

$N_w = 1.476$; the crystals are uniaxial (—).

Long-Chain Ammonium Polyphosphate. The preparations of the long-chain ammonium polyphosphate showed consistent optical properties, x-ray diffraction pattern, and chemical composition—that of $(\text{NH}_4)_{n+2}\text{P}_n\text{O}_{3n+1}$, approaching $(\text{NH}_4\text{FO}_3)_x$. It crystallized as microscopic stubby rods that were rectangular prismatic and showed parallel extinction; $N_\alpha = 1.485$ (elongation axis), $N_\gamma = 1.500$. The symmetry appears to be orthorhombic or higher, in accordance with its relatively simple x-ray diffraction pattern. Crystals large enough for detailed optical examination or for single-crystal x-ray study have not been prepared, but study of the material is being continued.

This ammonium polyphosphate

showed no close similarity to Maddrell's or Kurrol's salts in optical properties or x-ray diffraction pattern; the features of its infrared absorption spectrum were similar to those of the form IV Kurrol salts and unlike those of the cyclic alkali metal metaphosphates. The infrared spectrum contained no evidence of the presence of any -P-N-P- linkages. The salt has the desirable fertilizer property of being a slowly soluble, single source of both nitrogen and phosphorus.

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PHOSPHORUS AVAILABILITY

Correlations among Soil Phosphorus Fractions, Extractable Phosphorus, and Plant Content of Phosphorus

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Greenhouse and laboratory studies were conducted to determine relationships among soil phosphorus fractions, soil test methods, and millet growth and phosphorus content on three New Jersey soils, obtained from field plots previously adjusted to three levels each of phosphorus and potassium. Aluminum and iron phosphates were the predominant forms of active phosphorus in these soils. Previously applied phosphate fertilizer was found to have been fixed mostly as aluminum phosphate in the three soils. The phosphorus content of millet tops was chiefly correlated with the aluminum phosphate fraction of the three soils studied. Different soil test methods for phosphorus differed in their degree of correlation with this aluminum phosphate fraction.

ELECTRODIALYSIS is currently employed by the Soil Testing Laboratory in New Jersey for extracting soil phosphorus. In general, the phosphorus released by electro dialysis of New Jersey soils correlated with crop response (17, 18). The correlation of phosphorus and certain soils and crops has, however, been poor, and the reason for this lack of correlation needs investigation.

Three of the more active forms of phosphorus in soils are the aluminum, iron, and calcium phosphate fractions (6, 22). Some greenhouse experiments have indicated that a substantial proportion of the phosphorus required by plants can be supplied by pure iron and aluminum phosphates (31, 33), but in other experiments these phosphates have been shown to be relatively poor sources of phosphorus for plants (10, 28).

Various phosphorus extraction methods

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employed in soil testing laboratories remove and measure differing proportions of these phosphate forms (3, 7). Harper (20), Dean (17), and more recently Hanna (17) indicated that electro dialysis removed more phosphorus from calcium, magnesium, and manganese phosphates than from aluminum and iron phosphates. Cho and Caldwell (9) reported that the phosphorus extracted from soils by a 0.025*N* HCl + 0.003*N* NH₄F solution and a 0.1*N* HCl + 0.03*N* NH₄F solution as described by Bray and Kurtz (4), a 1% solution of citric acid, and a 0.5*M* sodium bicarbonate solution was highly correlated with aluminum and iron phosphates in soils. Cho and Caldwell also found that phosphorus extracted from soils by 10% sodium acetate in 3.0% acetic acid solution was well correlated with calcium phosphate. Chang and Juo (8) showed that the extent of correlation between the amounts of phosphorus extracted by several chemical methods and the total

amount of each discrete form of phosphate depends on the dominant form of soil phosphorus. Susuki, Lawton, and Doll (30) found that aluminum phosphate in soils was significantly correlated with a number of soil tests for phosphorus, while calcium phosphate and organic phosphorus were not related to any of the soil tests. Pratt and Garber (26) found that phosphorus extracted from soils by the 0.025*N* HCl + 0.03*N* NH₄F solution of Bray and Kurtz (4) was positively correlated with NH₄Cl-soluble and NH₄F-soluble phosphorus and negatively correlated with clay content.

