1.3810; sap. equiv., 103 (calcd. 102); m. p. of the *p*-toluidide of the acid, 122–124°. When this experiment was repeated using absolute alcohol instead of water a decided evolution of heat was noticed and resulting ethyl orthopropionate boiled at 157–158° (752 mm.); $n^{25}\mathrm{D}$ 1.4000. The yields of ester in each of these cases were practically quantitative.

Summary

Ketene diethylacetal and methylketene diethylacetal have been prepared in excellent yields by the action of sodium on the corresponding α-bromo-orthoesters. This method appears to be of general applicability for the higher homologs of ketene acetal. The properties of methylketene diethylacetal are described for the first time.

MADISON, WISCONSIN RECEIVED APRIL 4, 1940

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

Osage Orange Pigments. IV. Degree of Unsaturation and Flavone Nature[1]

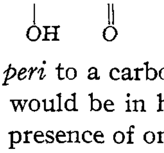
BY M. L. WOLFROM, P. W. MORGAN AND F. L. BENTON

The publication of the determination of the degree of unsaturation of osajin and pomiferin, the two pigments of the fruit of the osage orange (*Maclura pomifera* Raf.), has been withheld until enough data were obtained to warrant a satisfactory explanation. We believe that this can now be done.

Osajin could be hydrogenated catalytically at atmospheric pressure with platinum in a stepwise fashion. One double bond hydrogenated with great ease to yield dihydro-osajin. The second double bond also hydrogenated readily, although more slowly than the first, to yield tetrahydro-osajin. At this point further hydrogenation proceeded very slowly but a hexahydro-osajin was obtained. All of these hydrogenated derivatives showed the presence of the one easily acetylatable and of the one difficultly acetylatable hydroxyl group of the original osajin, a monoacetate and a diacetate of each hydrocompound being obtained. Hydrogenation thus produced no new hydroxyl groups and it was determined also that no carboxyl groups were formed. Similar results were obtained with pomiferin, except that the hexahydropomiferin has not yet been isolated. A diacetate and a triacetate of both dihydropomiferin and tetrahydropomiferin were obtained, this behavior on acetylation being identical with that of pomiferin. No carboxyl groups were produced.

Table I shows the results of the application of the perbenzoic acid titration procedure to the determination of the degree of unsaturation of the two pigments and of their reduction products. Osajin and pomiferin were found to undergo extensive general oxidation with perbenzoic acid, but when protected by acetylation, this effect was minimized, although not eliminated. If we consider the relatively low values given by the tetrahydro derivatives as a subtractable blank, it is seen that the data indicate the presence of two active double bonds in both osajin and pomiferin. The data indicate also that the third unsaturation, as represented by hexahydro-osajin, is of a different type and is not a simple aliphatic double bond. A negative Diels–Alder test with maleic anhydride denoted that the two active double bonds are not conjugated.

The nature of the unsaturation of this third double bond of osajin was therefore a presented problem. It was found that hexahydro-osajin gave a negative result with the boric acid test described by Wilson.[2] On the other hand, Table II shows that osajin and pomiferin and their dihydro and tetrahydro derivatives gave a positive color reaction. According to Wilson, flavanones give no color reaction with boric acid, and the grouping shown below is among those that do give a positive color reaction, the α,β-unsaturated carbonyl and a suitable *peri* auxochromic group, as the hydroxyl, being essential.



A phenolic group *peri* to a carbonyl group in osajin and pomiferin would be in harmony with the known fact of the presence of one hydroxyl group that is difficultly methylatable. This type of phenolic group is also frequently quite acidic and

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(1) Previous publications in this series: (a) THIS JOURNAL, **60**, 574 (1938); (b) **61**, 2832 (1939); (c) **62**, 651 (1940).

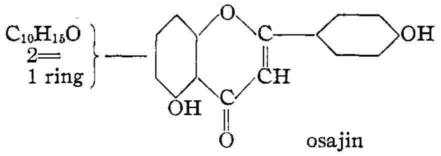
(2) C. W. Wilson, *ibid.*, **61**, 2303 (1939).

would explain the titratable phenolic acidity (one equivalent) of osajin, although pomiferin consumes less than one equivalent of alkali on direct titration.

