

ing nicotine to nornicotine probably by trans-methylation.

*Nicotiana glauca* contains principally anabasine. When grafted to *N. tabacum* roots<sup>3</sup> or when hybridized with the latter species<sup>4</sup> the leaves have been reported to contain predominantly anabasine. Repetition of these experiments in this laboratory has disclosed that the supposed anabasine of the grafts and of the hybrids is actually a mixture of anabasine and nornicotine with usually more nornicotine than anabasine. The difficult separation of anabasine from nornicotine in mixtures of the two was accomplished by repeated fractional crystallizations of the picrates and of the methylated picrates after removal of nicotine by the method of Smith and Smith.<sup>4</sup> To show that the nornicotine present in the leaves of these plants actually arose *in situ* and at the expense of nicotine translocated from the roots, *N. glauca* scions were grafted to *N. tabacum* roots. After a period of growth, a tomato scion was grafted to the apex of each *N. glauca* scion. Ultimately, these three-tiered plants were examined for alkaloids. The *N. glauca* scions contained one part of nicotine to fifty parts of mixed anabasine and nornicotine, while the tomato scions contained only nicotine.

It is now clear that the replacement of the methyl group of nicotine in the plant leaf by the hydrogen atom of nornicotine accounts for the increase in secondary amine content (previously attributed to anabasine<sup>3</sup>) of such graft combinations and genetical hybrids. It follows that expectations<sup>4</sup> of the development of hybrids between *N. tabacum* and *N. glauca* that would be suitable for the commercial extraction of anabasine are without justification.

(3) Schmuck, Kostoff and Borozabina, *Compt. rend. acad. sci. U. R. S. S. (Doklady)*, **25**, 477 (1939).

(4) Smith and Smith, *J. Agr. Research*, **65**, 347 (1942).

BIOLOGY DEPARTMENT  
PRINCETON UNIVERSITY  
PRINCETON, NEW JERSEY  
RAY E. DAWSON  
RECEIVED FEBRUARY 7, 1945

#### RESOLUTION OF 9-HYDROXYFLUORENE-2-CARBOXYLIC ACID

Sir:

The question whether fluorene has a folded or planar structure is a subject of controversy.<sup>1</sup> It might be thought that the classical methods of stereochemistry should furnish an answer but their application has been precluded by the inability to resolve fluorene compounds containing a 9-asymmetric carbon atom.<sup>2</sup>

We have now succeeded in resolving 9-hydroxyfluorene-2-carboxylic acid into its dextro and levo isomers.

(1) Rieveschl and Ray, *Chem. Rev.*, **23**, 378 (1938).

(2) Bennett and Noyes, *Rec. trav. chim.*, **48**, 895 (1929); *This Journal*, **52**, 3437 (1930); Bader, Thesis, Ludwig Maximilian University of Munich, pp. 9, Vienna, 1926.

To 11.3 g. of 9-hydroxyfluorene-2-carboxylic acid (m. p. 240°) in 125 cc. of 95% ethanol was added 16.7 g. of strychnine in 125 cc. of chloroform. The resulting solution was distilled to remove the greater part of the chloroform. It was then filtered and placed in a pan of hot water and the whole allowed to come to room temperature. The following morning crystals in the form of rosetts, weighing 13.2 g., were obtained. These, recrystallized from 700 cc. of ethanol, sintered at 190° and melted at 203°. This strychnine salt was dissolved in a mixture of 100 cc. of ethanol and 200 cc. of 1% sodium hydroxide. This was poured into a liter of water containing 20 cc. of 6 *N* hydrochloric acid. The white fluffy precipitate was recrystallized from 60 cc. of ethanol and fine needles melting at 263° (block) were obtained.

*Anal.* Calcd. for C<sub>14</sub>H<sub>10</sub>O<sub>3</sub>: mol. wt., 226. Found: mol. wt. (pinene dibromide), 237; equivalent weight, 226.

