

in recrystallizing the picrate of 2,8-dimethyl-1,2,3,4-tetrahydroquinoline and filtrates from this recrystallization were yellow after standing for thirty days.)

When the deep red filtrate from the recrystallization of the picrate of 2,6-dimethyl-1,2,3,4-tetrahydroquinoline was allowed to stand for thirty days, orange crystals separated. They were recrystallized from alcohol, m. p. 185-186°; mixed m. p. with the picrate of 2,6-dimethylquinoline (m. p. 186-187°) 186-187°. No crystals separated from the orange filtrate from the recrystallization of the picrate of 2,8-dimethyl-1,2,3,4-tetrahydroquinoline.

1,2,6-Trimethyl-1,2,3,4-tetrahydroquinoline hydriodide was prepared by mixing 17.6 g. of methyl iodide and 20.6 g. of the crude tetrahydroquinoline. So vigorous a reaction immediately took place that the mixture boiled violently. The resulting sticky red product was crystallized from alcohol giving 24 g. of a mixture of yellow and white crystals. Two crystallizations from water dissolved the yellow crystals to leave the white crystals, m. p. 187-188.5°. A mixed melting point of these with the hydriodide of 1,2,6-trimethyl-1,2,3,4-tetrahydroquinoline prepared below (m. p. 187.5-188.5°) was 187-188°.

1,2,6-Trimethyl-1,2,3,4-tetrahydroquinoline was prepared by refluxing 22 g. of 1,2,6-trimethylquinoline hy-

driodide with excess tin and hydrochloric acid for seven hours. The product obtained as in preceding preparations weighed 8.3 g. (64%); b. p. 145° (20 mm.); n_D^{20} 1.5611; d_4^{20} 0.9906; M_D calcd. 57.29; M_D found 57.31.

The hydriodide prepared by mixing equal volumes of the base and hydriodic acid of sp. gr. 1.50 crystallized from water in white crystals, m. p. 187.5-188.5°.

Anal. Calcd. for $C_{12}H_{13}NI$: I, 41.8. Found: I, 41.8.

The picrate after four crystallizations from alcohol appeared as yellow crystals, m. p. 141-142°.

Anal. Calcd. for $C_{12}H_{13}O_7N_3$: N, 13.88. Found: N, 13.76.

Summary

2,6-Dimethyl-1,2,3,4-tetrahydroquinoline has been found to be very much more unstable and reactive than 2,8-dimethyl-1,2,3,4-tetrahydroquinoline. Its N-methyl derivative, however, is stable. Eleven new compounds in the 2,6- and 2,8-dimethylquinoline series have been prepared and characterized.

URBANA, ILLINOIS

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Osage Orange Pigments. II. Isolation of a New Pigment, Pomiferin¹

BY M. L. WOLFROM, F. L. BENTON, A. S. GREGORY, W. W. HESS, J. E. MAHAN AND P. W. MORGAN

The isolation of a new yellow pigment from the fruit of the osage orange (*Maclura pomifera* Raf.) has been reported previously² from this Laboratory. The name osajin was assigned to the substance and the data reported were shown to be in harmony with a provisional formula of $C_{26}H_{22}O_3(OH)_2$.

Osajin melts at 189°³. In the preparation of further material from the natural source it was found that material of this same melting point could be prepared which, however, depressed the melting point of highly purified samples of osajin that melted at the same point. Further investigation showed that two yellow pigments were present, the original osajin of melting point 189° and a second of melting point 200.5°. The name pomiferin is suggested for this second product. The data so far obtained for pomiferin and its derivatives indicate a probable formula of $C_{25}H_{21}O_3(OH)_3$, thus differing from osajin by the presence of one additional oxygen atom combined as an

hydroxyl group. We now find that the substance described by us² as osajic acid di-*p*-toluenesulfonate was actually pomiferin di-*p*-toluenesulfonate (m. p. 148°) of high purity. The correct *p*-toluenesulfonate derivative of osajin has been prepared and has been found to be a mono-*p*-toluenesulfonate (m. p. 152°) crystallizing in beautiful, lustrous plates of a golden yellow color. We have also established the melting point of osajin diacetate as 164°. Other than this, the properties of osajin (m. p. 189°), osajin monoacetate (m. p. 159°), and of osajin diacetate (m. p. 164°) have been found correct as previously reported.