The correlation of phosphorus extracted from soils by chemical procedures with crop yield and phosphorus content should depend in part on the relative amounts of each chemical form of phosphorus in the soil and on the relative availability of each form to extraction by the plant and by the chemical procedure used. Many factors other than chemical

form of soil phosphorus influence the amount of phosphorus absorbed from a soil by a plant. A few of these are climate, physical and chemical characteristics of the soil, nature of the plant, associated biological activity in the soil, plant and animal residues in the soil, and the physical and chemical properties of added fertilizers, if any.

Poor correlations between soil phosphorus levels and crop response might possibly be partially explained by differences among soils in the forms of soil phosphorus. The major objectives of this investigation, therefore, were to determine if the amounts of phosphorus released by electro dialysis and other soil test methods are correlated with the forms of phosphorus in certain soils, and if the lack of correlation between electro dialyzable phosphorus and growth and phosphorus content of millet on certain soils can be partially explained on the basis of the forms of phosphorus present in these soils.

Experimental Procedures

Greenhouse Experiment. A greenhouse experiment was carried out to obtain plant yield and phosphorus content data which could be correlated with soil phosphorus forms and phosphorus extracted by soil test methods.

Three soils from New Jersey, among which there is poor correlation between electro dialyzable phosphorus and plant response, were selected for study. Aura coarse sandy loam is a red-yellow podzolic soil on the coastal plains of southern New Jersey. Nixon loam is a red-yellow podzolic soil, situated near the boundary of the coastal plains and the Piedmont plateau. Dutchess slaty silt loam is a gray-brown podzolic soil

derived from shales and slates, located in the highlands of northern New Jersey.

Bulk samples of these soils were taken from the soil test correlation plots at Glassboro, New Brunswick, and Beersville, respectively. There was little variation in soil pH either between soils or between treatments within each soil. The fertility status of these plots had been adjusted by previous fertilization to low, medium, and high levels of phosphorus and potassium. No additional phosphorus or potassium was added to the soils, so that residual levels of these nutrients were used in the greenhouse experiment. Soil type was used as the third factor, Aura, Nixon, and Dutchess soils being classified as possessing, respectively, low, medium, and high phosphorus-fixing capacity. After sieving and air-drying, 6 pounds of soil were placed in asphalted cans and a uniform application of nitrogen (equivalent to approximately 100 pounds an acre) was given to the soil in each can. Soil samples were taken from each can as it was being filled, screened through a 2-mm. sieve, and stored for analysis.

A 3³ complete factorial randomized block design was used in the greenhouse, the treatments being replicated four times. Six plants of foxtail millet were grown per can, and the above-ground portions of the plants were harvested 57 days after sowing. The dry weight of millet tops per can and the content of phosphorus in the plant tops were used as indices of plant response.

Laboratory Determinations. Plant samples were digested with nitric and perchloric acids according to the method described by Toth *et al.* (32). Phosphorus was determined on a Lumetron colorimeter by the Denigès colorimetric method as modified by Truog and Meyer (34) and Bertramson (2). Potassium was determined on a Perkin-Elmer

flame photometer using lithium as an internal standard.

Aluminum phosphate, iron phosphate, and calcium phosphate were determined by the method of Chang and Jackson (7), using successive extractions with 0.5*N* NH₄F, 0.1*N* NaOH, and 0.5*N* H₂SO₄. The NH₄F reagent was adjusted to pH 8.3 as suggested by Fife (15). Total and organic phosphorus was determined according to the method of Mehta *et al.* (24).

Readily extractable phosphorus was determined by means of the following procedures.

A. Two and one-half grams of soil were shaken by hand for 1 minute with 25 ml. of a 0.025*N* HCl + 0.03*N* NH₄F solution (4, 12).

B. Five grams of soil were electro dialyzed for 20 minutes in 75 ml. of 0.05*M* boric acid (19).

C. Two grams of soil were shaken mechanically for 1 hour with 20 ml. of 0.083*M* 2-ketogluconic acid and filtered through Whatman No. 40 paper, and phosphorus in the extract was determined as in B. This acid has been shown to be produced by certain bacteria that are efficient dissolvers of phosphates (13).

