

reacted at pH 8 with a solution of 200 mg chloromercuriacetic acid *N*-hydroxysuccinimide ester in 1 ml of anhydrous tetrahydrofuran, as described for the corresponding phenoxyacetylation procedure (Gillam *et al.*¹) The reaction product isolated by ethanol precipitation was dissolved in 10 ml of Gillam's¹ solution A and was applied (2800 A_{260} units, 11.4×10^6 cpm) to the previously mentioned BD-cellulose column. The column was eluted with Gillam's solutions A, B, E, and finally with 1.5 M NaCl solution containing 10 % ethanol, 0.01 M $MgCl_2$ and 0.01 M sodium acetate buffer pH 4.5. The chromatogram obtained is shown in Fig. 2. It is evident from the figure, that non-radioactive material, *i.e.* unesterified tRNA is eluted with the solution B at the same position as in Fig. 1 (peak I). No ^{14}C -valyl-tRNA seems to be present in the product, since we have found such aminoacyl-tRNA to be eluted with the solution B immediately after the unesterified tRNA.

The material eluted with 1.5 M NaCl should be chloromercuriacetylated ^{14}C -valyl-tRNA because of its coinciding UV-absorption and radioactivity, and because of the similar high affinity to the column that has been found for all *N*-acylated aminoacyl-tRNA:s studied by Gillam *et al.*¹

The fraction (II) indicated in Fig. 2 was precipitated by 3 volumes of ethanol, collected by centrifugation and dissolved in 4 ml of water. This solution contained 310 A_{260} units (560 μ moles, calculated with the value of 1.8 μ moles tRNA per A_{260} units⁶) and 10.2×10^6 cpm (440 μ moles) giving a ratio tRNA/ ^{14}C -L-valine of 1.27.

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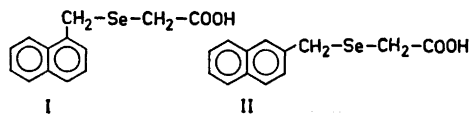
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Naphthylmethylseleno-substituted Alkanoic Acids

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In the course of current work on the biological effects of organoselenium compounds the acids I, II and 18 homologues (Tables 1 and 2) have been prepared. The end in view was to test the growth-regulating activity, the factor-3-effect and

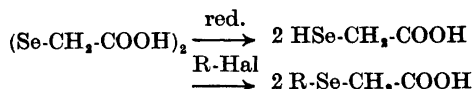


possibly other biological effects. The work on the growth-regulating activity, which also included some acids with selenium attached directly to the naphthalene ring prepared in this institute,^{1,2} was carried out by Professor B. Åberg.* It has in part been published³⁻⁴ and indicates that the selenium compounds have an anti-auxin effect, more pronounced than that of the corresponding sulphur compounds. The acid II is perhaps the most powerful anti-auxin known.⁴

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The work on the factor-3-effect is carried out in collaboration with Professor Klaus Schwarz* and will be published elsewhere. The present paper deals with the synthesis of the compounds.

Diseleno-dicarboxylic acids were reduced in alkaline solution to selenosubstituted acids. These were not isolated but directly reacted with 1-naphthylmethyl chloride⁵ or 2-naphthylmethyl bromide.⁴



The data for the acids are summarised in Tables 1 and 2.

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Experimental. The reduction was carried out in aqueous ammonia, either with zinc powder or with sodium formaldehydesulfoxylate (rongalite). The acids were generally recrystallised once or twice from formic acid and then from another organic solvent (carbon tetrachloride, cyclohexane, ligroin). If the last crystallisation is carried out from formic acid, traces of the solvent will remain in the product and cause discolouration and slight decomposition on long standing. Detailed descriptions for preparing four of the acids are given below.

1-Naphthylseleno-acetic acid (I). 2.76 g (0.01 mole) of diseleno-diacetic acid⁷ were dissolved in 10 ml concentrated aqueous ammonia + 10 ml water. Zinc powder was added in small portions with shaking until the yellow colour of the diselenide had disappeared. The solution was then filtered by suction into an 150 ml flask and the zinc on the filter was washed with 15 ml aqueous

Table 1. 1-Naphthylmethylseleno-substituted acids.

| Acid | m.p. °C | Calculated | | | Found | | |
|--------------|-------------|------------|------|-------|-------|------|-------|
| | | C | H | Se | C | H | Se |
| Acetic (I) | 115–116 | 55.92 | 4.33 | 28.28 | 55.90 | 4.36 | 28.29 |
| 2-Propionic | 99–100 | 57.34 | 4.81 | 26.93 | 57.32 | 4.94 | 26.93 |
| 3-Propionic | 81.5–82.5 | 57.34 | 4.81 | 26.93 | 57.14 | 4.90 | 26.96 |
| 2-Butyric | 119–121 | 58.64 | 5.25 | 25.70 | 58.75 | 5.27 | 25.60 |
| 3-Butyric | 76–77.5 | 58.64 | 5.25 | 25.70 | 58.96 | 5.37 | 25.42 |
| 4-Butyric | 72–73 | 58.64 | 5.25 | 25.70 | 58.50 | 5.28 | 25.59 |
| 2-Isobutyric | 115.5–116.5 | 58.64 | 5.25 | 25.70 | 58.53 | 5.25 | 25.81 |
| 3-Isobutyric | 72.5–73.5 | 58.64 | 5.25 | 25.70 | 58.64 | 5.24 | 25.50 |
| 5-Valeric | 110.5–112 | 59.80 | 5.65 | 24.58 | 59.73 | 5.72 | 24.61 |

