applicable to 9-alkyl- and 3,9-dialkylcarbazoles, and many carbazole aldehydes can thus be prepared.

2. Some reactions of these aldehydes (reduction, bromination, nitration) have been investigated, and several new compounds have been prepared in connection herewith.

PARIS (V), FRANCE RECEIVED MAY 31, 1950

[CONTRIBUTION FROM THE BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE, AGRICULTURAL RESEARCH ADMINISTRATION, U. S. DEPARTMENT OF AGRICULTURE]

Constituents of *Heliopsis* Species. I. Scabrin, an Insecticidal Amide from the Roots of *H. scabra* Dunal[1]

BY MARTIN JACOBSON

The isolation of an insecticidal amide from the roots of a Mexican plant submitted to this Bureau as *Erigeron affinis* D. C., and its identification as N-isobutyl-2,6,8-decatrienamide (I), were reported in 1945 by Acree, *et al.*[2] In 1947 the plant was shown to be actually *Heliopsis longipes* (A. Gray.) Blake[3] (family *Compositae*), and a detailed report of its insecticidal activity was published by McGovran, *et al.*[4]

$$CH_3CH{=}CHCH{=}CH(CH_2)_2CH{=}CHCNHCH_2CH(CH_3)_2 \quad (I)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad O$$

An investigation was undertaken to determine the insecticidal activity of three species of *Heliopsis* native to the United States, and it was found[5] that all of these species—namely, *H. scabra* Dunal., *H. gracilis* Nutt., and *H. parvifolia* A. Gray—particularly the roots, were toxic to house flies (*Musca domestica* L.). The roots of *H. scabra* were especially toxic to this insect.

Heliopsis scabra Dunal. is indigenous to most of the United States, growing as a weed from 2.5 to 4.5 feet tall. The only reference in the literature to the chemistry of the plant is that by Kuhn and Winterstein,[6] who reported the isolation of lutein, m. p. 193°, and its palmitic acid ester, m. p. 92°, from the flower heads of *H. scabra* var. *major* and *H. scabra* var. *cinniaeflorae*.

A quantity of air-dried *H. scabra*[7] was obtained from Ruidoso Canyon in the White Mountains of New Mexico and the roots were separated from the rest of the plant. Successive extraction of the roots with petroleum ether, ethyl ether, chloroform, and ethanol showed that only the petroleum ether extractive was toxic to house flies.[8]

The insecticidal material was extracted from the hydrocarbon solution with nitromethane, which was then removed and the residue taken up in ethyl ether. The neutral fraction, obtained following extraction with dilute acid and alkali, was chromatographed on successive columns of alumina, and the main toxic fraction was obtained in pure form in 0.12% yield (based on dry root) as a pale yellow, viscous oil which could not be distilled without decomposition, even under high vacuum.

A trace of this material, when placed on the tongue, produced, after about ten minutes, an intense burning, paralytic effect on the tongue and lips lasting for about two hours. It proved to be appreciably more toxic than the pyrethrins to house flies.

In addition to this toxic oil, there was obtained, in 0.08% yield, a very viscous, yellow oil showing strong blue fluorescence, which also possessed considerable toxicity to house flies, but which was not pungent. It appears to contain a small amount of impurity which is very difficult to separate. There were also isolated from the neutral fraction a colorless crystalline compound, $C_{20}H_{22}O_6$, m. p. 133.5–135.0°, and a yellow crystalline compound, $C_{10}H_6O_3$, m. p. 235°, showing strong blue fluorescence in solution, neither of which is insecticidal. The latter compound contains a lactone structure. The detailed investigation of these compounds will be reported separately.

The non-fluorescent, active substance, for which the name "scabrin" is proposed, is not stable at room temperature for more than a week, changing to a dark orange resin which is neither pungent nor insecticidal. However, it is stable in the cold for several weeks under nitrogen or in sealed ampoules. It is also stable in solution at room temperature, a property which is also shown by herculin from *Zanthoxylum clava-herculis* bark.[9]

Scabrin contained nitrogen and rapidly decolorized a dilute carbon tetrachloride solution of bromine. Acid hydrolysis yielded an acid which was too unstable to be characterized, and a nitrogenous base which was identified as isobutylamine by means of melting point and chlorine determination of its hydrochloride, by melting point of the chloroplatinate, and by comparison with authentic materials. The compound was thus established as the isobutylamide of an unsaturated acid.