D. Two grams of soil were shaken for 4 hours with 40 ml. of 0.1*N* ammonium lactate in 0.4*N* acetic acid (14).

E. Five grams of soil were shaken for 5 minutes with 20 ml. of 0.05*N* HCl + 0.025*N* H₂SO₄ (24).

Soil pH was determined on a Beckman pH meter (27).

Electro dialyzable potassium (19) was determined on a Technicon Auto-Analyzer with flame photometer.

Analysis of variance and correlation analyses were carried out on an IBM 1620 computer. Significant differences between means were calculated by the method of Tukey as presented by Steel and Torrie (29).

Table I. Dry Weight and Phosphorus Content of Millet Tops, Chemical Forms of Phosphorus, and Phosphorus Extracted by Various Methods from Three Soils

Level of P Fertilization	Av. Yields of Millet Tops ^a , G. Dry Wt./Pot	P Content of Millet Tops ^b , Mg. P/Pot	Phosphorus Forms in Soils					Phosphorus Extracted by Various Methods					
			Aluminum Phosphate	Iron Phosphate	Calcium Phosphate	Organic Phosphate	Inactive Inorganic P	Total P	Electro-dialysis	2-Ketogluconic Acid	Lactate-acetate	HCl + H ₂ SO ₄	HCl + NH ₄ F
P.P.M. P in Soil													
AURA SOIL													
Low	7.3	11.5	100	75	61	47	44	327	4.6	32.5	27.5	22.1	24.5
Medium	8.1	13.2	122	83	70	56	64	395	5.4	34.7	27.9	23.9	24.7
High	10.9	25.0	175	80	69	54	81	459	6.6	40.8	34.7	29.0	31.6
NIXON SOIL													
Low	8.8	15.2	74	145	56	116	204	595	1.3	6.3	6.5	5.1	7.4
Medium	12.1	18.3	96	158	56	127	165	602	1.6	9.2	9.0	6.8	9.6
High	14.1	24.1	156	184	70	125	190	725	3.0	14.5	14.1	10.3	14.5
DUTCHESS SOIL													
Low	4.7	7.8	147	258	63	268	225	951	0.2	1.7	3.0	2.1	6.6
Medium	10.6	14.5	244	302	71	288	228	1123	0.4	5.1	6.4	4.0	10.5
High	16.4	19.1	346	330	73	251	253	1253	0.7	10.3	11.0	7.2	14.8

^a In low, medium, and high K soils.

^b Average of low, medium, and high K treatments.

Results and Discussion

Plant Content of Phosphorus. The influence of soil levels of phosphorus on phosphorus content of foxtail millet tops is shown in Table I. There was more phosphorus in millet at the high phosphorus level of all soils than at either the low or medium levels. The millet tops grown on Dutchess soil also contained more phosphorus at the medium than at the low soil phosphorus level.

The data obtained from the greenhouse experiment appear satisfactory for use in correlating soil phosphorus forms and phosphorus extracted by soil test methods with plant response.

Soil Phosphorus Fractionation. Data for the effect of soil type and of phosphorus level of the aluminum, iron, and calcium phosphate fractions of the soils are presented in Table I.

Dutchess soil contained more iron and aluminum phosphates than either Aura or Nixon soil and more calcium phosphate than Nixon soil. Aura soil contained more aluminum and calcium phosphates and less iron phosphate than Nixon soil.

Iron and aluminum phosphates were the main forms of active inorganic phosphorus in Dutchess soil. The dominant form of phosphorus was aluminum phosphate in Aura soil and iron phosphate in Nixon soil. The higher proportion of aluminum phosphate in Aura than in the remaining soils is probably due to the higher proportion of gibbsite in the clay fraction of Aura (23). Haseman, Brown, and Whitt (27) reported that the decreasing order in which several minerals fixed phosphate was gibbsite, goethite, illite, kaolinite, and montmorillonite, the rate for gibbsite being much higher than for any of the others.

In all soils, the proportion of aluminum phosphate increased with increasing soil phosphorus level. The proportions of iron and calcium phosphated did not vary with the level of soil phosphorus in Nixon and Dutchess soils and decreased with increasing phosphorus level in Aura soil. The proportion of organic phosphorus remained constant at different phosphorus levels of Aura and Nixon soils and decreased with increasing phosphorus level in Dutchess soil. The relative amount of inactive inorganic phosphorus remained unchanged at different phosphorus levels of Aura and Dutchess soils, and decreased with increasing phosphorus levels of Nixon soil.

