alcohol and petroleum ether successfully separates the inhibitors from vitamin E in the case of tomato and carrot but from wheat germ oil the inhibitor as well as vitamin E are preferentially soluble in petroleum ether. From this fact and from the distillation ranges under diminished pressures it appears that the inhibitors in these three materials and in lettuce are probably all different substances. Similar evidence points to the identity of the vitamin E as obtained from different sources. Carrots contain only small amounts of vitamin E.

3. Lycopene, like carotene, is pro-oxygenic and shortens the induction period of autoxidizable fats. It is not active either as vitamin A or E. Crude carotene may be antioxygenic due to associated inhibitor.

4. There are probably other types of inhibitors in plant tissues aside from those found in the unsaponifiable portion of the lipids and the glucosides.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NEBRASKA]

Arsenicals Derived from 2-Amino-6-nitronaphthalene

BY LEON A. SWEET AND CLIFF S. HAMILTON

In 1915 Friedländer and Littner[1] stated that the products of nitration of β-acetnaphthalide were 2-amino-1-nitro-, 2-amino-8-nitro- and 2-amino-5-nitronaphthalene. Veselý and Jakeš[2] studied the reaction and were unable to find any trace of the 2,5-isomer, but obtained 2-amino-6-nitronaphthalene. Recently, Saunders[3] devised a method by which the three isomeric aminonitronaphthalenes were easily separated in two stages. His method was used in this work for the preparation of 2-amino-6-nitronaphthalene and although good yields were obtained the desired isomer comprised only 8% of the product. The nitration was studied for a range of temperatures but the ratio of yields was not altered. In view of the conflicting statements concerning the identity of this isomer, its structure was proved by reduction to 2,6-diaminonaphthalene, thus confirming the finding of Veselý and Jakeš.

2-Amino-6-nitronaphthalene was converted by the Bart[4] reaction into 2-arsono-6-nitronaphthalene. This was reduced with ferrous hydroxide to the corresponding amine.

Experimental

2-Amino-6-nitronaphthalene was prepared according to the method of Saunders.[3] It was reduced by means of tin and hydrochloric acid to give 2,6-diaminonaphthalene; m. p. 220° (Lange,[5] 216–218°). With benzoyl chloride in pyridine solution it formed **2-benzoylamino-6-nitronaphthalene,** which crystallized from ethanol in light yellow needles of m. p. 206°.

Anal. Calcd. for $C_{17}H_{12}N_2O_3$: C, 69.84; H, 4.14. Found: C, 69.67; H, 4.24.

2-Arsono-6-nitronaphthalene.—A solution of 2-amino-6-nitronaphthalene (9.4 g.) in 100 cc. of 6 *N* hydrochloric acid was stirred mechanically while cooled in a salt–ice mixture. A calculated volume of sodium nitrite solution (5 g. in 25 cc. of water) was added slowly during one hour. Meanwhile an arsenite solution was prepared by dissolving 20 g. of sodium metaarsenite and a few crystals of copper sulfate in a liter of water, and then made up to 1.5 liters by adding crushed ice. The arsenite solution was stirred mechanically while 85 cc. of 6 *N* sodium hydroxide was added slowly from one dropping funnel and the cold diazonium solution from another. The addition of alkali was begun, and after 5 cc. had been added both solutions were added simultaneously in such a ratio that the solution remained slightly alkaline. Stirring was continued for two hours, and then the temperature was raised to 60° for one hour. The solution was filtered and the arsonic acid precipitated by making acid to Congo red paper with hydrochloric acid; weight, 7.0 g. It was purified by dissolving in 0.5 *N* sodium carbonate solution and reprecipitating with acid, forming tiny glistening needles.

2-Arsono-6-aminonaphthalene was prepared from 2-arsono-6-nitronaphthalene by the method of Jacobs, Heidelberger and Rolf,[6] an alkaline ferrous hydroxide reduction. Reaction with acetic anhydride in glacial acetic acid yielded **2-arsono-6-acetylaminonaphthalene.** The amine in 0.5 *N* sodium carbonate solution condensed with

SUBSTITUTED 2-ARSONO-NAPHTHALENES

Substituents	Yield, %	Formula	Arsenic analyses, % Calcd.	Found	
6-Nitro-	47	$C_{10}H_8O_5NAs$	25.25	25.39	25.35
6-Amino-	87	$C_{10}H_{10}O_3NAs$	28.07	28.07	28.11
6-Acetylamino-	87	$C_{12}H_{12}O_4NAs$	24.25	24.28	24.14
6-Carbethoxyamino-	95	$C_{13}H_{14}O_5NAs$	22.12	22.27	22.32
6-β-Hydroxyethylamino-	90	$C_{12}H_{14}O_4NAs$	24.11	24.17	24.26

(1) Friedländer and Littner, *Ber.*, **48**, 330 (1915).
(2) Veselý and Jakeš, *Bull. soc. chim.*, [4] **33**, 942 (1923).
(3) Saunders, THIS JOURNAL, **54**, 636 (1932).
(4) Bart, *Ann.*, **429**, 55 (1922).
(5) Lange, *Chem. Zeit.*, **12**, 856 (1888).
(6) Jacobs, Heidelberger and Rolf, THIS JOURNAL, **40**, 1581 (1918).

ethyl chlorocarbonate to form **2-arsono-6-carbethoxyaminonaphthalene.** A sealed flask reaction with ethylene oxide in 0.5 *N* sodium carbonate solution gave **2-arsono-6-β-hydroxyethylaminonaphthalene.**

These arsenicals were white, difficultly soluble in water, and did not melt or decompose below 250°.

