952. *Synthesis of Plant-growth Regulators. Part V.** *(3-Substituted 2-naphthyloxy)-*n*-alkanecarboxylic Acids.*

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Various (3-substituted 2-naphthyloxy)-*n*-alkanecarboxylic acids have been prepared for testing as parthenocarpic and fungistatic agents. 3-Fluoro-2-naphthol has been prepared and characterised and 3-methyl-2-naphthol has been prepared by an improved method.

Many substituted 2-naphthyloxyacetic acids are plant-growth regulators and the effect of various nuclear substituents on the activity of the original acid has recently been reported.[1] The complete inactivity of 3-hydroxy-2-naphthyloxyacetic acid,[2] contrasting sharply with the high activity of the corresponding 3-chloro-compound[3] in the tomato ovary test, made it desirable to synthesise and investigate other 3-substituted acids.

3-Methyl-2-naphthol was first prepared by Wolff–Kishner reduction of 3-hydroxy-2-naphthaldehyde, though no analytical details were given.[4] Difficulties in the preparation of the aldehyde led us to prepare 3-methoxy-2-naphthaldehyde by a modified McFadyen–Stevens reaction, Wolff–Kishner reduction of the semicarbazone giving, in addition to

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* Part IV, *J.*, 1955, 577.

[1] Luckwill and Woodcock, " Chemistry and Mode of Action of Plant Growth Substances," Butterworths, London, 1956, p. 195.

[2] *Idem*, unpublished work.

[3] *Idem*, *J. Hort. Sci.*, 1955, **30**, 109.

[4] Tishler, Fieser, and Wendler, *J. Amer. Chem. Soc.*, 1940, **62**, 2866.

3-methyl-2-methoxynaphthalene, a phenolic alcohol which was shown to be 3-hydroxymethyl-2-naphthol Of the 3-halogeno-2-naphthols, the 3-fluoro-compound has not been previously described. Diazotisation of 3-methoxy-2-naphthylamine followed by addition of an aqueous solution of sodium fluoroborate gave 2-methoxy-3-naphthalenediazonium fluoroborate as stable, though photosensitive, orange crystals. This was decomposed by heat to 3-fluoro-2-methoxynaphthalene, and demethylation by hydrobromic acid then gave 3-fluoro-2-naphthol. 3-Bromo-2-naphthol was conveniently prepared from 1 : 3-dibromo-2-naphthol, preferential reduction taking place with hydriodic acid contrary to Clemo and Spence's findings.[5] 3-Cyano-2-naphthol was obtained from the corresponding methyl ether by demethylation with pyridine hydrochloride, since refluxing hydrobromic acid caused hydrolysis in addition to demethylation, forming 3-hydroxynaphthalene-2-carboxyamide. In attempts to obtain 3-iodo-2-naphthol[6] in improved yield, demethylation of 3-iodo-2-methoxynaphthalene gave only β-naphthol, whilst treatment of 3-bromo-2-naphthol with *n*-propyl-lithium, followed by iodine, gave 3-bromo-1-iodo-2-naphthol as a result of hydrogen–lithium exchange in preference to halogen–lithium exchange.[7]

3-*Substituted* 2-*naphthyloxyacetic acids.*

			Found (%)				Required (%)		
Substituent	M. p.	Solvent	C	H	N	Formula	C	H	N
F	169—170°	Aq. MeOH	66·0	4·5	—	$C_{12}H_9O_3F$	65·45	4·1	—
Br	175—176	C_6H_6–$COMe_2$	51·1	3·0	—	$C_{12}H_9O_3Br$	51·3	3·2	—
I	173—174	,,	44·0	2·8	—	$C_{12}H_9O_3I$	43·9	2·7	—
Me	188—189	AcOH	71·8	5·6	—	$C_{13}H_{12}O_3$	72·2	5·6	—
OH [a]	166	H_2O	66·3	4·6	—	$C_{12}H_{10}O_4$	66·1	4·6	—
OMe	175—176	Aq. MeOH	66·9	5·3	—	$C_{13}H_{12}O_4$	67·2	5·2	—
NO_2	188—189	,,	57·9	3·6	5·5	$C_{12}H_9O_5N$	58·3	3·6	5·7
CN	147	MeOH	68·9	4·4	6·0	$C_{13}H_9O_3N$	68·7	4·0	6·2
$CO{\cdot}NH_2$	251	,,	63·0	4·7	5·2	$C_{13}H_{11}O_4N$	63·0	4·5	5·7
CO_2H [b]	220—221	AcOH	63·6	4·1	—	$C_{13}H_{10}O_5$	63·4	4·1	—

