temperature of the reaction was kept at 20°, requiring fifteen minutes for the addition, stirred for an additional hour. At this stage two layers were present as well as some solid salt. The mixture was distilled to remove the chloroform formed and the alcohol. On cooling, the sodium salt of the α-ethyl-β-anisylvaleric acid solidified. Dissolved in water, clarified with Norite, followed by hydrochloric acid acidification gave 5 g. of a light tan solid melting at 125°, a 21% yield. Recrystallized from 75% acetic acid, aqueous alcohol or petroleum ether (40–60°) the racemic form melted at 135–136°. The amide melted at 139–142°.

Anal. Calcd. for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53; neut. equiv., 236.3. Found: C, 70.93; H, 8.66; neut. equiv., 237.6.

The *meso*-form was isolated from the mother liquors as a liquid.

Ethyl (α-β-Diethyl-*p*-methoxy)-cinnamate.—To a stirred mixture of 17.3 g. (0.105 mole) of *p*-methoxypropiophenone, 30 ml. each of benzene and toluene, 7 g. (0.107 mole) of zinc dust, 21 g. (0.108 mole) of ethyl α-bromobutyrate was added dropwise. An iodine crystal aided in starting the reaction. The ester completely added, the mixture was refluxed and stirred for an hour. Poured into 100 ml. of cold 20% sulfuric acid the benzene-toluene layer was separated, washed with water, dilute sodium carbonate solution, water. Removal of the solvents and distillation of the oil gave 21.3 g. of product boiling at 124–126° at 0.3 mm., $n^{20}D$ 1.5174, 86% yield.

Ethyl (2-Ethyl-3-anisyl)-valerate.—Some 13.2 g. (0.05 mole) of the ethyl (α,β-diethyl-*p*-methoxy)-cinnamate was reduced in 75 ml. of ethanol in the Parr hydrogenator at 60 lb. hydrogen pressure over 0.1 g. of platinum oxide and 0.1 g. of palladium black. The hydrogen uptake was complete in four hours. The catalyst was filtered off, the alcohol removed, distillation of the oil at 0.8 mm. gave 12.9 g. boiling at 122°, $n^{20}D$ 1.4935, 97% yield.

α-Ethyl-β-anisylvaleric Acid.—Saponification of the ethyl (2-ethyl-3-anisyl)-valerate with methanolic alkali gave the racemic acid melting at 133° after recrystallization from aqueous methanol. Recrystallized from petroleum ether (40–60°) the acid melted at 135–137°, yield 42%. A mixed melting point with the acid obtained by the synthesis from the *p*-methoxystyryl methyl ketone gave no depression. The products were identical.

Reaction of α-Ethyl-β-anisylvaleryl Chloride with Anisole.—Four grams (0.0169 mole) of the α-ethyl-β-anisylvaleric acid was warmed with 10 ml. of thionyl chloride under reflux for an hour. The excess thionyl chloride was removed under reduced pressure. To the residue was added 10 ml. of ethylene dichloride followed by 8.4 g. (0.063 mole) of aluminum chloride. The mixture was chilled and 4 g. (0.037 mole) of anisole added dropwise. After three hours the mixture was poured into 100 g. of crushed ice containing 10 ml. of concd. hydrochloric acid. Extracted with benzene, washed with water, dilute sodium carbonate solution, dried, distilled at 4–5 mm., 3.1 g. of material boiling at 190–194°, 61% yield, was obtained. Recrystallized twice from methanol after a Norite treatment, the solid melted at 81–82°. A mixed melting point determination with the solid ketone prepared from *p*-methoxybutyrophenone[4] gave no depression. The products were identical.

Summary

A new and independent synthesis from α-ethyl-β-anisylvaleric acid substantiates the structure of benzestrol[4] as a 1,2,3-tri-alkyl substituted 1,3-di-(*p*-hydroxyphenyl)-propane derivative.

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

The Synthesis of a Geometrical Isomer of Pellitorine[1,2]

BY MARTIN JACOBSON

Pellitorine, isolated from the roots of *Anacyclus pyrethrum* DC.,[3] has previously been shown[3,4] to be N-isobutyl-2,6-decadienamide (VIII). In view of the insecticidal activity of this compound,[4] its synthesis was attempted in this laboratory.