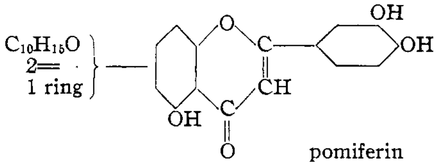
Asahina and co-workers[3] have shown that flavanones are reducible by both sodium amalgam and magnesium and hydrochloric acid; flavones are reducible by sodium amalgam and not by magnesium–hydrochloric acid; flavanols unsubstituted in position three are reducible by magnesium–hydrochloric acid and not by sodium amalgam; flavonols substituted in position three by a methoxyl group or a sugar residue are reducible by both methods. All reduction products exist in or separate from hydrochloric acid solutions as red substances of a flavylium salt nature. Application of these tests to our substances showed that hexahydro-osajin was reducible with magnesium–hydrochloric acid and that osajin, tetrahydro-osajin, pomiferin, and tetrahydropomiferin were not reducible by this reagent. Sodium amalgam, however, reduced all of the compounds, as shown in Table III.

The above results are indicative that osajin and pomiferin possess flavone structures and that the third double bond reduced in osajin was that between carbons two and three in a γ-pyrone nucleus, producing a flavanone structure. The absorption spectra obtained[1a,1b] for osajin and pomiferin (one band with maxima at 2730 and 2750 Å., respectively) are in harmony with the presence of a carbonyl group. These conclusions are based on color reactions and must be considered as tentative until supported by definite degradative results. Such confirmation has been obtained in part by the isolation of anisic acid from osajin dimethyl ether and of veratric acid from pomiferin trimethyl ether by oxidation with alkaline hydrogen peroxide.[1c]

If a flavone structure be subtracted from the molecular formulas of osajin ($C_{25}H_{24}O_5$) and of pomiferin ($C_{25}H_{24}O_6$), there is left a $C_{10}H_{15}O$ group. This is a monoterpene residue and would be attached very probably as shown in the formulas below. In this residue there must be two active double bonds which, when saturated, would produce the separate entity $C_{10}H_{20}O$. The one oxygen atom is unreactive, indicative of an oxide linkage. This entity has a deficiency of two atoms of hydrogen, indicative of one ring. On this basis, the formulas of osajin and pomiferin may be developed as shown below, although they are distinctly tentative and must be corroborated by further degradative work.



osajin



pomiferin

Further work on the structure of these two substances is in progress in this Laboratory.

Experimental[4]

Dihydro-osajin.—Platinum dioxide catalyst was freshly prepared and then dried for twenty-four to forty-eight hours in a vacuum desiccator over potassium hydroxide. The catalyst (0.10 g.) was suspended in 10 cc. of absolute ethanol and saturated with hydrogen. A solution of osajin (1 g. in 40 cc. of absolute ethanol) was then introduced and hydrogenation (atmospheric pressure) was stopped when 1 mol of hydrogen (55 cc., S. T. P.) had been absorbed. The time required varied with the activity of the particular catalyst preparation but with the amount of osajin cited it was generally about five minutes.

The catalyst was removed by filtration, the filtrate was concentrated to 30 cc. and the product was crystallized by the addition of water to the hot solution until turbidity appeared; yield 0.9 g. of m. p. 194.5° and 0.05 g. of m. p. 173–175°. The melting point was raised to 197°[5] by repeated crystallization from methanol and was unchanged on further crystallization from methanol, 95% ethanol or propylene chloride; yield 0.74 g.

The substance crystallized from methanol in fine, cottony needles of a light, dull yellow color. It was soluble in ethanol, less so in methanol and was moderately soluble in benzene. In alcoholic solution, it gave a dark green ferric chloride color, turning to a bright wine-red on the addition of ammonium hydroxide. In glacial acetic acid solution, it gave an immediate orange color on the addition of a few drops of concentrated sulfuric acid. In pyridine solution, it reduced Tollens reagent.

Anal. Calcd. for $C_{25}H_{26}O_5$: C, 73.87; H, 6.45; mol. wt., 406.5. Found: C, 73.88; H, 6.32; mol. wt. (Rast), 400, 380.

Dihydro-osajin Monoacetate.—Dihydro-osajin (0.44 g.) was acetylated overnight at icebox temperature with pyridine (10 cc.) and acetic anhydride (15 cc.) and the product obtained crystalline by pouring the acetylation mixture into ice and water; yield 0.48 g., m. p. 155°. Recrystal-

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[3] Y. Asahina and M. Inubuse, *Ber.*, **61**, 1646 (1928); **64**, 1256 (1931); Y. Asahina, G. Nakagome and M. Inubuse, *ibid.*, **62**, 3016 (1929).