[a] Shibata and Okuyama(*Bull. Chem. Soc. Japan*, 1936, **11**, 117) give 153°. [b] For details of this preparation see below.

Attempts to prepare 3-amino-2-naphthyloxyacetic acid from the corresponding naphthol by condensation with ethyl bromoacetate gave 3 : 4-dihydro-2-oxonaphtho-[2,3-*b*]-1 : 4-oxazine, but alkaline hydrolysis of this compound gave a solution of the sodium salt suitable for use in the tomato ovary test. The corresponding 2-oxonaphtho-[2,3-*b*]-1 : 4-dioxan was obtained in one attempted methylation of 3-hydroxy-2-naphthyloxyacetic acid.

It is hoped to publish the biological results elsewhere later.

EXPERIMENTAL

3-*Methoxy*-2-*naphthylamine.*—In the method of Jambuserwala *et al.*[8] it was found more convenient to use *iso*pentyl rather than the more volatile ethyl nitrite, in the preparation of ethyl 3-methoxy-2-naphthylcarbamate. The latter was hydrolysed by 40% aqueous sodium hydroxide to the amine in 85—98% yield.

3-*Methoxy*-2-*naphthalenediazonium Fluoroborate.*—3-Methoxy-2-naphthylamine (10 g.) was dissolved with stirring in a warm mixture of concentrated hydrochloric acid (15 ml.) and water (25 ml.), cooled to 0°, and diazotised by sodium nitrite (4·1 g.) in a little water. After 2 hours' stirring at 7° an ice-cold solution of sodium fluoroborate (8·2 g.) in water (10 ml.) was added and stirring continued for a further 0·5 hr. After the addition of 5% aqueous sodium fluoroborate

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[5] Clemo and Spence, *J.*, 1928, 2811.

[6] Goldstein and Cornamusaz, *Helv. Chim. Acta*, 1932, **15**, 935; Goldstein and Gardiol, *ibid.*, 1937, **20**, 516.

[7] Cf. Jones and Gilman, "Organic Reactions," Vol. VI, p. 349.

[8] Jambuserwala, Holt, and Mason, *J.*, 1931, 373.

(40 ml.), the *product* was collected and washed with a little ethyl alcohol followed by dry ether. It crystallised from acetone in orange needles (10·6 g., 68%), m. p. 153° (decomp.), which slowly decompose on exposure to light (Found: N, 10·3. $C_{11}H_9ON_2F_4B$ requires N, 10·3%).

3-*Fluoro*-2-*methoxynaphthalene*.—The above diazonium salt (5 g.) was decomposed *in vacuo* at 150—160° (bath-temp.). The *product* (1·3 g., 41%) which distilled was purified by sublimation at 80°/1 mm., followed by crystallisation from light petroleum (b. p. 40—60°). It formed nacreous plates, m. p. 90—91° (Found: C, 75·1; H, 5·2. $C_{11}H_9OF$ requires C, 75·0; H, 5·1%).

