of sodium methoxide (*ca.* 0.1 equiv) causes a decrease in height and broadening of the original ring proton resonances. This resonance usually totally disappears within 5–10 min without the formation of any new resonances. The solution immediately turns from a light red to a dark green (looks almost black) as soon as the sodium methoxide is added. Additional sodium methoxide (0.3–1.0 equiv) causes the appearance of two new upfield resonances which are characteristic of the ring protons of **10**. When these new resonances appear, the color of the solution changes to a dark red. The amino compound (**9**, R = NH_2) turns a dark green with the addition of sodium methoxide and the original ring proton resonance disappears. However, no new resonances are observed in an excess of sodium methoxide (*ca.* 3.0 equiv) nor is there a further change in the color of the solution. The reaction of this compound is probably complicated by abstraction of an amino hydrogen (Crampton, 1969), which would deactivate the compound toward nucleophilic attack. Furthermore, if an intermediate corresponding to **10** were formed there is a possibility that it might have some radical character, and, hence, not be easily seen by "normal" nmr techniques. This is observed for the corresponding carboxy compound (X, R = COOH). The addition of either water or sodium bicarbonate to a methanolic solution of this compound causes a broadening and eventual disappearance of the proton resonances. There is also a corresponding change in color from light orange to dark red; however, no new resonances appear.

On the basis of observed nmr spectra and the known chemistry of similar compounds it can be concluded that the reaction of dinitroaniline plant growth regulators with a nucleophile to produce intermediates represented by **10** is a general reaction of 4-substituted-2,6-dinitro-*N*,*N*-di-*n*-propylanilines which do not have ionizable substituents (*e.g.*, COOH, NH_2). The reaction pathway leading to **10**, as observed by nmr, can vary depending upon the electronic nature of the substituent. It is interesting to note that activity is very low (Hall, 1971) for compounds such as **9**, R = COOH or NH_2, which do not readily form Meisenheimer intermediates. On the basis of the generality of Meisenheimer intermediate formation, it can be conceived that activity of the dinitroanilines is derived from their nucleophilic reactivity. The possible role of these intermediates will be presented when detailed structure–activity relationships have been concluded.

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Synthesis of L-*N*-[(1-Naphthyl)acetyl]glutamic Acid

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L-*N*-[(1-Naphthyl)acetyl]glutamic acid was synthesized. The synthesis involved coupling the dibenzyl ester of L-glutamic acid with 1-naphthaleneacetic acid in the presence of Woodward's reagent (*N*-ethyl-5-phenylisoxazolium-3′-sulfonate). The final product was obtained when toluene was removed from the glutamic acid moiety by hydrogenolysis. Assay by gas–liquid chromatography–mass spectrometry, infrared and ultraviolet spectroscopy, and thin-layer chromatography confirmed the purity and structure of the final product.

While investigating conversion rates by leaf tissue of 1-naphthaleneacetic acid (NAA) to *N*-[(1-naphthyl)acetyl]aspartic acid a compound was discovered which was thought to be *N*-[(1-naphthyl)acetyl]glutamic acid (NAGlu) (Brenner and Tonkinson, 1974). NAGlu was synthesized in order to confirm the identity of the natural product and characterize some of its properties. Coupling of the NAA and the glutamic acid was accomplished using a carboxyl activating reagent described by Woodward *et al.* (1961). The two-step sequence involved in the coupling and isolation of the end product by partitioning makes this procedure quite simple and direct.

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PROTECTION OF CARBOXYL GROUPS OF GLUTAMIC ACID

The dibenzyl ester of the L-glutamic acid was prepared according to Good's (1956) modification of a method developed by Cipera and Nicholls (1955). The resulting benzenesulfonate salt of the ester was recrystallized from a 1:4 methanol–ether solution before conversion to the HCl salt. The yield of the HCl salt was 27%. The low yield was possibly due to formation of γ-lactam under the refluxing conditions and to dimer formation in carbon tetrachloride.

Dibenzyl esterification was confirmed by an infrared spectrum of the L-dibenzyl glutamate-HCl. Absorption at 690 and 725 cm^{-1} indicated the presence of benzene rings and that at 1200 cm^{-1} indicated an ester linkage.

