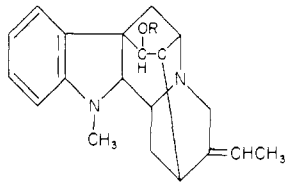
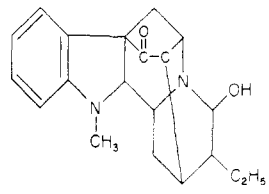
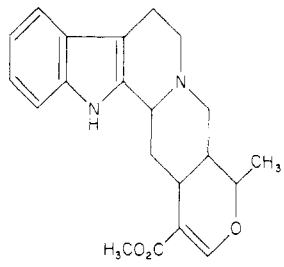
mitine is the trimethoxybenzoate of tetraphyllicine and must possess structure II.



I R = H
II R = 3,4,5-$(CH_3O)_3C_6H_2CO$-



III



IV

Biogenetically, the presence of the ethylidene function (reminiscent of curare alkaloids such as mavacurine[10]) is attractive in the light of current views[7] on the natural precursors of yohimbé alkaloids; the relationship of I to the heterocyclic, oxygen-ring containing alkaloids of the serpentine-ajmalicine (IV) series is particularly clear. It is appropriate to point out that various representatives of this group have been isolated together with tetraphyllicine from two *Rauwolfia* species.[2,8,11]

We are indebted to the American Heart Association and to Chas. Pfizer and Co. for financial assistance in the form of fellowships (M.G. and S.C.P.)

(10) H. Bickel, H. Schmid and P. Karrer, *Helv. Chim. Acta*, **38**, 649 (1955).

(11) Serpinine, isolated in minute quantity from *R. serpentina* (S. Bose, *Naturwiss.*, **42**, 71 (1955)), may be identical with tetraphyllicine.

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RECEIVED FEBRUARY 24, 1956

CRYSTALLIZABLE POLYSTYRENE

Sir:

Natta, *et al.*,[1,2] reported some physical properties of a crystalline polystyrene, but no preparative method was disclosed.

We have found that Alfin-polymerized polystyrene can be crystallized to various degrees by a suitable crystallization solvent. Morton[3] in his work dealing with Alfin-catalyzed polystyrene probably prepared samples of the crystallizable polymer, the crystallizability of which was not recognized at that time. Natta[2] reported that the polystyrene prepared in his work contained crystalline and non-crystalline fractions, the non-crystalline fraction being removable by extraction with aliphatic hydrocarbons.

When Alfin-catalyzed polystyrene of moderate molecular weight was extracted with boiling *n*-heptane, no soluble polymer was removed, yet partially crystalline polystyrene resulted. Since the interplanar spacings and relative intensities of the seven strongest X-ray reflections are in close agreement with those reported by Natta,[2] the crystalline phase is the same. The hot extraction solvent served only as a crystallization medium supplying the necessary energy and swelling effect for the polymer to crystallize. X-Ray investigation before treatment revealed a completely amorphous polymer, while after treatment, the polystyrene showed moderate crystallinity. Suitable crystallization media are: *n*-hexane, *n*-heptane, *n*-octane, *n*-decane, hexene-1, and, to a less efficient extent, butanol-1, heptanol-1, octanol-1, cyclohexanol, 2-methoxyethanol, and ethylene glycol. Methanol and *n*-pentane failed to cause crystallization because of their low boiling points or failure to penetrate the polymer. At higher temperatures under pressure, *n*-pentane functioned well as a crystallizing solvent.

Crude Alfin-polystyrene containing a high proportion of isotactic chains can be crystallized readily by heat alone at 150°.

When the crystallized polystyrene is reprecipitated from benzene into methanol, the polymer is completely amorphous. Crystallinity can be restored by the hot solvent technique. X-Ray examination of the Alfin-crystalline polystyrene shows that it can be heated up to 200° without loss of crystallinity. Between 200 and 220°, there is a gradual reduction in crystallinity, and the polymer becomes completely amorphous after heating above 220°.

