in the sulfur mode gave good response to 1-naphthyl-2,5-dichlorobenzenesulfonate, as seen in Figure 8. A Research Specialties gas chromatographic oven, Model 660, was equipped with an FPD which had the metal base lined with Teflon tubing throughout the carrier gas portion. A 6 ft × 0.25 in. × 5 mm i.d. glass column was packed with 5% LSX 3-0295 packing and operated at 60 ml/min and 220°.

DISCUSSION

Somewhat low, but consistent (relative standard deviation <12%), recoveries were obtained for those levels of carbamate approaching 1 ppm (Figure 4). Most of this loss was found to be due to hydrolysis of the carbamate when the benzene phase containing the pesticide is washed with the cold 0.25 *N* NaOH. However, this washing procedure removed almost all of the interferences and was considered to contribute greatly to the simplicity of the procedure.

The thermal stability of the sulfonates was demonstrated by sealing microgram quantities in glass ampoules for various lengths of time. After heating at 250° for 1 hr and then analyzing by GC it was determined that no measurable amount of loss had occurred.

If competing side reactions occurred in the derivatization they were not indicated, as evidenced by the complete absence of multiple peaks and by the 100%+ conversion efficiency of the derivatization reaction.

The Varian Model 1520B gas chromatograph used in this study was modified by removing the stainless steel connecting lines running from the column over to the detector base and replacing them with short sections of glass tubing. This produced an essentially all glass system which was found to be necessary to minimize the catalytic degradation of the sulfonates. Even then the 1520B was found not to be as sensitive as other instruments of somewhat newer design. Figure 9 is a typical chromatogram obtained with a glass column equipped Varian 1200 showing a limit of detection of about 1 pg compared to 50 pg which is the limit of detection for a Varian 1520B.

The sulfonates have not only found great use in this laboratory as derivatives of carbamates but also of certain ring hydroxylated compounds, such as 2,4-dichlorophenol, a metabolite of 2,4-dichlorophenoxyacetic acid. This usage will be reported at a later date.

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Preservation of Grain with Aliphatic 1,3-Diols and Their Esters

John W. Frankenfeld,* Raam R. Mohan, and Robert L. Squibb

A series of linear, aliphatic 1,3-diols and certain of their monoesters have been found to be safe, effective preservatives for raw grain and animal feeds. The safety of these materials was established by rat feeding experiments which showed them to be nontoxic and readily metabolized. In antifungal tests, using tube dilution methods, several of the diols and esters were significantly more active than either calcium propionate or calcium sorbate. The most effective diols are those with carbon numbers ranging from 7 to 9. The best esters have carbon contents, diol plus acid fragments, in the range of C_{10} to C_{15}. The most promising new compounds were evaluated as preservatives for chick feeds and for raw grains at various humidity levels. They appeared to be at least as effective as current, acidic grain preservatives and to possess certain unique advantages. These include greater safety, lack of corrosivity, and improved odor and flavor characteristics.

Deterioration of grain due to microbial attack during storage continues to be a serious problem. Moldy grain is unpalatable, difficult to handle, and malodorous. Damaged flour, for example, has a deleterious effect on bread making (Daftary et al., 1970). In addition, the mycotoxins produced by many molds present a serious health threat to both humans and animals (Ciegler et al., 1971). Traditionally, grain is preserved from microbial attack by drying to 14% moisture content or less (Huitson, 1968; Christensen and Kaufmann, 1969) although refrigeration and aeration processes are also employed (Christensen and Kaufmann, 1969). Recently, various types of chemical preservatives have been added to stored grain. For the most part these have been aliphatic acids, especially acetic and propionic acid, and their calcium and sodium salts. These materials, while effective, have drawbacks in

Exxon Research and Engineering Company, Linden, New Jersey 07036 (J.W.F., R.R.M.) and Laboratories of Disease and Environmental Stress, Rutgers, The State University, New Brunswick, New Jersey 08903 (R.L.S.).

