two urea-water-formamide solutions is shown in Table II. The salting-out temperature of a solution containing 34.6% nitrogen was lowered from 67° to 32° F. at the eutectic (18% ammonium nitrate). The eutectic of a 35.0% nitrogen solution (40° F.) was reached by adding about 21% by weight of ammonium nitrate.

In corrosion tests with solutions containing formamide, specimens of mild steel (A.S.T.M. designation A-285) and aluminum alloy (A.S.A. designation 1100-H14) were moved constantly for 28 days in 750 ml. of liquid held at 120° F. in thermal block equipment. Compositions of the solutions are shown in Table III. Corrosion rate in all the tests was less than 1 mil per year. Some loss of ammonia from the solutions was indicated by a lowering of pH during the tests—about 3 pH units for straight formamide and 1 unit for the other liquids. When the solutions were stored for 4 weeks at 120° F. in vented containers made of the same metals, however, the nitrogen contents, salting-out temperatures, and specific gravities remained essentially constant. Change of pH was significant only with the straight formamide. The liquids can be considered noncorrosive and stable in contact with steel and aluminum.

Low-Pressure Nitrogen Solutions

Large quantities of low-pressure nitrogen solutions are used for ammoniation of superphosphate and for direct subsurface application to the soil. Introduction of free ammonia into nitrogen solutions containing ammonium nitrate and urea increases their nitrogen content and lowers the cost per unit of nitrogen.

Formamide was substituted for water in solutions of this type to yield products containing 40 to 45% nitrogen and having vapor pressures below 25 p.s.i.g. at 104° F. Salting-out temperatures of the solutions containing formamide generally were well above those of the corresponding commercial products containing water, however, and this use of formamide was concluded to be impractical.

Liquid Mixed Fertilizers

A factor contributing to low concentration of liquid mixed fertilizers is the low solubility of potassium nitrate. Potassium nitrate, the least soluble salt encountered in liquid fertilizers made from conventional materials, may be formed by reaction of materials in the formulation, commonly urea–ammonium nitrate solution and potassium chloride (*6*).

In tests of formamide as a means for lowering the salting-out temperature of potassium-containing liquid fertilizers, potassium chloride, formamide, and water were mixed with ammoniated superphosphoric acid (11–37–0 solution) (*4*). Urea and ammonium nitrate were sources of additional nitrogen in some of the tests. The mixtures, Table IV, covered most of the nutrient ratios found in commercial fertilizers.

Salting-out temperatures of the formamide mixtures generally were considerably below those of commercial solutions of the same grade with urea–ammonium nitrate solution as the source of supplemental nitrogen. An exception was 10–10–10, for which formamide gave no advantage. The new mixtures containing small amounts of urea and ammonium nitrate along with formamide had even lower salting-out temperatures—a point that was not investigated thoroughly.

Economic Considerations

Although formamide can be used to advantage in liquid fertilizers containing no free ammonia, its cost at its present level of consumption is too high. Production on a much larger scale might bring its cost to a level acceptable for a major component of fertilizers. Also, lower costs may be found in new methods of synthesis. These possibilities are being explored.

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QUATERNARY AMMONIUM COMPOUNDS

Derivatives of (+)-Limonene: Quaternary Ammonium Compounds That Retard Plant Growth

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Ten new quaternary ammonium derivatives synthesized from (+)-limonene have a high order of growth-retarding activity on young bean seedlings. The chemistry and structure-activity relationships of these compounds are discussed. Thirty-four other miscellaneous limonene derivatives had little or no such activity.

Wirwillie and Mitchell (*9, 14*) first reported that certain quaternary ammonium compounds reduced stem elongation of bean plants without gall formation or other formative changes. The most active compound was a quaternary ammonium carbamate, designated Amo-1618, prepared from the expensive terpene thymol by R. L. Shriner. The most critical part of the molecule was found to be the terpene moiety. This is illustrated by the work of Cathey (*3*) with carvadan, a position isomer of Amo-1618 made from carvacrol, which was a growth retardant on poinsettias whereas Amo-1618 was not. Krewson *et al.* (*7*) studied the synthesis of Amo-1618 and prepared eight additional new, related compounds which were potent growth retardants.

