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THE EFFECT OF ULTRA-VIOLET LIGHT ON 1-NAPHTHALENE-ACETIC ACID

D. A. M. WATKINS

Long Ashton Research Station, University of Bristol

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Abstract—Irradiation of an aqueous solution of 1-naphthalene acetic acid (NAA) with light of wavelength 253·7nm gave 1-naphthaldehyde, 1-naphthylcarbinol, 1-naphthoic acid, 1-methylnaphthalene and naphthalene. After 3 days only 9% NAA remained. In ethanolic solution phthalic acid was also produced in addition to ethyl 1-naphthoate and ethyl 1-naphthyl acetate.

INTRODUCTION

1-NAPHTHALENE acetic acid (NAA) is a plant-growth regulator, used as a fruit-thinning agent for apples, and for reducing the pre-harvest drop of apples and pears. Interest in the effect of ultra-violet light on pesticides sprayed on plant surfaces,[1(a)–(c)] prompted an investigation into the irradiation of NAA. Several previous reports had indicated that there is considerable breakdown by decarboxylation and liberation of carbon dioxide. Zeeuw and Leopold[2] found less than 1 per cent change in 3 hr exposure to u.v. light but Luckwill and Lloyd-Jones[3] reported 80 per cent loss of radioactivity from ^{14}C carboxyl labelled NAA over 4 days. Leeper, Gowing and Stewart,[4] working with carboxyl labelled NAA deposited on either pineapple leaves or aluminium foil, observed the evolution of $^{14}CO_2$ on exposure to sunlight and concluded that this decarboxylation was not due mainly to metabolism. Recently, a report on the determination of NAA by the American Association of Analytical Chemists[5] mentions that results of the study were inconclusive because of the apparent decomposition of the NAA solutions used.

If there is considerable breakdown by sunlight then this will influence and may even control the field performance of NAA. Also, the products so formed may themselves have biological activity or leave toxic residues in or on the plant. Preliminary work on the breakdown in ethanolic solution has been published[6] and this has been extended to aqueous solutions. In the present work no attempt was made to carry out any experiments in an oxygen-free solution since *in vivo* NAA is in contact with the air.

RESULTS AND DISCUSSION

Solutions of NAA were circulated continuously past a low-pressure mercury vapour discharge tube emitting light mainly at 253·7 nm. Solubility considerations and the instability

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[3] L. C. LUCKWILL and C. P. LLOYD-JONES, *J. Hort. Sci.* **37**, 190 (1962).
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of silicone rubber in the apparatus to certain solvents led initially to the use of an ethanolic solution. Samples were taken after 5 hr and then at daily intervals for 1 week for direct GLC analysis on Column A. This showed the presence of six major and seventeen minor peaks. No new peaks emerged after 5 hr although they all increased in size with time. The quantity of NAA was determined by peak area comparison and finally 9 per cent remained unchanged. The residue, after evaporation of the alcohol, was chromatographed on a silica gel column (Table 1, column 1).

The presence of ethyl esters complicated the separation, so finally an aqueous solution was used and, due to the low solubility of NAA in water, a larger volume of solution was circulated at a much higher rate. Samples taken at various intervals were extracted continuously with ether overnight before being analysed. The residual aqueous solution contained a large proportion of organic material but on acidification and re-extraction almost quantitative recovery resulted. The latter extract consisted mainly of NAA with a little 1-naphthoic acid.

Experiments, where samples were taken at 30-min intervals for 3 hr and then at daily intervals for a week, showed that all four major peaks in the GLC analysis (column A) were present in the first sample and increased in height with time. Analysis of the 3-day sample showed that 9% NAA was left, and of the residue 30 per cent appeared to have polymerized increasing to 50 per cent after 1 week.

The combined unacidified extract of five 24-hr experiments was chromatographed on silica gel in petroleum ether (Table 1, column 2). The u.v. and i.r. spectra of the petrol eluate A indicated a hydrocarbon with a naphthalene nucleus. GLC on columns B and D gave two peaks and preparative GLC on the former column gave samples with spectra and retention data identical to those of naphthalene and 1-methylnaphthalene. The oil in fraction B had an i.r. spectrum of an aromatic aldehyde and the thin-layer chromatogram, sprayed with 2,4-dinitrophenylhydrazine solution, showed a yellow spot at relative R_f 1·65. The compound was identified as 1-naphthaldehyde by preparation of the DNP derivative. The next two fractions (C and D) were crystalline and were shown by undepressed mixed melting points to contain 1-naphthoic acid and NAA. Fraction E crystallized from a solution in petroleum ether (b.p. 60–80°) containing a little benzene. The i.r. spectrum, in a KBr disc had a broad band at 3300 cm^{-1} but in CCl_4 solution a sharp band at 3620 cm^{-1}, and a band at 1075 cm^{-1} indicating a primary hydroxyl group. The compound was shown to be 1-naphthylcarbinol by comparison of GLC, TLC and i.r. data with those of a synthetic specimen and by an undepressed mixed melting point. The 100% ether and methanol eluates appeared to contain polymers and no pure compounds could be isolated.

