

Researches on Plant Growth Substances

I. On 1-Naphthylacetaldehyde 1*

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Recently Poul Larsen¹ presented evidence for the function of 3-indole-acetaldehyde as a growth hormone in higher plants. To procure more direct evidence that this compound is actually a growth hormone it would be of great interest to test the action of synthetically prepared 3-indoleacetaldehyde. This compound has, however, not hitherto been described in the literature, and experiments on synthesizing it were beset by such difficulties that we at last chose to try the different methods of preparing aldehydes on a model substance, which could be made from a more easily accessible starting material. For this purpose 1-naphthylacetaldehyde was selected. This substance would also be of interest from the point of view of growth hormone action, since 1-naphthylacetic acid is almost as active as 3-indoleacetic acid. Indeed our preparations of 1-naphthylacetaldehyde have been shown by Larsen² to possess activity as a growth hormone.

Of course not all methods leading to 1-naphthylacetaldehyde could be applied to the indole analogue, because the indole nucleus has a rather reactive hydrogen atom. But one could be fairly sure that there would be little use in trying methods of preparing 3-indoleacetaldehyde, which could not also be applied to the naphthalene analogue. As a matter of fact several of the usual methods of preparing aldehydes gave none or little 1-naphthylacetaldehyde, so this compound must be characterized as rather difficultly accessible.

1-Naphthylacetaldehyde has only been described once in the literature, by Tiffeneau and Daudel³, who prepared it by the reaction between 1-vinylnaphthalene, mercuric oxide and iodine. The boiling point of the aldehyde was given as 163—166° at 13 mm and the melting point of the semicarbazone as

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208°. According to our investigations, however, this is nearer the melting point of 1-naphthaldehyde semicarbazone, and therefore the aldehyde of Tiffeneau and Daudel was not pure. On the other hand we were able to show that some naphthylacetaldehyde can be obtained by the method of Tiffeneau and Daudel.

1-Naphthylacetaldehyde may easily be oxidized to 1-naphthaldehyde, and in some preparations 1-naphthylacetaldehyde may be contaminated by 1-naphthaldehyde used as starting material or formed by side reactions. It was, therefore, of great importance for us to be able with certainty to distinguish between these two aldehydes. From 1-naphthaldehyde and from a pure sample of 1-naphthylacetaldehyde, prepared from 1-naphthyl-2,3-propanediol (see later), we prepared several derivatives, the melting points of which have been compared in the following table (the figures in parantheses are those found by Coles and Dodds⁴ who previously prepared several derivatives of 1-naphthaldehyde). The melting points were determined on a Kofler stage.

Table 1.

	1-Naphthaldehyde-	1-Naphthylacet- aldehyde
phenylhydrazone	82 (82)	—
<i>as</i> -methylphenylhydrazone	92	—
4-nitrophenylhydrazone	235 (237)	—
2,4-dinitrophenylhydrazone	260—62 (254)	184
oxime	98—99 (98)	123—24
semicarbazone	218—19 (219)	190—91
4-phenylsemicarbazone	205—06	166
thiosemicarbazone	222—23 (217)	179
3-nitrobenzhydrazone	217—18	150—51

As a rule the derivatives of 1-naphthylacetaldehyde are more soluble than the derivatives of 1-naphthaldehyde and with the exception of the oxime, their melting points are lower. The phenylhydrazone, *as*-methylphenylhydrazone and 4-nitrophenylhydrazone of 1-naphthylacetaldehyde are unsuited for identification; they were only obtained by addition of water to their alcoholic solutions as oily or semisolid precipitates.