The steps employed in this synthesis are shown in the accompanying chart. Dihydropyran (I) was chlorinated, to give 2,3-dichlorotetrahydropyran (II) in 91% yield, by a slight modification of the method of Paul.[5] Treatment of II with *n*-propylmagnesium bromide gave a 73% yield of 3-chloro-2-*n*-propyltetrahydropyran (III). Treatment of III with sodium split the ring to give 4-octen-1-ol (IV) in 86% yield, a general procedure previously used to obtain 4-penten-1-ol[6] and 4-nonen-1-ol.[5,7] Dichromate oxidation of the unsaturated alcohol (IV) by the low-temperature method of Delaby and Guillot-Allègre[8] resulted in a 35% yield of 4-octene-1-al (V). Treatment of the aldehyde (V) with malonic acid in pyridine with piperidine as catalyst (Doebner reaction) gave the acid fragment of pellitorine (2,6-decadienoic acid) (VI) in 17% yield. The acid chloride (VII) was prepared in 96% yield by use of thionyl chloride in low-boiling petroleum ether, and addition of VII to isobutylamine in ether solution yielded 95% of N-isobutyl-2,5-decadienamide (VIII).

There are four possible *cis* and *trans* isomers having structure VIII, namely, *cis–cis*, *cis–trans*, *trans–cis*, and *trans–trans*. The compound synthesized by the procedure described above, although showing approximately the same boiling point (150° at 0.1 mm.) as natural pellitorine (155–165° at 0.3–0.5 mm.),[4] melted at 54–55°, whereas the natural isomer melts at 72°.[9] Both materials are

(1) Report of a study made under the Research and Marketing Act of 1946. Article not copyrighted.

(2) Presented before the Division of Organic Chemistry, at the Atlantic City Meeting of the American Chemical Society, September 21, 1949.

(3) Gulland and Hopton, *J. Chem. Soc.*, 6 (1930).

(4) Jacobson, THIS JOURNAL, **71**, 366 (1949).

(5) Paul, *Compt. rend.*, **218**, 122 (1944).

(6) Paul and Normant, *Bull. soc. chim.*, [5] **10**, 484 (1943).

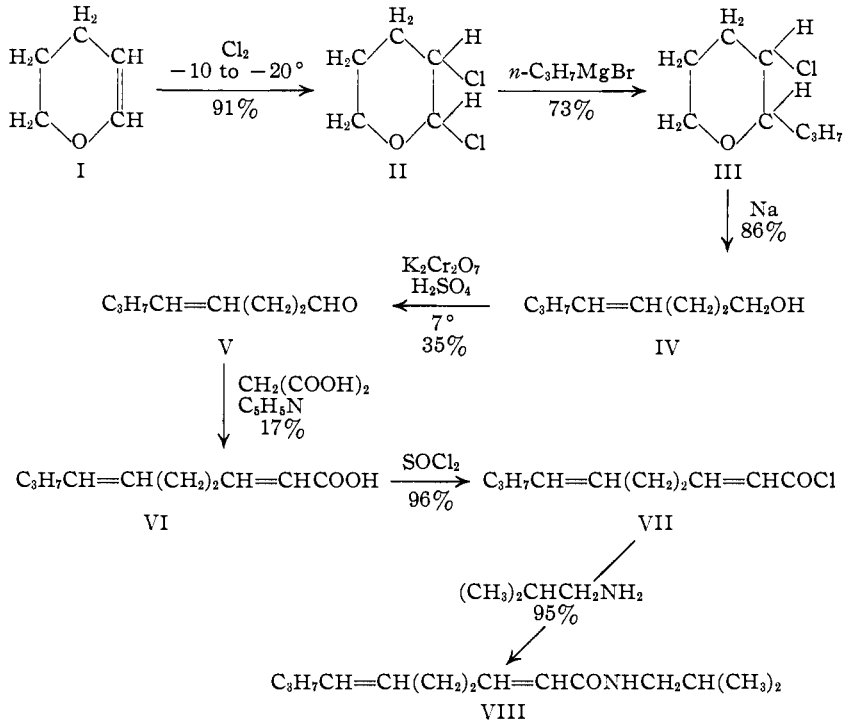
(7) Paul and Riobé, *Compt. rend.*, **224**, 474 (1947).

(8) Delaby and Guillot-Allègre, *Bull. soc. chim.*, [4] **53**, 301 (1933).

(9) After this paper was submitted for publication, the synthesis of the *cis–cis* and *cis–trans* isomer of pellitorine, was reported by Raphael and Sondheimer (*Nature*, **164**, 707 (1949)) and by Crombie and Harper (*ibid.*, **164**, 1053 (1949)), respectively. These isomers are identical with neither the natural product nor our solid isomer and indications point to the latter as being the *trans–trans* isomer.

very soluble in organic solvents, but insoluble in water, acid and alkali.