We also postulated the probable presence of a lactone group in osajin. We now believe that no lactone group is present but that the consumption of one equivalent of alkali by osajin is due to the presence of an acidic phenolic group, such as is present in gossypol and in other naturally occurring phenolic structures.

Pomiferin has been characterized by a number of derivatives. It forms a diacetate and a triacetate, a dimethyl ether and a trimethyl ether, and also a dimethyl ether monoacetate.

Both osajin and pomiferin are isomerized to

(1) Presented before the Division of Organic Chemistry at the 97th Meeting of the American Chemical Society, Baltimore, Maryland.

(2) E. D. Walter, M. L. Wolfrom and W. W. Hess, *THIS JOURNAL*, **60**, 574 (1938).

(3) All melting points herein reported are uncorrected.

high melting, colorless products by the action of sulfuric acid in glacial acetic acid. These substances have been designated iso-osajin and iso-pomiferin, respectively. Iso-osajin gives no phenolic ferric chloride test, while iso-pomiferin does. Pomiferin di-*p*-toluenesulfonate, which initially gives a phenolic ferric chloride test and possesses a slight tinge of yellow color, is isomerized under these same conditions to a colorless isomer which no longer gives a phenolic test with ferric chloride and which is identical with the product obtained by the reaction of the isomerized pomiferin with *p*-toluenesulfonyl chloride. It would thus appear that a phenolic or enolic group is concerned in this isomerization.

The relationship of the various derivatives of osajin and pomiferin described in this paper are given in Fig. 1.

Further work on these two pigments of the fruit of the osage orange is in progress in this Laboratory.

Experimental

Isolation and Properties of a Second Pigment (Pomiferin) from the Osage Orange.—The ground and dried meal of the whole, ripe fruit of the osage orange tree (*Maclura pomifera* Raf.) was extracted with petroleum ether and ether as described previously.² The ether-soluble material was recrystallized repeatedly from xylene until material of melting point 200.5° was obtained. This material was unchanged in melting point on further recrystallization from xylene, benzene or ethanol. The crystals were of a yellow color and were of a deeper tinge than osajin. The substance was slightly less soluble than osajin in the same organic solvents. The properties of the substance were similar to those of osajin and it exhibited the same general behavior with chemical reagents as described previously for osajin.² It also showed the same evidence of possessing phenolic rather than carboxylic acidity, as described below for osajin.

Both osajin and pomiferin give only yellow colorations with pyroboracetate in acetic anhydride and with alcoholic nickel acetate.

*Anal.*⁴ Calcd. for $C_{26}H_{24}O_6$: C, 71.42; H, 5.75; mol. wt., 420.4; Found: C, 71.47, 71.36; H, 5.90, 5.90; mol. wt. (Rast), 388, 361.

The mother liquor material from the pomiferin isolation was repeatedly recrystallized from ethanol and yielded the previously described osajin² of melting point 189°.

Evidence of Phenolic Nature of Osajin Acidity.—Osajin (1 g.), dissolved in 50 cc. of ether, was placed in a 200-cc. separatory funnel and the air displaced with methane

(natural gas). The top of the funnel was connected to the outlet of a 60-cc. separatory funnel containing 20 cc. of a 10% sodium hydroxide solution. As the sodium hydroxide was allowed to drop, with shaking, into the ether solution of osajin, the yellow color in the ether layer gradually disappeared and the aqueous hydroxide layer became the characteristic greenish-yellow color of alkaline osajin. After the ether layer had become completely colorless, the upper funnel was removed and a stream of carbon dioxide was passed into the funnel containing the two layers. The color in the aqueous layer disappeared completely and the yellow color of osajin returned to the ether layer. Osajin was recovered on evaporation of the ether layer.

Pomiferin exhibited the same behavior when subjected to the identical treatment described above for osajin.