These results indicate that applied phosphate fertilizer is fixed chiefly in the form of aluminum phosphate. The literature apparently supports this conclusion (1, 16, 36). In long-term experiments, however, where no phosphorus had been added to the soil for several years, the proportion of iron phosphate

increased and often exceeded that of aluminum phosphate (5, 35).

Soil Test Methods. Four of the soil test methods—electrodialysis, 2-ketogluconic acid, lactate-acetate, and Mehlich's HCl-H₂SO₄—extracted more phosphorus from Aura than from Nixon or Dutchess soils. The fifth soil test method, Bray No. 1, differed from the others in that it extracted the greatest amount of phosphorus from Dutchess soil; it also, however, released more phosphorus from Aura than from Nixon soil.

When the amounts of phosphorus extracted from each soil type (Table I) are expressed as percentages of the total phosphorus in each soil, all soil test methods, including Bray No. 1, extracted a greater proportion of the total phosphorus from Aura than from either Nixon or Dutchess soils. Except for electro dialysis, which released a larger proportion of phosphorus from Nixon, the soil test methods appeared to release about the same fraction of the total phosphorus from Nixon as from Dutchess soil.

Investigations by Pratt and Garber (26) of the soil inorganic phosphorus fractions before and after extraction with Bray's and Olsen's reagents indicated that the reagents so reacted with soil minerals other than phosphates that high clay content decreased their efficiencies as phosphorus extractants. The high efficiency of all soil test methods in extracting phosphorus from the Aura soil may be due, therefore, to the low clay content and highly siliceous nature of this soil.

The complete reaction of the solvent with soil minerals cannot, however, account for the relatively small fraction of the total phosphorus removed by electro dialysis of Dutchess in comparison with Aura soil; this hypothesis is also inconsistent with the fact that the proportion of phosphorus removed by each soil test method increased with increasing phosphorus level within each soil. It is suggested, therefore, that the phosphorus removed from fertilized soils

by Chang and Jackson's procedure does not consist of discrete chemical compounds but of various types of aluminum, iron, and calcium phosphates which differ in their availability to phosphorus extractants and to plant uptake. Support for this suggestion is found in the investigations of Olsen and Watanabe (25), who concluded that surface phosphate attached to exchangeable iron, aluminum, and calcium ions of the clay and hydrous oxides includes the fraction of all phosphate compounds which will equilibrate with P³². Aluminum, iron, and calcium phosphate were regarded as containing a certain fraction of their phosphorus as readily available surface phosphate. From the studies of Dunbar and Baker (7) on the rate of P³² equilibration with soil phosphorus forms, it may be concluded that aluminum phosphate contained the greatest proportion of surface phosphate. Since aluminum phosphate represents a greater proportion of the total phosphorus in the Aura soil, it is possible that readily available surface phosphate represents a greater fraction of the soil phosphorus in the Aura than in the other soils. This would account for the relative ease with which phosphorus is released from the Aura soil by various soil test methods.

Soil Phosphorus Fractions and Plant Uptake of Phosphorus

Table II shows the coefficients for the multiple correlation, *R*, of phosphorus uptake by millet and various measures of soil phosphorus. Since potassium fertilization influenced plant response to soil phosphorus level, electro dialyzable potassium was included as a factor in the multiple regression. Both logarithmic and quadratic models were tested in the multiple regression. Since the quadratic fit was generally better for the data of all soils, *R* values for the quadratic model are given in this column. On the other hand, since the logarithmic model gave a better fit when multiple correlation coefficients were computed for the data

Table II. Coefficients of Multiple Correlation, *R*, of Phosphorus Content of Millet Tops and Various Measures of Soil Phosphorus

Measure of Soil Phosphorus	<i>R</i> Values			
	All soils	Aura	Nixon	Dutchess
Soil phosphorus fractions				
Al phosphate	0.32	0.88	0.75	0.83
Al + Fe phosphate	0.11 N.S. ^a	0.65	0.85	0.83
Al + Fe + Ca phosphate	0.11 N.S.	0.66	0.82	0.83
Inorganic phosphate	0.14 N.S.	0.75	0.61	0.78
Soil test methods				
Bray No. 1	0.47	0.89	0.84	0.83
Electrodialysis	0.62	0.74	0.80	0.73
2-Ketogluconic acid	0.60	0.84	0.86	0.85
Lactate-acetate	0.65	0.85	0.85	0.85
Mehlich's HCl-H ₂ SO ₄	0.61	0.87	0.86	0.86

^a N.S. Not significant. All other correlations significant at 999 to 1 level.

of the individual soils, *R* values for this model are given in the columns for the individual soils.