[4] All experimental work by Mr. P. W. Morgan, except where otherwise noted.

[5] All melting points recorded are uncorrected and were taken on a 360° thermometer with immersion to the −20° mark.

lization from 95% ethanol raised the melting point to 156.5° (yield 0.36 g.), unchanged on further crystallization from 95% ethanol or benzene.

The substance crystallized from ethanol as long, silky needles of a very light yellow tinge. It was very soluble in chloroform and was only moderately soluble in 95% ethanol, acetone and benzene. It gave an apple-green ferric chloride–alcohol test and gave a yellow color with sulfuric acid–acetic acid.

Anal. Calcd. for $C_{25}H_{25}O_6(CH_3CO)$: C, 72.30; H, 6.29; CH_3CO, 2.23 cc. 0.1 *N* NaOH per 100 mg.; mol. wt., 448.5. Found: C, 72.25; H, 6.19; CH_3CO,[6] 2.16 cc.; mol. wt. (Rast), 400.

Dihydro-osajin Diacetate.—Dihydro-osajin (0.6 g.) was acetylated by refluxing for three hours with fused sodium acetate (5 g.) and acetic anhydride (30 cc.) and the product isolated by pouring the acetylation mixture into ice and water; yield 0.7 g., m. p. 150°. Recrystallization from 95% ethanol and from methanol raised the melting point to 154° (yield 0.45 g.) unchanged on further recrystallization from 95% ethanol or benzene–petroleum ether; mixed m. p. with dihydro-osajin monoacetate (m. p. 156.5°), 142°.

The substance crystallized in radiating clusters of colorless, elongated plates, was very soluble in acetone and benzene and was only moderately soluble in cold alcohol. It gave no coloration with ferric chloride–alcohol and gave a yellow color slowly with sulfuric acid–acetic acid.

Anal. Calcd. for $C_{25}H_{24}O_5(CH_3CO)_2$: C, 71.03; H, 6.17; CH_3CO, 4.08 cc. 0.1 *N* NaOH per 100 mg.; mol. wt., 490.5. Found: C, 71.03; H, 6.01; CH_3CO, 4.16 cc.; mol. wt. (Rast), 460.

Dihydro-osajin diacetate also was obtained by similar treatment of dihydro-osajin monoacetate and was identified by melting point and mixed melting point.

Tetrahydro-osajin.—Osajin (1.0 g.) was reduced with hydrogen (platinum catalyst) at atmospheric pressure as described for the preparation of dihydro-osajin except that the hydrogenation was stopped when 2 mols of hydrogen (111 cc., S. T. P.) had been absorbed. With most catalyst preparations, this point was attained readily (about fifteen minutes) and further reduction proceeded very slowly. The substance was isolated as described for dihydro-osajin; yield 0.78 g., m. p. 198–200°. Pure material was obtained on recrystallization from benzene; yield 0.60 g., m. p. 206°, mixed m. p. with dihydro-osajin (m. p. 197°) 188–190°. This melting point was unchanged on further crystallization from propylene chloride. The substance crystallized from benzene or propylene chloride in the form of long, silky needles of a pale yellow color. If allowed to stand overnight in a benzene–petroleum ether mixture these needles slowly changed to short prisms of a lemon-yellow color, having the same melting point. This change in habit occurred more readily if the material was impure.

The solubilities and properties of the substance were similar to those of dihydro-osajin. In alcoholic solution, it gave an apple-green ferric chloride color, turning wine-red on the addition of ammonium hydroxide.

Anal. Calcd. for $C_{25}H_{28}O_5$: C, 73.50; H, 6.91; mol. wt., 408.5. Found: C, 73.70; H, 6.84; mol. wt. (Rast), 390, 360.

Tetrahydro-osajin also was obtained on further hydrogenation of dihydro-osajin and was identified by melting point and mixed melting point.

Tetrahydro-osajin Monoacetate.—Tetrahydro-osajin (0.25 g.) was acetylated with pyridine and acetic anhydride as described for the preparation of dihydro-osajin monoacetate. Pure material was obtained on recrystallization from benzene–petroleum ether; yield 0.19 g., m. p. 179.5°, unchanged on further crystallization from benzene or ethanol.