Osajin Mono-*p*-toluenesulfonate.—Osajin (1 g.) was dissolved in 10 cc. of dry pyridine and treated with a solution of *p*-toluenesulfonyl chloride (4 g.) in 15 cc. of dry pyridine. The solution stood at room temperature for eighteen hours and was then poured into 400 cc. of ice and water. The resultant gum hardened readily on standing at ice-box temperature for a few hours. It was removed

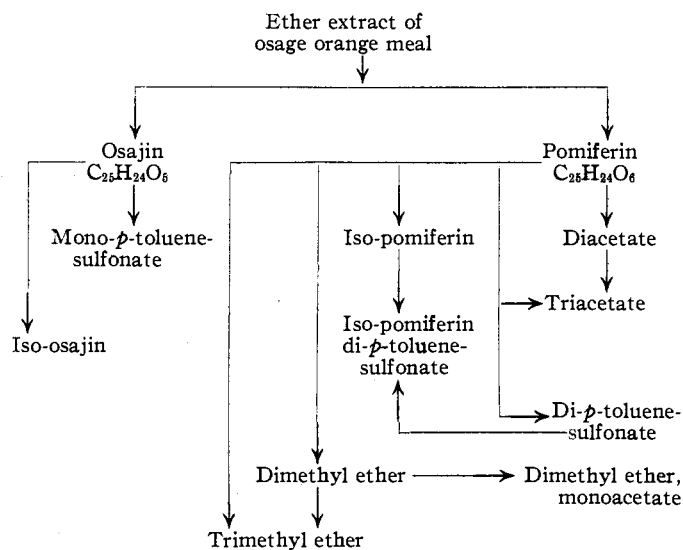


Fig. 1.

by filtration, washed with water and recrystallized from absolute ethanol. Pure material was obtained on several recrystallizations from absolute ethanol; m. p. 152°, unchanged on further recrystallizations from either absolute ethanol or xylene-methanol. The substance crystallized as lustrous plates of a golden yellow color and gave a green coloration, in alcoholic solution, with ferric chloride.

Anal. Calcd. for $C_{26}H_{23}O_4(OSO_2C_6H_4CH_3)$: C, 68.79; H, 5.41; S, 5.73; mol. wt., 558.5. Found: C, 68.84, 68.83; H, 5.42, 5.40; S, 5.79; mol. wt. (Rast), 584, 531.

Iso-osajin.—Osajin (5 g.) was dissolved in 75 cc. of boiling glacial acetic acid and 3 cc. of concentrated sulfuric acid added dropwise to the hot solution. The resulting dark orange solution was allowed to stand overnight at room temperature, after which an equal volume of water

(4) All combustion analyses herein reported were made by Dr. Ing. A. Schoeller, Berlin.

was added. The thick, curdy mass which separated crystallized on standing at ice-box temperature for an hour. The light yellow crystals were separated by filtration and washed several times with water; yield 4.1 g., m. p. 200–201°. Concentration of the mother liquors under reduced pressure yielded additional material; 0.56 g., m. p. 139°; total yield, 4.66 g. Recrystallization from absolute ethanol yielded pure colorless crystals, m. p. 285° (dec.).⁵

Iso-osajin is more difficultly soluble in organic solvents than osajin. An alcoholic solution of the substance shows no coloration with ferric chloride; it reduces Fehling's solution and, in pyridine solution, reduces Tollens' reagent. Iso-osajin was recovered unchanged when treated with an alcoholic solution of hydroxylamine acetate (refluxed for ten minutes and allowed to stand overnight). Iso-osajin is insoluble in cold 20% potassium hydroxide, but dissolves on boiling to give a greenish-yellow solution from which the substance can be recovered unchanged by acidification. The addition of a few drops of concentrated sulfuric acid to a solution of iso-osajin in glacial acetic acid gave only a deep yellow coloration. A negative test for sulfur was obtained by sodium fusion methods and by the Parr bomb. Iso-osajin also can be prepared by using an equivalent amount of concentrated hydrochloric acid in place of the sulfuric acid.

Anal. Calcd. for $C_{26}H_{24}O_5$: C, 74.25; H, 5.98; mol. wt., 404.4. Found: C, 74.24, 74.33; H, 6.00, 5.88; mol. wt. (Rast), 396, 361, 364.