Table I. Toxicity and Nutritional Data for Various Grain Preservatives[a]

Dihydroxy compd[b]	Oral LD_{50}, g/kg[c]	Obsd metabolic energy, kcal/g	% utilized[d]	Ref.
1,3-Butanediol	29	6.0	88	
1,2-Pentanediol	>15	2.1	28	
1,3-Pentanediol	20	7.8	100	
1,5-Pentanediol	2	NU[e]		
1,3-Hexanediol	>20	6.6	85	
1,5-Hexanediol	>20	NU[e]		
2,5-Hexanediol	2	NU[e]		
1,6-Hexanediol	5	NU[e]		
1,3-Heptanediol	>20	8.0	98	
1,3-Octanediol	>20	5.8	71	
1,3-Nonanediol	>20	7.5	85	
1,3-Butanediol 1-monooctanoate	>20			
1,3-Octanediol 1-monopropionate	>20			
Sorbic acid	10			Spector (1955)
Sodium sorbate	6–7			Spector (1955)
Propionic acid	4			Smyth et al. (1962)
Acetic acid	3.3			Spector (1955)

[a] Data for diols and esters taken from Frankenfeld and Miller (1974) and Giron (1968). [b] Test compounds were maintained in a sterile condition. [c] Lethal dose for 50% kill; single dose in rats. [d] Determined by dividing observed metabolic energy (kilocalories) by theoretical metabolic energy (kilocalories); see Frankenfeld and Miller (1974), Giron (1968), and Miller (1964) for details. [e] NU, not utilized, animals lost weight or died.

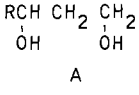
Table II. Inhibition of Mold Growth on Raw Grain Treated with Various Preservatives[a] (50% Relative Humidity)

		Mold growth after days[c]								
		Soy flakes			Cracked corn			Wheat grains		
Additive	Method of addition[b]	10	20	30	10	20	30	10	20	30
None		±	+++		+	+++		−	+	++
1,3-Nonanediol	B	−	−	−						
1,3-Nonanediol (50%) +	A				−	+	++	−	−	−
1,3-butanediol 1-monooctanoate	B	−	−	−	−	−	−			
(50%)	C				−	±	+	−	−	−
Ethanol	A	±	++		+	+++				

[a] Preservatives added at level of 1% based on dry weight of grain. [b] Methods of addition of active ingredient: A, undiluted; B, in ethanol solution; C, as aqueous emulsion with commercial surfactant. [c] Mold growth evaluated as: −, no growth; ±, questionable; +, light; ++, moderate; +++, heavy.

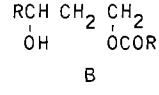
their odors, corrosivity, and difficulty in application. In addition, they prevent germination and cannot be used on seed grain.

As part of our search for new food and feed preservatives we have found that a number of linear, aliphatic 1,3-diols and certain of their monoesters are uniquely safe and effective preservatives. Because they are readily metabolized, energy dense materials (Giron, 1968) they also serve to improve the nutritional quality of products to which they are added. This paper describes some initial studies in the evaluation of these materials having the general chemical structures shown below (A and B) as nutritionally valuable grain preservatives (Frankenfeld et al., 1973).



A

1,3-Diols



B

Diol Esters

MATERIALS AND METHODS

Test Chemicals. The 1,3-diols used in this study were prepared by reduction of the corresponding hydroxy esters (Frankenfeld and Werner, 1969) with lithium aluminum hydride in ether (Gaylord, 1956). Purity of 99.5% or better was verified by gas chromatography. Food grade preservatives for comparison were obtained from commercial sources and used without purification.

Nutritional Evaluation and Animal Toxicity Determinations. These were carried out as described by Frankenfeld and Miller (1974) and Giron (1968).