The substance crystallized as silky needles of a very light yellow tinge. It was soluble in benzene and propylene chloride and was moderately soluble in ethanol. It gave an apple-green color with ferric chloride–alcohol.

Anal. Calcd. for $C_{25}H_{27}O_5(CH_3CO)$: C, 71.98; H, 6.71; CH_3CO, 2.22 cc. 0.1 *N* NaOH per 100 mg.; mol. wt., 450.5. Found: C, 71.96; H, 6.68; CH_3CO, 2.21 cc.; mol. wt. (Rast), 395, 370.

Tetrahydro-osajin was recovered from the acetyl[6] analysis by pouring the alcoholic solution into a large excess of water, removing the separated solid by filtration, and recrystallizing from benzene–petroleum ether (identification by m. p. and mixed m. p.).

Tetrahydro-osajin Diacetate.—Tetrahydro-osajin (0.30 g.) was acetylated with acetic anhydride and sodium acetate as described for the preparation of dihydro-osajin diacetate. The substance crystallized from 95% ethanol as colorless needles; yield 0.21 g. of m. p. 186°, unchanged on further crystallization from methanol. It gave no color with ferric chloride–alcohol.

Anal. Calcd. for $C_{25}H_{26}O_5(CH_3CO)_2$: C, 70.71; H, 6.55; CH_3CO, 4.06 cc. 0.1 *N* NaOH per 100 mg.; mol. wt., 492.6. Found: C, 70.89; H, 6.47; CH_3CO, 4.00 cc.; mol. wt. (Rast), 450.

This substance also was obtained by similar treatment of tetrahydro-osajin monoacetate (identification by m. p. and mixed m. p.). Tetrahydro-osajin was recovered from the acetyl analysis (identification by m. p. and mixed m. p.).

Hexahydro-osajin.[7]—This substance was prepared by the reduction of osajin (1.5 g.) with an active catalyst as described for the preparation of dihydro-osajin but allowing the hydrogenation to proceed until 3 mols of hydrogen (250 cc., S. T. P.) were absorbed. This required about three hours. It was isolated in the same manner and was purified by crystallization from methanol–water and benzene–petroleum ether; yield 1.0 g. of m. p. 162°.

The substance crystallized in the form of pale yellow needles. When impure, it crystallized with difficulty. It was water-insoluble but was soluble in the common organic solvents except low-boiling petroleum ether. It gave a dark dull-green color with ferric chloride–alcohol, turning to a dull wine-red color with ammonium hydroxide. In acetic acid solution, it gave an immediate yellow color on the addition of a few drops of concentrated sulfuric acid. In pyridine solution it reduced Tollens reagent. The compound was recovered unchanged on refluxing with either a pyridine or an alcoholic solution of hydroxylamine for two hours.

Anal. Calcd. for $C_{25}H_{30}O_5$: C, 73.15; H, 7.37; mol. wt., 410.5. Found: C, 73.16; H, 7.30; mol. wt. (Rast), 380.

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[6] All acetyl analyses recorded were made according to the procedure of K. Freudenberg and M. Harder, *Ann.*, **433**, 230 (1923).

[7] Preliminary experimental work by Mr. W. W. Hess.

The substance absorbed one equivalent of alkali when titrated directly in acetone solution according to the procedure described for osajin.[1a] This behavior is identical with that observed for osajin and accordingly no acid groups were formed in the reduction.

Hexahydro-osajin was obtained on further hydrogenation of tetrahydro-osajin (identification by m. p. and mixed m. p.).

Hexahydro-osajin Monoacetate.—This substance was prepared from hexahydro-osajin (0.50 g.) as described for the preparation of dihydro-osajin monoacetate and was purified by crystallization from 95% ethanol; yield 0.45 g., m. p. 138°, unchanged on recrystallization from benzene–petroleum ether.

The substance crystallized in radiating clusters of needles possessing a slight yellow tinge and was soluble in the common solvents except water and petroleum ether. It gave an apple-green color with ferric chloride–alcohol.