Pomiferin Di-*p*-toluenesulfonate.—Pomiferin (2 g.) was treated as described for the preparation of osajin mono-*p*-toluenesulfonate²; yield 2.9 g., m. p. 148°. This substance was identical (mixed m. p. unchanged) with the product of m. p. 148° previously described² as osajic acid di-*p*-toluenesulfonate.

*Anal.*² Calcd. for $C_{26}H_{22}O_4(OSO_2C_6H_4CH_3)_2$: C, 64.3; H, 4.98; S, 8.80; mol. wt., 728.8. Found: C, 64.4; H, 5.08; S, 8.75; mol. wt. (Rast), 680.

Iso-pomiferin.—Pomiferin was isomerized with sulfuric acid in glacial acetic acid as described for the preparation of iso-osajin and was purified by recrystallization from absolute ethanol; m. p. 265°. The substance formed colorless needles and gave a green coloration with ferric chloride, changing to violet on the addition of ammonium hydroxide. It reduces Fehling's solution and, in pyridine solution, reduces Tollens' reagent. In cold 20% potassium hydroxide it turns yellow but does not dissolve; upon boiling, brownish yellow flocs form and the solution becomes dark yellow. Concentrated sulfuric acid added to a glacial acetic acid solution of the substance produces only a deep yellow color.

Anal. Calcd. for $C_{26}H_{24}O_6$: C, 71.42; H, 5.75; mol. wt., 420.4. Found: C, 71.53, 71.53; H, 5.69, 5.83; mol. wt. (Rast), 423, 399.

Iso-pomiferin Di-*p*-toluenesulfonate.—Pomiferin di-*p*-toluenesulfonate (1 g.) was isomerized with sulfuric acid in glacial acetic acid as described for the preparation of iso-osajin and the product was purified by recrystallization from alcohol followed by recrystallization from xylene by the addition of methanol; yield 0.72 g., m. p. 194°.

(5) Taken on a modified Berl-Kullman block as described by F. W. Bergstrom, *Ind. Eng. Chem., Anal. Ed.*, **9**, 340 (1937).

An alcoholic solution of the product shows no coloration with ferric chloride and does not reduce Fehling's solution or Tollens' reagent. A few drops of concentrated sulfuric acid added to a glacial acetic acid solution of the substance impart a very light yellow color. The compound was recovered unchanged after refluxing with acetic anhydride and sodium acetate for two hours.

Iso-pomiferin di-*p*-toluenesulfonate was also prepared by treating iso-pomiferin in pyridine solution with a pyridine solution of *p*-toluenesulfonyl chloride. The identity of the products was established by melting point and mixed melting point.

Anal. Calcd. for $C_{26}H_{22}O_4(OSO_2C_6H_4CH_3)_2$: C, 64.3; H, 4.98; S, 8.80; mol. wt., 728.6. Found: C, 64.1, 64.0; H, 5.11, 5.11; S, 8.55; mol. wt. (Rast), 645, 633.

Pomiferin Diacetate.—Pomiferin (1 g.) was dissolved in 12 cc. of pyridine and 24 cc. of acetic anhydride and placed in the ice-box overnight. This solution was poured into water and the crude material which separated was crystallized from methanol by the addition of water. The crystals were in the form of bright yellow plates; yield 1 g., m. p. 134.5°. Recrystallization from benzene and petroleum ether gave long, radiating needles. The melting point was not raised by recrystallization from benzene or ethanol.

The reactions and solubilities of this compound are similar to those of the monoacetate of osajin previously described.² The substance gave a green coloration, in alcoholic solution, with ferric chloride. Yellow crystals, m. p. 198.5°, were recovered after treatment of the compound with sodium hydroxide at ice-box temperature for three hours followed by acidification. The saponification was carried out in an atmosphere of nitrogen. A mixed melting point with pomiferin and this product showed no depression.

Anal. Calcd. for $C_{26}H_{22}O_4(OCOCH_3)_2$: C, 69.03; H, 5.59; saponification equivalent, 252.3 (3.96 cc. of 0.1 N NaOH per 100 mg.); mol. wt., 504.5. Found: C, 69.02, 69.22; H, 5.61, 5.57; saponification equivalent (Freudenberg method⁶), 255, 258 (3.93 cc. and 3.88 cc. of 0.1 N NaOH per 100 mg.); mol. wt. (Rast), 430.