The broad variation in effect of quaternary ammonium compounds on plants is illustrated by the fact that some compounds are so phytotoxic that they have been considered as herbicides (*4*, *10*). In contrast to this, Marth, Preston, and Mitchell (*8*) screened 80 quaternary ammonium derivatives and found only seven which induced relatively marked inhibition of stem elongation. Four of these seven compounds were approximately as effective as Amo-1618.

Portions of previous papers have dealt with the synthesis of a number of new amino alcohols (*11*) and a quaternary ammonium compound (*12*) from the inexpensive citrus terpene (+)-limonene. These were prepared in connection with a study of limonene derivatives having possible physiological activity. Certain structural features of these compounds were considered sufficiently similar to those of Amo-1618 to warrant testing them for plant growth-retarding activity.

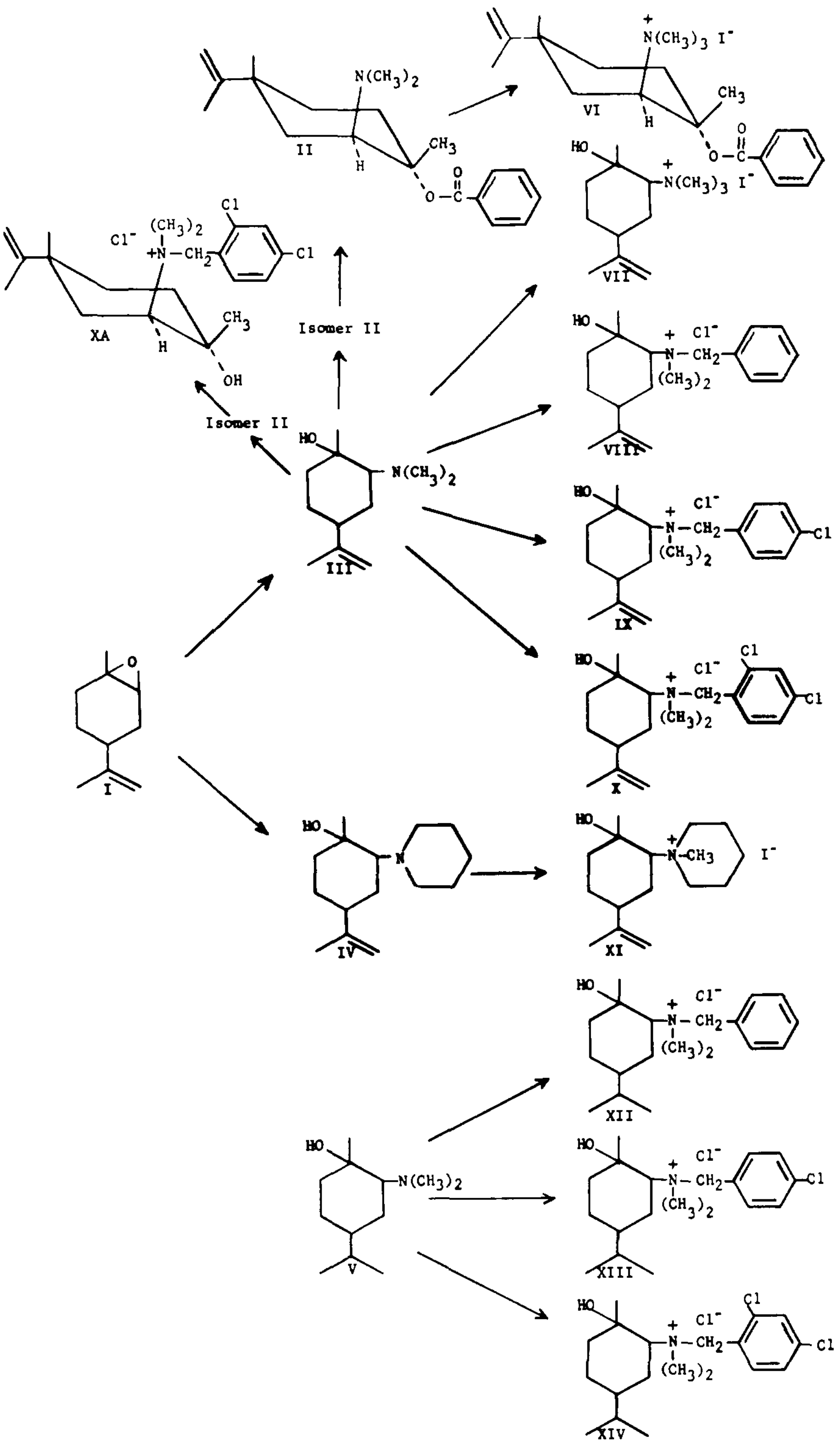

Figure 1. Synthetic route to the 10 quaternary ammonium compounds used in this study

