

EXPERIMENTAL

β-2-Naphthylxypropionic Acid.—*β*-Propiolactone (3.6 g.) was added dropwise during 10 min. to a boiling stirred solution of *β*-naphthol (7.2 g.) and sodium hydroxide (2 g.) in water (30 ml.). After being heated for a further 15 min., the solution was cooled, acidified, and extracted with ether. The acid, isolated from the ethereal solution by shaking it with sodium hydrogen carbonate solution and acidifying it, was washed with water and dried at 100°. It (1.8 g.) crystallised from methyl alcohol in rhombic prisms, m. p. 143—144° (Found: equiv., 216.8. Calc. for C₁₅H₁₂O₃: equiv., 216). Chakravarti and Dutta, (*J. Indian Chem. Soc.*, 1939, 16, 639) give m. p. 144—145°.

3-2'-Naphthylxypropyl Chloride.—*β*-Naphthol (7.2 g.) was added to sodium ethoxide [from sodium (1.15 g.) and ethyl alcohol (40 ml.)], and the solution added dropwise during 1 hr. to a boiling mixture of 1-bromopropyl chloride (10 ml.) and ethyl alcohol (20 ml.). After being refluxed for 4 hr., the solution was cooled, diluted with water, and extracted with ether; an ether-insoluble solid (*A*) was filtered off. The ethereal solution after being washed with sodium hydroxide and water was dried, the solvent removed, and the residue distilled. The fraction, b. p. 138—142°/0.5 mm., solidified, and the chloride then crystallised from light petroleum (b. p. 40—60°) in small prisms (4.2 g.), m. p. 51—52° (Found: C, 70.9; H, 5.8; Cl, 15.8. C₁₅H₁₃OCl requires C, 70.8; H, 5.9; Cl, 16.1%). The solid (*A*) crystallised from benzene in nacreous plates, m. p. 146—147° (Found: C, 83.8; H, 6.0. C₂₃H₂₀O₂ requires C, 84.1; H, 6.1%).

3-2'-Naphthylxypropyl Cyanide.—The chloride (8.7 g.) and sodium cyanide (2.5 g.) were heated in ethyl alcohol (40 ml.) under reflux for 18 hr. The alcohol was distilled off, water added, and the product extracted with ether. The residue, after removal of the ether, was distilled (b. p. 152—160°/0.5 mm.). The solid distillate of cyanide crystallised from ethyl alcohol—light petroleum (b. p. 40°) in nacreous plates, m. p. 41—42° (Found: C, 79.5; H, 6.2. C₁₄H₁₃ON requires C, 79.6; H, 6.2%).

γ-2-Naphthylxybutyric Acid.—The cyanide (7.8 g.) was hydrolysed with a boiling solution of potassium hydroxide (2.5 g.) in water (5 ml.) and ethyl alcohol (20 ml.) for 18 hr. The solution was cooled, diluted with water, and extracted with ether. Extraction of the ethereal solution with aqueous sodium hydrogen carbonate, followed by acidification of the extract gave the required acid, which crystallised from benzene—light petroleum (b. p. 40°) in aggregates of small rhombs, m. p. 122—123° (Found: C, 73.3; H, 6.1. Calc. for C₁₄H₁₄O₃: C, 73.0; H, 6.2%). This acid was prepared by Synerholm and Zimmerman (*loc. cit.*) who claimed it as a new compound, but it had been previously reported by Nair and Peacock (*J. Indian Chem. Soc.*, 1935, 12, 318) who gave m. p. 122°.

δ-2-Naphthylxyvaleric Acid.—A solution of the above chloride (13.6 g.) in ethyl alcohol (30 ml.) was refluxed for 6 hr. with sodiomalonic ester (from 8.4 g. of diethyl malonate and 1.2 g.

Substituted ω-2-naphthylxyalkanecarboxylic acids, C₁₀H₇O·[CH₂]_{*n*}CO₂H
(substituents in the naphthalene system).