In addition to the breakdown products already cited, ethyl 1-naphthoate and phthalic acid were also identified in the ethanol solution experiment[6] (Table 1, column 1). An equivalent experiment using NAA in ethanolic solution, but run in the dark, showed that there was no dark reaction and no esterification. A solution of 1-naphthoic acid was irradiated for 7 days but apart from a slight darkening in colour no change could be detected. The retention times of diethylphthalate and phthalic acid/anhydride on column A used for analysis were identical but they could be separated on column E. No diethylphthalate could be detected in the mixture. Although no ethyl naphthyl acetate was isolated from the silica column a peak corresponding in retention time appeared in the GLC analysis.

Neither the order of formation of the products nor the photochemical pathway was determined. The major product appears to be 1-naphthaldehyde which is readily oxidized in air to 1-naphthoic acid; hence the presence of the latter may not be due to a photochemical process. The production of naphthalene and 1-methylnaphthalene is to be expected by simple

TABLE 1. DETAILS OF SILICA COLUMN RUNS AND IDENTIFICATION OF COMPOUNDS

Fraction	Eluent	Alcohol solution	Aqueous solution	Compounds identified	Identification*
A	Petrol. ether (b.p. 60–80°)	0·15 g	0·015 g	Naphthalene	u.v. 267, 277, 288 nm
				1-Methylnaphthalene	u.v. 272, 283, 293 nm
B	(1) Petrol. ether + 5% ether (b.p. 60–80°)	1·1		Ethylnaphthoate	i.r., M.S. NMR†
	(2) Petrol. ether + 5% ether (b.p. 60–80°)	0·6	0 6	1-Naphthaldehyde	i.r. 1690, 2720 cm^{-1} DNP, m.p. 257–258°[10]
C	Petrol. ether + 10% ether (b.p. 60–80°)	1·0	0·04	1-Naphthoic acid	m.p. 160°
D	Petrol. ether + 25% ether (b.p. 60–80°)	2·1	1·1	NAA	m.p. 132°
E	(1) Petrol. ether + 50% ether (b.p. 60–80°)	0·45	0·15	1-Naphthylcarbinol	m.p. 59°[11] i.r. KBr 3300, CCl_4 soln. 3620 cm^{-1}
	(2) Petrol. ether + 50% ether (b.p. 60–80°)	2·2		Phthalic acid	i.r., M.S.‡
F	Ether	1·0	0·09		
G	Methanol	0·6	0·10		

* All compounds had identical GLC, TLC data with authentic specimens as in Table 1.

† I.r. 1720 cm^{-1}: M.S.[12] *m/e* 200, 155, 127 (M-$COOC_2H_5$): NMR ($CDCl_3$), multiplet τ=2·2 (aromatic), quadruplet and triplet τ=5·6, 8·6 (—C_2H_5).

‡ I.r. 1705, 3000 (broad) cm^{-1}, after GLC 1780, 1850 cm^{-1} (anhydride formation): Esterification, GLC column C M.S. *m/e* 222, 177, 149, 76 corresponding to diethylphthalate.[12]

decarboxylation to a radical which could add on hydrogen. These however were minor products. Although phthalic acid is found in the ethanolic solution experiment it was not found in the water experiment. The oxidation of 1-methylnaphthalene is known to give hemi-mellitic acid besides naphthoic and phthalic acids. The retention data of hemi-mellitic acid was determined and no peak corresponding to it was found in the breakdown products. Hammond and Leermakers[7] state that the reduction of an aldehyde group conjugated to a naphthalene nucleus does not undergo normal photoreduction. They found that 1-naphthaldehyde could be reduced to 1-naphthylcarbinol in the presence of a good hydrogen donor, tributylstannane.

A wheat coleoptile assay of the crude product from the ethanolic solution showed a decrease in percentage growth equivalent to the decrease in proportion of NAA present.