Antimicrobial Activity Determination. Preliminary screening studies to determine minimum inhibitory concentrations (MIC's) were carried out as follows. Nutrient broth was used as the basal nutrient medium for the growth of all microorganisms tested. Five milliliters of nutrient broth (Difco Co.) was placed in 18 mm × 150 mm test tubes and sterilized with steam at 15 psi for 15 min. After cooling, a sufficient amount of the various compounds was added to the basal medium to give the required concentrations. After mixing the chemicals with nutrient broth, the tubes were innoculated with the various test microorganisms. The microorganisms were grown 45 hr earlier in nutrient broth and 1 drop of the dense microbial suspension containing approximately 10^9 cells/ml was added to the tubes. The tubes containing the test chemicals and microorganisms were then incubated at the

Table III. Inhibition of Mold Growth on Soy Flakes at 100% Humidity[a]

Additive	Replicate	Mold growth after days[b]					
		4	7	10	15	20	30
None	1	++	+++	+++			
	2	++	+++	+++			
	3	+	+++	+++			
Propionic acid	1	−	−	±	++	+++	+++
	2	−	−	−	−	−	−
	3	−	−	−	−	−	−
	4	−	−	−	−	+	+++
	5	−	−	−	−	+	+++
1,3-Nonanediol	1	−	−	±	±	++	+++
(50%) + 1,3-butanediol	2	−	−	±	±	++	+++
1-monooctanoate (50%)	3	−	−	±	±	++	+++
	4	−	−	−	−	+	+
	5	−	−	+	++	++	+++
1,3-Heptanediol	1	−	−	−	−	−	−
	2	−	−	−	−	−	−
	3	−	−	−	−	±	±
	4	−	−	−	−	±	±
	5	−	−	−	−	+	+

[a] Propionic acid was added undiluted; other preservatives were added in ethanol solution; levels in all cases were 1% based on dry weight of grain. [b] −, no growth; ±, questionable; +, light; ++, moderate; +++, heavy.

optimal growth temperatures (30 or 37°) reported for each microorganism tested. Growth in control tubes, as well as those containing chemicals, was observed visually. After a suitable incubation period, a small aliquot of the test solutions was streaked on an agar plate. This was done in order to confirm the visual readings and the viability of the test microorganism.

Studies with Raw and Ground Grain. In preliminary studies, cracked corn, roughly ground soy flour, and whole wheat grains were employed. Weighed amounts of the grains were sprayed with 50 wt % solutions of the test chemicals in absolute ethyl alcohol until the grain had absorbed the desired amount of preservative. The treated grains were tumbled in open jars until the ethanol had evaporated (1.25 hr) and then spread out in petri dishes and stored under ambient conditions (50% relative humidity). Daily examinations for mold growth were conducted. Controls consisting of untreated grain and grain sprayed with ethanol alone were handled similarly. A similar test was conducted with propionic acid as a control preservative. In this experiment, the covers of the petri dishes were fitted with filter paper disks soaked with water in order to increase the relative humidity to 100% and enhance the rate of mold growth.

More detailed experiments at various relative humidities and with different levels of preservatives were carried out as follows. Wheat, milo, and corn with initial moisture contents of 13.8, 14.6 and 15.6%, respectively, were used as experimental materials. The grains were reconstituted with water to raise the moisture content to 25.0%. They were then treated with a mixture of 1,3-nonanediol and 1,3-butanediol 1-monooctanoate (1:1) at levels of 0.05, 0.50, and 1.00% with controls provided by untreated grain and either ethanol or propionic acid treated grains.

The grains were then stored in glass beakers of 300 g capacity in relative humidity chambers (constituted by sulfuric acid–water mixture) at a room temperature of 22°.

The samples were observed on alternate days for visual appearance of mold growth at any of the three levels of added preservative. Presence of mold was recorded by a + sign and in the case of uncertainty (+)? was recorded.

In a separate experiment, the grains, after 15 days storage, were placed on a sterile plate containing nutrient agar. The number of grains which produced mold colonies were noted and the type of mold determined microscopically.