Substi- tuent	<i>n</i>	Route	Solvent *	M. p.	Found, %			Formula	Required, %		
					C	H	Cl		C	H	Cl
H	4	<i>b</i>	C ₆ H ₆ - <i>A</i>	111—112°	74.1	6.6	—	C ₁₆ H ₁₆ O ₃	73.8	6.6	—
H	5	<i>a</i>	{ aq. MeOH aq. MeOH	126—127 94—95	74.5 74.8	7.0 7.0	—	C ₁₆ H ₁₈ O ₃ C ₁₆ H ₁₈ O ₃	74.4 74.4	7.0 7.0	—
H	6	<i>b</i>	Et ₂ O- <i>B</i>	96—97	74.9	7.2	—	C ₁₇ H ₂₀ O ₃	75.0	7.4	—
H	7	<i>b</i>	<i>B</i>	91—92	75.2	7.7	—	C ₁₈ H ₂₂ O ₃	75.5	7.7	—
H	8	<i>a</i>	Et ₂ O- <i>B</i>	98—99	76.4	8.0	—	C ₁₈ H ₂₄ O ₃	76.0	8.0	—
H	9	<i>a</i>	Benzene	114—115	76.0	8.3	—	C ₂₀ H ₂₆ O ₃	76.4	8.3	—
H	11	<i>b</i>	EtOH	96—97	77.1	8.8	—	C ₂₂ H ₃₀ O ₃	77.2	8.8	—
3-Cl	2	—	MeOH	173—174	62.4	4.3	14.4	C ₁₃ H ₁₁ O ₃ Cl	62.3	4.4	14.2
3-Cl	3	<i>a</i>	aq. AcOH	174—175	63.3	5.0	13.3	C ₁₄ H ₁₃ O ₃ Cl	63.5	4.9	13.4
3-Cl	5	<i>a</i>	aq. MeOH	114—115	65.2	5.8	12.0	C ₁₆ H ₁₇ O ₃ Cl	65.6	5.8	12.1
3-Cl	7	<i>b</i>	aq. MeOH	74—75	67.8	6.6	11.0	C ₁₈ H ₂₁ O ₃ Cl	67.4	6.6	11.1
3-Cl	9	<i>a</i>	Et ₂ O- <i>B</i>	90—91	68.8	6.9	10.5	C ₂₀ H ₂₅ O ₃ Cl	68.8	7.2	10.2
1-Cl	2	—	MeOH	170—171	62.3	4.4	14.6	C ₁₃ H ₁₁ O ₃ Cl	62.3	4.4	14.2
1-Cl	3	<i>a</i>	MeOH	139—140	63.3	4.9	13.3	C ₁₄ H ₁₃ O ₃ Cl	63.5	4.9	13.4
1-Cl	5	<i>a</i>	MeOH	144—145	65.9	6.2	12.3	C ₁₆ H ₁₇ O ₃ Cl	65.7	5.8	12.1
8-Cl	3	<i>a</i>	AcOH	159—160	63.5	4.9	13.2	C ₁₄ H ₁₃ O ₃ Cl	63.5	4.9	13.4
8-Cl	5	<i>a</i>	Et ₂ O- <i>B</i>	122—123	65.5	6.0	12.2	C ₁₆ H ₁₇ O ₃ Cl	65.7	5.8	12.1
3 : 4-Cl ₂	2	—	MeOH	163—169	54.7	3.4	25.0	C ₁₃ H ₁₀ O ₃ Cl ₂	54.8	3.5	24.9
3 : 4-Cl ₂	3	<i>a</i>	Dioxan	175—177	56.5	4.0	23.7	C ₁₄ H ₁₃ O ₃ Cl ₂	56.2	4.1	23.7

Substituted ω -2-naphthylalkyl halides and cyanides, $C_{10}H_7O \cdot [CH_2]_n \cdot X$ (substituents in the naphthalene system).