Iso-pomiferin was recovered from the Freudenberg acetyl analyses and identified by melting point and mixed melting point. Pomiferin subjected to the conditions of this analysis yielded iso-pomiferin and no volatile esters.

Pomiferin Triacetate.—Pomiferin (1 g.) was refluxed for three hours with 75 cc. of acetic anhydride and 6 g. of fused sodium acetate. The mixture was poured into water and kept overnight at ice-box temperature. The crystalline material was removed by filtration; yield 1.2 g., m. p. 154°, unchanged on recrystallization from alcohol or from benzene by the addition of petroleum ether. The substance crystallized as colorless needles and gave no coloration, in alcoholic solution, with ferric chloride. Its solubilities and other reactions were much like those of osajin diacetate.

This compound also was prepared by treating pomiferin diacetate in the same manner.

Anal. Calcd. for $C_{26}H_{20}O_8(OCOCH_3)_3$: C, 68.1; H, 5.53; saponification equivalent, 182.2 (5.49 cc. of 0.1 N NaOH per 100 mg.); mol. wt., 546.6. Found: C, 68.07,

(6) K. Freudenberg and M. Harder, *Ann.*, **433**, 230 (1923).

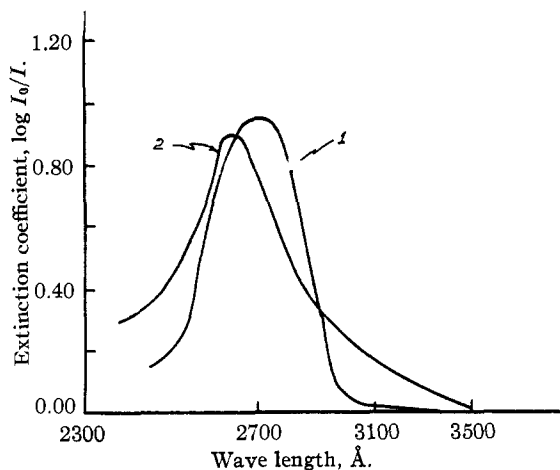


Fig. 2.—Curve 1—Absorption spectra of osajin: maximum at 2730 Å.; solvent, absolute ethyl alcohol; concentration 0.00166 g./100 cc. Cell 0.4 cm. Curve 2—Absorption spectra of iso-osajin: maximum at 2660 Å.; solvent, absolute ethyl alcohol; concentration 0.00142 g./100 cc. Cell, 0.4 cm.

68.08; H, 5.59, 5.57; saponification equivalent (Freudenberg method,⁶ 190, 191 (5.26 cc. and 5.25 cc. of 0.1 *N* NaOH per 100 mg.); mol. wt. (Rast), 540, 570.

Iso-pomiferin was recovered from the Freudenberg acetyl analyses and identified by melting point and mixed melting point.

Osajin acetylated as above yielded the previously described² diacetate, m. p. 164°.

Pomiferin Dimethyl Ether.—Pomiferin (1 g.) was methylated in 45 cc. of methyl alcohol under an atmosphere of nitrogen, by first adding a solution of 2.5 g. of potassium hydroxide in 40 cc. of methanol, cooling the mixture to 0° and, finally, adding 18 cc. of dimethyl sulfate with vigorous shaking of the mixture. The mixture was allowed to stand for an hour and was then poured into ice and water, filtered, and thrice recrystallized from ethanol; yield 1.1 g., m. p. 132°.

The substance crystallizes in fluffy masses of light yellow needles and is soluble in the common organic solvents. An alcoholic solution of the substance gives a green coloration with ferric chloride, but no violet coloration on the further addition of ammonia. In glacial acetic acid solution, it gives an orange coloration on the addition of sulfuric acid. It does not reduce Fehling's solution or Tollens' reagent (in pyridine solution). In carbon tetrachloride solution it shows bromine and iodine absorption. It is insoluble in hot aqueous solutions of sodium carbonate and potassium hydroxide. The substance shows no loss in weight on heating at 125–130° for several hours over phosphorus pentoxide under reduced pressure.