Analysis and molecular weight determination indicated the formula $C_{22}H_{35}NO$ for scabrin. Hydrogenation with platinum oxide catalyst yielded decahydroscabrin, $C_{22}H_{45}NO$, m. p. 77–

(1) Report of a study made under the Research and Marketing Act of 1946. Article not copyrighted. This paper was presented before the Division of Organic Chemistry, at the Chicago meeting of the American Chemical Society, September 5, 1950.

(2) F. Acree, Jr., M. Jacobson and H. L. Haller, *J. Org. Chem.*, **10**, 236 (1945); **10**, 449 (1945).

(3) (a) M. Jacobson, F. Acree, Jr., and H. L. Haller, *J. Org. Chem.*, **12**, 731 (1947); (b) E. L. Little, *J. Wash. Acad. Sci.*, **38**, 269 (1948).

(4) E. R. McGovran, *et al.*, Bur. Ent. and Plant Quar. E-736, 5 pp. (1947).

(5) W. A. Gersdorff and N. Mitlin, *J. Econ. Entom.*, **43**, 554 (1950).

(6) R. Kuhn and A. Winterstein, *Naturwiss.*, **18**, 754 (1930).

(7) This material was very kindly collected by Prof. A. H. Berkman, Texas Western College, and its identity was verified by S. F. Blake, Bureau of Plant Industry, Soils, and Agricultural Engineering, U. S. Department of Agriculture, Beltsville, Md.

(8) The tests against house flies were made by W. A. Gersdorff and N. Mitlin of this Bureau.

(9) M. Jacobson, THIS JOURNAL, **70**, 4234 (1948).

78°, showing the presence of five double bonds, one double bond and two triple bonds, or three double bonds and a triple bond.

Acid hydrolysis of decahydroscabrin yielded isobutylamine and an acid fraction, m. p. 69–70°, which was identified as stearic acid by neutralization equivalent, by preparation of the *p*-phenylphenacyl ester, m. p. 97°, and by comparison of the acid and ester with authentic specimens. A mixed melting point determination of decahydroscabrin with synthetic N-isobutylstearamide, m. p. 77–78°, showed no depression. Scabrin was thus shown to be the N-isobutylamide of an unsaturated 18-carbon straight-chain acid, and it remained only to determine the points of unsaturation in the molecule.

Oxidation of scabrin with alkaline permanganate resulted in the isolation of butyric, oxalic, succinic and N-isobutyloxamic acids only. There were therefore only six theoretically possible structures (II–VII) for scabrin, exclusive of *cis–trans* isomers. Although oxalic and succinic acids were each obtained in yields only slightly above one mole, this is probably due to polymerization in the oxidation mixture.

The ultraviolet absorption curve of scabrin is represented in Fig. 1. The absorption band at 222 mμ is such as would be given by a conjugated diene or enal structure, and the absorption at 263 mμ (ϵ = 31,800) indicates a conjugated triene or dienal system.[10,11]

Consideration of this spectrum makes structures II and VI untenable. Scabrin is, therefore, the N-isobutylamide of either 2,4,8,10,14-, 2,4,8,12,14-, 2,6,8,10,14- or 2,6,10,12,14-octadecapentaenoic acid or a mixture of these isomers.

