a steam-bath. The material was almost white and sintered at 156–158°, m.p. 210° dec. The yield was 77% (14.7 g.). After recrystallization from glacial acetic acid the substance effervesced at 176°, resolidified, and then melted at 212–214°.

Anal. Calcd. for $C_5H_5N_3O_3S$: C, 32.1; H, 2.70; N, 22.5; S, 17.1. Found: C, 32.1; H, 2.80; N, 22.4; S, 17.1.

1,2,4-Triazine-3,5-dione-6-carboxylic Acid.—The methylthiol above (14.7 g., 0.078 mole) was heated with concentrated hydrochloric acid (30 ml.) and glacial acetic acid (55 ml.) under reflux for 5 hours. The solution was filtered; the insoluble matter was washed with a little boiling glacial acetic acid and the washings were added to the filtrate. The product which crystallized out on standing overnight at 4°, decomposed with evolution of gas at 237–238°; yield 55% (6.75 g.). After further recrystallization from glacial acetic acid, gas was evolved from the material at 241°.

Anal. Calcd. for $C_4H_3N_3O_4$: C, 30.6; H, 1.93; N, 26.8. Found: C, 31.0; H, 1.89; N, 26.4.

When concentrated, the original mother liquors yielded more material which effervesced at 227–229°. When this was recrystallized from glacial acetic acid, gas was evolved at 233–234°; the amount (1.3 g.) brought the total yield up to 65%.

1,2,4-Triazine-3,5-dione (6-Azauracil).—When the above carboxylic acid (III, R = COOH) was heated at 230–250° (10 mm.) in a sublimation tube, a vigorous effervescence occurred and almost the theoretical yield of 6-azauracil sublimed onto the cold inner surface of the apparatus. This material sintered at 272°, lit.[4] m.p. 272°.

Anal. Calcd. for $C_3H_3N_3O_2$: C, 31.9; H, 2.68; N, 37.1. Found: C, 31.7; H, 2.64; N, 36.9.

Since paper chromatography revealed the presence of a trace of impurity, the sublimed product was recrystallized twice from water; its m.p. remained unchanged.

Anal. Found: C, 31.8; H, 2.93; N, 37.0.

NEW HAVEN, CONN.

COMMUNICATIONS TO THE EDITOR

THE STRUCTURES OF TETRAPHYLLICINE, AJMALIDINE AND RAUVOMITINE[1]

Sir:

Recently, there has been described[2] the isolation from *R. tetraphylla L.* of a new *Rauwolfia* alkaloid, tetraphyllicine, with the apparent empirical formula $C_{20}H_{26}N_2$ (calcd.: C, 81.58; H, 8.90; N, 9.52). The similarity of this alkaloid, especially along spectroscopic lines, with ajmaline led to the suggestion that tetraphyllicine might be the oxygen-free parent substance of the ajmaline group.

The accumulation of additional quantities of this alkaloid has now permitted further degradation experiments. Selenium dehydrogenation furnished ind-N-methylharman, a characteristic degradation product of ajmaline,[3] thus providing further support for the supposed structural similarity of the two alkaloids. Tetraphyllicine was found to contain one active hydrogen atom and in order to determine whether N(b) was secondary, the alkaloid was acetylated. The resulting product was clearly an O-acetate (infrared spectrum) and mild saponification regenerated the parent alkaloid. These results raised serious doubt as to the correctness of the original $C_{20}H_{26}N_2$ formula which had been based on seven combustion analyses from three different analytical laboratories. Three of these analyses showed C, 81.24–81.52; H, 8.29–8.51, while the remaining ones ranged from C, 78.23–78.76. These latter analyses were ignored since they were assumed to be due to incomplete combustion of the high melting alkaloid. Repeated analyses,[4] including direct oxygen determinations (found: C, 77.97, 78.23; H, 7.89, 8.08; N, 8.91; O, 5.28, 5.20) now clearly show that tetraphyllicine possesses the empirical formula $C_{20}H_{24}N_2O$ (calcd.: C, 77.88; H, 7.84; N, 9.08; O, 5.19). The infrared spectrum closely resembles that of desoxyajmaline[5] and the rotatory dispersion curves between 700–320 $m\mu$ are very similar in shape except that the values for desoxyajmaline are consistently higher by *ca.* 100° over the 375–320 $m\mu$ range. Catalytic hydrogenation of tetraphyllicine yielded dihydrotetraphyllicine which proved to be identical by mixture melting point determination, infrared comparison and virtual coincidence of the rotatory dispersion curves[6] (700–320 $m\mu$) with desoxyajmaline. The position of the double bond was proved by ozonolysis of tetraphyllicine which yielded 55% of acetaldehyde. These results coupled with the recently established structure[7] of ajmaline require the expression I for tetraphyllicine.

Ajmalidine, a new alkaloid ($C_{20}H_{24}N_2O_2$) isolated[8] in trace amounts together with ajmaline and tetraphyllicine from *Rauwolfia sellowii* shows striking similarities to ajmaline but contains a cyclopentanone ring as demonstrated by its infrared spectrum; it is likely, therefore, that ajmalidine is best represented by structure III.

Quite recently, two groups[9] have announced the isolation of a new ester alkaloid, rauvomitine ($C_{30}H_{34}N_2O_5$)[9a] from *R. vomitoria* Afz., which on hydrolysis yielded trimethoxybenzoic acid and a new base, $C_{20}H_{24}N_2O$. Direct comparison of this cleavage product (kindly provided by Dr. E. Haack,[9a] C. F. Boehringer, Mannheim-Waldhof) with tetraphyllicine has now established the identity of the two substances. Consequently, rauvo-

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[1] Paper XI in the Wayne series "Alkaloid Studies."

[2] C. Djerassi and J. Fishman, *Chem. and Ind.*, 627 (1955).

[3] F. A. L. Anet, D. Chakravarti, R. Robinson and E. Schlittler, *J. Chem. Soc.*, 1242 (1954); *cf.* A. Chatterjee and S. Bose, *Experientia*, **9**, 254 (1953).

[4] Carried out by Mr. G. M. Maciak (Eli Lilly and Co.) and Dr. A. Bernhardt (Mülheim).

[5] R. Robinson, *Chem. & Ind.*, 285 (1955).

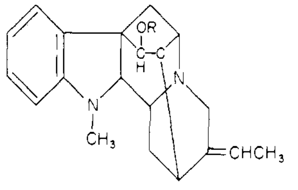
[6] These will be published in a detailed paper.

[7] R. B. Woodward, *Angew. Chem.*, **68**, 13 (1956).

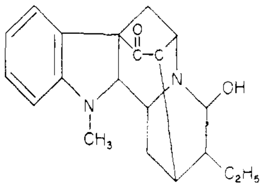
[8] S. C. Pakrashi, C. Djerassi, R. Wasicky and N. Neuss, THIS JOURNAL, **77**, 6687 (1955).

[9] (a) E. Haack, A. Popelak and H. Spingler, *Naturwiss.*, **42**, 627 (1955); (b) J. Poisson, R. Goutarel and M. M. Janot, *Compt. rend.*, **241**, 1840 (1955).

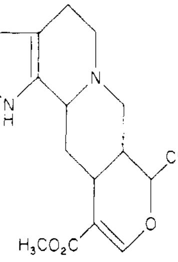
mitine is the trimethoxybenzoate of tetraphyllicine and must possess structure II.



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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RECEIVED FEBRUARY 17, 1956

[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).

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] 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).