Substituent	n	X	Solvent *	M. p.	Found, %			Formula	Required, %		
					C	H	Halogen		C	H	Halogen
H	2	Br	B	94—95°	57.5	4.5	31.8	$C_{12}H_{11}OBr$	57.4	4.4	31.8
H	3	Br	A	56—57	59.2	5.0	29.9	$C_{13}H_{13}OBr$	58.9	4.9	30.2
H	3	Cl	A	51—52	70.9	5.8	15.8	$C_{13}H_{13}OCl$	70.8	5.9	16.1
H	5	Br	liquid	¹	61.5	6.2	27.5	$C_{15}H_{17}OBr$	61.4	5.8	27.3
H	6	Br	A	40—41	62.5	6.3	26.2	$C_{16}H_{19}OBr$	62.5	6.2	26.1
H	8	Br	EtOH	47—48	64.6	7.1	23.6	$C_{18}H_{23}OBr$	64.5	6.9	23.9
H	10	Br	EtOH	54—55	66.0	7.4	21.9	$C_{20}H_{27}OBr$	66.1	7.4	22.0
3-Cl	3	Cl	A	64—65	60.9	4.8	28.0	$C_{13}H_{12}OCl_2$	61.2	4.7	27.8
3-Cl	5	Br	A	64—65	55.0	4.9	Cl, 10.6	$C_{15}H_{16}OBrCl$	55.0	4.9	Cl, 10.8
3-Cl	6	Br	A	67—68	56.1	5.6	Cl, 10.3	$C_{16}H_{18}OBrCl$	56.2	5.3	Cl, 10.4
1-Cl	3	Cl	liquid	²	61.4	4.8	27.7	$C_{13}H_{12}OCl_2$	61.2	4.7	27.8
1-Cl	5	Br	A	48—49	55.1	4.8	Cl, 10.7	$C_{15}H_{16}OBrCl$	55.0	4.9	Cl, 10.8
8-Cl	3	Cl	liquid	³	61.5	4.5	—	$C_{13}H_{12}OCl_2$	61.2	4.7	27.8
8-Cl	5	Br	EtOH	58—60	54.8	5.1	—	$C_{15}H_{16}OBrCl$	55.0	4.9	Cl, 10.8
3 : 4-Cl ₂	3	Cl	EtOH	92—93	53.9	3.6	36.6	$C_{13}H_{11}OCl_3$	53.9	3.8	36.8
3 : 4-Cl ₂	5	Br	EtOH	66—67	49.6	4.2	Cl, 19.4	$C_{15}H_{15}OBrCl_2$	49.7	4.1	Cl, 19.6
H	3	CN	EtOH-A	41—42	79.5	6.2	—	$C_{14}H_{13}ON$	79.6	6.2	—
H	5	CN	Et ₂ O-A	59—60	80.2	7.1	—	$C_{16}H_{17}ON$	80.3	7.1	—
H	8	CN	aq. MeOH	51—52	80.7	8.0	—	$C_{18}H_{23}ON$	81.1	8.2	—
H	9	CN	liquid	⁴	81.5	8.7	—	$C_{20}H_{26}ON$	81.4	8.5	—
3-Cl	3	CN	EtOH	96—97	67.9	5.1	14.6	$C_{14}H_{12}ONCl$	68.4	4.9	14.4
3-Cl	5	CN	EtOH	109—110	69.9	6.1	13.0	$C_{16}H_{16}ONCl$	70.2	5.9	13.0
1-Cl	3	CN	Et ₂ O-B	82—83	68.4	4.6	14.6	$C_{14}H_{12}ONCl$	68.4	4.9	14.5
1-Cl	5	CN	EtOH	74.5—75	70.2	5.8	13.0	$C_{16}H_{16}ONCl$	70.2	5.9	13.0
8-Cl	3	CN	EtOH	56—57	68.7	5.0	14.6	$C_{14}H_{12}ONCl$	68.4	4.9	14.5
8-Cl	5	CN	EtOH	74—76	70.1	5.7	—	$C_{16}H_{16}ONCl$	70.2	5.9	13.0
3 : 4-Cl ₂	3	CN	MeOH	85—86	59.6	3.9	25.6	$C_{14}H_{11}ONCl_2$	60.0	3.9	25.4
3 : 4-Cl ₂	5	CN	MeOH	81—82	62.0	4.7	23.3	$C_{16}H_{15}ONCl_2$	62.4	4.9	23.0

Substituted ω -2-naphthylalkylmalonic acids, $C_{10}H_7O \cdot [CH_2]_n \cdot CH(CO_2H)_2$ (substituents in the naphthalene system).