RESULTS AND DISCUSSION

Toxicity and Nutritional Value of Test Compounds. A major goal of this research was to discover safe, new preservatives which might actually enhance the nutritive value of foods and feeds. Consequently, the first screening experiments on candidate preservatives were designed to determine their toxicity and nutritional properties. The results of toxicity (LD_{50}) determinations are given in Table I. Literature values (Spector, 1955; Smyth et al., 1962) for some common feed preservatives are also shown. The linear 1,3-dihydroxy structure is unique in being both completely nontoxic and well utilized as a source of metabolic energy (calories). All other diols including branched 1,3-diols or esters we have studied were either toxic or poorly utilized by the test animals (Frankenfeld and Miller, 1974; Miller, 1964). These data indicate that the 1,3-diols may actually enhance the food value of grains used as animal feeds. The organoleptic properties of the diols and esters have not been extensively explored. The flavor of undiluted 1,3-diols may be described as "bitter" and they impart a warm or "burning" sensation to the tongue. It is not known whether treated grains would be unacceptable to animals at the low levels required for mold protection. Diets containing up to 10% of the test compounds were well tolerated by rats. Modification and/or improvement of flavor characteristics can be achieved in some measure by mixing of diols or conversion to monoester derivatives. The diesters, while having improved flavor characteristics, are not effective preservatives.

Antifungal Properties of Diols and Esters. These experiments were carried out by tube dilution methods for the purpose of identifying the most promising new fungicides. The best 1,3-diols were those which contained seven or more carbon atoms. In general, the best monoesters were those which contained a total of 10–15 carbon atoms in the diol and ester portions of the molecule. The new preservatives were tested against a variety of fungi including *A. niger, A. flavus, P. roquefortii, C. globosum,* and *Fusa-*

Table IV. Preservation of Raw Corn with Various Levels of 1,3-Nonanediol (50%) plus 1,3-Butanediol 1-Monooctanoate (50%)[a]

Additive	Concn, %	Rel humidity, %	Mold growth at days after storage[b] 2	4	8	12	16	20	24
None		100	+						
			−						
			−						
		90	+						
			+						
			+						
		80	+						
			+						
			+						
Ethanol	1.00	100	+	+	+				
			−	−	+				
			−	−	+				
		90	−	−	+				
			−	−	+				
			−	−	+				
		80	−	−	+				
			−	−	+				
			−	−	+				
1,3-Nonanediol (50%) + 1,3-butanediol 1-monooctanoate (50%)	0.05	100	+	+	+				
			−	−	+				
			−	−	+				
		90	−	−	−	+			
			−	−	−	+			
			−	−	−	+			
		80	−	−	−	+			
			−	−	−	+			
			−	−	−	+			
	0.50	100	−	−	+	+	+	+	
			−	−	−	−	+	+	
			−	−	−	−	−	−	
		90	−	−	−	−	−	+	
			−	−	−	−	−	+	
			−	−	−	−	−	+	
		80	−	−	−	−	−	+	
			−	−	−	−	−	+	
			−	−	−	−	−	+	
	1.00	100	−	−	+	+	+	+	+
			−	−	−	−	−	+[c]	+
			−	−	−	−	−	−	+[d]
		90	−	−	−	−	−	−	(+ / + / +)?
			−	−	−	−	−	(+)?	
			−	−	−	−	−	−	
		80	−	−	−	−	−	−	−
			−	−	−	−	−	−	−
			−	−	−	−	−	−	−

[a] Moisture content: 25%; three replicates at each level. [b] −, no growth; (+)?, questionable growth; +, definite growth. [c] Growth definite on day 18. [d] Growth definite on day 22.

rium sp. (ATCC No. 10911). The minimum inhibitory concentrations (MIC's) for the most active compounds ranged from 80 ppm for *A. niger* to 500–1000 ppm for *C. globosum*. Commercial preservatives, calcium propionate and calcium sorbate, were included in some of the tests. They were less effective than the best diols and esters, having MIC's ranging from 2000 to >20,000 ppm in these tests. This was true both at pH 7 and 5. A 50:50 mixture of 1,3-nonanediol and 1,3-butanediol 1-monooctanoate, when used in combination, gave lower MIC's than equivalent amounts of either test compound alone. However, this effect was not observed in tests for preservation of the grain itself. Additional results of antimicrobial screening studies may be found in Frankenfeld et al. (1974).

