides and/or the lack of intramolecular hydrogen bonding seem to be essential for high and fast desiccation effect. This is in agreement with the over-all activity of XXXIII and XXXV, which is lower than that of XV. Of the two isomers (XV and XXV), the latter has an OH *o*-positioned to SO_2F and is less active; XIII and XIV also are less active than I. This trend, however, cannot be substantiated by the two isomeric pairs XXVIII/XXIX and XLII/XLIII. If hydroxybenzenesulfonic acids are active metabolites of the correspondingly substituted hydroxybenzenesulfonyl fluorides, these metabolites must be formed at the site of action to cause activity, since XLVIII was—surprisingly—completely inactive. This observation probably explains the inertness of the hydroxybenzenesulfonyl chlorides, which are hydrolyzed to the corresponding sulfonic acids faster than the respective hydroxybenzenesulfonyl fluorides.

The data of the preliminary screening show that for high over-all plant response and for high and fast desiccation effect the optimum structures of the hydroxybenzenesulfonyl fluorides must meet the following specifications: phenolic OH *p*-positioned to SO_2F ; and ring substitution by one or two chlorine (or fluorine) atoms which are not adjacent to each other and at least one of which is *o*-positioned to OH.

The greenhouse-tree test demonstrated the desiccation superiority of the free phenols over the temporarily blocked phenols. It virtually substantiated the requirements for the optimum structure mentioned in the preceding paragraph with an indication for a slight modification; if two Cl atoms are present in the ring of the *p*-hydroxybenzenesulfonyl fluoride, both should preferably be *o*-positioned to the phenolic OH. Structure XV exhibited somewhat better desiccation and defoliation activity than XXVI.

The hope to improve the speed of the defoliation effect of the fluorosulfonated phenols by substituting the phenolic hydroxyl with various moieties did not materialize. In most cases the defoliation was relatively slow when compared with the desiccation effect. Many compounds exhibited substantial defoliation (75 to 100%) at 1.0 pound per acre and comparatively fast (2 to 7 days) herbicidal activity at 10 pounds per acre in the bean test.

The field test data confirmed the greenhouse-tree and the preliminary screening results. 3,5-Dichloro-4-hydroxybenzenesulfonyl fluoride (XV) was a somewhat better desiccant than I, XXV, or XXVI. All four are very fast desiccants also under field conditions. They were much faster desiccating

agents than the formulations of sodium cacodylate (LV), picloram isooctyl ester (LVI), or a 1-to-1 mixture of butyl esters of 2,4-D and 2,4,5-T (LVII) used in the tests.

SYNTHESES

Analytical data and reaction and recrystallization solvents for all products are listed in Tables I and II. Compounds III to VIII were synthesized by a method described for the preparation of X. Methanesulfonyl chloride (for III), *N,N*-dimethylsulfonyl chloride (for IV), acetyl chloride (for V), chloroacetyl chloride (for VI), trichloroacetyl chloride (for VII), and ethyl chloroformate (for VIII) were used instead of *N,N*-diethylcarbamyloxy chloride. The reaction mixtures were refluxed for 2 instead of 30 hours. All temperatures are given in °C.

3-Chloro-4-(*N*-ethylcarbamyloxy)benzenesulfonyl Fluoride (IX). To a mixture of 21.1 grams (0.1 mole) of 3-chloro-4-hydroxybenzene sulfonyl fluoride(I) and 8.4 grams (0.12 mole) of ethyl isocyanate was added 10 drops of Et_3N under stirring. An exothermic reaction took place and the reaction mixture solidified. It was recrystallized from 250 ml. of petroleum ether (60 to 110°)—benzene mixture (4 to 1) to obtain 24.0 grams (85%) of the pure product (m.p. 97–98°).

3-Chloro-4-(*N,N*-diethylcarbamyloxy)benzenesulfonyl Fluoride (X). A solution of 31.6 grams (0.15 mole) of 3-chloro-4-hydroxybenzenesulfonyl fluoride (I), 16.0 grams (0.16 mole) of triethylamine, and 22.0 grams (0.16 mole) of *N,N*-diethylcarbamyloxy chloride in 200 ml. of benzene was stirred and refluxed for 30 hours. The precipitated triethylamine hydrochloride was filtered off; the filtrate was Darco-treated and filtered hot; the filtrate was concentrated in vacuo to a pale amber-colored sirup which crystallized upon cooling. The crude product was recrystallized from 80% aqueous ethanol to obtain 29.5 grams of pure product (m.p. 55–57°).