Anal. Calcd. for $C_{20}H_{22}O_4(OCH_3)_2$: C, 72.3; H, 6.29; OCH_3 , 13.8; mol. wt., 448.4. Found: C, 72.2; H, 6.33; OCH_3 , 13.6; mol. wt. (Rast), 428, 387.

The compound gives no positive saponification value even when heated at 90° with alcoholic sodium hydroxide for several hours.

Pomiferin Dimethyl Ether Monoacetate.—Pomiferin dimethyl ether (0.4 g.) was treated with 2 g. of anhydrous

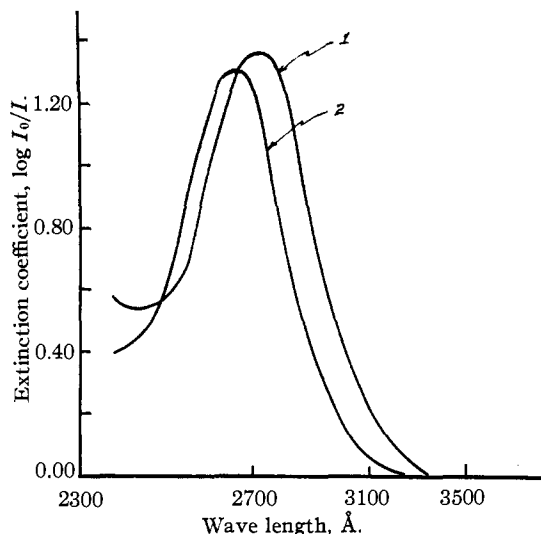


Fig. 3.—Curve 1—Absorption spectra of pomiferin: maximum at 2750 Å.; solvent, absolute ethyl alcohol; concentration 0.00303 g./100 cc.; cell 0.4 cm. Curve 2—Absorption spectra of iso-pomiferin: maximum at 2680 Å.; solvent, absolute ethyl alcohol; concentration, 0.00289 g./100 cc.; cell, 0.4 cm.

sodium acetate and 20 cc. of acetic anhydride and the mixture refluxed for three hours. The mixture was poured into ice and water, allowed to stand overnight and the product removed by filtration; yield, 0.43 g. Pure material was obtained on recrystallization from ethanol; m. p. 128–129°.

The substance crystallized as a fluffy mass of white needles. When dissolved in alcohol, it gives no coloration on the addition of ferric chloride. In glacial acetic acid solution, it gives a light yellow coloration on treatment with sulfuric acid. It gives no positive tests with Fehling's solution or Tollens' reagent (in pyridine). It is insoluble in aqueous sodium hydroxide.

Anal. Calcd. for $C_{25}H_{21}O_8(OCH_3)_2(OCOCH_3)$: C, 71.00; H, 6.16; sap. equiv., 490.4 (2.04 cc. of 0.1 *N* NaOH per 100 mg.); mol. wt., 490.4. Found: C, 71.16, 70.96; H, 6.14, 6.19; sap. equiv. (Freudenberg method,⁶ 472, 483 (2.12 cc. and 2.07 cc. of 0.1 *N* NaOH per 100 mg.); mol. wt. (Rast), 458, 454.

Pomiferin Trimethyl Ether.—Pomiferin (2 g.) was dissolved in 130 cc. of acetone under reflux and to this solution, maintained at the boiling point, was added 24 cc. of dimethyl sulfate followed by six alternate portions of 6 cc. each of dimethyl sulfate and 8 cc. of 50% aqueous potassium hydroxide, all added as rapidly as possible. The solution was refluxed for two hours, during which time a white precipitate of potassium methyl sulfate separated, leaving a clear yellow solution. The mixture was cooled to room temperature, poured into one liter of ice and water and the excess methyl sulfate just neutralized with 10% potassium hydroxide. The white crystalline product which separated was removed by filtration and washed with water; yield 2.3 g., m. p. 120–125°. Pure material was obtained on recrystallization from ethanol; m. p. 139.5°, unchanged on further recrystallization. The substance was unchanged in weight on heating

at 110° for several hours over phosphorus pentoxide under reduced pressure.