Experimental

The structural formulas and preparation of the active growth retardants used in this study are outlined in Figure 1. Each of the 11 structures, except I, drawn as planar cyclohexane rings represents a mixture of the possible trans isomers with respect to the hydroxyl and nitrogen substituents. The obtaining of mixed, isomeric products is inherent in this reaction scheme, in that limonene oxide (I), the precursor of III, and *p*-menthane oxide, the precursor of V, are equal mixtures of two isomers. The preparation of the quaternary ammonium precursors (III and V) as well as the separation of their isomers has been discussed in previous publications (*11*, *12*). The three compounds (XA, II, and VI, Figure 1) drawn as chair forms of cyclohexane are single derivatives of known stereochemistry. Each is derived from isomer II of compound III which has been shown to have the *trans*-1,2-*cis*-1,4 configuration in which both the hydroxyl and nitrogen substituents are axial (*12*).

Since the procedures for preparing the 10 quaternary ammonium compounds (Figure 1) were similar and involved only slight changes in reaction conditions in some cases, these are summarized in Table I. Yields of the 2,4-dichlorobenzyl derivatives were consistently low because of the steric effect of the *o*-chloro substituent. The preparations of II and IV have not been described previously and are presented in detail.

Preparation of *trans*-2-Dimethylamino-$\Delta^{8(9)}$-*p*-menthen-1-ol Benzoate (II). A solution of 30 grams (0.15 mole) of 2-dimethylamino-$\Delta^{8(9)}$-*p*-menthen-1-ol (isomer II) (*12*) in 150 ml. of dry acetone was stirred and maintained at 0° C. during the dropwise addition of a solution of 25 ml. (0.22 mole) of benzoyl chloride in 30 ml. of dry acetone. Stirring was maintained at 0° C. for 15 minutes after the addition was completed. A heavy precipitate of amine hydrochloride formed. The mixture was allowed to warm slowly to room temperature over a period of 30 minutes and was then warmed at 40° to 50° for an additional 30 minutes. The clear solution was poured into excess aqueous sodium bicarbonate solution and stirred for 15 to 20 minutes to decompose excess benzoyl chloride. The product was isolated by extraction four times with ethyl ether. The combined ether extracts were washed two times with water and dried over anhydrous sodium sulfate and the ether was removed under reduced pressure. This procedure afforded 41.3 grams of almost colorless, oily benzoate (II). This crude product was dissolved in methanol and excess solid picric acid added. Yellow prisms separated from the solution on cooling (51.2 grams, m.p. 127–33°, 64% yield). Recrystallization from methanol gave 47.8 grams (m.p. 132–34°).

Table I. Preparation of Quaternary Ammonium Compounds[a]

	Compound	Reaction Time, Hours	Yield, %	Nitrogen,[b] %	
				Calcd.	Found
VI	*trans-p*-Menth-8-en-1-ol-benzoate, 2-dimethylamino-, methiodide	4	70	3.16	3.11
VII	Mixed *trans-p*-menth-8-en-1-ol,2-dimethylamino-, methiodides	4	98	4.13	3.71
VIII	Mixed *trans-p*-menth-8-en-1-ol,2-dimethylamino-, benzyl chlorides	70	77	4.33	4.35
IX	Mixed *trans-p*-menth-8-en-1-ol,2-dimethylamino-, *p*-chlorobenzyl chlorides	70	81	3.91	3.95
X	Mixed *trans-p*-menth-8-en-1-ol,2-dimethylamino-2,4-dichlorobenzyl chlorides	70	44	3.57	3.73
XA	*trans-p*-Menth-8-en-1-ol,2-dimethylamino-2,4-dichlorobenzyl chloride	120	20	3.57	3.70
XI	Mixed *trans-p*-menth-8-en-1-ol,2-piperidyl methiodides	70	83	3.69	3.00
XII	Mixed *trans*-1-*p*-menthanol,2-dimethylamino-, benzyl chlorides	70	81	4.29	3.91
XIII	Mixed *trans*-1-*p*-menthanol,2-dimethylamino-, *p*-chlorobenzyl chlorides	70	86	3.88	3.32
XIV	Mixed *trans*-1-*p*-menthanol,2-dimethylamino-, 2,4-dichlorobenzyl chlorides	70	35	3.55	3.33