3-Chloro-4-(*N*-phenylcarbamyloxy)benzenesulfonyl Fluoride (XI) and 3-Chloro-4-(*N-m*-chlorophenylcarbamyloxy)benzenesulfonyl Fluoride (XII) were obtained by the method applied for IX, using phenyl isocyanate and *m*-chlorophenyl isocyanate, respectively, instead of ethyl isocyanate.

3,5-Dichloro-4-hydroxybenzenesulfonyl Fluoride (XV). To 103.0 grams (1.03 moles) of fluorosulfonic acid was added 28.9 grams (0.172 mole) of 2,6-dichlorophenol over a period of 15 minutes. The solution was then heated at 70° for 1 hour, cooled, and poured into cracked ice. The resulting oil solidified in approximately 15 minutes and the solid was filtered off to give a crude, tan-colored product. Recrystallization from CCl_4 gave 26.0 grams (62%) of the product (m.p. 90.5–91.5°).

3,5-Dichloro-4-methoxybenzenesulfonyl Fluoride (XVI). To a cooled, stirred solution of 17.2 grams (0.07 mole) of 3,5-dichloro-4-hydroxybenzenesulfonyl fluoride (XV) in 150 ml. of ether was added over 0.75 hour a solution of 4.2 grams (0.1 mole) of diazomethane in 160 ml. of ether. When nitrogen evolution had ceased, several drops of glacial acetic acid were added to destroy the excess of diazomethane. The mixture was concentrated in vacuo to an orange-colored, liquid residue. After standing for 12 days it crystallized. It was recrystallized from 95% EtOH (Darco) to obtain 15.3 grams (85%) of product (m.p. 43–45°).

Ethyl 2,6-Dichloro-4-fluorosulfonylphenoxyacetate (XXIII). To a cold solution of 35.0 grams (0.143 mole) of 3,5-dichloro-4-hydroxybenzenesulfonyl fluoride (XV) in 150 ml. of absolute EtOH was slowly added a cold solution of 3.4 grams (0.143 atom) of sodium metal in 150 ml. of absolute EtOH. After 15 minutes the ethanolic solution was con-

centrated in vacuo to a white solid; the white solid was washed with several portions of ether, filtered, dried, and then refluxed for 40 hours in an excess of ethyl bromoacetate. The mixture was poured into 500 ml. of ether and the suspended solid was filtered off. The filtrate was evaporated in vacuo and the residue was fractionally distilled to obtain 20.5 grams (43%) of product XXIII (b.p. 150–55°/0.5 mm., n_D^{25} 1.5206).

Ethyl 2,5-Dichloro-4-fluorosulfonylphenoxyacetate (XXVII). A stirred mixture of sodium 2,5-dichloro-4-fluorosulfonylphenolate [prepared from 24.5 grams (0.1 mole) of XXVI and 2.3 grams of sodium], 100 grams of ethyl bromoacetate, 100 ml. of xylene, and a pinch of copper powder was refluxed for 15 hours. The mixture was filtered and the residue was washed with boiling toluene (2×75 ml.). The solvent and the excess of ethyl bromoacetate were removed from the filtrate under vacuum. The residual oil was recrystallized from ether–petroleum ether to give 9.0 grams (27%) of the product (m.p. 84–85°).

3-Chloro-4-hydroxy-5-nitrobenzenesulfonyl Fluoride (XXXIII). To a stirred mixture of 88 grams (1.25 moles) of 90% nitric acid and 100 grams of concentrated H_2SO_4 at 35° was added in small portions 52.6 grams (0.25 mole) of 3-chloro-4-hydroxybenzenesulfonyl fluoride (I) over 30 minutes. Ice bath cooling was used to maintain a reaction temperature of 35°. After all had been added, the solution was stirred and heated at 45° for 30 minutes and then poured onto 1 kg. of ice. The gummy product became crystalline after repeated washings with water. It was filtered off, dissolved in 65% aqueous ethanol, cooled, and filtered to obtain 35.5 grams (56%) (m.p. 82–83.5°). A recrystallization from *n*-hexane did not change the melting point.

3-Amino-5-chloro-4-hydroxybenzenesulfonyl Fluoride (XXXIV). A solution of 25.6 grams (0.1 mole) of 3-chloro-4-hydroxy-5-nitrobenzenesulfonyl fluoride (XXXIII) in 200 ml. of absolute EtOH was hydrogenated at 60 p.s.i.g. in a Parr shaker using 3 grams of Raney nickel as catalyst. The catalyst was filtered off; the filtrate was diluted to 3 liters with water and sodium chloride was added until all the product had been salted out. It was filtered off and air-dried to give 20.0 grams (88.5%) of the pure product (m.p. 115–18°).