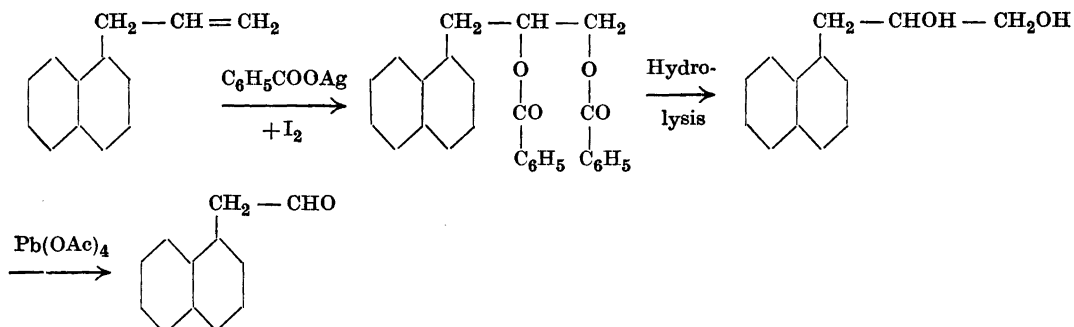
Especially characteristic for 1-naphthylacetaldehyde is the semicarbazone, which separates as white crystals by addition of semicarbazide hydrochloride (without addition of acetate) to aqueous solutions or suspensions of the aldehyde. The melting point is also suited for differentiation between the two aldehydes. The semicarbazone was prepared in most cases for isolating and

characterizing 1-naphthylacetaldehyde formed by different methods. From mixtures of the two aldehydes the semicarbazone of 1-naphthylacetaldehyde is easily obtained in the pure form. As the melting point of the semicarbazone of Tiffeneau and Daudel was given as 208° , their aldehyde must have contained an appreciable amount of 1-naphthaldehyde, and perhaps mainly consisted of this.

A point of great importance for the isolation of pure 1-naphthylacetaldehyde was the observation that the aldehyde is volatile with steam. The distillate has a very faint odour, somewhat resembling that of phenylacetaldehyde. By addition of semicarbazide hydrochloride to the aqueous distillate the semicarbazone separates in pure form.

The other derivatives mentioned under 1-naphthylacetaldehyde are also well suited for differentiation between the two aldehydes. For identification we have often used the 2,4-dinitrophenylhydrazone. It is, however, to be noted that the 2,4-dinitrophenylhydrazone of 1-naphthaldehyde is so slightly soluble, that this compound separates from mixtures of the aldehydes even when they only contain little 1-naphthaldehyde. The dinitrophenylhydrazone of 1-naphthaldehyde is darker red than that of 1-naphthylacetaldehyde.

As mentioned above the method of Tiffeneau and Daudel gives a little 1-naphthylacetaldehyde. This method is, however, not suited for preparation of the pure aldehyde and the same applies to most other methods we have investigated. The best method we have found for preparing pure 1-naphthylacetaldehyde is the aldehyde synthesis of Hershberg ⁵. By application of this method to the problem in question, 1-allylnaphthalene was transformed into 1-(1-naphthyl)-2,3-propanediol, and this was oxidized with lead tetraacetate:



The preparation goes over two intermediary products, but the yields are good and the aldehyde is obtained in a high state of purity.

We have further investigated the following methods with a view to preparing 1-naphthylacetaldehyde (more details of some of the experiments are to be found in the experimental part).

a. Oxidation and dehydrogenation of β -1-naphthylethanol

The oxidation of β -1-naphthylethanol with chromic acid gave preparations consisting mainly of 1-naphthaldehyde. The aldehyde (isolated by extraction with ether, purifying *via* the hydrogensulphite compound and distilling) gave a semicarbazone, thiosemicarbazone, 4-phenylsemicarbazone, p-nitrophenylhydrazone, 2,4-dinitrophenylhydrazone and methylphenylhydrazone melting as crude products at 210°, 214°, 194°, 215°, 260° and 88–89° respectively. After recrystallization the melting points were the same as indicated in Table 1.

Shumeiko ⁶ has described a method of obtaining phenylacetaldehyde by oxidation of β -phenylethanol with chromic acid in the presence of an indifferent solvent (benzene, toluene *etc.*). By application of this method to β -1-naphthylethanol we obtained 1-naphthylacetaldehyde, but only in slight yield and containing an appreciable amount of 1-naphthaldehyde.

By oxidation of β -1-naphthylethanol with CrO_3 in acetic acid a little 1,4-naphthoquinone was formed; most of the naphthylethanol could be recovered unchanged.

By oxidation of β -1-naphthylethanol with lead dioxide and sulphuric acid, with hypobromite and with chloramine-T, 1-naphthaldehyde was obtained.