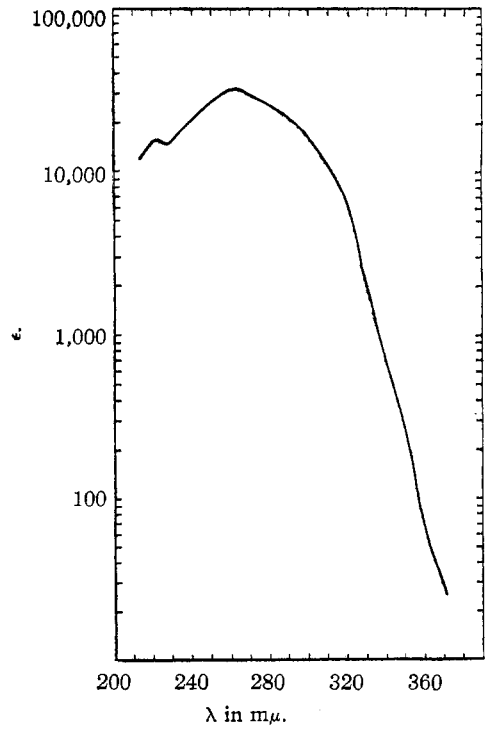
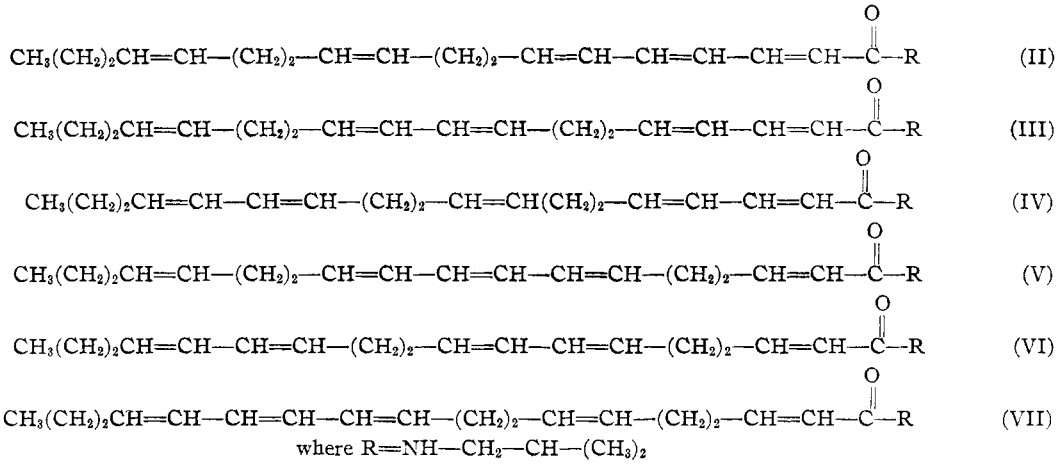


Fig. 1.—Absorption curve of scabrin in absolute ethanol: concentration, 2 × 10^{-5} mole per liter; ϵ = 31,800, max. 263 mμ (major peak); ϵ = 16,600, max. 222 mμ (minor peak).



Experimental[12]

Isolation of Scabrin.—For preliminary trial, 350 g. of finely ground roots of *H. scabra* was extracted successively, in a Soxhlet extractor, with petroleum ether, b.p. 30–40° (Skellysolve A), ethyl ether, chloroform, and ethanol. Only the petroleum ether extract (5.46 g., 1.6%) was toxic to house flies after removal of the solvent.

Therefore, 2826 g. of ground roots was exhaustively extracted in a Soxhlet extractor with Skellysolve A. The extract was concentrated down to 500 ml., during which time a small quantity of orange oil separated from solution. The solution was decanted into a separatory funnel, and the separated oil was taken up in 100 ml. of nitromethane, which was then used to extract the hydrocarbon solution. The solution was then extracted twice with 100-ml. portions and twice with 75-ml. portions of nitromethane. The combined nitromethane solution was concentrated down to 375 ml. and passed through an 8- by 1.5-inch column of activated carbon (Norite). After elution with 600 ml. of nitromethane, the recovered solution was freed of solvent under reduced pressure, leaving 32.00 g. (1.1%) of viscous orange oil with strong blue fluorescence.

This oil was taken up in ethyl ether, and the ether solution was washed thoroughly with water, 5% hydrochloric acid solution, 10% sodium hydroxide solution, and finally with water. After being dried over sodium sulfate, the ether solution of the neutral fraction was concentrated down

(10) K. Dimroth, *Angew. Chem.*, **52**, 545 (1939); R. B. Woodward, THIS JOURNAL, **64**, 72 (1942).