Preliminary Tests with Chick Starter Diet. A commercial chick starter diet (Squibb, 1961) was used as a

Table V. Preservation of Milo with 1,3-Nonanediol (50%) plus 1,3-Butanediol 1-Monooctanoate (50%)[a]

Additive	Concn, %	Rel humidity, %	Mold growth at days after storage							
			2	4	8	12	16	20	24	26
None		100	+							
			+							
			+							
		90	+							
			+							
			+							
		80	+							
			+							
			+							
Ethanol control (1%)	1.00	100	+	+	+					
			−	−	+					
			−	−	+					
		90	−	−	+					
			−	−	+					
			−	−	+					
		80	−	−	+					
			−	−	+					
			−	−	+					
1,3-Nonanediol (50%) + 1,3-butanediol 1-monooctanoate (50%)	0.05	100	+	+	+					
			−	−	+					
			−	−	+					
		90	−	−	(+)?					
			−	−						
			−	−						
		80	−	−	(+)?	+				
			−	−		+				
			−	−		+				
	0.50	100	−	−	+	+	+			
			−	−	−	+	+			
			−	−	−	−	+			
		90	−	−	−	−	(+)?	+[b]		
			−	−	−	−		+		
			−	−	−	−		+		
		80	−	−	−	−	(+)?	+[b]		
			−	−	−	−		+		
			−	−	−	−		+		
	1.00	100	−	−	+	+	+		+	
			−	−	−	−	−		+[c]	
			−	−	−	−	−		+	
		90	−	−	−	−	−		(+)?	+
			−	−	−	−	−			+
			−	−	−	−	−			+
		80	−	−	−	−	−		−	−
			−	−	−	−	−		−	−
			−	−	−	−	−		−	(+)

[a] For explanation of symbols see footnotes to Table IV. [b] Growth definite on day 18. [c] Growth definite on day 22.

vehicle for preliminary testing of 1,3-heptanediol as a grain preservative. The test compound was added to the diet in undiluted form at levels of 0.5, 0.75, and 1.00 wt %. After 72 hr storage at 100% relative humidity, the treated samples showed evidence of slight mold growth at the 0.5% level, questionable to no growth at 0.75%, and no evidence of mold growth at 1.0%. Untreated control groups were heavily overgrown with molds in the same time period.

Preliminary Tests with Raw Grain. The best compounds from the antifungal screening tests were evaluated as preservatives for various raw grains. Results are shown in Tables II and III. The best results over untreated controls were obtained with whole wheat grains while cracked corn and soy were somewhat more difficult to preserve. The synergistic effects of a combination of a diol and ester were not observed. This is brought out most strongly in the case of 100% humidity (Table III). The 1,3-heptane-

Table VI. Preservation of Wheat with 1,3-Nonanediol (50%) plus 1,3-Butanediol 1-Monooctanoate (50%)[a]