Anal. Calcd. for $C_{25}H_{29}O_5(CH_3CO)$: C, 71.66; H, 7.13; CH_3CO, 2.21 cc. 0.1 *N* NaOH per 100 mg.; mol. wt., 452.5. Found: C, 71.57; H, 7.03; CH_3CO, 2.28 cc.; mol. wt. (Rast), 390.

Hexahydro-osajin was recovered from the acetyl analysis (identification by m. p. and mixed m. p.).

Hexahydro-osajin Diacetate.—This substance was prepared from hexahydro-osajin (0.20 g.) as described for the synthesis of dihydro-osajin diacetate and was purified by crystallization from 95% ethanol; yield 0.17 g., m. p. 190°, unchanged on crystallization from benzene–petroleum ether, mixed m. p. with tetrahydro-osajin diacetate (m. p. 186°) 170–174°.

The substance crystallized in radiating clusters of fine, colorless needles. Its solubilities were similar to those of hexahydro-osajin monoacetate. It gave no color with ferric chloride–alcohol.

Anal. Calcd. for $C_{25}H_{28}O_5(CH_3CO)_2$: C, 70.44; H, 6.93; CH_3CO, 4.04 cc. 0.1 *N* NaOH per 100 mg.; mol. wt., 494.6. Found: C, 70.39; H, 6.82; CH_3CO, 4.01 cc.; mol. wt. (Rast), 450.

This substance also was obtained by similar treatment of hexahydro-osajin monoacetate (identification by m. p. and mixed m. p.). Hexahydro-osajin was recovered from the acetyl analysis (identification by m. p. and mixed m. p.).

Dihydropomiferin.[8]—This substance was prepared from pomiferin (2 g.) as described for the preparation of dihydro-osajin. It was purified by crystallization from propylene chloride, trichloroethylene and from ethanol–water; yield 1.3 g. of m. p. 212°.

The substance crystallized from ethanol–water as fine, lustrous, light yellow needles. It was very soluble in acetone, methanol and ethanol; moderately so in benzene and propylene chloride; and was insoluble in water. It gave an apple-green color with ferric chloride–alcohol, turning deep violet with ammonia. The compound gave an orange color with acetic acid–sulfuric acid.

Anal. Calcd. for $C_{25}H_{26}O_6$: C, 71.07; H, 6.20; mol. wt., 422.5. Found: C, 70.75; H, 6.10; mol. wt. (Rast), 390.

The substance consumed less than one equivalent of alkali when titrated directly in acetone solution according to the procedure described for osajin.[1a] This behavior is identical with that observed for pomiferin.

Dihydropomiferin Diacetate.—Dihydropomiferin (0.50 g.) was acetylated as described for the preparation of dihydro-osajin monoacetate and the product was purified from 95% ethanol; yield 0.50 g. of m. p. 166°, unchanged on crystallization from benzene–petroleum ether.

The compound formed long, silky needles of a slight yellow tint. It was readily soluble in acetone, benzene and chloroform; moderately so in 95% ethanol and carbon tetrachloride; practically insoluble in water and petroleum ether. The substance gave an apple-green color with ferric chloride–alcohol. It gave a deep yellow color with acetic acid–sulfuric acid.

Anal. Calcd. for $C_{25}H_{24}O_6(CH_3CO)_2$: C, 68.77; H, 5.97; CH_3CO, 3.95 cc. 0.1 *N* NaOH per 100 mg.; mol. wt., 506.5. Found: C, 68.80; H, 5.90; CH_3CO, 3.91 cc.; mol. wt. (Rast), 450.

Dihydropomiferin Triacetate.—Dihydropomiferin (0.60 g.) was acetylated as described for the preparation of dihydro-osajin diacetate and the product was purified from 95% ethanol and from methanol; yield 0.59 g. of m. p. 165.5°, unchanged on crystallization from benzene–petroleum ether, mixed m. p. with dihydropomiferin diacetate (m. p. 166°) 142–149°.

The substance crystallized from methanol as glistening plates and from benzene–petroleum ether as clusters of radiating needles. It was very soluble in benzene; moderately so in acetone, ethanol and methanol; practically insoluble in water and petroleum ether. It gave no color with ferric chloride–alcohol.

Anal. Calcd. for $C_{25}H_{23}O_6(CH_3CO)_3$: C, 67.84; H, 5.88; CH_3CO, 5.47 cc. 0.1 *N* NaOH per 100 mg.; mol. wt., 548.6. Found: C, 68.06; H, 5.85; CH_3CO, 5.41 cc.; mol. wt. (Rast), 520.