[a] Each quaternary ammonium compound was prepared by heating 10 grams of the appropriate amino alcohol and 20 ml. of the required alkyl halide in methyl ethyl ketone. After refluxing, the solutions were concentrated at reduced pressure, the residues dissolved in water and the aqueous solutions washed five times with ethyl ether. Concentration of the neutral, aqueous phases to dryness afforded the quaternary compounds.

[b] Nitrogen analyses were made using a semimicro-Kjeldahl-Gunning procedure. This was necessary because most compounds were amorphous, hygroscopic glasses which were difficult to purify, dry, and weigh.

Analysis. Calculated for $C_{25}H_{30}N_4O_9$: C, 56.60; H, 5.70; N, 10.56. Found: C, 56.63; H, 5.67; N, 10.47.

The free base (II) regenerated from the picrate by treatment with excess aqueous sodium hydroxide followed by ether extraction was a colorless oil having the following physical constants: d^{25} 1.0320, n_D^{25} 1.5236, $[\alpha]_D^{25}$ + 75.7.

Preparation of *trans*-2-Piperidyl-$\Delta^{8(9)}$-*p*-menthen-1-ols(IV). This reaction required an extended period of heating because of the steric requirements of the large piperidyl group.

Two sealed tubes were prepared, each containing 18 grams (0.12 mole) of limonene-1,2-epoxide (I) and 25 ml. (0.25 mole) of piperidine. The tubes were heated at 145° for 5 days. After cooling, the contents were combined and concentrated on a film evaporator at 70° to remove excess piperidine. The dark viscous liquid product was vacuum-distilled. At 124–27°/0.55 mm., 20.5 grams (73%) of colorless product (IV) distilled as a medium viscous liquid, n_D^{25} 1.5021, $[\alpha]_D^{25}$ + 2.52.

Analysis. Calculated for $C_{15}H_{27}NO$: C, 75.89; H, 11.47; N, 5.90. Found: 75.29; H, 11.05; N, 5.96.

Infrared absorption curves were obtained using thin films of the amorphous quaternary ammonium compounds (Table I) prepared, in each case, by evaporating a few drops of a dilute methanol solution directly on a sodium chloride window. These spectra were consistent with the assigned structures (Figure 1). All derivatives exhibited strong absorption at 2.96 microns (OH) and 3.37 microns (C—H). The unsaturated compounds had a sharp peak of medium intensity at 6.08 microns and a strong broad peak at 11.2 to 11.3 microns, both of which were absent from the saturated derivatives.

Method of Application of Chemicals to Bean Plants

One per cent concentrations of the test compounds were prepared in lanolin containing 2.5% Tween-80 as the emulsifying agent. This is the formulation used by Krewson *et al.* (7), except that Tween-20 was used as the emulsifier by these authors. The same method of application of the lanolin mixtures below the second node of young bean plants of the Black Valentine variety was also used. Treated plants were grown under greenhouse conditions for 7 to 9 days and measurements of the second internode and the fresh weights of the terminal growth above the second node were compared with comparable data from control plants. Results were expressed as per cent activity—i.e., average per cent reduction (−) or per cent increase (+) in growth or weight of growth as compared to the controls.

In the preliminary screening, three bean plants were treated with each compound. Active growth retardants were then screened more extensively (Table II).

Results and Discussion

During preliminary screening of (+)-limonene derivatives, considerable differences in growth were observed between untreated control plants and controls treated with Tween-lanolin mixtures. Therefore, one experiment was conducted to determine the growth-retarding effects of various Tweens *per se*. This effect varied inversely with the Tween number—i.e., Tween-20 caused a 45% reduction of internode growth and Tween-85 caused only 3% reduction. Tween-80 was chosen for all further testing because it showed the least effect on both length of internode and weight of terminal growth. However, a test of three compounds applied to beans in Tween-80–lanolin or Tween-20–lanolin mixtures gave identical per cent growth retardation compared to their respective controls. Application of all active compounds without an emulsifying agent reduced effectiveness by approximately one third.