When the data for all soils are considered, only the aluminum phosphate fraction correlated with phosphorus uptake by millet. On each of the individual soils, however, phosphorus content of millet tops correlated highly with all soil phosphorus fractions containing aluminum phosphate. Phosphorus content of millet growing on Aura soils correlated most highly with aluminum phosphate, and the degree of correlation decreased when other soil phosphorus fractions were included with the aluminum phosphate. On Dutchess soils, there was little difference among the correlations between phosphorus content and the various soil phosphorus fractions containing aluminum phosphate. On Nixon soil, however, phosphorus content of millet was most closely

related to the combined aluminum and iron phosphate fractions. It may be concluded, therefore, that iron phosphate as well as aluminum phosphate contributed to uptake of phosphorus from Nixon soil, while aluminum phosphate was the main source of phosphorus available to millet growing on Aura and Dutchess soils. It also appears that soil type may be an important factor in determining the relationship between soil phosphorus forms and phosphorus uptake by plants. In Nixon loam, iron phosphate is the dominant form of phosphorus and plays a greater role in the phosphorus-supplying capacity of this soil than in that of Aura and Dutchess.

Soil Test Methods and Phosphorus in Millet Tops

The use of multiple regression analysis (Table III) indicates that phosphorus

contained in millet tops correlated highly with the phosphorus extracted by all soil test methods. When the data for all soils are considered, the phosphorus extracted by Bray's method shows the least relationship to the phosphorus in millet tops. Correlations for the individual soils, however, indicate that electro-dialyzable phosphorus may correlate less with phosphorus in millet tops than the phosphorus extracted by the other soil test methods.

Soil Phosphorus Fractions and Soil Test Methods

The simple linear correlation coefficients for relationships between soil phosphorus fractions and phosphorus extracted by soil test methods are shown in Table III.

All the soil test methods except electro-dialysis correlated with the amount of aluminum phosphate in the soils. To a lesser degree, the phosphorus from all of the soil test methods, again with the exception of that from electro-dialysis, also correlated with the calcium phosphate fraction of the soils. The phosphorus extracted by Bray's No. 1 reagent correlated with iron phosphate and with all the remaining phosphorus fractions except organic phosphorus. The correlation of phosphorus extracted by other soil test methods, however, was not significantly positive with any phosphorus fractions except aluminum and calcium phosphates.

When the correlations between various soil phosphorus fractions and the phosphorus extracted by soil test methods are considered for the individual soils (Table IV), all soil test methods are found to correlate highly with aluminum phosphate and the various inorganic phosphorus fractions containing aluminum phosphate fraction. For Nixon and Dutchess soils, however, there was little variation among the correlation coefficients for relationships between soil phosphorus fractions and soil test methods.

It has been reported (8) that the correlation coefficients between the values of readily extractable phosphorus and the amounts of each soil phosphorus fraction depend on the dominant form of phosphorus in the soil. The closer relationship between aluminum phosphate and phosphorus extractable by soil test methods in Aura than in Nixon and Dutchess soils may be related to the greater proportion of aluminum phosphate in Aura soil.

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Table III. Correlation between Soil Phosphorus Fractions and Phosphorus Extracted by Soil Test Methods

Soil Phosphorus Fractions	Simple Linear Correlation Coefficients ^a				
	Bray No. 1	Electro-dialysis	2-Ketogluconic acid	Lactate-acetate	Mehlich's HCl-H ₂ SO ₄
Al phosphate	0.86***	0.14 N.S.	0.28**	0.49***	0.30**
Fe phosphate	0.34***	-0.64***	-0.38***	-0.16 N.S.	-0.37***
Ca phosphate	0.34***	0.10 N.S.	0.22*	0.26**	0.21*
Al + Fe phosphate	0.63***	-0.44***	-0.08 N.S.	0.15 N.S.	-0.06 N.S.
Al + Fe + Ca phosphate	0.65***	-0.42***	-0.06 N.S.	0.17 N.S.	-0.04 N.S.
Total P	0.44***	-0.58***	-0.31**	0.09 N.S.	-0.29**
Inorganic P	0.52***	-0.51***	-0.22*	0.02 N.S.	-0.20*
Organic P	0.19 N.S.	-0.67***	-0.51***	-0.32***	-0.47***

^a Data for all soils.