This substance also was produced by similar treatment of dihydropomiferin diacetate (identification by m. p. and mixed m. p.).

Tetrahydropomiferin.—This substance was prepared from pomiferin (1 g.) as described for the preparation of tetrahydro-osajin and the product was purified by crystallization from trichloroethylene–petroleum ether; yield 0.91 g. of m. p. 201.5°, unchanged on crystallization from 95% ethanol or benzene–petroleum ether.

The substance crystallized from trichloroethylene–petroleum ether as yellow plates. Its solubilities and properties were similar to those of dihydropomiferin. The substance was recovered unchanged on refluxing with a pyridine solution of hydroxylamine hydrochloride for four hours.

Anal. Calcd. for $C_{25}H_{28}O_6$: C, 70.71; H, 6.65; mol. wt., 424.5. Found: C, 70.71; H, 6.57; mol. wt. (Rast), 380.

The substance consumed less than one equivalent of alkali when titrated directly in acetone solution according to the procedure described for osajin.[1a] This behavior is identical with that observed for pomiferin. Tetrahydropomiferin also was obtained by further hydrogenation of dihydropomiferin (identification by m. p. and mixed m. p.).

Tetrahydropomiferin Diacetate.—Tetrahydropomiferin (0.35 g.) was acetylated as described for the preparation of

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(8) Preliminary experimental work by Mr. F. L. Benton.

dihydro-osajin monoacetate and the product was purified from methanol; yield 0.35 g. of m. p. 154.5°, unchanged on crystallization from 95% ethanol or benzene–petroleum ether.

The compound crystallized from methanol as very long, radiating needles of a slight yellow tinge. Its solubilities and properties were similar to those of dihydropomiferin diacetate.

Anal. Calcd. for $C_{25}H_{26}O_6(CH_3CO)_2$: C, 68.49; H, 6.34; CH_3CO, 3.93 cc. 0.1 *N* NaOH per 100 mg.; mol. wt., 508.6. Found: C, 68.65; H, 6.41; CH_3CO, 3.96 cc.; mol. wt. (Rast), 500, 480.

Tetrahydropomiferin was recovered from the acetyl analysis (identification by m. p. and mixed m. p.).

Tetrahydropomiferin Triacetate.—Tetrahydropomiferin (0.50 g.) was acetylated as described for the preparation of dihydro-osajin diacetate and the product was purified from 95% ethanol; yield 0.62 g. of m. p. 181.5°, unchanged on crystallization from propylene chloride–petroleum ether or benzene–petroleum ether.

The compound crystallized from 95% ethanol as fine, colorless needles. Its solubilities and properties were similar to those of dihydropomiferin triacetate.

Anal. Calcd. for $C_{25}H_{25}O_6(CH_3CO)_3$: C, 67.62; H, 6.22; CH_3CO, 5.45 cc. 0.1 *N* NaOH per 100 mg.; mol. wt., 550.6. Found: C, 67.56; H, 6.15; CH_3CO, 5.38 cc.; mol. wt., 540, 490.

This substance was produced by similar treatment of tetrahydropomiferin diacetate and also was obtained by reduction of pomiferin triacetate[1b] (identifications by m. p. and mixed m. p.). Tetrahydropomiferin was recovered from the acetyl analysis (identification by m. p. and mixed m. p.).

Maleic Anhydride Treatment of Osajin and Pomiferin.—Osajin (0.30 g.) was recovered unchanged (0.20 g., identification by m. p. and mixed m. p.) on refluxing for two hours in xylene (20 cc.) containing 0.7 g. of maleic anhydride. Similar results were obtained with pomiferin.

Flavone and Flavanone Color Tests.—The substance to be tested[9] (10 mg.) was dissolved in 3 cc. of 95% ethanol, a small drop of mercury and 5 drops of concentrated hydrochloric acid were then introduced and the mixture heated to 40° and maintained at that temperature. Powdered magnesium was then added and from time to time more powdered magnesium and a few drops more of hydrochloric acid were added in order to maintain a constant evolution of hydrogen. A quercitin control gave a cherry-red coloration in ten minutes. No colorations were developed in five hours time by osajin, tetrahydro-osajin, pomiferin and tetrahydropomiferin. Hexahydro-osajin, however, developed on orange color in twenty minutes. This color deepened to a reddish-orange in one hour and when observed at five hours, the color was a dark cherry-red.