By the action of lead tetraacetate on β -1-naphthylethanol in benzene solution (*cf.* Criegee ⁷) no reaction took place.

It was further attempted to prepare 1-naphthylacetaldehyde by catalytic dehydrogenation of β -1-naphthylethanol (the method of Bouveault ⁸). An all-glass apparatus similar to that described by Weygand ⁹ was used. As catalyst we used either freshly reduced copper oxide (*cf.* Weygand ⁹) or copper-silver on pumice (Davies and Hodgson ¹⁰). The catalyst chamber was electrically heated to 240° and the apparatus thoroughly flushed with hydrogen. Then the alcohol was slowly distilled through the catalyst at a pressure of 12–15 mm. No aldehyde was formed, but from the distillate 1-ethylnaphthalene could be isolated. Evidently the alcohol is dehydrated to 1-vinylnaphthalene, which in its course is hydrogenated to 1-ethylnaphthalene. It was then attempted to use copper oxide as a catalyst; in this case, when removing the stopper at the top of the catalyst chamber, the characteristic odour of 1-naphthylacetaldehyde could be perceived, but no aldehyde could be detected in the distillate.

Finally we tried to repare 1-naphthylacetaldehyde by the Oppenauer method¹¹, *i. e.* oxidation of the alcohol with ketones (acetone, cyclohexanone) in the presence of aluminium *tert.*-butoxide, but no 1-naphthylacetaldehyde could be isolated.

b. From 1-vinylnaphthalene

By reaction of 1-vinylnaphthalene with iodine and mercuric oxide 1-naphthylacetaldehyde was obtained, but only in small yield.

1-Naphthylacetaldehyde could also be obtained by rearrangement of naphthylethyleneoxide, prepared from 1-vinylnaphthalene and perbenzoic acid.

c. 1-Naphthylmethylmagnesium chloride and ethyl orthoformate

This method failed, because the Grignard process resulted mainly in 1,2-dinaphthylethane.

d. 1-Naphthylmagnesium bromide and bromoacetal

No 1-naphthylacetaldehyde was obtained.

e. 1-Naphthylmagnesium bromide and ethoxyacetal

By the reaction of phenylmagnesium bromide with ethoxyacetal Späth¹² has prepared phenylacetaldehyde. No 1-naphthylacetaldehyde could be obtained by application of this method to 1-naphthylmagnesium bromide.

f. The glycidic ester synthesis of Claisen-Darzens¹³

Several reactions of ethyl chloro- or bromoacetate with 1-naphthaldehyde were performed using sodium, sodamide or sodium ethoxide as condensing agents. Only small yields of 1-naphthylacetaldehyde were obtained, the best ones when sodium ethoxide was used.

g. β -1-naphthylacrylic acid and hypochlorite or hypobromite

By reaction of cinnamic acid with hypochlorite or hypobromite good yields of phenylacetaldehyde are obtained (Erlenmeyer¹⁴); this is one of the best methods of preparing phenylacetaldehyde. By application to the naphthalene

analogue, however, no 1-naphthylacetaldehyde was obtained. Most of the β -1-naphthylacrylic acid remained unchanged (no addition of hypochlorous or hypobromous acid taking place), but some of it was oxidized to 1-naphthaldehyde.

h. Hydrolysis of 1-naphthylacetaldehyde oxime

By reduction of α -(1-naphthyl)- β -nitro-ethylene with aluminium amalgam, Mayer and Stieglitz¹⁵ prepared the oxime of 1-naphthylacetaldehyde, but they did not hydrolyse this compound. By hydrolysis of the oxime with 1 *N* hydrochloric acid + ethanol (1 : 1) we prepared the aldehyde in a 70 % yield (isolated as the semicarbazone after steam distillation).

According to these experiments the most satisfactory method of preparing 1-naphthylacetaldehyde is the oxidation of 1-(1-naphthyl)-2,3-propanediol with lead tetraacetate. By distillation in a high vacuum the aldehyde was obtained as a colourless liquid (b. p. 112° at 0.7 mm) which crystallized by cooling in solid carbon dioxide and then had the melting point 33.5°. In the course of some weeks or months the crystalline substance is transformed into a viscous oil and later into a glassy mass. Without doubt this aldehyde undergoes polymerisations in the same manner as is known for phenylacetaldehyde (Stobbe and Lippold¹⁶), and accordingly the viscous oil and glassy substance are chain polymers.