3-*Fluoro*-2-*naphthol*.—A solution of the above methyl ether (1 g.) in acetic acid (6 ml.) was refluxed for 4 hr. with hydrobromic acid (*d* 1·5; 4 ml.), cooled, diluted with water, and extracted with ether. Naphtholic material, extracted in dilute sodium hydroxide solution, was recovered by acidification and isolation with ether, the ethereal solution dried (Na_2SO_4), and the solvent removed. The residue (0·8 g.), m. p. 70—75°, was purified by sublimation at 80°/1 mm. and crystallised from light petroleum (b. p. 40—60°) in nacreous plates, m. p. 90—91° (Found: C, 74·9; H, 4·1. $C_{10}H_7OF$ requires C, 74·1; H, 4·3%). 3-*Fluoro*-2-*naphthol* depressed the m. p. of its methyl ether to 62°.

N-(3-*Methoxy*-2-*naphthoyl*)-N′-*toluene*-p-*sulphonylhydrazine*.—3-Methoxy-2-naphthhydrazide[8] (18·8 g.) was dissolved in pyridine (50 ml.), cooled, and treated with toluene-*p*-sulphonyl chloride (20 g.) in pyridine (20 ml.). After being heated at 100° for 30 min. the mixture was diluted with water (200 ml.) and acidified with hydrochloric acid, and the crude oily product collected. Washing with dilute hydrochloric acid followed by dissolution in dilute sodium hydroxide and re-precipitation with acid gave a more tractable *product* (22·5 g., 58%) which crystallised from dioxan in monoclinic prisms, m. p. 218° (Found: C, 61·9; H, 4·9; N, 7·9. $C_{19}H_{18}O_4N_2S$ requires C, 61·6; H, 4·9; N, 7·6%).

3-*Methoxy*-2-*naphthaldehyde*.—The above hydrazide (1 g.) in diethylene glycol (20 ml.) was heated and stirred at 160° during addition of anhydrous sodium carbonate (2·5 g.) and afterwards until the evolution of carbon dioxide had ceased. The mixture was cooled, diluted with water, and extracted with ether. Removal of the solvent from the dried extract gave a brownish-yellow gum which was purified by sublimation at 100°/1 mm. The *aldehyde* crystallised from light petroleum (b. p. 40—60°) in yellow rhombic plates (0·2 g.), m. p. 87—89° (Found: C, 77·2; H, 5·3. $C_{12}H_{10}O_2$ requires C, 77·4; H, 5·4%).

The *semicarbazone* was prepared from the aldehyde in the usual way, or more conveniently by the following modification of the McFadyen–Stevens reaction: the preceding hydrazide (30 g.) and semicarbazide hydrochloride (10 g.) were heated and stirred in diethylene glycol (600 ml.) at 160° until all had dissolved. After addition of anhydrous sodium carbonate (75 g.) stirring was continued for 20 min., until gas evolution had ceased. The pale yellow suspension was poured into water (5 l.), and the product collected and dried (21·5 g.). It crystallised from dioxan in colourless plates, m. p. 233—234° (Found: C, 64·2; H, 5·4; N, 16·8. $C_{13}H_{13}O_2N_3$ requires C, 64·2; H, 5·3; N, 17·3%).

2-*Methoxy*-3-*methylnaphthalene*.—The above semicarbazone (2 g.) in a solution from sodium (1 g.) in ethyl alcohol (50 ml.) was heated at 190—200° for 18 hr. When cold, the mixture was extracted with ether and the extract was washed with 10% sodium hydroxide solution and water, and dried (Na_2SO_4). Removal of solvent gave a crystalline *product* (1·2 g.) which after distillation *in vacuo* crystallised from light petroleum (b. p. 40°) in plates, m. p. 74—75° (Found: C, 84·1; H, 7·0. $C_{12}H_{12}O$ requires C, 83·7; H, 7·0%). Acidification of the alkaline washings gave a substance which after isolation with ether crystallised from acetone–benzene in nacreous plates, m. p. 187—188° (Found: C, 75·8; H, 6·0%). It gave a positive ceric ammonium nitrate test for an alcoholic group and did not depress the m. p. of 3-hydroxymethyl-2-naphthol described below.