(11) These data were kindly interpreted by Harry Bastron of the Bureau of Animal Industry.

(12) All melting points are corrected. Analyses were performed by J. C. Ard of the Bureau of Agricultural and Industrial Chemistry, and by Clark Microanalytical Laboratory, Urbana, Ill.

to 50 ml. and Skellysolve A was added until a cloudiness appeared. The solution, on standing at 5° overnight, deposited a quantity of yellow solid, which was filtered off and washed with ether. Recrystallization from ethanol gave 1.0 g. of yellow crystalline solid, m.p. 235°, which showed a strong blue fluorescence in ultraviolet light and in solution. The material was recovered unchanged upon acidification of a hot aqueous potassium hydroxide solution, indicating a lactone structure.

Anal. Calcd. for $C_{10}H_6O_3$: C, 68.98; H, 3.45. Found: C, 69.10; H, 3.58. The compound was non-toxic to house flies.

The ether–Skellysolve filtrate obtained above was freed of solvent completely, leaving 27.0 g. (0.96%) of viscous orange oil with strong blue fluorescence.

Thirteen and five-tenths grams of this oil was dissolved in a small quantity of benzene and put on a 15- by 1-inch column of adsorption alumina, 80 to 200 mesh. Benzene was used to develop the bands, and the progress of fluorescent materials down the column was followed by use of an ultraviolet light (long wave 3660 Å.). A brown band remained at the top of the column and below this a yellow band showing blue fluorescence moved slowly down the column with gradual widening. A lower yellow band showing no fluorescence was weakly adsorbed, moving down rapidly on further development. Half-way down the column the fluorescent yellow band stopped moving, and further development with benzene quickly brought out the non-fluorescent yellow band (Fraction A). The developing solvent was now changed to benzene–ethyl ether (1:1), which brought out the fluorescent yellow zone (Fraction B), leaving the brown band stationary at the top of the column. Further development with straight ethyl ether gave a colorless filtrate (Fraction C), and elution with chloroform and ethanol failed to remove anything further from the column.

Fraction A, after removal of solvent under reduced pressure, consisted of 1.7 g. (0.06%, based on dry root) of pale yellow, viscous oil. Chromatographic adsorption on a fresh column of alumina and development with benzene brought the fraction down the column as a sharp, well-defined yellow band. After elution with benzene and removal of the solvent, it still weighed 1.7 g., and was considered to be pure. It was very pungent and appreciably more toxic than pyrethrins to house flies.

Fraction B was freed of solvent and the thick, orange, fluorescent residue was adsorbed on a fresh column of alumina. Development with benzene failed to yield any further Fraction A. Benzene–ethyl ether (1:1) brought out a yellow band showing blue fluorescence, and development with ethyl ether gave a colorless filtrate which, on removal of solvent, left 2.1 g. of colorless shining prisms, m.p. 133.5–135.0° after recrystallization from ethanol. The yellow fluorescent filtrate, after removal of solvent, gave 1.0 g. (0.04%) of viscous orange oil with strong blue fluorescence. It was non-pungent, but possessed considerable toxicity to house flies. However, its behavior on the column showed it to be a mixture, which will be further investigated.

Fraction C was freed of solvent and stirred with a few ml. of absolute ether which caused sudden crystallization. One recrystallization from ethanol gave 7.9 g. of clusters of shining prisms, m.p. 133.5–135°, identical with the crystals obtained from the rechromatography of Fraction B. The total yield was 10.0 g. (0.35%). It was non-toxic to house flies.

Anal. Calcd. for $C_{26}H_{22}O_6$: C, 67.02; H, 6.19. Found: C, 66.89; H, 6.27.

This chromatographic procedure was repeated on the remaining 13.5 g. of neutral fraction obtained above, providing total yields of 3.4 g. (0.12%) of non-fluorescent, yellow oil (scabrin), 2.0 g. (0.08%) of fluorescent, yellow oil and 20.0 g. (0.70%) of crystals, m.p. 133.5–135.0°.