EXPERIMENTAL

1-(1-Naphthyl)-2,3-propanediol-dibenzoate. A mixture of 15 g of 1-allylnaphthalene (prepared from 1-naphthylmagnesium bromide and allyl bromide. Yield 74 %. B. p. 135–136° at 15 mm), 40 g of dry silver benzoate, 21 g of iodine and 250 ml of dry benzene was refluxed for 14 hours. The silver iodide was filtered by suction and washed with benzene, and the benzene solution was washed with sodium hydrogen carbonate solution and with water and then dried over calcium chloride. The benzene was distilled off on a water bath, when the dibenzoate was left as a brownish oil. By dissolving the oil in petroleum ether and evaporating in vacuo the dibenzoate crystallized. It was purified by dissolving in hot methanol, cooling in ice and seeding with some of the crystals formed in petroleum ether solution. Yield 21.9 g = 60 %. M. p. 83°.

$C_{27}H_{22}O_4$ (410.4)	Calc.	C	79.01	H	5.40
	Found	»	79.62	»	5.37

1-(1-Naphthyl)-2,3-propanediol. The dibenzoate (20 g) was hydrolyzed by refluxing with a solution of 11 g of sodium hydroxide in 50 ml of water + 125 ml of methanol for 2 hours. The solution was then almost neutralized with sulphuric acid, the methanol removed in vacuo and water added. Most of the glycol separated, a little more could be

isolated by extraction of the solution with ether. The melting point of the crude product was 110°, after recrystallization from water the m. p. was 111°. Yield 8.9 g = 90 %.

$C_{13}H_{14}O_2$ (202.2)	Calc.	C	77.21	H	6.98
	Found	»	77.23	»	6.97

1-Naphthylacetaldehyde. The glycol (3.2 g) was treated with lead tetraacetate (8.9 g) in benzene (27 ml) for 1 ½ hour at room temperature. Then acetic acid (8 ml) was added and the mixture was heated at 50° for ½—1 hour. The solution was cooled, washed with water and sodium hydrogen carbonate solution. The aqueous layer was extracted with ether. The ether and benzene layers were combined, the solution dried with sodium sulphate, filtered and evaporated in vacuo. The residue was a faintly yellow oil. Yield 2.5 g = 92 %.

By distillation in a high vacuum of the crude aldehyde obtained by oxidation of 8.9 g of the glycol 3.7 g of 1-naphthylacetaldehyde = 60 % was obtained. The loss by distillation could presumably be much diminished. M. p. 33.5°. B. p. 112° at 0.7 mm.

$C_{12}H_{10}O$ (146.2)	Calc.	C	84.69	H	5.92
	Found	»	84.98	»	5.72

Derivatives of 1-naphthylacetaldehyde

2,4-Dinitrophenylhydrazone: Red-yellow precipitate by addition of the aldehyde to an alcoholic solution of 2,4-dinitrophenylhydrazine containing a little hydrochloric acid. Recrystallized from toluene it forms orange-red crystals with m. p. 184°.

$C_{18}H_{14}O_4N_4$ (350.3)	Calc.	N	15.99
	Found	»	16.02

Oxime: The aldehyde was added to a concentrated aqueous solution of hydroxylamine hydrochloride + sodium acetate, the solution heated to boiling and alcohol added to obtain a clear solution. Colourless crystals were obtained on cooling, m. p. 123—124°.

$C_{12}H_{11}ON$ (185.2)	Calc.	N	7.56
	Found	»	7.46

Semicarbazone: White crystals by addition of an aqueous solution of semicarbazide hydrochloride to an alcoholic solution of the aldehyde. Recrystallized from alcohol it had m. p. 190—191°.

$C_{13}H_{13}ON_3$ (227.2)	Calc.	N	18.49
	Found	»	18.38

4-Phenylsemicarbazone: White crystals from rather concentrated alcoholic solution (1 ml/0.15 g) of the components. Recrystallized from alcohol. M. p. 166°.