The sodium amalgam reductions were performed according to the general directions of Asahina and co-workers.[3] The substance (10 mg.) to be tested was dissolved in 3 cc. of 95% ethanol and the air displaced with nitrogen. Sodium amalgam (3%) was added and the tube stoppered. Standing at room temperature for ten hours or heating at 40° for two hours gave the same results. At the end of this treatment, the solution was decanted quickly from the excess amalgam and acidified with an excess of concentrated hydrochloric acid. The colored precipitates obtained were formed on dilution with water. Sodium chloride sometimes separated but redissolved on dilution. The results obtained are tabulated in Table III and indicate that osajin, pomiferin and their tetrahydro compounds possess the flavone structure and that hexahydro-osajin has the flavanone structure.

TABLE I

DEGREE OF UNSATURATION OF OSAJIN AND POMIFERIN AS DETERMINED BY PERBENZOIC ACID TITRATION[a]

Substance	No. double bonds 2 hr.	24 hr.
Osajin diacetate	1.48	2.13
Dihydro-osajin diacetate	1.16	1.52
Tetrahydro-osajin diacetate	0.21	0.33
Hexahydro-osajin diacetate	.14	.60
Pomiferin triacetate	1.56	2.20
Dihydropomiferin triacetate	1.14	1.33
Tetrahydropomiferin triacetate	0.23	0.21

[a] Experimental work by Mr. F. L. Benton.

TABLE II

BORIC ACID COLOR REACTION (ACCORDING TO WILSON[2]) OF OSAJIN, POMIFERIN AND THEIR HYDRO COMPOUNDS[a]

Substance	Nature of test	Time for initiation of yellow color, min.
Quercitin	+	Immediate
Osajin	+	2
Dihydro-osajin	+	3
Tetrahydro-osajin	+	3
Hexahydro-osajin	−	
Pomiferin	+	2
Dihydropomiferin	+	3
Tetrahydropomiferin	+	3

[a] Experimental work by Mr. J. E. Mahan.

TABLE III

SODIUM AMALGAM REDUCTION OF OSAJIN, POMIFERIN AND THEIR HYDRO COMPOUNDS

Substance	Color of final HCl soln.	Color of ppt.
Osajin	Bright red	Dark red
Tetrahydro-osajin	Reddish-orange	Rust
Hexahydro-osajin	Reddish-orange	Brick-red
Pomiferin	Dark red	Purple
Tetrahydropomiferin	Cherry-red	Purple

We are indebted to Mr. John Walker (W. P. A. Project 18062) for assistance rendered in the analytical determinations and to Messrs. E. J. Penka and J. H. Tracht (N. Y. A. Project O. S. U. 181) for assistance in preparing the plant material.

Summary

1. Osajin has been hydrogenated stepwise to produce a dihydro, tetrahydro and hexahydro derivative, each of which has been characterized as a monoacetate and diacetate.

2. Pomiferin has been hydrogenated stepwise to produce a dihydro and a tetrahydro derivative,

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[9] *Cf.* R. Willstätter, *Ber.*, **47**, 2874 (1914).

each of which has been characterized as a diacetate and triacetate.

3. Perbenzoic acid titrations and non-reactivity with maleic anhydride indicate the presence of two non-conjugated, active double bonds in both osajin and pomiferin.

4. By a combination of the Wilson boric acid color reaction and the Asahina reduction tests, it is shown that a flavanone structure for hexahydro-osajin and a flavone structure for osajin and pomiferin are probable.