Summary

1. 2-Amino-6-nitronaphthalene was prepared by the method of Saunders. A study of the reaction over a range of temperatures showed that the ratio of the isomers formed was not altered.

2. The structure of this isomer was confirmed by reduction to 2,6-diaminonaphthalene. A new derivative, 2-benzoylamino-6-nitronaphthalene, was described.

3. 2-Arsono-6-nitronaphthalene was formed by the Bart reaction. Reduction of this compound with ferrous hydroxide yielded 2-arsono-6-aminonaphthalene. Three derivatives, formed by reaction of the amine with acetic anhydride, ethylene oxide and ethyl chlorocarbonate, were described.

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Arsenated Phenoxyalkanols

BY LEON A. SWEET[1] AND CLIFF S. HAMILTON

β-4-Arsonoanilinoethanol and γ-4-arsonoanilinopropanol[2] have been prepared by condensing arsanilic acid with ethylene and trimethylene chlorohydrins. Similarly, the oxygen analogs were prepared by condensation with 4-hydroxyphenylarsonic acid.[3] In the present investigation two series of arsenated phenoxyalkanols were derived from the parent compounds, β-4-arsonophenoxyethanol and γ-4-arsonophenoxypropanol.

Condensations of ethylene and trimethylene chlorohydrins with 4-hydroxyphenylarsonic acid were readily effected by refluxing with 6 *N* sodium hydroxide. Under similar conditions ethylene chlorohydrin and 3-nitro-4-hydroxyphenylarsonic acid did not condense.

Nitration of β-4-arsonophenoxyethanol using three molecular proportions of nitric acid (sp. gr. 1.50) in an excess of concentrated sulfuric acid resulted in a mixture of β-2-nitro-4-arsonophenoxyethyl nitrate and the mono- and di-nitro compounds. Heating at 95° yielded a mixture of β-2,6-dinitro-4-arsonophenoxyethanol and 2,6-dinitro-4-arsonophenol. The use of nitric acid (sp. gr. 1.50) alone resulted in a complete conversion to the nitro ester and further reaction introduced one nuclear nitro group. Oxidation of the side chain to the corresponding acid accompanied nitration whenever sulfuric acid was not used. After reaction for twenty-four hours at room temperature the only product was 2-nitro-4-arsonophenoxyacetic acid. γ-4-Arsonophenoxypropanol behaved in a similar manner, although oxidation occurred more readily than with the ethanol homolog, necessitating a lower temperature and a longer time of reaction for the preparation of γ-2-nitro-4-arsonophenoxypropyl nitrate.

β-2-Nitro-4-arsonophenoxyethyl nitrate and γ-2-nitro-4-arsonophenoxypropyl nitrate were readily hydrolyzed by refluxing with 3 *N* hydrochloric acid. Reduction of the hydrolysates by means of alkaline ferrous hydroxide gave the corresponding amines.

Newbery, Phillips and Sticklings[4] observed that reduction of 2-nitro-4-arsonophenoxyacetic acid led to the cyclic compound 3-hydroxy-1,4-benzisoxazine-6-arsonic acid. In connection with our work on arsenated phenyl ethers it seemed of interest to prepare methyl-2-nitro-4-arsonophenoxyacetate to determine whether on reduction a straight chain or cyclic compound would result. Esterification did not prevent ring closure, the intermediate 2-amino compound losing a molecule of methanol to form 3-hydroxy-1,4-benzisoxazine-6-arsonic acid.

Experimental

β-4-Arsonophenoxyethanol[5] and its Sodium Salt.—To a solution of 218 g. of 4-hydroxyphenylarsonic acid in 500

(1) Parke, Davis & Company Fellow.

(2) Hamilton, THIS JOURNAL, **45**, 2751 (1923).

(3) Unpublished work, Chemical Laboratory, Northwestern University. The compounds β-4-arsonophenoxyethanol, γ-4-arsonophenoxypropanol and β-2-acetylamino-4-arsonophenoxyethanol are identified by the numbers 141, 132 and 133, respectively, in our arsenical series. The last mentioned has appeared recently in the patent literature; Benda and Sievers, German Patent 552,267; English Patent 373,071.

(4) Newbery, Phillips and Sticklings, *J. Chem. Soc.*, **130**, 3056 (1928).

(5) Prepared by Cislak and Hamilton, Chemical Laboratory, Northwestern University.