3-*Hydroxymethyl*-2-*naphthol*.—2-Hydroxy-3-naphthoic acid (9·45 g.) in dry ether (200 ml.) was added dropwise to lithium aluminium hydride (4·75 g.) in dry ether (150 ml.) stirred in a stream of nitrogen. After 1 hr. water (10 ml.) was cautiously added and the solution acidified with hydrochloric acid. After extraction with ether, the extract was washed with sodium hydrogen carbonate solution, dried (Na_2SO_4), and evaporated. The residual solid (8·5 g.), m. p. 185°, crystallised from ethyl alcohol in prismatic plates, m. p. 187—188° (Found: C, 76·0; H, 5·5. $C_{11}H_{10}O_2$ requires C, 75·9; H, 5·75%). The *di*-p-*nitrobenzoyl derivative* crystallised from acetone in needles, m. p. 169° (Found: C, 63·8; H, 3·5; N, 5·8. $C_{25}H_{16}O_8N_2$ requires C, 63·6; H, 3·4; N, 5·9%).

3-*Methyl*-2-*naphthol*.—2-Methoxy-3-methylnaphthalene (4·7 g.) was refluxed with acetic acid (40 ml.) and hydrobromic acid (*d* 1·5; 15 ml.) for 4 hr. The cooled mixture was diluted with water and extracted with ether, and the ethereal solution washed with sodium hydrogen carbonate to remove acetic acid. The naphthol (2·1 g.) isolated by means of 10% aqueous sodium hydroxide crystallised from benzene–light petroleum (b. p. 40—60°), in plates, m. p. 159·5—160·5° (Found: C, 83·5; H, 6·2. $C_{11}H_{10}O$ requires C, 83·5; H, 6·3%).

3-*Bromo*-2-*naphthol*.—1 : 3-Dibromo-2-naphthol[9] (10 g.), acetic acid (60 ml.), hydriodic acid (*d* 1·7; 4 ml.), and a trace of red phosphorus were refluxed for 4 hr. The filtered solution was diluted with water and extracted with ether. After being washed with water and sodium hydrogen carbonate solution, the ethereal extract was dried (Na_2SO_4) and evaporated. 3-Bromo-2-naphthol (5·2 g.) crystallised from light petroleum (b. p. 40—60°) in colourless plates, m. p. 80—81° (Found: C, 53·7; H, 3·0. Calc. for $C_{10}H_7OBr$: C, 53·8; H, 3·1%). Clemo and Spence[5] give m. p. 80—81°.

3 : 4-*Dihydro*-3-*oxonaphtho*[2,3-*b*]-1 : 4-*oxazine*.—3-Amino-2-naphthol (3·2 g.) in ethyl alcohol (50 ml.) containing sodium (0·46 g.) was refluxed with ethyl bromoacetate (2·5 ml.) for 4 hr. After cooling, a solid [1·6 g.; m. p. 265° (decomp.)] was collected and the filtrate diluted with water and shaken with ether. The ethereal solution was washed successively with dilute sodium hydroxide, hydrochloric acid, and water, dried (Na_2SO_4), and evaporated, more solid (1 g.) being obtained. The combined crops of naphtho-oxazine crystallised from methyl alcohol in needles, m. p. 268° (decomp.) (Found: C, 72·3; H, 4·3; N, 7·2. Calc. for $C_{12}H_9O_2N$: C, 72·3; H, 4·5; N, 7·0%) (no aminonaphthyloxyacetic ester was obtained by basifying the acid washings). Fries, Walter, and Schilling[10] give m. p. 270°.

3-*Cyano*-2-*methoxynaphthalene*.—3-Amino-2-methoxynaphthalene (6·9 g.) in water (70 ml.) and concentrated hydrochloric acid (12 ml.) was stirred at 0—5° during the dropwise addition of sodium nitrite (3 g.) in water (10 ml.) and for a further 0·75 hr. This diazonium mixture was then added with stirring to a solution of potassium cuprocyanide (from 16 g. of copper sulphate and 16 g. of sodium cyanide) in water (100 ml.), the temperature being maintained at 70—80°, and the whole was steam-distilled. The distillate was extracted with ether, and the extract washed with dilute sulphuric acid, water, and dried (Na_2SO_4). Removal of the solvent gave the *cyanide* (4 g.) which after sublimation *in vacuo* had m. p. 125° (Found: C, 78·7; H, 5·0; N, 7·75. $C_{12}H_9ON$ requires C, 78·7; H, 4·9; N, 7·65%).