COLUMBUS, OHIO RECEIVED APRIL 8, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY]

Optically Active α,γ-Diphenyl-α-carbomethoxy-γ-naphthylallene

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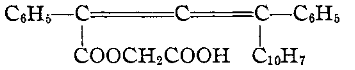
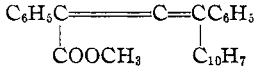
The glycolic acid ester of α,γ-diphenyl-γ-naphthylallene carboxylic acid (I) was recently



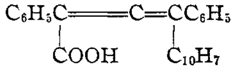
$$\underset{\mathrm{COOCH_2COOH}}{\mathrm{C_6H_5{-}C}}{=}\mathrm{C}{=}\underset{\mathrm{C_{10}H_7}}{\mathrm{C}}\mathrm{{-}C_6H_5} \qquad \text{(I)}$$

resolved in this Laboratory,[2] and we now describe the preparation and behavior of the optically active forms of the corresponding allenic methyl ester (II).



$$\underset{\mathrm{COOCH_3}}{\mathrm{C_6H_5C}}{=}\mathrm{C}{=}\underset{\mathrm{C_{10}H_7}}{\mathrm{C}}\mathrm{C_6H_5} \qquad \text{(II)}$$

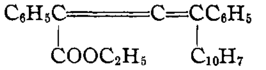
The solid inactive glycolic acid ester (I), with diazomethane, yielded its methyl derivative, but the active forms of (I), on similar treatment, or when subjected to hydrolysis in the attempt to prepare active forms of the simple allenic acid (III), gave only oily products.



$$\underset{\mathrm{COOH}}{\mathrm{C_6H_5C}}{=}\mathrm{C}{=}\underset{\mathrm{C_{10}H_7}}{\mathrm{C}}\mathrm{C_6H_5} \qquad \text{(III)}$$

The optically active methyl esters of the simple allenic acid (II), however, were synthesized by at least two of the following methods: (1) the active glycolic acid ester (I) was hydrolyzed by a large excess of alcoholic potassium hydroxide, the active form of the simple allenic acid (III) was converted into the silver salt, and the latter, with methyl iodide, to the active methyl ester (II); (2) the active allenic acid (III), prepared by the hydrolysis of active (I), was treated with diazomethane and yielded the active methyl ester (II); and (3) the active glycolic acid ester (I) was converted to the active methyl ester (II) by absolute methyl alcoholic potassium hydroxide.

A study of the formation of the active and inactive methyl esters (II) by the third method, as well as the rapid conversion of the inactive glycolic acid ester (I) to the inactive ethyl ester (IV)

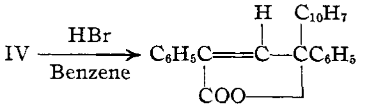


$$\underset{\mathrm{COOC_2H_5}}{\mathrm{C_6H_5C}}{=}\mathrm{C}{=}\underset{\mathrm{C_{10}H_7}}{\mathrm{C}}\mathrm{C_6H_5} \qquad \text{(IV)}$$

by ethyl alcoholic potassium hydroxide, indicated that the reaction proceeded by ester interchange. The pure methyl esters (II) were obtained in yields increasing with the amount of potassium hydroxide used up to two equivalents. With 1.1 mole of potassium hydroxide (0.08 *M*), during one hour, 62% yield of methyl ester was obtained, but 80% was obtained with two moles (0.25 *M*) during a quarter hour. The sign of rotation of each optically active ester was the same as that of the parent glycolic ester no matter which method of transformation was employed.

That these enantiomeric methyl esters retained the allenic system was demonstrated by dissolving together equimolecular quantities of each in ether, and isolating from the solution only an inactive ester which proved to be identical with the inactive methyl ester (II) prepared by a method leaving no doubt as to its structure.[2]

Solutions of the active forms of the glycolic acid ester (I) and of the methyl ester (II) in benzene and in ethyl acetate remained optically active during long periods when kept in the dark, but on exposure to sunlight for a few days the solution developed a yellow color, became inactive, and the inactive form of (I) or (II) (50–60% yield) was isolated together with a yellow resin.



$$\mathrm{IV} \xrightarrow[\text{Benzene}]{\text{HBr}} \underset{\mathrm{COO}}{\mathrm{C_6H_5C}}{=}\overset{\mathrm{H}}{\mathrm{C}}{-}\overset{\mathrm{C_{10}H_7}}{\mathrm{C}}\mathrm{C_6H_5} \qquad \text{(V)}$$

It has been shown that the inactive ethyl ester (IV) with hydrogen bromide in benzene solution yields the crotono lactone[3] (V).

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[1] The experimental work described in this manuscript was completed before the death of Professor Kohler. The present manuscript has been prepared since that time by the junior author.

[2] Kohler, Walker and Tishler, THIS JOURNAL, **57**, 1743 (1935).

[3] Unpublished work of Dr. Max Tishler.