Scabrin was a pale yellow, viscous oil, $n^{25}D$ 1.5685, which could not be distilled without decomposition, even under high vacuum. It could not be induced to crystallize. It contained nitrogen, rapidly decolorized a 5% solution of bromine in carbon tetrachloride, and was soluble in all organic solvents except petroleum ether. Its ultraviolet absorption curve showed maxima at 222 mμ (ϵ = 16,600) and 263 mμ (ϵ = 31,800).

Anal. Calcd. for $C_{22}H_{35}NO$: C, 80.18; H, 10.71; N, 4.25; $2CH_3$, 9.1; mol. wt., 329.5. Found: C, 80.11; H, 10.62; N, 4.35; CH_3, 10.0; mol. wt. (Rast), 333.5.

Hydrolysis of Scabrin.—A mixture of 1.00 g. of scabrin, 15 ml. of ethanol, and 2.5 ml. of concentrated hydrochloric acid was heated in a sealed tube at 100° for 121 hours and then cooled. The reaction mixture was diluted with three volumes of water and then extracted with ether. The aqueous acid solution was evaporated to dryness on the steam-bath, and the residue (0.31 g.) was stirred with 10 ml. of boiling ethyl acetate and filtered. On cooling, the solution deposited 0.26 g. (79%) of shining colorless plates, m.p. 174–175° after three recrystallizations from ethyl acetate. It was identified as isobutylamine hydrochloride by the mixture melting point determination with authentic material, m.p. and mixed m.p. 174–175°.

Anal. Calcd. for $C_4H_{11}N\cdot HCl$: Cl, 32.35. Found: Cl, 32.15.

The chloroplatinate was prepared by the addition of 3 drops of a saturated aqueous solution of chloroplatinic acid to 100 mg. of the base-hydrochloride dissolved in 1 ml. of absolute ethanol. The crystalline product that precipitated was filtered, washed with ethanol, and dried. It melted at 227–228° (dec.) (239–240° dec. in a preheated bath), undepressed by admixture with an authentic specimen, m.p. 227–228° (dec.).

The ether extract of the original reaction mixture was washed free of mineral acid and dried, and the solvent was removed. The residue was refluxed for one hour with 0.5 g. of potassium hydroxide in 20 ml. of ethanol; the reaction mixture, after being cooled and acidified, was extracted with ether. The dried ether solution was freed from solvent, leaving a dark red, oily acid residue (0.69 g., 83%) which was completely soluble in sodium bicarbonate solution, but which could not be characterized at this stage because of its instability.

Preparation of Decahydroscabrin.—An absolute ethanol solution of 0.2271 g. of scabrin was hydrogenated with 100 mg. of reduced platinum oxide catalyst. In seven minutes 77 ml. (cor.) of hydrogen was taken up, and the reaction then ceased. (The theoretical requirement for 5 moles of hydrogen for the above weight of a substance of molecular weight 330 is 77 ml.) The reaction mixture was separated from the catalyst, and the solvent was removed at reduced pressure, leaving a white solid. One recrystallization from ethanol gave a quantitative yield of the saturated compound as clusters of colorless needles, m.p. 77–78°.

Anal. Calcd. for $C_{22}H_{45}NO$: C, 77.81; H, 13.36; N, 4.13. Found: C, 78.21; H, 13.54; N, 4.31.

The product was found to be identical with N-isobutylstearamide, m.p. 77–78°, by mixed m.p. (77–78°) with an authentic specimen prepared by the following procedure. Thirteen grams of pure stearic acid and 8.1 g. (50% excess) of thionyl chloride were heated on the steam-bath for 3.5 hours. Excess thionyl chloride was removed under reduced pressure and the residue was distilled to give 8.8 g. (64%) of stearoyl chloride as a colorless liquid, b.p. 207° (15 mm.). To an ice-cold solution of 8.6 g. (100% excess) of isobutylamine in anhydrous ether was added slowly with stirring an anhydrous ether solution of the acid chloride. After the mixture had stood at room temperature overnight the precipitated amine hydrochloride was dissolved by the addition of dilute hydrochloric acid, and the ether layer was washed with water, 5% potassium hydroxide solution and water, then dried and evaporated. The residue, after recrystallization from ethanol, weighed 8.9 g. (90%) and melted at 77–78°.