H	3	—	Et ₂ O-B	171—172 (dec.)	66.6	5.6	—	$C_{16}H_{16}O_5$	66.7	5.6	—
H	5	—	Et ₂ O-B	153—154 (dec.)	68.2	6.2	—	$C_{18}H_{20}O_5$	68.3	6.3	—
H	6	—	AcOH	161—162 (dec.)	69.0	6.9	—	$C_{18}H_{22}O_5$	69.3	6.7	—
H	10	—	aq. AcOH	134—135	71.5	7.8	—	$C_{22}H_{30}O_5$	71.5	7.8	—
3-Cl	6	—	aq. AcOH	149—150 (dec.)	62.2	5.8	9.7	$C_{18}H_{21}O_5Cl$	62.5	5.8	9.7

1 : ω -Bis-2'-naphthylalkanes, $C_{10}H_7O \cdot [CH_2]_n \cdot O \cdot C_{10}H_7$ (substituents in naphthalene system).

H	2	—	Dioxan	215—216	84.1	5.8	—	$C_{22}H_{18}O_2$	84.1	5.7	—
H	3	—	Benzene	146—147	83.8	6.3	—	$C_{23}H_{20}O_2$	84.1	6.1	—
H	5	—	A	74—76	84.0	7.0	—	$C_{25}H_{24}O_2$	84.3	6.7	—
H	6	—	Benzene	152—153	84.3	7.1	—	$C_{26}H_{26}O_2$	84.3	7.0	—
H	8	—	Benzene	129—130	84.2	7.5	—	$C_{28}H_{30}O_2$	84.4	7.5	—
H	9	—	C ₆ H ₆ -A	128—129	84.5	7.6	—	$C_{29}H_{32}O_2$	84.5	7.8	—
H	10	—	Benzene	126—127	84.5	7.9	—	$C_{30}H_{34}O_2$	84.5	8.0	—
3-Cl	3	—	C ₆ H ₆ -A	192—193	69.3	4.7	18.0	$C_{23}H_{18}O_2Cl_2$	69.5	4.5	17.9
3 Cl	5	—	C ₆ H ₆ -A	144—145	71.1	5.5	16.0	$C_{26}H_{24}O_2Cl_2$	71.1	5.5	16.2

* Solvents, other than those named are: A light petroleum (b. p. 40—60°); B, light petroleum (b. p. 60—80°).

¹ B. p. 180—184°/0.2 mm. ² B. p. 170—172°/0.5 mm. ³ B. p. 162—164°/0.5 mm. ⁴ B. p. 180—184°/0.5 mm.

of sodium). 40% Sodium hydroxide (50 ml.) was then added, and after a further hour's refluxing the solution was cooled, diluted with water, and extracted with ether. Acidification of the alkaline layer gave the 2'-naphthylalkylmalonic acid, m. p. 167° (decomp.), which crystallised from acetone-benzene in monoclinic prisms, m. p. 171—172° (decomp.) (Found: C, 66.6; H, 5.6. $C_{16}H_{16}O_5$ requires C, 66.7; H, 5.6%). Decarboxylation was carried out at

185° for 1 hr. The *valeric acid* crystallised from benzene-light petroleum (b. p. 40°) in rhombic plates, m. p. 111—112° (Found: C, 74.1; H, 6.6. $C_{15}H_{16}O_3$ requires C, 73.8; H, 6.6%).

6-2'-Naphthylxyhexanoic Acid.—5-2'-Naphthylxypentyl cyanide was hydrolysed with ethyl alcoholic potassium hydroxide as described above. When the ethereal extract was shaken with sodium hydrogen carbonate solution an insoluble sodium salt was formed which was washed with ether and decomposed with concentrated hydrochloric acid. The *acid*, isolated by ether, crystallised from aqueous methyl alcohol in wedge-shaped prisms, m. p. 94—95° (Found: C, 74.8; H, 7.0. $C_{16}H_{18}O_3$ requires C, 74.4; H, 7.0%). In another experiment, under apparently identical conditions, the product crystallised from aqueous methyl alcohol in nacreous plates, m. p. 126—127° (Found: C, 74.5; H, 7.0%). This product did not depress the m. p. of the isomeric acid, but we have so far failed to demonstrate dimorphism by the mutual seeding of solutions in aqueous methyl alcohol. The *S-benzylthiuronium* salt from the low-m. p. form only crystallised from aqueous ethyl alcohol in rectangular prisms, m. p. 156—157° (Found: C, 68.0; H, 6.6; S, 7.5. $C_{24}H_{28}O_3N_2S$ requires C, 67.9; H, 6.6; S, 7.5%).

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