In contrast to natural pellitorine, the synthetic material is neither pungent nor toxic to house flies.[10] It is, however, fairly stable. A small sample exposed to the air at room temperature showed signs of discoloration only after four weeks, whereas natural pellitorine, under the same conditions, turned yellow after one week. However, both isomers were less stable when kept in petroleum ether solution at room temperature, although both the pure crystalline materials and their solutions could be kept unchanged in the cold for several months.



The synthetic material was shown to have structure VIII by hydrogenation with platinum oxide to N-isobutylcapramide, and by oxidation to yield butyric, succinic and N-isobutyloxamic acids in excellent yields, identical with the oxidation products of natural pellitorine.[4]

An attempt to convert the synthetic to the natural isomer by exposure to ultraviolet light was unsuccessful, 90% of the material being recovered unchanged after eighteen hours of exposure. The remaining 10% was converted to a resin-like material which could not be made to crystallize.

Experimental[11,12]

2,3-Dichlorotetrahydropyran (II).—Dihydropyran[13] was distilled (b. p. 85–86°, $n^{25}D$ 1.4573), and dried over sodium before use.

Chlorine was passed rapidly into a solution of 300 g. of dihydropyran in 975 ml. of dry, redistilled carbon tetrachloride, while the temperature was maintained between −10 and −20°. When the theoretical quantity (253 g.) of chlorine had been added, the solution was freed of solvent under reduced pressure and the residue was distilled to give 483 g. (91%) of colorless, mobile liquid, b. p. 79–83° (13 mm.); $n^{25}D$ 1.4930 (lit.[14] b. p. 89–90° at 20 mm.; $n^{17}D$ 1.49582).

Anal. Calcd. for $C_5H_8Cl_2O$: Cl, 45.74. Found: Cl, 45.70.

The temperature at which this chlorination is carried out is a critical factor, as Hawkins[15] has reported that chlorination of dihydropyran in carbon tetrachloride at 0° results in a 90% yield of 3-chloro-5,6-dihydropyran, b. p. 141–142°.

3-Chloro-2-*n*-propyltetrahydropyran (III).—To an ether solution of *n*-propylmagnesium bromide (prepared from 600 g., 4.96 moles, of dry, redistilled *n*-propyl bromide and 127 g., 5.22 moles, of magnesium turnings) in a five-liter, three-necked flask equipped with a reflux condenser and calcium chloride drying tube, mercury-sealed stirrer and dropping funnel, was added, with stirring, a solution of 482 g. (3.11 moles) of 2,3-dichlorotetrahydropyran in one liter of anhydrous ether. The solution was added at such a rate that gentle refluxing of the ether occurred, although cooling of the mixture with an ice-bath was sometimes necessary. As the reaction proceeded, the mixture thickened and a gray solid separated, necessitating the addition of ether from time to time to facilitate stirring. After addition was complete (4.5 hours), the mixture was cooled in an ice-bath and carefully hydrolyzed with ice and hydrochloric acid (1:1). The ether layer was separated, washed with water, and dried over anhydrous sodium sulfate. Removal of the ether and distillation of the residue gave 367.6 g. (73%) of colorless liquid with a menthol odor, b. p. 72–80° (13 mm.); $n^{25}D$ 1.4550.

Anal. Calcd. for $C_8H_{16}ClO$: C, 58.70; H, 9.86; Cl, 21.66. Found: C, 58.73; H, 9.80; Cl, 21.62.

4-Octen-1-ol (IV).—One hundred and fifteen grams of sodium (10% excess) was powdered under toluene in a five-liter three-necked flask. The toluene was decanted and the sodium was washed three times with small portions of anhydrous ether and then covered with a layer of anhydrous ether. The flask was then equipped with a reflux condenser and calcium chloride drying tube, a mercury-sealed Hershberg stirrer, and a dropping funnel.

To this vigorously stirred ether suspension of sodium was added a solution of 366.0 g. (2.23 moles) of 3-chloro-2-*n*-propyltetrahydropyran in 450 ml. of anhydrous ether. The addition was carried out at such a rate that steady refluxing of the ether took place, and no cooling was neces-

(10) The tests against house flies were made by W. A. Gersdorff of this Bureau.

(11) All melting points are corrected; boiling points are uncorrected.