Hydrolysis of Decahydroscabrin.—Decahydroscabrin (0.31 g.) was dissolved in 10 ml. of hot ethanol, 2 ml. of concentrated hydrochloric acid was added, and the mixture was heated in a sealed tube at 100° for 72 hours. After the reaction mixture had cooled, it was diluted with water and extracted with ether. From the aqueous acid solution there was obtained, by the procedure described under hydrolysis of scabrin, 80 mg. of isobutylamine hydrochloride, m.p. 174–175°.

The ether solution was washed and dried, and the residue, following removal of solvent, was refluxed for one hour with 0.5 g. of potassium hydroxide in 10 ml. of ethanol. After the mixture had cooled, water was added (a voluminous white solid separated) and the mixture was acidified and extracted with ether. The ether solution was then washed with water and dried. Removal of the solvent left yellowish glistening crystals and recrystallization from methanol yielded 0.23 g. (90%) of colorless leaflets, m.p. 69–70°.

Anal. Calcd. for $C_{18}H_{36}O_2$: neut. equiv., 284. Found: neut. equiv., 283.

The acid was identified as stearic acid by mixed m.p. with an authentic specimen, and by preparation of the *p*-phenylphenacyl ester, m.p. and mixed m.p. with an authentic sample 97°.

Oxidation of Scabrin.—To a stirred suspension of 1.8 g. of scabrin in 120 ml. of water, maintained at 60°, 11.6 g. of finely powdered potassium permanganate (equivalent to 10 moles of oxygen) was added in small portions. When the reaction mixture had become colorless, the manganese dioxide was filtered and washed thoroughly with warm water. The combined aqueous filtrates were concentrated down to 35 ml. and made acid to congo red with sulfuric acid. The solution was steam distilled to remove completely the volatile acids and then extracted with ether in a continuous extractor. The ether solution was freed of solvent, and the partly crystalline residue was subjected to sublimation in a micro sublimator. Five hundred and seventy mg. of colorless solid was obtained, which sublimed at 100–110° (15 mm.) and melted at 185–186° (dec.). It rapidly reduced an aqueous solution of potassium permanganate.

Anal. Calcd. for $C_2H_2O_4$: neut. equiv., 45. Found: neut. equiv., 45.

The substance was identified as anhydrous oxalic acid by a mixture melting point determination with an authentic specimen (m.p. 186–187° dec.) and by preparation of the di-*p*-phenylphenacyl ester, m.p. and mixed m.p. with authentic material 165.5° (dec.).

The yield of oxalic acid was 58% (1.16 moles).

The sublimation residue, after recrystallization from ethyl acetate, yielded 561 mg. of colorless crystals, m.p. 187–188°.

Anal. Calcd. for $C_4H_6O_4$: neut. equiv., 59. Found: neut. equiv., 58.

The substance was identified as succinic acid by a mixture melting point determination, m.p. 187.5–188.0°, and by preparation of the di-*p*-phenylphenacyl ester, m.p. 208°. An additional 220 mg. of succinic acid (total yield 61%, 1.22 moles) was obtained from the ethyl acetate mother liquors, together with a tarry residue which could not be made to crystallize, and which was obviously polymerized material.

The solution of steam-volatile acids obtained above was neutralized with sodium hydroxide solution, concentrated to a small volume on the steam-bath, and acidified to congo red with sulfuric acid. The solution was rapidly steam distilled until all material acid to congo red had distilled over. The distillate was neutralized with 0.1 *N* NaOH solution (47.50 ml. was required), the neutral solution was evaporated to dryness, and the *p*-phenylphenacyl ester was prepared. It melted at 82° and a mixed melting point determination with authentic *p*-phenylphenacyl butyrate, m.p. 82°, showed no depression. The yield of butyric acid, therefore, amounted to approximately 87%.

