

However, the presence of alkaloids, epimeric to I and II in the 2-benzylmalate part of the molecule, can only be excluded safely by identification of the ester obtained in the methanolysis. We have not succeeded in detecting any phalaenopsine in extracts from *Ph. gigantea* or *Ph. lindenbergii* (only one attempt was made).

It is noteworthy that whereas the configuration of the amino alcohol part of phalaenopsine varies, the 2-benzylmalate residue has had the same absolute configuration (still unknown) in all hitherto methanolysed alkaloid samples.

Experimental. The suppliers of the plant material are given in Table 1. Isolations and methanolyses of the alkaloids as well as GLC and NMR measurements were performed as previously described.^{2,3} Analytical GLC on V-VIII and their acetates, however, was carried out using a 20% rather than a 3% SE-52 column. Mass spectra were measured on an LKB 9000 instrument equipped with a GLC inlet system (2.8 m 1% SE-30 for compounds I-IV and 2.8 m 20% SE-52 for compounds V-VIII and their acetates). Specific rotations were measured in ethanol, c 1-3.

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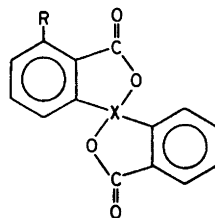
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Synthesis and Partial Resolution of 7-Carboxy-3,3'-spirobi(3-selenaphthalide)

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It is known that benzophenone-dicarboxylic acid is easily transformed into its anhydride,¹ which is assumed to be a dilactone (I).



I: X = C, R = H

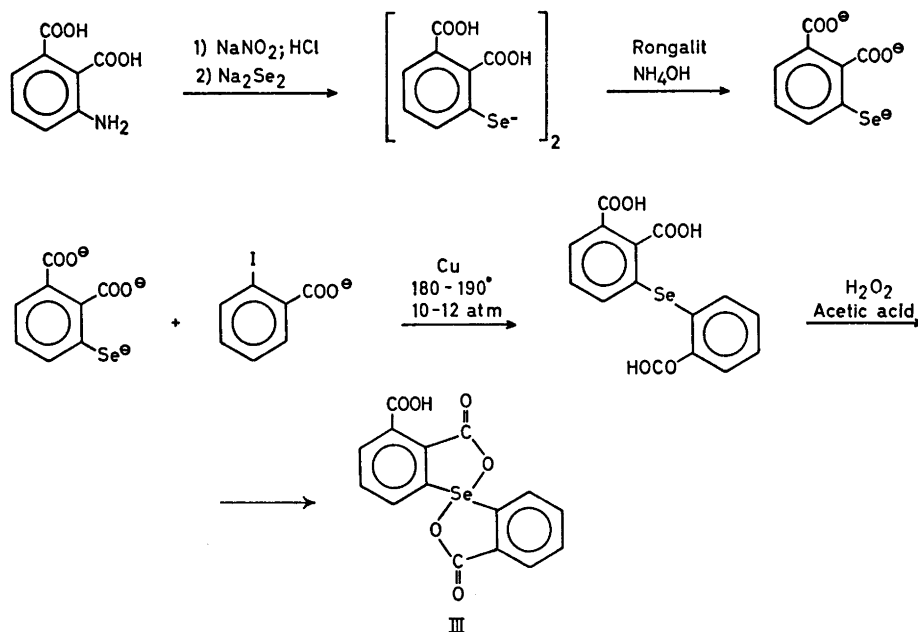
II: X = Se, R = H

III: X = Se, R = COOH

A selenium analogue (II) has been reported by Lesser and Weiss,² and Agenäs and Lindgren³ have recently synthesized an analogous aliphatic spiro-selena-dilactone.

As this ring system is chiral, a good proof for its formation would include the separation of a compound, with this ring structure, into its optical antipodes. To resolve this type of compound by general methods, a basic or acidic substituent has to be introduced into the ring system. Thus, in this paper the synthesis and partial resolution of 7-carboxy-3,3'-spirobi(3-selenaphthalide) are briefly reported.

The 7-carboxy group was introduced in the ring system by diazotizing the amino group of 3-amino-phthalic acid hydrochloride and by reacting the resulting diazonium salt with sodium diselenide. The organic diselenide was reduced with sodium formaldehydesulfoxylate (rongalit) in dilute ammonia. To the reaction mixture was added 2-iodo-benzoic acid and copper powder. This mixture was heated in an autoclave for 5-6 h at 180-190°. Upon acidification of the reaction mixture the 2,3,2'-tricarboxy-diphenyl selenide was



Scheme 1.

isolated. Oxidation of this compound with hydrogen peroxide in acetic acid gave the 7-carboxy-3,3'-spirobi(3-selenaphthalide) (III). The compound isolated was insoluble in many organic solvents except trifluoroacetic acid, DMSO and DMF. The product was purified by dissolving it in dilute sodium hydroxide followed by acidification with dilute sulfuric acid. M.p. 282–283°. (Found: C 49.54; H 2.23; Se 21.67. Calc. for $C_{18}H_8O_6Se$: C 49.60; H 2.22; Se 21.74.)

Preliminary resolution tests with bases have been made. In some cases diastereomeric salts were isolated. A quinine salt, obtained from a mixture of ethyl acetate and methanol, gave free acid with a specific rotation of $[\alpha]_{365}^{25} = -145.1^\circ$ ($c = 1.1$; DMSO). Acid isolated from the mother liquor gave a specific rotation of $[\alpha]_{365}^{25} = +11.2^\circ$ ($c = 1.1$; DMSO). As acid with both positive and negative specific rotation was isolated, this optical activity cannot be due to contamination with base, and the proposed spiro-selenadilactone structure is proved. None of the bases used has given the plus form with any high activity.

The complete resolution of the 7-carboxy-3,3'-spirobi(3-selenaphthalide) is now being attempted. These experiments as well as details of the synthesis will be published later.

The selenium analyses were performed by a microanalytical method developed by Bengtsson,⁴ which is very similar to the method of Gould.⁵

The optical rotatory measurements were made on a Perkin Elmer 141 polarimeter. The melting points are uncorrected.

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