3-Chloro-5-fluorosulfonyl-4-hydroxybenzenesulfonyl Fluoride (XXXV). To 160 grams (1.6 moles) of fluorosulfonic acid was added with stirring 63.2 grams (0.3 mole) of 3-chloro-4-hydroxybenzenesulfonyl fluoride (I). The mixture was heated at 140° to 150° for 30 minutes and at 120° to 130° for 2.5 hours, cooled, and poured onto 600 grams of crushed ice. An oil separated out. It solidified on standing, and was filtered off. The aqueous filtrate was extracted with benzene (3×250 ml.). The benzene solution was worked up to obtain a residue which was combined with the above solid and recrystallized from benzene–petroleum ether (b.p. 60° to 110°) and then from petroleum ether (b.p. 60° to 110°) to obtain 23.5 grams (27%) of the product (m.p. 98–99°).

3-Fluoro-4-hydroxybenzenesulfonyl Fluoride (XXXVI) and Bis(3-fluoro-4-hydroxyphenyl) Sulfone (XLIX). To 773 grams (7.73 moles) of fluorosulfonic acid was slowly added 168 grams (1.50 moles) of *o*-fluorophenol at 0° to 5°. The reaction solution was stirred for 18 hours at room temperature and poured onto 4 kg. of ice. The aqueous mixture was extracted with 5×300 ml. of ether and the ether solution was washed with 300 ml. of a saturated sodium chloride solution,

dried, and evaporated to give a brown oil. It was washed with 500 ml. of cold benzene to give 60 grams of off-white solid (m.p. 175–90°). Recrystallization from 25% aqueous EtOH gave 35 grams (16%) of the sulfone (XLIX) (m.p. 200–02°). The benzene filtrate was evaporated and the residue recrystallized from carbon tetrachloride to give 70 grams (24%) of the benzenesulfonyl fluoride (XXXVI) (m.p. 65–70°); upon recrystallization from CCl_4 the melting point of XXXVI was raised to 70–71°; the yield was reduced to 16%.

3,5-Dichloro-2-hydroxybenzenesulfonyl Chloride (XLVI). To 291 grams (2.5 moles) of chlorosulfonic acid was added with stirring 81.5 grams (0.5 mole) of 2,4-dichlorophenol over a 0.5-hour period. The reaction was not exothermic and after all the phenol had been added the mixture was homogeneous. After standing for 16 hours at room temperature, the mixture was cautiously poured with stirring into 2 kg. of ice. The acid layer was decanted, and the product was washed with three 300-ml. portions of ice water and filtered off. After drying, the crude product was dissolved in 1300 ml. of CCl_4 , filtered hot, concentrated in vacuo to ca. 200 ml., and filtered. There was obtained 77.5 grams (59%) of product (m.p. 82.5–83.5°). The melting point did not change after recrystallization from CCl_4 .

3-Chloro-4-hydroxybenzenesulfonamide (XLVII). A suspension of 63.2 grams (0.3 mole) of 3-chloro-4-hydroxybenzenesulfonyl fluoride (I) in 200 ml. of concentrated NH_4OH was stirred at room temperature for 72 hours. The mixture was then acidified with concentrated HCl and cooled. The solid product was filtered off, washed with ice water, and air-dried. There was obtained 53.5 grams (86%) of product (m.p. 195–98°). A recrystallization from 25% aqueous EtOH raised the melting point to 196–99°.

***p*-Chlorobenzenesulfonyl Fluoride (LIV).** To 160.0 grams (1.6 moles) of fluorosulfonic acid was added dropwise 56.3 grams (0.5 mole) of chlorobenzene while stirring at 5° to 10°. The reaction mixture was then heated for 3 hours at 80–85°, cooled, and slowly added to 2 kg. of crushed ice. The product was filtered, washed with water, dried, and recrystallized from isopropyl ether to obtain 63.2 grams (65%) [m.p. 48.5–50°; lit. (Davies and Dick, 1931) m.p. 47–48°]. Calculated for $C_6H_4ClFO_2S$ (LIV): C, 37.00; H, 2.52; Cl, 18.25; F, 9.58; S, 16.45. Found: C, 36.96; H, 2.54; Cl, 18.30; F, 9.77; S, 16.49.

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