A total of 44 derivatives of (+)-limonene were tested. Ten quaternary ammonium compounds, prepared by quaternization of the tertiary nitrogens of II, III, IV, and V (Figure 1) strongly retarded the growth of young bean plants. Six exhibited typical growth-retardant activity and caused plants to grow short and sturdy with intense green foliar coloration. The results of four growth tests using these compounds and their precursors are summarized in Table II. The dates of beginning and termination are listed for each experiment because daylight hours and temperatures were constantly increasing. The potent growth retardant, N-dimethylaminosuccinamic acid (B995), was included in all experiments as a reference standard.

There was a great increase in activity on introduction of the onium pole, characteristic of quaternary nitrogen, in both III and V (Table II). Compounds VI, VII, and XI caused injury and/or death of the apical bud in many cases. This was probably a function of concentration of compound and may be related to the fact that these are the only quaternary iodides included in this study. A similar difference in toxicity between Amo-1618, a chloride, and Amo-1619, the corresponding iodide, has been reported (7). Compound XII caused abscission in all seven plants with no visible injury in experiment 1. However, this effect was observed again only in the case of two plants in experiment 3. The fact that several compounds gave slightly different results in experiment 2 was thought to be due to a sudden change in light intensity in the greenhouse. It was necessary to apply shade paint to the greenhouse during the course of the experiment, causing all plants to become etiolated. However, the compounds tested had virtually the same order of growth-retardant activity in all four experiments.

Some structure-activity trends can be observed among the 10 active quaternary ammonium derivatives. However, at the concentrations used, the differences in activity were small, making such correlations speculative at best. The saturated compounds (XII, XIII, and XIV)

Table II. Results of Screening Tests on Quaternary Ammonium Compounds and Their Precursors[a]

	Activity, %							
	Expt. 1 (3/22–3/29)		*Expt. 2 (3/26–4/2)*		*Expt. 3 (4/12–4/20)*		*Expt. 4 (4/29–5/6)*	
Compound	*Second internode length*	*Terminal growth wt.*	*Second internode length*	*Terminal growth wt.*	*Second internode length*	*Terminal growth wt.*	*Second internode length*	*Terminal growth wt.*
I	−17	−17	+1	−17	−3	−1		
III	−14	−25	−3	−10	−17	−15		
V	−11	−14	+5	+5	−14	−10		
VI	Death of apical bud		−53	−52	−63 (injury)	−49		
VII	Death of apical bud		−19	−36	Death of apical bud			
VIII	−78	−73	−65	−57	−81	−72		
IX	−86	−82	−78	−74	−74	−50		
X	−92	−81	−85	−69	−85	−75	−68	−53
XA							−77	−69
XI	Death of apical bud		−71 (injury)	−60	Death of apical bud			
XII	Abscission		−93	−93	−90	(2 abscissions)		
XIII	−92	−87	−78	−69	−89	−82		
XIV	−94	−87	−87	−74	−89	−85	−72	−60
B995	−94	−79	−88	−79	−90	−78	−84	−64

[a] Results calculated from mean of seven plants in experiments 1, 2, and 3 and from mean of eight plants in experiment 4.

Table III. Growth-Regulant Activity of Miscellaneous (+)-Limonene Derivatives[a]