(12) All microanalyses except neutralization equivalents and chlorine determinations were made by Oakwold Laboratories, Alexandria, Va.

(13) This material was very generously supplied by the Electrochemicals Department, E. I. du Pont de Nemours and Co., Wilmington, Del.

(14) Normant, *Compt. rend.*, **226**, 185, 733 (1948).

(15) Hawkins, *et al.*, British Patent 571,265, Aug. 14, 1945.

sary. As the reaction proceeded, a white solid separated and the mixture took on a deep blue color which disappeared when addition was complete (four hours). The mixture was refluxed for an additional hour with stirring and then cooled in an ice-bath. Water was carefully added to decompose the excess sodium present, and then hydrochloric acid (1:1) until the aqueous layer was acid to congo red. After separation of the layers, the aqueous layer was washed with several 75–100 ml. portions of ether. The combined ether solutions were washed with water and dried over anhydrous sodium sulfate. Removal of the solvent and distillation of the residue gave the desired product (248.0 g., 86%) as a colorless liquid with a pleasant, fruity odor, b. p. 84–88° (12 mm.); $n^{25}D$ 1.4435.

Anal. Calcd. for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 74.97; H, 12.51.

The 3,5-dinitrobenzoate crystallized from ethanol in colorless prisms, m. p. 44°.

Permanganate Oxidation of 4-Octen-1-ol.—To a stirred suspension of 3 g. of the alcohol in 300 ml. of water, maintained at 50°, 7.4 g. of finely powdered potassium permanganate 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 30 ml. and made acid to congo red with sulfuric acid. The solution was steam-distilled to remove the volatile acids and then extracted with ether in a continuous extractor. The ether solution was freed of solvent, and the residue was recrystallized from a small amount of ethyl acetate to give 2.1 g. (80%) of colorless needles, m. p. 188–189°.

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

A mixed melting point with an authentic sample of succinic acid, m. p. 188–189°, showed no depression.

The solution of steam-volatile acids obtained above was neutralized with sodium hydroxide solution, evaporated to dryness on the steam-bath, and converted to the *p*-phenylphenacyl ester, melting point and mixed melting point with an authentic sample of *p*-phenylphenacyl butyrate, 81–82°.

Isolation of the above oxidation products showed conclusively that the unsaturated alcohol did possess the assigned structure IV.

4-Octen-1-al (V).—To a stirred solution of 414 g. of potassium dichromate and 414 g. of concentrated sulfuric acid in 2760 ml. of water, cooled to 7° in an ice-bath, there was added, all at once, 124 g. of 4-octen-1-ol emulsified with 138 ml. of water. The solution became dark brown and the temperature rose to 14°. After three minutes the temperature began to drop, and the mixture was immediately transferred to a separatory funnel and extracted with five 200-ml. portions of ether. The combined ether solution was washed with a saturated solution of sodium bicarbonate and then with water, and dried over sodium sulfate. Removal of the solvent and distillation of the residue gave, after a small forerun, 42.2 g. (35%) of colorless, mobile liquid, b. p. 80–84° (13 mm.); $n^{25}D$ 1.4463. By repeating the procedure with another sample of 120 g. of the octenol, an additional 37.7 g. of the aldehyde was obtained, giving a total yield of 80.0 g. (35%).

Anal. Calcd. for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.13; H, 11.20.

The 2,4-dinitrophenylhydrazone formed glistening, orange prisms, m. p. 108°, out of ethanol.

2,6-Decadienoic Acid (VI).—A solution of 79.0 g. (0.63 mole) of 4-octen-1-al, 80.0 g. (0.77 mole) of malonic acid, 125 ml. of dry pyridine, and 3 drops of piperidine was heated at 115° for four hours. During this time carbon dioxide was evolved vigorously. The clear yellow solution was then cooled in an ice-bath, made acid to congo red with dilute sulfuric acid, and extracted with several portions of ether. The combined ether solution was washed with water and then extracted with 10% sodium carbonate solution. This alkaline solution was extracted twice with small portions of ether and then made acid to congo red with dilute sulfuric acid. The acid solution was extracted with ether, and the extract was then dried over sodium sulfate. Evaporation of the solvent and distillation of the residue gave 19.1 g. (17%) of colorless, viscous liquid, b. p. 130° (1.5 mm.), which rapidly solidified to a mass of colorless plates, m. p. 35°.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59; neut. equiv., 168.2. Found: C, 71.30; H, 9.57; neut. equiv., 167.9.