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ISOLATION FROM RUTABAGA SEED OF PROGOITRIN, THE PRECURSOR OF THE NATURALLY OCCURRING ANTITHYROID COMPOUND, GOITRIN (L-5-VINYL-2-THIOÖXAZOLIDONE)[1]

Sir:

In earlier studies on the goitrogenic effects of various foods in man, it became apparent that the antithyroid effect of rutabaga and turnip seemed to be contained in a compound which was liberated from a precursor in the plant by enzymatic hydrolysis when the cells were crushed but was otherwise not present. Although both raw rutabaga and raw turnip exerted an inhibitory effect on the radioiodine uptake in man, this effect was not present if the vegetables were cooked before being fed.[2] The liberated antithyroid compound was later isolated and proved to be L-5-vinyl-2-thiooxazolidone,[3] henceforth called goitrin.

(1) G. Natta, P. Pino, P. Corradini, F. Danusso, E. Mantica, G. Mazzanti and G. Moraglio, THIS JOURNAL, **77**, 1708 (1955).

(2) G. Natta, *J. Polymer Sci.*, **16**, 143 (1955).

(3) A. A. Morton, *Ind. Eng. Chem.*, **42**, 1488 (1950).

(1) I am indebted to Eugene V. Clark and Howard L. Erwin for excellent technical assistance and to Drs. Theodore A. Geissman, Harry Wood and M. G. Ettlinger for valuable advice and suggestions.

(2) M. A. Greer and E. B. Astwood, *Endocrinology*, **43**, 105 (1948).

Seeds of the genus *Brassica* contain a higher concentration of goitrin than do the edible portions of rutabaga and turnip. In studies of these seeds, it was found that goitrin was not formed when the enzyme was destroyed by suspending the seeds in boiling water. Subsequent treatment of the filtrate with a purified myrosin preparation liberated goitrin. The precursor was found to have a specific absorption at 225–227 mμ compared to 240 mμ for goitrin, greatly facilitating its fractionation. Since the precursor was heat stable, water soluble, and ether insoluble and the goitrin could be delivered by enzymatic hydrolysis, it was suggested that the compound might be similar to known mustard oil precursors.[4] It has now been possible to isolate, crystallize and identify this precursor, henceforth called progoitrin.

Rutabaga seed was ground in a coffee mill, extracted three times with ether and dried. Approximately 300 g. of the ether-extracted ground seed was poured slowly into approximately 2 liters of boiling water and boiled for 30 minutes. The suspension was cooled and filtered and the residue resuspended in 1 liter of cold water overnight. This was again filtered; the filtrates were combined and evaporated *in vacuo* at a temperature of 38°. The concentrated extract was made up to 80% ethanol by volume to precipitate the protein and was again filtered and concentrated. The concentrate was dissolved in a small volume of 80% ethanol and placed on an 80% ethanol washed alumina column. After developing with two column volumes of 80% ethanol the column was eluted with 60% ethanol and approximately 70% of the progoitrin in greatly purified form was obtained. This purified progoitrin was then rechromatographed in a similar manner three times. The material from the last chromatogram was evaporated to dryness and dissolved in a small volume of hot 95% ethanol. After standing several months in the cold, crystals eventually formed. Subsequent seeding of chromatographically purified material allowed crystallization of relatively large quantities of fine needle-like white crystals. After several recrystallizations from 80 to 95% ethanol, the material gave a constant decomposition point. After thorough desiccation, the crystals began to turn brown at 128–130° and melted at 135–140°. Optical rotation was $[\alpha]_D$ −22.3° (water). Elemental analysis was consistent with the empirical formula listed below. The pure compound could easily be split by a purified myrosin preparation yielding stoichiometric amounts of goitrin, glucose, sulfate and sodium.