The distillated above was neutralized with sodium hydroxide solution, concentrated on the steam-bath to 15 ml., acidified to congo red with sulfuric acid, and extracted with ether in a continuous extractor. The ether solution was dried and freed of solvent. The crystalline residue sublimed completely at 90–95° (15 mm.). One recrystallization from Skellysolve B gave 0.55 g. (69%) of colorless feathery needles, m.p. 107°, containing nitrogen.

Anal. Calcd. for $C_5H_{11}NO_3$: N, 9.66; neut. equiv., 145. Found: N, 9.74; neut. equiv., 145.

The substance was identified as N-isobutyloxamic acid by a mixture melting point determination with a synthetic sample, m.p. 107°.

Summary

A pungent isobutylamide of an unsaturated C_{18} acid has been isolated from the roots of *Heliopsis scabra* Dunal. The substance, for which the name "scabrin" is proposed, is appreciably more toxic than the pyrethrins to house flies.

Hydrogenation of the amide gave N-isobutylstearamide, and on oxidation it yielded butyric, oxalic, succinic and N-isobutyloxamic acids.

On the basis of these degradations and of its ultraviolet absorption spectrum, scabrin was shown to be the N-isobutylamide of either 2,4,8,10,14-, 2,4,8,12,14-, 2,6,8,10,14- or 2,6,10,12,14-octadecapentaenoic acid, or a mixture of these isomers.

Also isolated from the roots were two crystalline compounds, and a fluorescent oil which is also considerably toxic to house flies. These compounds will be investigated further.

BELTSVILLE, MARYLAND RECEIVED JUNE 26, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY]

α-Halogenation of Secondary Nitriles[1,2]

BY CALVIN L. STEVENS AND T. H. COFFIELD

Recently the reaction of isobutyronitrile with phosphorus pentachloride and phosphorus pentabromide to give α-chloro- and α-bromoisobutyronitrile[3] in good yield was reported. The purpose of this paper is to extend the scope of this reaction for secondary aliphatic nitriles.

Phosphorus pentachloride has been used by Von Braun, *et al.*,[4] to α-chlorinate aliphatic secondary iminochlorides in good yield at the temperature of refluxing benzene. At about 200°, phosphorus pentachloride is reported[5] to chlorinate α-methylbutyryl chloride in unspecified yield. α-Chloroisobutyronitrile has been obtained by the direct chlorination of isobutyronitrile in sunlight.[6] The action of bromine on aliphatic nitriles has been reported[7] to give 85–95% of bromonitriles from which the α-bromonitriles could not be isolated in pure form.

In this work, four aliphatic secondary nitriles (IX): α-methylbutyronitrile, α-ethylbutyronitrile, α-ethylcapronitrile and cyclohexanecarbonitrile were chlorinated and brominated with the phosphorus pentahalides under mild conditions in the absence of solvents to give the α-halonitriles (X) in 70–95% yield (see Table I, compounds I to VIII).

$$\underset{\text{IX}}{R_1R_2CHCN} + PX_5 \longrightarrow \underset{\text{X}}{R_1R_2CXCN} + HX + PX_3$$

Evidence that the halogen entered the α-position was obtained by acid hydrolysis of the bromo- and chlorocyclohexanecarbonitrile and the bromo- and chloro-α-ethylbutyronitrile to give 70–95% of known amides (see Table II). Hydrolysis of the halonitriles with unsymmetrical alkyl groups gave amides that melted at or below room temperature.

(1) This work was supported in part by a Research Corporation Grant-in-Aid and in part by an Ethyl Corporation Fellowship.

(2) Presented before the Organic Division of the American Chemical Society in Atlantic City in Sept., 1949.

(3) Stevens, THIS JOURNAL, **70**, 165 (1948).

(4) Von Braun, Jostes and Münch, *Ann.*, **453**, 127 (1927).

(5) *Ibid.*, **453**, 146 (1927).

(6) Loder, U. S. Patent, 2,175,810, Oct. 10, 1939.

(7) Merckx and Bruylants, *Bull. soc. chim. Belg.*, **43**, 200 (1934).