Additive	Concn, %	Rel humidity, %	Mold growth at days after storage						
			2	4	8	12	16	20	30
None		100	+	+					
			+	+					
			+	+					
		90	−	+					
			−	+					
			−	+					
		80	−	+					
			−	+					
			−	+					
Ethanol	1.00	100	−	+	+				
			−	−	+				
			−	−	+				
		90	−	−	+	+			
			−	−	−	+			
			−	−	−	+			
		80	−	−	(+ + +)?				
			−	−					
			−	−					
1,3-Nonanediol + 1,3-butanediol 1-monooctanoate	0.05	100	−	−	+				
			−	−	+				
			−	−	+				
		90	−	−	−	+			
			−	−	−	+			
			−	−	−	−			
		80	−	−	−	+			
			−	−	−	+			
			−	−	−	+			
	0.50	100	−	−	+	+	+	+	
			−	−	−	−	+	+[b]	
			−	−	−	−	−	+	
		90	−	−	−	−	+	+	
			−	−	−	−	−	+[b]	
			−	−	−	−	−	+	
		80	−	−	−	−	−	+	
			−	−	−	−	−	+	
			−	−	−	−	−	+	
	1.00	100	−	−	(+)?	(+)?	+	+	(+ + +)?
			−	−	−	−	−	−	
			−	−	−	−	−	−	
		90	−	−	−	−	−	−	−
			−	−	−	−	−	−	−
			−	−	−	−	−	−	−
		80	−	−	−	−	−	−	−
			−	−	−	−	−	−	−
			−	−	−	−	−	−	−

[a] For explanation of symbols see footnotes to Table IV. [b] Growth definite on day 18.

diol was more effective than the mixture at the same level of addition. The method of addition, undiluted, in solution or as an emulsion, had no significant influence on the efficacy of the preservatives in these preliminary tests. However, in certain trials spotty mold growth was observed after a few days when material was added undiluted indicating incomplete coverage of the grains. In the high (100%) humidity trial, propionic acid was included as a control. The propionic acid was somewhat more effective than the diol–ester combination but not quite so effective as 1,3-heptanediol. The acid treated grains were discolored and had an offensive odor not noticed with the diols or esters.

An interesting observation, which remains to be confirmed, was the effect of the new preservatives on grain weevils. In these preliminary experiments, a number of

Table VII. Effects of Various Levels of 1,3-Nonanediol (50%) plus 1,3-Butanediol 1-Monooctanoate (50%) on Individual Mold Species in Different Grains[a,b]

Grain	Rel humidity, %	Additive, %	% of grains affected by[c]							
			Fusarium	*Alternaria*	*A. flavus*	*A. niger*	*A. glaucus*	*Penicillium*	*Rhizopus*	Some fungi[d]
Wheat	100	None	44	2	60	70	2	70	0	100
		Ethanol (1%)	2	2	98	12	0	74	0	100
		0.05	10	0	96	22	4	50	6	100
		0.50	2	10	96	0	8	8	0	100
		1.00	0	10	22	2	0	0	0	32
	90	None	18	22	16	4	40	6	0	90
		Ethanol (1%)	0	0	14	0	84	2	0	90
		0.05	0	2	8	0	94	0	0	96
		0.50	0	4	28	0	0	0	0	24
		1.00	0	0	6	0	0	0	0	6
	80	None	38	4	32	6	18	6	4	94
		Ethanol (1%)	2	4	0	0	100	0	0	100
		0.05	0	0	10	2	96	2	0	100
		0.50	2	0	0	0	0	0	0	2
		1.00	0	4	2	0	0	0	0	4
Milo	100	None	52	36	0	0	0	36	0	100
		Ethanol (1%)	22	70	24	6	0	38	6	100
		0.05	14	70	42	0	0	46	24	100
		0.50	26	30	68	0	12	20	26	100
		1.00	32	14	26	0	0	2	48	88
	90	None	8	90	0	0	0	6	0	100
		Ethanol (1%)	2	60	78	2	8	4	0	100
		0.05	0	30	68	0	34	0	0	94
		0.50	0	4	46	0	14	0	0	64
		1.00	2	10	26	0	0	0	0	32
	80	None	18	98	0	0	0	0	0	100
		Ethanol (1%)	2	48	26	0	34	2	0	98
		0.05	6	18	18	0	52	8	0	90
		0.50	0	4	2	0	0	0	0	6
		1.00	0	2	4	0	0	0	0	6
Corn	100	None	96	N[e]	64	8	0	0	32	100
		Ethanol (1%)	88	N	40	72	0	0	28	100
		0.05	100	N	84	24	4	0	0	100
		0.50	36	N	88	0	4	0	32	100
		1.00	36	N	60	0	4	0	16	68
	90	None	88	N	68	28	8	0	8	100
		Ethanol (1%)	48	N	0	0	72	0	4	100
		0.05	36	N	0	0	100	0	0	100
		0.50	0	N	0	0	12	0	0	12
		1.00	4	N	0	0	0	0	0	8
	80	None	88	N	12	16	20	4	8	100
		Ethanol (1%)	60	N	4	0	68	4	4	100
		0.05	12	N	0	0	76	0	0	84
		0.50	4	N	0	0	4	0	0	12
		1.00	0	N	0	0	0	0	0	0