These had the following rotations for red, yellow and green light for a solution of 0.7000 g. in 50 cc. of ethanol in a 2-dm. tube:  $\alpha^{27}_{656.3} + 0.82^{\circ}$ ;  $\alpha^{27}_{589.3} + 1.11^{\circ}$ ;  $\alpha^{27}_{516.3} + 1.39^{\circ}$ ;  $[\alpha]^{27}_{656.3} + 29.3^{\circ}$ ;  $[\alpha]^{27}_{589.3} + 39.6^{\circ}$ ;  $[\alpha]^{27}_{516.3} + 49.6^{\circ}$ .

The levo isomer was isolated similarly. It melted at 260° (block). A solution of 0.7500 g. in 50 cc. of ethanol in a 2-dm. tube gave:  $\alpha^{27}_{656.3} - 0.83^{\circ}$ ;  $\alpha^{27}_{589.3} - 1.09^{\circ}$ ;  $\alpha^{27}_{516.3} - 1.35^{\circ}$ ;  $[\alpha]^{27}_{656.3} - 27.6^{\circ}$ ;  $[\alpha]^{27}_{589.3} - 36.3^{\circ}$ ;  $[\alpha]^{27}_{516.3} - 45.0^{\circ}$ .

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF CINCINNATI  
CINCINNATI 21, OHIO

FRANCIS EARL RAY

ELIZABETH KREISER

RECEIVED FEBRUARY 10, 1945

#### INTRODUCTION OF THE ANGULAR METHYL GROUP

Sir:

In a previous report<sup>1</sup> we described the preparation of *cis*- and *trans*-9-methyldecalone-1, using Koebner and Robinson's excellent method for directing the alkylation to the angular position,<sup>2</sup> complemented by a scheme for removal of the protective arylidene group. Although this affords a good source of these particular ketones, there are, as recently pointed out by Birch and Robinson,<sup>3</sup> certain objections to our method from the point of view of more general applicability. We have been engaged for some time in a search for another protective group more easily removed than the arylidene group, and are reporting some of our findings now, because of the appearance of work along somewhat similar lines recently announced by the English workers.<sup>3</sup>

The condensation of decalone-1 with ethyl formate according to a previously described procedure<sup>1</sup> gave excellent yields of the colorless

(1) Johnson, *This Journal*, **65**, 1317 (1943).

(2) Koebner and Robinson, *J. Chem. Soc.*, 500 (1931).

(3) Birch and Robinson, *ibid.*, 501 (1944).

(4) See the preparation of 2-formyl-3-methylhydride-1 by Johnson, Anderson and Sjöberg, *This Journal*, **66**, 218 (1944).

liquid 2-formyldecalone-1. Without distillation this was treated with isopropyl iodide and potassium carbonate in acetone according to Claisen's method for O-alkylation.<sup>5</sup> Almost colorless, crystalline enol ether, m. p. 67–72°, was thus obtained in 94% over-all yield from decalone-1. The recrystallized 2-isopropoxymethylenedecalone-1 melted at 77–78° (cor.), and gave a slowly developing violet color with ferric chloride. *Anal.* Calcd. for C<sub>14</sub>H<sub>22</sub>O<sub>2</sub>: C, 75.63; H, 9.98. Found: C, 75.31; H, 9.77. Angular methylation was effected by treatment with potassium amide in ether followed by methyl iodide. The alkylated enol ether was hydrolyzed with dilute hydrochloric acid to give 2-formyl-9-methyldecalone-1 which was separated by alkaline extraction, and cleaved to the ketone by distillation of the alkaline solution. The steam-volatile material consisted of a mixture of *cis*- and *trans*-9-methyldecalone-1 obtained in about 30% over-all yield from decalone-1. Further work, as yet incomplete, indicates that this yield can be increased. The ketones were easily separated by taking advantage of the

(5) Cf. v. Auwers, *Ber.*, **71B**, 2082 (1938).

differential rates of formation of the semicarbazones.<sup>1</sup> Almost pure *trans* derivative separated rapidly, m. p. after recrystallization 218–218.5° (cor.), undepressed by an authentic specimen.<sup>1</sup> The *cis* semicarbazone, which formed slowly, melted at 224–225.5° (cor.) after recrystallization. A mixture with authentic material<sup>1</sup> showed no depression of the melting point.