2,6-Decadienoyl Chloride (VII).—Twenty-one grams (0.18 mole) of thionyl chloride (purified by distillation with quinoline and then with linseed oil) was added to a solution of 19.0 g. (0.12 mole) of the acid VI in 60 ml. of dry petroleum ether (b. p. 30–40°). The solution was allowed to stand overnight at room temperature, and was then refluxed on the steam-bath for three hours. After removal of the solvent and excess thionyl chloride under reduced pressure, the residue was distilled to give 20.3 g. (96%) of colorless, mobile liquid, b. p. 118° (17 mm.), possessing a sharp odor.

Anal. Calcd. for $C_{10}H_{15}ClO$: Cl, 19.00. Found: Cl, 18.93.

N-Isobutyl-2,6-decadienamide (VIII).—To an ice-cold solution of 32.0 g. (100% excess) of redistilled isobutylamine in 100 ml. of anydrous ether was added slowly, with stirring, an anhydrous ether solution of 20.1 g. (0.11 mole) of the acid chloride prepared above. After the mixture had stood at room temperature for two hours, the precipitated amine hydrochloride was dissolved by the addition of cold dilute hydrochloric acid, and the ether layer was washed with water, 5% potassium hydroxide solution and water, then dried and evaporated. Distillation of the residue in an atmosphere of nitrogen yielded 22.8 g. (95%) of colorless, viscous oil, b. p. 150° (0.1 mm.), which rapidly solidified to a mass of feathery needles, m. p. 54–55°. The melting point was unchanged after recrystallization from ice-cold petroleum ether (b. p. 30–40°).

Anal. Calcd. for $C_{14}H_{25}NO$: C, 75.28; H, 11.28; N, 6.27. Found: C, 75.24; H, 11.22; N, 6.22.

The substance was soluble in all organic solvents, and insoluble in water, acid and alkali. It rapidly decolorized a 5% solution of bromine in carbon tetrachloride.

Hydrogenation of VIII.—An ethanol solution of 0.9997 g. of compound VIII was hydrogenated with 50 mg. of reduced platinum oxide catalyst. In thirty minutes 204.3 ml. (cor.) of hydrogen was taken up, and the reaction then ceased. (The theoretical requirement for 2 moles of hydrogen for this weight of a substance of molecular weight 223 is 200.8 ml.) The reaction mixture was separated from the catalyst, and the solvent was removed at reduced pressure, leaving 1.0 g. of a colorless oil which crystallized in rosettes of needles, m. p. 37.5–38.0°.

The product was found to be identical with N-isobutylcapramide, m. p. 38–38.5°, by mixed melting point (37.5–38.0°) with an authentic specimen.

A sample of natural pellitorine weighing 0.8066 g. absorbed 168.0 ml. of hydrogen (theory 163 ml.), yielding colorless needles, m. p. 38°, undepressed by admixture with hydrogenated VIII.

Oxidation of VIII.—Three grams of compound VIII was oxidized at 55–60° with 11.3 g. of potassium permanganate by the procedure already given for the permanganate oxidation of 4-octenol. The non-volatile acid residue was extracted with two small portions of boiling Skellysolve B. Cooling of the hydrocarbon solution caused the separation of 1.6 g. (80%) of colorless, feathery needles, m. p. 106°.

Anal. Calcd. for $C_6H_{11}NO_3$: neut. equiv., 145. Found: neut. equiv., 145.

The mixed melting point with an authentic sample of N-isobutyloxamic acid was 106°.

The insoluble residue from the Skellysolve B extraction above was taken up in a little chloroform. Cooling in an ice-bath yielded 1.0 g. (67%) of colorless crystals as clusters of needles, m. p. 189°.

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

The product was identified as succinic acid by a mixed melting point determination with an authentic specimen (m. p. 189°).

The solution of steam-volatile acids was neutralized with sodium hydroxide solution and evaporated to dryness on the steam-bath, and the residue was converted to the *p*-phenylphenacyl ester, melting point and mixed melting point with an authentic sample of *p*-phenylphenacyl butyrate, 81–82°.

Exposure of VIII to Ultraviolet Light.—One gram of compound VIII was exposed on a watch glass for eighteen hours to the direct light from an ultraviolet lamp. The resulting orange viscous oil was taken up in a few milliliters of Skellysolve A, in which a very small quantity remained insoluble, and cooled in Dry Ice–acetone mixture. The mass of colorless needles that appeared weighed 0.9 g. (90%) after filtration and drying. A melting point and mixed melting point of 54–55° showed the material to be unchanged VIII.