The structure of the compound has tentatively been assigned as a glucoside related to L-2-hydroxy-3-butenyl isothiocyanate (I). Progoitrin has a specific absorption at 227 mμ very similar to sinigrin[5]; the spectral shift to 240 mμ during enzymatic hydrolysis indicates that cyclization to goitrin (II) occurs. It seems probable that progoitrin is analogous in structure to sinigrin but contains an extra CHOH group. If Gadamer's structure for

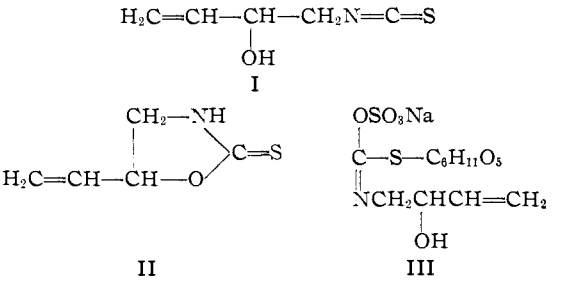

Fig. 1.—(I) 2-Hydroxy-3-butenyl isothiocyanate; (II) 5-vinyl-2-thioöxazolidone; (III) possible structure of progoitrin.

sinigrin[6] is accepted, progoitrin may then be written as III. The molar extinction of progoitrin at 227 mμ is 7700; its infrared spectrum is consistent with the structure advanced above.

	Elemental Analysis for ($C_{11}H_{18}O_{10}NS_2Na$)				
	C	H	N	S	Na
Found	32.44	4.59	3.39	15.27	5.52
Calcd.	32.11	4.38	3.41	15.56	5.59

(3) E. B. Astwood, M. A. Greer and M. G. Ettlinger, *J. Biol. Chem.*, **181**, 121 (1949).

(4) M. A. Greer, M. G. Ettlinger and E. B. Astwood, *J. Clin. Endocrinology*, **9**, 1069 (1949).

(5) Obtained through the courtesy of Drs. M. G. Ettlinger and A. J. Lundeen.

(6) J. Gadamer, *Arch. Pharm.*, **235**, 44 (1897).

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RECEIVED FEBRUARY 6, 1956

THE ELECTRONIC SPECTRA AND STRUCTURE OF THE PLEIADIENES

Sir:

The unusual peri-condensed aromatic hydrocarbons, acepleiadiene, pleiadiene, and acepleiadylene, have been synthesized recently by Boekelheide and co-workers.[1,2] The study of such aromatic systems provides an excellent opportunity to test the various theories of electronic structure of complex molecules.

The study of the electronic spectra of aromatic hydrocarbons in dilute mixed crystals at low temperatures has led to a detailed analysis of the vibrational structure and polarization properties of the electronic transitions of numerous catacondensed aromatic hydrocarbons.[3–6] Accordingly, the spectra of acepleiadiene and acepleiadylene have been measured in dilute solid solutions in pyrene, using single crystals and polarized light. The polarization properties which are observed for the lowest transition in each of these molecules conclusively demonstrate that the transition at 17 kk.[7] (log ϵ = 2.3) in acepleiadiene is polarized along the transverse direction ($^1B_1 \leftarrow$

(1) V. Boekelheide, W. E. Langeland and C. T. Liu, THIS JOURNAL, **73**, 2432 (1951).

(2) V. Boekelheide and G. K. Vick, *ibid.*, **78**, 653 (1956).

(3) Naphthalene: D. S. McClure, *J. Chem. Phys.*, **22**, 1668 (1954); **24**, 1 (1956).

(4) Azulene: J. W. Sidman and D. S. McClure, *ibid.*, **24**, in press.

(5) Anthracene and tetracene: J. W. Sidman, *ibid.*, **24**, in press.

(6) Stilbene: R. H. Dyck and D. S. McClure, to be published.

(7) 1 kk. = 1 kilokayser = 1000 cm.$^{-1}$.