2-Methylcyclohexanone has been converted through the sequence of reactions described above into pure 2,2-dimethylcyclohexanone, b. p. 166–169°; over-all yield 31%; m. p. of oxime 93–93.5° (cor.); m. p. of semicarbazone 199–201° (cor.). Mixtures of these derivatives with samples obtained by an alternate synthesis<sup>1</sup> showed no depression of the m. p. The methylation step was promoted successfully with potassium *t*-butoxide in *t*-butyl alcohol.<sup>1,2</sup> When this procedure was used in the decalone series, however, the methylation was incomplete.

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF WISCONSIN  
MADISON, WISCONSIN

WILLIAM S. JOHNSON  
HARVEY POSVIC

RECEIVED JANUARY 22, 1945

## NEW BOOKS

**Varnish Constituents.** By H. W. CHATFIELD. Science Publishers, Inc., 215 Fourth Avenue, New York 3, N. Y., 1944. 496 pages. 14 × 22 cm. Price, \$7.00.

This book contains a detailed description of the many diverse materials which are available for use in the manufacture of oleoresinous varnishes. There is some discussion of the methods of manufacture of some of these raw materials, especially where variations in the manufacture results in different grades or varieties which the varnish maker needs to distinguish. The main emphasis is on the properties of the materials which influence or control their suitability for varnish making. The author evidently attempts to give definite numerical values of measurable properties wherever feasible. A substantial fraction of the book is devoted to tables in which the numerical values of significant properties are systematically tabulated for easy reference and comparison. There are such tables for Varnish Oils; Acids; Monoglycerides; Synthetic Resins (47 pages); Solvents and Diluents (22 pages); Plasticizers (16 pages); Driers, Salts and Soaps; Asphalts and Pitches, Waxes; besides numerous small tables of varied sorts. Numerous references to the technical and patent literature are given. The text contains much descriptive matter and comments on performance and usefulness of the materials with a discussion of the possibility of substitution of one material by another and the influence of such replacements on the properties of the finished varnish. Since these comments are written by an experienced English expert they should be of value to American formulators in these days when shortages of materials and priorities may make substitutions necessary.

Statistical data as to production and international commerce in these materials are omitted and what little comment there are on such questions is apt to be weak. Thus under the heading Soya Bean Oil he says, "The oil is obtained from the beans of *Glycine* or *Soya hispida*,

indigenous to China, Japan and Manchuria. Some oil is produced in the United States of America, Russia and Europe, and a little from experimental sources in Great Britain." The author apparently is not aware that the production of soya bean oil has been gaining rapidly in the United States. In 1943 the production in the United States was 1226 million pounds, which was almost as much as the cottonseed produced (1312 million pounds) and substantially ahead of the linseed oil (917 million pounds).

GRINNELL JONES

**Annual Review of Biochemistry.** Vol. XII. JAMES MURRAY LUCK, Editor, Stanford University, JAMES H. C. SMITH, Associate Editor, Carnegie Institution of Washington, Stanford University, California. Annual Reviews, Inc., Stanford University P. O., California, 1943. ix + 704 pp. Illustrated. 15.5 × 23 cm. Price, \$5.00.

**Annual Review of Biochemistry.** JAMES MURRAY LUCK, Editor, Stanford University, JAMES H. C. SMITH, Associate Editor, Carnegie Institution of Washington, Stanford University, California. Vol. XIII. Annual Reviews, Inc., Stanford University P. O., California, 1944. ix + 795 pp. Illustrated. 15.5 × 23 cm. Price, \$5.00.

Since its inception in 1932, the "Annual Review of Biochemistry" has proven to be perhaps the most valuable publication of its kind in the field of Biochemistry. The high standards set in previous years are maintained in volumes XII and XIII, in spite of the many handicaps inherent in war conditions. It is to be regretted that the cosmopolitan character of pre-war issues is now lacking in these volumes. With the exception of a few English re-