The 100 mg. of orange resinous material insoluble in Skellysolve A could not be made to crystallize.

Summary

A stable, geometrical isomer of natural pellitorine (N-isobutyl-2,6-decadienamide) has been synthesized. In contrast to the natural isomer, it is non-pungent and non-toxic to house flies.

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

Exposure to ultraviolet light failed to transform the synthetic into the natural isomer.

BELTSVILLE, MD. RECEIVED SEPTEMBER 28, 1949

[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT AT THE FACULDADE DE FILOSOFIA, CIÊNCIAS E LETRAS DA UNIVERSIDADE DE SÃO PAULO]

Some Constituents of the Leaves of *Cassia alata L.*[1]

BY H. HAUPTMANN AND L. LACERDA NAZÁRIÔ

Cassia alata L., one of the 189 Brazilian *Cassia* species, is in its pharmacological action similar to senna leaves (*Cassia angustifolia Vahl* and *Cassia acutifolia Delile*) as Wasicky[2] pointed out some years ago. At the same time, based on the Borntraeger reaction,[3] the same author came to the conclusion that there are anthraquinone derivatives in reduced state either free or in glycosidal combination. Earlier studies on this plant[4] mention only hydroxymethylanthraquinones or "chrysophanic acid" as isolated compounds. Therefore, it seemed interesting to try the isolation and identification of its main constituents.

Cassia alata leaves were extracted with 25% alcohol[5] after a previous treatment with petroleum ether.[6] The alcoholic extract was submitted to two different treatments: (a) fractional precipitation with lead acetate similar to that used by several investigators[7] in their studies on senna leaves and (b) hydrolysis with sodium carbonate.

By the first procedure (a) all the anthraquinone compounds and their reduced derivatives were precipitated when an excess of saturated lead acetate solution was added to the ethanolic extract at room temperature. Heating should be avoided because at higher temperature the precipitation is not quantitative. By fractionating the lead salt precipitate different fractions A were obtained which all contained anthraquinonic substances either in reduced or in oxidized state. The first fraction (A1) obtained by extraction of the lead salt precipitate with alcohol was microcrystalline and showed a positive Borntraeger reaction only after several hours. It was extremely sensitive to air, darkened and liquefied within a few seconds when exposed. The dark oil gave immediately a positive Borntraeger reaction. This behavior leads us to the conclusion that the micro-crystalline fraction contained reduced anthraquinones which, on contact with the air, were very rapidly oxidized to anthraquinones.

It was impossible to isolate the anthraquinones formed by air oxidation; but oxidizing the microcrystalline precipitate of reduced anthraquinones with ferric chloride we obtained Rhein (1,8-dihydroxyanthraquinone-3-carboxylic acid, m. p. 310°) which was identified by direct comparison with an authentic sample. Further identification involved preparation of its acetate (m. p. 217–218°), methyl ester (m. p. 172–174°), methyl ester acetate[8] (m. p. 194–195°). The purification of Rhein was made difficult by the presence of very small quantities of another anthraquinone that, up to now, could not be identified. From the lead salt precipitate after decomposition with hydrogen sulfide two more fractions (A2 and A3) could be obtained by extraction with benzene and alcohol, respectively. A2 yielded Rhein directly without previous oxidation. From A3, which

(1) Extract from a Thesis presented by L. Lacerda Nazárió to the Faculdade de Filosofia, Ciências e Letras da Universidade de São Paulo, Brasil, for the degree "Doutor em Ciências."

(2) R. Wasicky, *Anias. Fac. Farm. Odont. Univ. S. Paulo*, **2**, 57 (1942).

(3) H. Borntraeger, *Z. anal. Chem.*, **19**, 165 (1880).

(4) Porte and Helbing, *Z. Österr. Apoth. Ver.*, 589 (1884), cited after C. Wehmer "Pflanzenstoffe," G. Fischer, Jena, 1929, p. 505; Gresshof, *Ber.*, **23**, 3540 (1890).

(5) Private communication of R. Wasicky.

(6) P. B. Murti and T. R. Seshadri, *Proc. Indian Acad. Sci.*, **10A**, 96 (1939).

(7) A. Tschirch, *Schweiz. Wochenschr. Pharm.*, **23**, 174 (1898); *Ber. deuts. Pharm. Ges.*, **8**, 174 (1898).

(8) This compound was found to be especially satisfactory for identification purposes (private communication of the Scientific Laboratory of Sandoz A. G., Basel).