An alcoholic solution of the product shows no coloration with ferric chloride and it does not reduce Fehling's solution. A chloroform solution of the substance absorbs bromine and it shows a yellow coloration in acetic acid on the addition of a few drops of sulfuric acid. The product was recovered unchanged after refluxing with acetic anhydride and sodium acetate for two hours. It was not affected by cold 20% potassium hydroxide but dissolved slowly on boiling to produce a light yellow solution.

Anal. Calcd. for $C_{25}H_{21}O_3(OCH_3)_3$: C, 72.7; H, 6.57; OCH_3 , 20.1; mol. wt., 462.4. Found: C, 72.9; H, 6.69; OCH_3 , 20.06; mol. wt. (Rast), 420, 437.

The same product was obtained by application of the same methylation procedure to pomiferin dimethyl ether. The identity of the products was established by melting point and mixed melting point.

Absorption Spectra.⁷—The absorption spectra of osajin, iso-osajin, pomiferin and iso-pomiferin were observed in absolute ethanol. The data are shown in Fig. 2 and Fig. 3. A single band spectrum was obtained for each compound.

Acknowledgment is gratefully made to the National Youth Administration for assistance rendered in this investigation.

Summary

1. A second yellow pigment has been isolated

(7) The absorption spectra measurements were made by Miss J. Appleton of this Laboratory, according to the method described in Brode, "Chemical Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1939, p. 273.

from the fruit of the osage orange tree (*Machura pomifera* Raf.). The name pomiferin is assigned to this substance and it is shown that the experimental data so far obtained harmonize with a provisional formula of $C_{25}H_{21}O_6$.

2. The basicity of osajin is shown to be more in harmony with an acidic phenolic structure than with a lactone structure.

3. The substance previously described as osajic acid di-*p*-toluenesulfonate² is shown to be pomiferin di-*p*-toluenesulfonate.

4. Osajin forms a mono-*p*-toluenesulfonate (m. p. 152°).

5. The melting point of osajin diacetate is established as 164°.

6. A diacetate, triacetate, dimethyl ether, trimethyl ether, and dimethyl ether monoacetate of pomiferin have been prepared.

7. Both osajin and pomiferin are isomerized by sulfuric acid-glacial acetic acid mixtures to high-melting, colorless, crystalline substances.

8. Pomiferin di-*p*-toluenesulfonate is isomerized under the same conditions and the product is identical with the reaction product formed between iso-pomiferin and *p*-toluenesulfonyl chloride.

9. The absorption spectra of osajin, iso-osajin, pomiferin and iso-pomiferin have been observed.

COLUMBUS, OHIO

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Dibenzofuran. XIII. Orientation and Substituted Amines¹

BY HENRY GILMAN, PAUL T. PARKER, JAMES C. BAILIE AND GEORGE E. BROWN

Introduction

Incidental to the determination of structure of substituted amines, it is now shown that the generalizations on orientation postulated previously² are adequate for the predominant products which result from polysubstitution of the dibenzofuran nucleus.

Nitration.—Nitration of a monosubstituted dibenzofuran having a strongly meta-orienting group proceeded heteronuclearly and the entering nitro group went largely to the 7-position, and the 8-position was involved only to a subordinate extent. The nitro acid obtained from nitration of 2-

acetyldibenzofuran was identical with that obtained from nitration of methyl 2-dibenzofurancarboxylate. The same acid resulted by oxidation of the acetyl-3-nitrodibenzofuran prepared by a Friedel-Crafts reaction with 3-nitrodibenzofuran.

The chief nitro ester obtained by nitration of methyl 3-dibenzofurancarboxylate was methyl 2-nitro-7-dibenzofurancarboxylate. The position of the nitro group was shown by hydrolysis to a nitro acid which on decarboxylation yielded 2-nitrodibenzofuran.

Nitration of 1-acetamino-4-methoxydibenzofuran took place homonuclearly, as might have been predicted, and the nitro group was directed ortho to the acetamino group. The structure of

(1) Paper XII, THIS JOURNAL, 61, 1371 (1939).

(2) Gilman, Brown, Bywater and Kirkpatrick, *ibid.*, 56, 2473 (1934); Gilman, Van Ess and Hayes, *ibid.*, 61, 643 (1939). See, also, Cullinane, *J. Chem. Soc.*, 2365 (1932).