3-*Cyano*-2-*naphthol*.—3-Cyano-2-methoxynaphthalene (3·5 g.) and pyridine hydrochloride (12 g.) were heated in a sealed tube at 200° for 4 hr. After cooling, the contents were diluted with water, acidified with hydrochloric acid, and extracted with ether, and naphtholic material further extracted with dilute aqueous sodium hydroxide. Acidification of the alkaline extract and extraction with ether gave the *naphthol* (2·45 g.), m. p. 180°. It crystallised from aqueous ethyl alcohol in monoclinic prisms, m. p. 185° (Found: C, 78·3; H, 4·13; N, 8·3. Calc. for $C_{11}H_7ON$: C, 78·2; H, 4·15; N, 8·3%). Lesser, Kranepuhl, and Gad[11] give m. p. 188—189°.

3-*Hydroxynaphthalene*-2-*carboxyamide*.—(*a*) 3-Cyano-2-methoxynaphthalene (2·3 g.) in acetic acid (8 ml.) was refluxed with hydrobromic acid (*d* 1·5; 3 ml.) for 4 hr. The solution was poured into water and extracted with ether, and naphtholic material removed from the extract by alkali. The alkaline solution was acidified and extracted with ether, the extract dried (Na_2SO_4), and the solvent distilled off. The residual amide (1·2 g.) crystallised from aqueous methyl alcohol in prismatic plates, m. p. 215° (Found: C, 70·9; H, 5·2; N, 7·1. Calc. for $C_{11}H_9O_2N$: C, 70·6; H, 4·8; N, 7·4%). Fries[12] gives m. p. 217°. (*b*) Demethylation of 3-methoxynaphthalene-2-carboxyamide[6] by hydrobromic acid (*d* 1·5) as above gave the phenolic amide, m. p. 215°, undepressed on admixture with the product from (*a*) above.

2-*Oxonaphtho*[2,3-*b*]-1 : 4-*dioxan*.—3-Hydroxy-2-naphthyloxyacetic acid (0·5 g.) was refluxed with acetic anhydride (5 ml.) for 2 hr., the reagent distilled off, and the product sublimed at 120° (bath-temp.)/0·5 mm. The sublimate of *naphthodioxan*, crystallised from ethyl alcohol, benzene, or ether–light petroleum (b. p. 40—60°), had m. p. 142—143° (Found: C, 71·9; H, 3·9. $C_{12}H_8O_3$ requires C, 72·0; H, 4·0%). Repeated crystallisation of the sublimate from aqueous methyl alcohol gave a product, m. p. 89—92°, which was insoluble in sodium hydrogen carbonate solution and gave a red colour with *p*-nitrobenzenediazonium fluoroborate. It crystallised from ether–light petroleum (b. p. 60—80°) in colourless rectangular

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[9] James and Woodcock, *J.*, 1951, 3418.
[10] Fries, Walter, and Schilling, *Annalen*, 1935, **516**, 248.
[11] Lesser, Kranepuhl, and Gad, *Ber.*, 1925, **58**, 2109.
[12] Fries, *ibid.*, p. 2845.

prisms, m. p. 93—94° (Found: C, 67·4; H, 5·2%), undepressed on admixture with methyl 3-hydroxy-2-naphthyloxyacetate prepared as below.