[a] Preservative added by method B (see footnotes to Table IV). [b] Molds identified microscopically (see Materials and Methods Section). [c] After 15 days storage. [d] Numbers in this column refer to percent of individual grains with some evidence of mold growth. [e] N = not observed.

the control samples had weevil larvae in evidence after several days of incubation. No larvae were observed in any of the samples treated with diols or esters.

Evaluation of Diol and Ester Mixture under Controlled Conditions. A 50:50 mixture of 1,3-nonanediol and 1,3-butanediol 1-monooctanoate was used in these tests since, at that time, this mixture was thought to be synergistic. The results of the first series of tests, at various relative humidities, are shown in Tables IV-VI. Some protection is noted at all levels. Concentrations as low as 0.05% of the test compounds extended the storage time of corn to 12 days as compared to 4 for controls and 8 for ethanol treated samples (Table IV). Noteworthy protection was achieved with 1% of the test mixture where samples of corn were kept free of mold up to 30 days and wheat for even longer periods. Milo was somewhat more difficult to preserve but the efficacy of the preservative is obvious (Table V). The effects of the diol-ester mixture on individual fungi are summarized in Table VII. *A. flavus*, *A. glaucus*, and *Penicillium* were the most common types observed. At 80 and 90% humidities >90% of the grains treated with 1% of the additive had no viable fungi after 15 days and almost as good protection was noted with 0.5%.

Table VIII. Comparison of Mixture of 1,3-Nonanediol (50%) and 1,3-Butanediol 1-Monooctanoate (50%) with Propionic Acid as Preservatives for Moist Grain[a,b]

% on moist corn	Days to heavy mold infestation	
	Diol–ester mixture	Propionic acid
0	2–4	2–4
0.05	8–14	6–8
0.50	14–22	24–>38
1.00	18–>38	>38

[a] Initial moisture content, 25%; storage conditions 80, 90, and 100% relative humidity; range of values reflects these differences. [b] Summary data for diol-ester mixture contains results of tests with milo and wheat as well as corn. Data for propionic acid are for corn alone.

Comparison of Diol-Ester Mixture with Propionic Acid. Other tests similar to those shown in Tables IV-VI were carried out with propionic acid as the positive control. The results are summarized in Table VIII. In these tests the diol-ester combination was approximately as effective as propionic acid except at the lowest level where it was slightly better. None of the other new preservatives were employed in these trials.

In most of the experiments summarized above some difficulty was encountered in properly dispersing the test compounds. This led to spotty mold growth and, consequently, lower preservative scores.

The mode of action of the new preservatives is, as yet, unknown. It would be particularly interesting to determine the effect of 1,3-diols and their esters on the biosynthesis and in situ production of mycotoxins by the infecting molds. Methods for accomplishing this are being explored.

CONCLUSIONS

This work suggests that certain 1,3-diols and their monoesters could be valuable as safe, noncorrosive grain preservatives. The chain length of the diol has an effect on the preservative action; the best compounds are those with carbon numbers of 7-9. Among the esters, the most effective compounds seem to be those whose total carbon content, diol plus acid, is in the range of C_{10} to C_{15}. The best preservatives for grain would seem to be the 1,3-diols used by themselves. A major difficulty in using these new additives lies in achieving uniform application. Once this is overcome, these materials should prove useful new preservatives for raw grain and feeds.

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