Compounds	*Activity, % (Second Internode Length)*
Dilimonene	+1
Limonene-1,2-epoxide	−28
Limonene dioxide	−5
trans-*p*-Menthane-1,2-diol	+26
trans-*p*-Menthane-1,2-dipropionate	+17
trans-*p*-Menthane-1,2-dibutyrate	−1
β-Dihydroterpineol	+11
β-Dihydroterpineol acetate	−9
β-Dihydroterpineol propionate	−7
Tetrahydrocarvone	−7
Tetrahydrocarvone semicarbazone	+20
1-Hydroxy-2-keto-*p*-menthane	+5
1-Hydroxy-2-keto-*p*-menthane oxime	−15
3-Isopropyl-cyclopentyl methyl ketone	+12
3-Isopropyl-cyclopentyl methyl ketone semicarbazone	+36
trans-1-Hydroxy-*p*-menthane-2-carbamonitrile	−4
1-(*trans*-1-Hydroxy-*p*-menth-2-yl)-2-thiourea	−27
trans-1-Hydroxy-*p*-menthane-2-isothiocyanate	−23
cis-2-Amino-1-*p*-menthanol	+4
cis-2-Amino-5-isopropyl-7a-methyl-3a,4,5,6,7,7a-hexahydrobenzoxazole	−18
trans-2-Amino-$\Delta^{8(9)}$-*p*-menthen-1-ols	+35
trans-2-Methylamino-$\Delta^{8(9)}$-*p*-menthen-1-ols	−4
trans-2-Dimethylamino-$\Delta^{8(9)}$-*p*-menthen-1-ols (III, Figure 1)	−16
trans-2-Piperidyl-$\Delta^{8(9)}$-*p*-menthen-1-ols (IV, Figure 1)	0
trans-2-Amino-1-*p*-menthanols	−16
trans-2-Methylamino-1-*p*-menthanols	+32
trans-2-Dimethylamino-1-*p*-menthanols (V, Figure 1)	+80
trans-2-Piperidyl-1-*p*-menthanols	−50
trans-1-Dimethylamino-$\Delta^{8(9)}$-*p*-menthen-2-ol	−7
trans-2-Dimethylamino-$\Delta^{8(9)}$-*p*-menthen-1-ol benzoate (II, Figure 1)	−13
**trans*-2-Dimethylamino-$\Delta^{8(9)}$-*p*-menthen-1-ol-*o*-methoxybenzoate (colorless, viscous liquid, n_D^{25} 1.5289, d^{25} 1.0618, picrate m.p. 167–69° C.)	+18
**trans*-2-Dimethylamino-$\Delta^{8(9)}$-*p*-menthen-1-ol hydrochloride (colorless needles, slightly hygroscopic, m.p. 153–54° C.)	−30
**trans*-2-Dimethylamino-$\Delta^{8(9)}$-*p*-menthen-1-ol acetate-hydrochloride (colorless needles, very hygroscopic, m.p. 154–55.5° C.)	−24
**trans*-2-Dimethylamino-$\Delta^{8(9)}$-*p*-menthen-1-ol benzoate-hydrochloride (colorless needles, m.p. 183–84° C.)	−26

[a] Prepared in this laboratory in connection with a continuing study of (+)-limonene derivatives. The four compounds marked with an asterisk are new derivatives of isomer II from compound III, Figure 1, not previously reported in the chemical literature. Therefore physical properties are included.

appeared to have slightly more activity than their unsaturated analogs (VIII, IX, and X). Among the saturated benzyl compounds, the addition of successive chlorine atoms to the molecule had very little effect on activity. In each series, the benzyl derivatives without chlorine were highly active. Some increase in activity with successive additions of chlorine atoms was evident, however, in the unsaturated group (VIII, IX, and X). Quaternary compounds (X, XIII, and XIV) showed virtually the same activity on beans as B995. In one test, the single, trans, diaxial isomer (XA) proved to be as highly active as the mixed trans isomers (X). This indicated that the activity of the mixed trans isomers was not due to a synergistic effect.

The remaining 34 limonene derivatives tested did not show sufficient growth-retarding activity compared to the 10 quaternary ammonium compounds (Table II) to warrant further investigation. The results of the preliminary screening tests of these compounds are summarized in Table III. Several compounds did cause a slight retardation of growth, whereas others appeared to accelerate growth. This latter effect may have some significance but has not been investigated further.

Although the active compounds reported herein have some chemical similarity to other terpene quaternary ammonium derivatives previously reported as growth retardants (*7*), they do not possess the structural features found by these authors to be essential for such activity. These features include: an aromatic terpene ring; a dichlorobenzyl group; two nitrogen atoms to the molecule, one as a quaternary and the other as a carbamate nitrogen.

The structural similarities of the quaternary ammonium compounds to certain inhibitors of animal cholinesterases (*5*) have suggested that dwarf plants may be produced as a result of abnormal choline metabolism (*2*). An enzyme related to acetylcholinesterase has been discovered in plants (*1*, *6*). It has been named acetylesterase because it hydrolyzes many acetic and propionic acid esters as well as acetylcholine. Compounds II, III, V, and VI (Figure 1) have been found to be inhibitors of pseudocholinesterase, which hydrolyzes a number of esters including acetylcholine and is found in blood serum (*13*). Whether this enzyme inhibition is in any way associated with growth-regulant activity is not known.