Methyl 3-*Hydroxy*-2-*naphthyloxyacetate*.—A solution of 3-hydroxy-2-naphthyloxyacetic acid in anhydrous ether was treated with ethereal diazomethane (1 equiv.). After 1 hr. the solution was washed with sodium hydrogen carbonate solution, dried, and evaporated. The residual *methyl ester* crystallised from ether–light petroleum (b. p. 60—80°) in prisms, m. p. 93—94° (Found: C, 67·05; H, 5·0. $C_{13}H_{12}O_4$ requires C, 67·2; H, 5·2%).

2 : 2-*Dimethyl*-3-*oxonaphtho*[2,3-*b*]-1 : 4-*dioxan*.—This *compound* was prepared for comparison with 2 : 3-dihydro-2-oxo-2′ : 3′-naphtho-1 : 4-dioxan. 2 : 3-Dihydroxynaphthalene (3·2 g.), in a solution from sodium (0·46 g.) in ethyl alcohol (30 ml.), was refluxed with ethyl α-bromo-α-methylpropionate (3 ml.) for 4 hr. and then for a further 1 hr. after the addition of excess of 10% aqueous sodium hydroxide. The solution was cooled and acidified with hydrochloric acid, and the *product* (1·5 g.) extracted with ether. It crystallised from ethyl alcohol in monoclinic prisms, m. p. 144—145° (Found: C, 73·5; H, 5·2. $C_{14}H_{12}O_3$ requires C, 73·7; H, 5·3%); it was insoluble in cold 10% aqueous sodium hydroxide but dissolved on gentle warming, acidification even with acetic acid re-forming the lactone.

α-(3-*Methoxy*-2-*naphthyloxy*)-α-*methylpropionic Acid*.—(*a*) 3-Methoxy-2-naphthol (0·9 g.), condensed with ethyl α-bromo-α-methylpropionate in the usual way, gave a *product* (0·6 g.) which crystallised from ether–light petroleum (b. p. 40—60°) in prisms, m. p. 105—106° (Found: C, 69·1; H, 6·1. $C_{15}H_{16}O_4$ requires C, 69·2; H, 6·15%). (*b*) A solution of 2 : 3-dihydro-2 : 3-dimethyl-3-oxo-2′ : 3′-naphtho-1 : 4-dioxan in a slight excess of warm 10% aqueous sodium hydroxide was treated dropwise with shaking with excess of dimethyl sulphate. The bicarbonate-soluble material was extracted with ether, the extract dried, and the ether distilled off. The product crystallised from aqueous methyl alcohol in prisms, m. p. 102—103° (Found: C, 69·0; H, 6·0%) undepressed on admixture with the product from (*a*). Refluxing with hydriodic acid (*d* 1·7) in acetic acid for 2 hr. gave 2 : 3-dihydro-2 : 2-dimethyl-3-oxo-2′ : 3′-naphtho-1 : 4-dioxan, m. p. and mixed m. p. 143—144°.

3-*Carboxy*-2-*naphthyloxyacetic acid*.—Ethyl 3-hydroxy-2-naphthoate (2·2 g.) was dissolved in a solution from sodium (0·23 g.) in ethyl alcohol (75 ml.) and refluxed with ethyl bromoacetate (1·2 ml.) for 8 hr. The solution was poured into water and extracted with ether, and unchanged naphtholic material removed by cold 0·1N-sodium hydroxide. After washing of the ethereal solution with water, the solvent was distilled off and the residue (1·86 g.) hydrolysed by refluxing 10% sodium hydroxide solution for 1 hr. The solution was then cooled, acidified, and extracted with ether, the ethereal solution washed with water and dried (Na_2SO_4), and the solvent removed. The *product* (1·1 g.) crystallised from ethyl alcohol or acetic acid in rhombic plates, m. p. 220—221°. Analytical details are given in the Table.