$C_{19}H_{17}ON_3$ (303.3)	Calc.	N	13.85
	Found	»	13.86

Thiosemicarbazone: An alcoholic solution of the aldehyde and an aqueous solution of thiosemicarbazide were mixed and heated to boiling. Water was added to opalescence and then alcohol to obtain a clear solution. By cooling colourless crystals, m. p. 179°.

$C_{13}H_{13}SN_3$ (243.3)	Calc.	N	17.27
	Found	»	17.54

m-Nitrobenzhydrazone: Yellow crystals from a solution of the components in aqueous alcohol. M. p. 150—151°.

$C_{19}H_{15}O_3N_3$ (333.4)	Calc.	N	12.63
	Found	»	12.33

Derivatives of 1-naphthaldehyde. For comparison the following derivatives of 1-naphthaldehyde were prepared:

Phenylhydrazone: Crystallized from a concentrated alcoholic solution of the components. M. p. 82°.

$C_{17}H_{14}N_2$ (246.3)	Calc.	N	11.38
	Found	»	11.29

α -Methyl-phenylhydrazone: Small yellow crystal aggregates from an alcoholic solution of the components. M. p. 92°.

$C_{18}H_{16}N_2$ (260.3)	Calc.	N	10.76
	Found	»	11.10

p-Nitrophenylhydrazone: From the components in dilute alcohol (1 : 1). Small yellow needles. M. p. 235°.

$C_{17}H_{13}O_2N_3$ (291.3)	Calc.	N	14.42
	Found	»	14.34

2,4-Dinitrophenylhydrazone: Recrystallized from toluene. Orange-red crystals. M. p. 260—262°.

$C_{17}H_{12}O_4N_4$ (336.3)	Calc.	N	16.66
	Found	»	16.69

Oxime: Colourless needles from dilute alcohol. M. p. 98—99°.

$C_{11}H_9ON$ (171.2)	Calc.	N	8.18
	Found	»	8.38

Semicarbazone: Colourless needles from alcohol. M. p. 218—219°.

$C_{12}H_{11}ON_3$ (213.2)	Calc.	N	19.71
	Found	»	19.78

4-Phenylsemicarbazone: White crystals from alcohol. M. p. 205–206°.

$C_{18}H_{15}ON_3$ (289.3)	Calc.	N	14.52
	Found	»	14.60

Thiosemicarbazone: Faint yellow, thin needles. Recrystallized from alcohol. M. p. 222–223°.

$C_{12}H_{11}SN_3$ (229.3)	Calc.	N	18.32
	Found	»	18.39

m-Nitrobenzhydrazine: Light yellow crystals from a hot alcoholic solution of the components. M. p. 217–218°.

$C_{18}H_{13}O_3N_3$ (319.3)	Calc.	N	13.17
	Found	»	13.31

Oxidation of β -1-naphthylethanol with chromic acid. To a solution of 6.5 g of sodium dichromate and 10 g of conc. sulphuric acid in 25 ml of water were added 50 ml of benzene and then, with vigorous shaking, a solution of 10 g of 1-naphthylethanol¹⁷ in 15 ml of benzene. The temperature rose to ca. 55°. The mixture was shaken until the temperature had fallen to room temperature; then 50 ml of water was added and the mixture was steam distilled. The distillation was continued until the distillate gave no further reaction with dinitrophenylhydrazine. The benzene layer was separated and the water layer extracted with ether. The combined extracts were dried with sodium sulphate and distilled *in vacuo*. Between 164 and 172° at 12 mm a small amount (1.9 g) of a faint yellow oil distilled. The aldehyde was analyzed by dissolving in ethanol, precipitating with an aqueous solution of semicarbazide hydrochloride and weighing the precipitate; according to this analysis the aldehyde contained 81 % of naphthylacetaldehyde. After one crystallization the semicarbazone melted at 186–187° and contained 18.16 % N (calc. 18.49). The oxime prepared from the oil had the correct melting point (123°). The 2,4-dinitrophenylhydrazone, however, after recrystallization from toluene had the melting point 261–262°, *i. e.* the melting point of 1-naphthaldehyde 2,4-dinitrophenylhydrazone. The crude product of the dinitrophenylhydrazone melted partially at 175°. By chromatographic adsorption on aluminium oxide the two dinitrophenylhydrazones could be separated (that derived from 1-naphthaldehyde forming the lower zone) and isolated after elution they had the melting points 262° and 184°.