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PHOSPHORIC ACID IMPURITIES

Precipitated Impurities in Wet-Process Phosphoric Acid

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The sludges in raw wet-process phosphoric acid consist mostly of calcium sulfate and sodium fluosilicate; those in merchant-grade acid are mostly $(Fe, Al)_3KH_{14}(PO_4)_8 \cdot 4\ H_2O$, whose precipitation depends upon the amount of potassium dissolved during the manufacture of the acid; and those in superphosphoric acid are mostly iron and aluminum tripolyphosphates and metaphosphates. Addition of potassium salts to merchant-grade acid precipitates iron and, to a smaller extent, aluminum, but removal of the precipitate entails considerable loss of phosphate. The optical properties and x-ray patterns of the sludge components are presented.

The sludges that precipitate in wet-process acid are composed of crystalline salts of the impurities that dissolve when phosphate rock is treated with sulfuric acid. Iron, aluminum, potassium, fluorine, and silica were the most important constituents of sludges recovered from acids from various sources. In addition to calcium sulfate, the principal constituents of these sludges were complex iron and aluminum phosphates, some of which contain potassium as an essential constituent, and sodium fluosilicate. The filtration and sedimentation characteristics of the sludges are governed by the rate of crystal growth of the principal sludge phase rather than by the chemical nature of the precipitating solids.

Solubilities in the aqueous systems of orthophosphoric acid and aluminum (*5*), ferric (*2, 7, 11*), and ferrous iron (*8*) are reported, and several iron and aluminum polyphosphates have been described (*24*). Some of the compounds described in these studies occur as components of sludges, but their characterizations were incomplete.

Precipitates from three concentrations of acid were examined: raw wet-process phosphoric acid, 12 to 14% P (28 to 32% P_2O_5); merchant-grade acid, 22 to 24% P (50 to 54% P_2O_5); and superphosphoric acid, 31% P (70% P_2O_5). The acids were obtained from several commercial and experimental sources and the details of their production usually were not available. Many of the acids received for examination had been partially clarified, so that the relations between the amounts of the residual sludges and the total amounts formed in production of the acids are not known, but the precipitated compounds were generally the same in all acids.

The precipitates were examined petrographically and by x-ray. Many of the compounds were new, and, when possible, these were synthesized in crystal form suitable for determination of their chemical composition (Table I), optical properties (Table II), and x-ray diffraction patterns (Table III). In the chemical analyses, iron was determined by titration with dichromate (*12*), aluminum colorimetrically with 8-quinolinol (*18*), potassium by atomic absorption spectrophotometry (*1*), phosphorus gravimetrically with quinolinium (*17*), magnesium (*9*) and zinc (*6*) by EDTA titration, silicon gravimetrically with quinolinium (*4*), fluorine by distillation and titration (*22*), and sulfur gravimetrically as barium sulfate (*13*). Total water (of constitution and hydration) was determined by difference, and condensed phosphates were detected by infrared spectroscopy and determined quantitatively by ascending paper chromatography (*23*).

Raw Wet-Process Acid

The precipitates in raw wet-process phosphoric acid (12 to 14% P, 28 to 32% P_2O_5) are largely sodium fluosilicate (usually with minor substitution of potassium for sodium) and calcium sulfate (anhydrous, hemihydrated, and dihydrated), with small amounts of calcium fluoride.

The compound with the empirical formula $Ca_4SO_4SiF_6AlF_6OH.12H_2O$ was detected in several raw acids, but never in merchant-grade acid. This compound, described in a patent on the clarification of phosphoric acid (*14*), is an isometric salt with an octahedral habit and a refractive index that make it indistinguishable from calcium fluoride, but it may be identified by x-ray or microchemical tests.

Merchant-Grade Acid

The solid phases in the sludges in most of the commercial merchant-grade acids (22 to 24% P, 50 to 54% P_2O_5) are mainly acidic iron and aluminum orthophosphates that contain potassium. Of these, the major portion is a mixture of members of the isomorphous series $(Fe,Al)_3KH_{14}(PO_4)_8.4H_2O$. Secondary phases are calcium sulfate, calcium fluoride, and mixed crystals of sodium and potassium fluosilicates. These secondary phases usually constitute a small fraction of the sludge; their amounts vary with the fluorine content and history of the acid—precipitation of the secondary phases usually accelerates after most of the iron and aluminum has precipitated.