EXPERIMENTAL

The apparatus described by Cohen, Mijovic, Newman and Pitts[8] was used whereby a thin film is continuously circulated down the inside of a glass tube (40 mm dia.) around the u.v. tube. Ethanolic solutions of 10 g NAA in 500 ml absolute ethanol were pumped at 800 ml/hr by a DCL micropump type T with silicone rubber and stainless steel in contact with the solution. Evaporation to dryness after 7 days gave a residual brown oil (9·7 g) which was chromatographed (Table 1, column 1). Aqueous solutions of 1·1 g NAA in 2 l. glass distilled water were circulated by a Charles Austen DYMK II pump with neoprene and stainless steel to give a higher flow rate of 10 l/hr. After 24 hr the solution was continuously extracted overnight and the combined extract of five runs (2·5 g) chromatographed (Table 1, column 2). The tube was a 2-ft low-pressure vapour discharge tube (Hanovia 6827, Bactericidal) giving light mainly at 253·7 nm.

Gas Chromatography

The GC analyses were carried out on Varian Aerograph A 700 or A 90-P3 instruments fitted with flame ionization detectors and linear temperature programmers.

The columns used were:

A. 2·5% diethylene glycol adipate (Analabs stabilized C5), 0·2% ortho-phosphoric acid on Chromosorb G (AW-DMCS) (80–100 mesh) packed in 10 ft × ⅛ in. stainless steel.
B. 5% Silicone OV.17, 15% Bentone 34 on Aeropak 30 (70–80 mesh) packed in 20 ft × ⅛ in. stainless steel, run at 162°.
C. 2·5% LAC-2R-446, 0·2% orthophosphoric acid on Chromosorb G (AW-DMCS) (80–100 mesh) packed in 6 ft × ¼ in. stainless steel, run at 210°.
D. 10% Silicone OV·17 on Aeropack 30 (70–80 mesh) packed in 10 ft × ⅛ in. stainless steel, run at 75°.
E. 1% diethylene glycol succinate (Analabs stabilized C6), 0 8% orthophosphoric acid on Chromosorb G (AW-DMCS) (80–100 mesh) packed in 10 ft × ⅛ in. stainless steel.

Unless otherwise stated, the gas flows through the columns were 100 ml/min with a split ratio of 1:3 to F.I.D., the temperatures (1) columns programmed 100–260° at 10°/min, (2) detector 300°, (3) injector 275°. All data is quoted relative to NAA (Table 2).

The extract from the aqueous experiment had peaks at relative retention times 0·28, 0·56, 0·71, 0·9 and 1 0 and the ethanol solution gave peaks at 0·28, 0·52, 0·56, 0·61, 0·65, 0·9 and 1·0.

Column Chromatography

Column chromatography was carried out using Koch-Light silica gel (100–200 mesh) previously activated overnight at 120° and packed in dry petroleum ether (b.p. 60–80°). Merck silica gel did not give as good a separation. Fractions were eluted with the same solvent containing successively increasing amounts of dry ether and then methanol, as shown in Table 1.

TLC

TLC was carried out on Merck silica gel G for analytical purposes and silica gel HR for preparative work and plates activated at 110° for 1 hr. The solvent system used was petroleum ether (b.p. 40–60°):ether:acetic acid (70:30:1) unless otherwise stated. TLC data is quoted relative to NAA (Table 1).

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TABLE 2. CHROMATOGRAPHIC DATA OF COMPOUNDS ISOLATED

	Relative* retention time on column A	Relative* R_f on silica gel G
1-Naphthalene acetic acid (NAA)	1·00	1·00
1-Naphthoic acid	0·9	1·38
1-Naphthylcarbinol	0·71	1·06
Ethyl 1-naphthyl acetate	0·65	
Ethyl 1-naphthoate	0 61	
1-Naphthaldehyde	0·56	1·65
Phthalic acid (as anhydride)	0·52	
Diethylphthalate	0·52	
1-Methylnaphthalene	0·28	
Naphthalene	0·2	

* Relative to NAA.

Chemicals

1-naphthaldehyde was prepared from 1-naphthoic acid via the acid chloride and reduction with lithium tri-*t*-butoxy aluminohydride.[9] The product was stored under N_2 in the refrigerator. The DNP derivative had m.p. 258°.[10] 1-naphthylcarbinol, prepared by reduction of 1-naphthoic acid with $LiAlH_4$ in ether, had m.p. 59–60°.[11]

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