L-*N*-[(1-NAPHTHYL)ACETYL]GLUTAMIC ACID SYNTHESIS

Recrystallized NAA (1.53 g, 0.008 mol) was dissolved in 10 ml of acetonitrile followed by the addition of 1.2 ml of triethylamine while stirring (solution A). *N*-Ethyl-5-phenylisoxazolium-3′-sulfonate (2.10 g) (Woodward's reagent) was dissolved in 10 ml of acetonitrile (solution B). Solution A was added to solution B and the mixture stirred for 4 hr at 4°. The hydrochloride salt of the L-dibenzyl glutamate (3.0 g) was added to the reaction mixture followed by triethylamine (1.2 ml) and the mixture stirred overnight at room temperature.

The reaction mixture was diluted with 10 ml of chloroform and the resulting solution was partitioned twice against 20 ml of water to remove the secondary product. The aqueous phase was discarded and the organic phase was concentrated to a syrup by evaporation with an air stream. The syrup was dissolved in 50 ml of *n*-butyl alcohol and added to 0.5 g of 5% palladium on barium sulfate which had been prewetted with 1.0 ml of water. The mixture was shaken overnight under 3.4 atm of hydrogen which caused subsequent removal of toluene from the protecting ester.

The catalyst was removed by filtration and the filtrate extracted, once with 0.1 *N* HCl and twice with water. The *n*-butyl alcohol phase was extracted with 5.0, 2.5, and 2.5 ml of 0.5 *N* sodium bicarbonate. The pooled bicarbonate extracts were partitioned against ether and the residual ether evaporated from the bicarbonate extracts under an air stream. The bicarbonate solution was acidified with 80% phosphoric acid to a slight turbidity and kept overnight at 4°. The resulting crystals were white. The melting point was 182–184° (uncorrected). The yield on a molar basis was 44% of the L-dibenzyl glutamate-HCl.

ANALYTICAL CONFIRMATION OF NAGlu

The infrared spectrum was obtained on a Perkin-Elmer Model 257 grating infrared spectrometer using a potassium bromide pellet. The following functional groups were confirmed: peptide bond 3250 (s), 1580 (s), 1650 (s), and carboxylic acids 1700 cm^{-1} (s). The presence of the naphthalene ring was confirmed by comparing the ultraviolet absorption spectrum in ethanol of the NAGlu with NAA alone. The spectra were identical showing maximum absorption at 282.5 nm and shoulders at 293 and 272.5 nm.

The final product was methyl esterified by the diazomethane method (Schlenk and Gellerman, 1960) and injected into a Beckman GC-45 gas–liquid chromatograph. The glass column was 1.22 m × 3 mm i.d. packed with 3% OV 101 on 100–120 mesh Gas Chrom Q (Applied Science Inc.). The flame ionization detector temperature was 300°, the injection port was 225°, and the column temperature was programmed from 170 to 254° with a 7°/min rate of rise. The helium flow was 40 cm^3/min, air flow was 300 cm^3/min, and H_2 flow was 28 cm^3/min. A 2-μl sample containing 1 μg/l. of NAGlu methyl ester was injected. The peak had a retention time of 10 min. No peak appeared at 2.3 min which is the retention time of NAA methyl ester.

The NAGlu methyl ester was analyzed with an LKB 9000 gas chromatograph–mass spectrometer with similar gc operating parameters. The most intense ions in the mass spectrum at 70 eV and at each 14 *m/e* units were: 74 (23); 115 (25); 140 (25), 141 (55); 145 (55); 168 (100), 169 (14); 174 (8); 321 (8); 343 (4).

THIN-LAYER CHROMATOGRAPHY

Samples of NAA and NAGlu were spotted separately on 250-μm thick silica gel G/MH precoated plates (Analtech Inc.) and the plates were developed in an 8:1:1 solution of isopropyl alcohol–ammonia–water to 15 cm. A covered glass chamber 30 × 27 × 10 cm was purged with nitrogen gas and 2 ml of bromine water was added. The tank was allowed to stand until the atmosphere was well saturated with bromine. The dry thin layer plate was quickly inserted, the chamber covered, and a 150-W reflector flood lamp directed toward the plate surface for 15 min. The naphthalene compounds were located by the brown spots produced as a result of bromination. The R_f for NAA was 0.63 and that for NAGlu was 0.27. There was no indication of NAA above the NAGlu spot.

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