2 : 3-*Dihydro*-2-*oxonaphtho*[2,3-*b*]*oxazole*.—3-Hydroxy-2-naphthhydrazide (75 g.) in ethyl alcohol (1 l.) was cooled to 0° after addition of dry ethanolic hydrogen chloride (135 ml. containing 19·8 g. of hydrogen chloride). *iso*Pentyl nitrite (54 ml.) was added portionwise with stirring, which was continued for a further 2 hr. After refluxing until nitrogen evolution had ceased (0·5 hr.), the solution was concentrated to 200 ml. and poured into water (1 l.). The product was collected, washed with water, dried, and crystallised from ethyl alcohol (58·4 g.). Recrystallisation from ethyl alcohol–ether (charcoal) gave colourless needles, m. p. 200—201° (Found: C, 71·7; H, 3·9; N, 7·3. Calc. for $C_{11}H_7O_2N$: C, 71·4; H, 3·8; N, 7·6%). Fries [12] gives m. p. 205°.

3-*Iodo*-2-*naphthol*.—3-Amino-2-naphthol (7·95 g. prepared from the above oxazole by hydrolysis with 40% aqueous sodium hydroxide) in hot water (100 ml.) containing sulphuric acid (12 ml.) was stirred at 10—15° during the dropwise addition of a solution of sodium nitrite (3·45 g.) in water (30 ml.), and for a further 1 hour. Urea (10 g.) in water (20 ml.) was then added, followed by potassium iodide (25 g.) in water (60 ml.), and sulphuric acid (8 ml.) in water (20 ml.), and stirring continued for 1 hour. Steam-distillation of the tarry product and ether-extraction of the distillate gave crude 3-iodo-2-naphthol (2·25 g., 16·6%) which by sublimation gave colourless needles, m. p. 104°. Goldstein and Gardiol [6] reported a 12% yield, m. p. 105°.

Attempted Preparation of 3-*Iodo*-2-*naphthol using* n-*Propyl-lithium*.—A solution of *n*-propyllithium (prepared from 0·16 g. of lithium according to " Organic Reactions," Vol. VI, p. 352) in anhydrous ether (50 ml.) was added dropwise to a solution of 3-bromo-2-naphthol (1 g.) in dry ether (20 ml.) and the whole was stirred for 1 hr. in an atmosphere of nitrogen. Iodine (1 g.)

in ether (20 ml.) was added and stirring continued for 0·5 hr., followed by refluxing 0·5 hr. The cooled ethereal solution was washed with sodium thiosulphate solution, and naphtholic material extracted with alkali. Acidification of the alkaline solution and isolation with ether gave a gum which after sublimation was repeatedly crystallised from light petroleum (b. p. 40°) until chromatographically pure. The naphthol, m. p. 86—87°, gave an *oxyacetic acid,* m. p. 207—208° (Found: C, 35·1; H, 2·1%), which did not depress the m. p. of the authentic specimen prepared as below.

3-*Bromo*-1-*iodo*-2-*naphthol*.—This *naphthol* was prepared from 3-bromo-2-naphthol by Marsh's method.[13] After repeated fractional sublimation (to remove 3-bromo-2-naphthol) it crystallised from light petroleum (b. p. 40°) in prisms, m. p. 82—83° (Found: C, 34·3; H, 2·0. $C_{10}H_6OBrI$ requires C, 34·4; H, 1·7%). The *oxyacetic acid* crystallised from aqueous methyl alcohol in colourless monoclinic prisms, m. p. 207—208° (Found: C, 35·7; H, 2·1. $C_{12}H_8O_3BrI$ requires C, 35·45; H, 2·0%).

3-*Substituted* 2-*naphthyloxyacetic Acids*.—Of these only the 3-chloro-[9] and 3-hydroxy-[14] are known. The acids listed in the Table were prepared by the method described previously,[15] 3-methoxy- and 3-nitro-2-naphthol being obtained by published methods.[16]

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[13] Marsh, *J.*, 1927, 3164.
[14] Shibata and Okuyama, *Bull. Chem. Soc. Japan*, 1936, **11**, 117.
[15] James and Woodcock, *J.*, 1951, 3418.
[16] Friedlander and Silberstern, *Monatsh.*, 1902, **23**, 513; Woodcock and Clifford, *J.*, 1957, 4139.