Levels for significance. N.S. Not significant
 * 19 to 1 level
 ** 99 to 1 level
 *** 999 to 1 level

Table IV. Correlations between Soil Phosphorus Fractions of Aura, Nixon, and Dutchess Soils and Phosphorus Extracted by Soil Test Methods

Soil Phosphorus Fractions	Simple Linear Correlation Coefficients ^a				
	Bray No. 1	Electro-dialysis	2-Ketogluconic acid	Lactate-acetate	Mehlich's HCl-H ₂ SO ₄
Aura					
Al phosphate	0.96	0.83	0.90	0.94	0.95
Al + Fe phosphate	0.73	0.68	0.75	0.81	0.77
Al + Fe + Ca phosphate	0.76	0.69	0.77	0.81	0.76
Inorganic P	0.80	0.79	0.82	0.80	0.82
Nixon					
Al phosphate	0.96	0.90	0.95	0.95	0.96
Al + Fe phosphate	0.92	0.89	0.94	0.93	0.94
Al + Fe + Ca phosphate	0.92	0.89	0.95	0.94	0.95
Inorganic P	0.87	0.81	0.84	0.92	0.85
Dutchess					
Al phosphate	0.94	0.85	0.93	0.94	0.92
Al + Fe phosphate	0.92	0.83	0.92	0.92	0.90
Al + Fe + Ca phosphate	0.92	0.83	0.92	0.92	0.90
Inorganic P	0.91	0.88	0.88	0.81	0.88

^a All correlations significant at 999 to 1 level.

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TERMINAL GROWTH CONTROL

Apical Dominance in Bean Plants Controlled with Phthalamic Acids

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Nine new phthalamic acids were found to be active growth regulators when applied to stems of young bean plants, six approximating the activity of the known regulator *N*-(1-naphthyl)phthalamic acid when applied at the rate of 125 μ g. per plant. These compounds inhibited terminal growth and accelerated growth of lateral buds. Applied to the stem, *N*-(3-nitro-1-naphthyl)phthalamic and *N*-(5-acenaphthenyl)phthalamic acids caused an abscission zone to develop in the second internode and abscission of the terminal bud. A fraction of 1 μ g. of the nitro-substituted acid induced abscission when applied to that area of stem capable of developing an abscission zone. Although very effective when applied to stems or roots, this acid did not affect terminal growth when applied to leaves. *N*-(5-Acenaphthenyl)phthalamic acid increased growth of lateral buds and decreased the amount of fruit that developed. Some of the phthalamates were apparently inactivated rapidly by the plant.

SOME growth-regulating compounds induce abscission when used to thin flowers and fruits and to defoliate plants. Others retard abscission of some kinds of fruits and leaves when used to prevent preharvest drop and to improve the appearance of decorative plants (7, 4). There is need, however, to control other kinds of abscission. For example, control of the abscission that results in seed shatter would reduce losses in such crops as carrots and lettuce. A means of defoliating tomato and grape would facilitate development of machines to harvest these crops.

In an earlier study of abscission, 30 compounds, some with widely different structures, retarded terminal growth and induced formation of an abscission zone in the stem near the terminal bud when applied to stems of young bean plants. Abscission of the terminal buds usually followed, thus inducing growth of lateral buds (2).

The purpose here is to describe the effects of some phthalamic compounds on apical dominance and terminal bud abscission. The practical significance of phthalamic compounds when used to induce the responses described is not

implied, however, since little is known regarding their toxicity.

Experimental

Sixty-four phthalamic acids were selected to determine their effects on apical dominance. Each compound was mixed separately with melted lanolin and the mixture cooled. Equimolar concentrations were not used in most cases, since differences in weight were relatively slight and marked plant responses were involved. However, in comparing the activity of *N*-(3-nitro-1-naphthyl)phthalamic acid, the most effective compound in terms of abscission, with