Transformation of 1-vinylnaphthalene into 1-naphthylacetaldehyde

a. With cooling in ice and vigorous shaking, 3 g of yellow mercuric oxide and 3.5 g of iodine were added to a solution of 1 g of 1-vinylnaphthalene¹⁸ in 10 ml of ether. Yellow mercuric iodide was formed at first, but when the mixture reached room temperature it was transformed into the red modification. The ethereal layer was decolourised with sodium thiosulphate, the ether was removed *in vacuo* and the residue steam-distilled. During the distillation some iodine was formed which was reduced with sodium thiosulphate. By addition of semicarbazide hydrochloride the semicarbazone of 1-naphthylacetaldehyde (m. p. 190°) was precipitated. The yield was only 0.110 g \sim 12 %.

The residue from the distillation was obviously a polymeride.

b. 1-Naphthylethylene oxide was prepared from 1-vinylnaphthalene by reaction with perbenzoic acid analogous to the preparation of styrene oxide¹⁹ as a colourless oil with boiling point 106° at 1.4 mm.

$C_{12}H_{10}O$ (170.2)	Calc.	C	84.69	H	5.92
	Found	»	84.28	»	5.70

One gram of 1-naphthylethylene oxide was added to a solution of anhydrous magnesium bromide in ether (prepared by addition of the calculated amount of bromine and a trace of iodine to 0.5 g of magnesium under 100 ml of anhydrous ether). The solution became turbid. The ether was removed by distillation and the residue steam distilled. The distillate gave 0.2 g of the semicarbazone of 1-naphthylacetaldehyde.

Condensation of 1-naphthaldehyde with ethyl bromoacetate

A mixture of 15.6 g of 1-naphthaldehyde²⁰ (0.1 mol) and 16.7 g (0.1 mol) of ethyl bromoacetate was added to a suspension of 0.1 mol of ethanolfree sodium ethoxide in ether (prepared from pulverized sodium and the calculated amount of ethanol in ether). After the addition the mixture was heated for one hour on a steam bath, then it was cooled, water was added and the ether layer dried with potassium carbonate and the ether removed by distillation. To the residue alcoholic sodium hydroxide was added. After standing for some days a white salt had separated which was filtered and washed with ether. Yield 10.2 g (+ 1.5 g from the filtrate). Analysis: 0.2241 g of the salt gave by steam distillation 0.085 g of a semicarbazone melting at 187–188°. The salt accordingly contained 39 % of the sodium salt of β -1-naphthylglycidic acid, and the yield of 1-naphthylacetaldehyde was 27 %, calculated on the 1-naphthaldehyde used.

After one crystallization the semicarbazone melted at 190°. The 2,4-dinitrophenylhydrazone, thiosemicarbazone and oxime prepared from the aldehyde formed by steam distillation melted at 181°, 180° and 118–120° respectively, showing the compounds to be derivatives of 1-naphthylacetaldehyde.

The oxime may also be prepared directly by boiling an aqueous solution of the salt with hydroxylamine hydrochloride, when the oxime separates.

By hydrolysis of the sodium salt of 1-naphthylglycidic acid with hydrochloric acid we once isolated a small amount of an acidic substance, which was insoluble in ether and melted at about 200° with evolution of carbon dioxide and formation of 1-naphthylacetaldehyde. According to these properties and analyses the compound is β -1-naphthylglyceric acid, $C_{10}H_7 \cdot CHOH \cdot CHOH \cdot COOH$.

$C_{13}H_{12}O_4$ (232.2)	Calc.	C	67.24	Eq.wt.	232
	Found	»	67.44	»	» 233

SUMMARY

1-Naphthylacetaldehyde was for the first time prepared in a pure state by oxidation of 1-(1-naphthyl)-2,3-propanediol with lead tetraacetate and characterized through derivatives. Other possible methods of obtaining this

aldehyde were investigated, but most of them gave none or little of the required product.

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