Table 2. 2-Naphthylmethylseleno-substituted acids.

| Acid | m.p. °C | Calculated | | | Found | | |
|---------------|-------------|------------|------|-------|-------|------|-------|
| | | C | H | Se | C | H | Se |
| Acetic (II) | 120–121 | 55.92 | 4.33 | 28.28 | 55.70 | 4.40 | 28.07 |
| 2-Propionic | 103–104 | 57.34 | 4.81 | 26.93 | 57.32 | 4.76 | 26.94 |
| 3-Propionic | 115.5–116.5 | 57.34 | 4.81 | 26.93 | 57.30 | 4.83 | 26.73 |
| 2-Butyric | 98–99.5 | 58.64 | 5.25 | 25.70 | 58.47 | 5.27 | 25.74 |
| 3-Butyric | 96–97 | 58.64 | 5.25 | 25.70 | 58.71 | 5.25 | 25.64 |
| 4-Butyric | 91–92 | 58.64 | 5.25 | 25.70 | 58.53 | 5.31 | 25.71 |
| 2-Isobutyric | 161–162.5 | 58.64 | 5.25 | 25.70 | 58.53 | 5.27 | 25.72 |
| 3-Isobutyric | 76.5–77.5 | 58.64 | 5.25 | 25.70 | 58.35 | 5.20 | 25.68 |
| 5-Valeric | 79–80 | 59.80 | 5.65 | 24.58 | 59.79 | 5.69 | 24.53 |
| 6-Caproic | 87.5–88.5 | 60.89 | 6.01 | 23.55 | 60.84 | 6.02 | 23.59 |
| 11-Undecanoic | 78–80 | 65.17 | 7.46 | 19.48 | 64.88 | 7.60 | 19.52 |

ammonia. 1-Naphthylmethyl chloride (3.7 g, 0.021 mole) dissolved in 40 ml ethanol was then added to the solution. After shaking for a few minutes, the milky suspension was practically transparent. After standing overnight, the solution was filtered and the greater part of the ethanol was evaporated with a ventilator. Some oil separated but dissolved again on adding ammonia. The solution was then diluted with water to about 250 ml and the acid precipitated by adding concentrated hydrochloric acid in excess. It separated as a gradually crystallising oil.

A rapid crystallisation and a purer product is obtained if some finely powdered acid is dispersed in the hydrochloric acid added; this material is obtained by first acidifying a small sample of the solution. The same procedure can be recommended for the other acids of this series.

The acid was filtered off, dried and recrystallised, once from formic acid and twice from carbon tetrachloride. Yield of crude product 5.28 g (95 %), and of pure acid 3.80 g (68 %). It forms small, prismatic crystals with m.p. 115–116°. Analyses, see Table 1.

1-Naphthylmethylseleno-3-isobutyric acid. 5.00 g (0.015 mole) diseleno-3,3'-diisobutyric acid⁸ were dissolved in 80 ml water + 20 ml concentrated ammonia and rongalite was added in portions with shaking until the yellow colour of the diselenide had disappeared. Some care must be taken since the reduction is not quite instantaneous. To prevent oxidation by air, the reaction is best carried out in an ordinary flask, closed by a cork stopper and opened only momentarily when the reactant is added. 1-Naphthylmethyl chloride (5.50 g, 0.031 mole) in 50 ml ethanol was then added and the flask shaken until the solution was practically clear. The solution was treated as described above, diluted to about 500 ml and acidified with concentrated hydrochloric acid. After one recrystallisation from formic acid and two from ligroin, the acid was obtained as glistening scales with m.p. 72–73°. The yield of crude product was practically quantitative and of pure acid 5.55 g (60 %). Analyses, see Table 1.

2-Naphthylmethylseleno-3-propionic acid. 3.04 g (0.01 mole) diseleno-3,3'-dipropionic acid⁹ were dissolved in 60 ml water + 15 ml concentrated ammonia and reduced with rongalite as described above. 2-Naphthylmethyl bromide (4.75 g, 0.022 mole), dissolved

in 125 ml ethanol was added and the milky emulsion was shaken. The reaction took place rapidly, but gradually a salt separated. After standing over-night, the salt was filtered off, washed with water and dried. The yield was 5.7 g. Decomposition with dilute sulphuric acid and extraction with ether yielded 5.40 g (92 %) of crude acid. Two recrystallisations from carbon tetrachloride gave 4.70 g (80 %) of pure acid as glistening scales with m.p. 115.5–116.5°. Analyses, see Table 2.

2-Naphthylmethylseleno-11-undecanoic acid. 0.8 g (0.0015 mole) diseleno-11,11'-diundecanoic acid⁸ was dissolved in 15 ml concentrated ammonia + 25 ml water + 15 ml ethanol (the ammonium salt of this acid is only sparingly soluble in water). After reduction with rongalite, 0.7 g (0.0032 mole) 2-naphthylmethyl bromide was added and the solution was shaken for one h. During the reaction a colourless salt separated. The following day it was filtered off and the acid was liberated as described above. Yield of pure acid 1.16 g (95 %). One recrystallisation from formic acid and one from cyclohexane gave 0.96 g (75 %) of pure acid, as a crystalline powder with m.p. 78–80°. Analyses, see Table 2.

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