

Osage Orange—A Potential Source of Edible Oil and Other Industrial Raw Materials

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THE FRUIT of the Osage orange tree has been found to be a valuable source of edible oil, sugars, resins, and pigments. When these are removed, there is left a palatable protein-rich food. Tremendous yields of the fruit are attainable.

Introductory Remarks

The Osage orange is a native tree of Arkansas, Oklahoma, and Texas, and now grows extensively throughout the southern, midwestern, and eastern states. It is a member of the mulberry family (*Moraceae*) and is known botanically as *Maclura pomifera* (also *Maclura aurantiaca*, *Toxylon pomiferum*, and *Ioxyton pomiferum*). Locally it is known by several other common names such as Bois d'Arc, Hedge apple, Horse apple, etc. It is planted principally for ornamental purposes and as a hedge fence. Osage Indians used the young trunks of this tree to make bows because of its unusual toughness and resiliency. They also used the sticky resins of the fruit as an adhesive for war paint, hence came the names Bois d'Arc and Osage orange. Mell (14) has written a brief history on Osage orange wood.

Present Uses

Osage orange wood is the source of a valuable dye (3, 4) which is sold on the market as Osage crystals. It is a yellow pigment resembling fustic (15), and may be used in place of fustic as a dye. According to Kressman (11), the dyeing principles of Osage crystals and fustic are the same and give practically identical results. However, in some respects they differ. One of the unusual characteristics of the Osage orange dyes is their mildew resistance. Cotton fabrics dyed with Osage orange were found still mildew resistant after six weeks weathering (6). A yield of approximately 15% Osage crystals is obtained from the wood of *Maclura pomifera*. For some reason it is claimed that dye obtained from northern-grown wood does not give good results. Orange-yellow, old gold, deep tan, olive, and chocolate shades obtained with chromium or iron mordants are equal to or better than those obtained with fustic (10). Osage orange crystals contain two coloring matters, marin and maclurin, which are apparently identical with those in fustic (17). The use of Osage orange wood pigments as a textile dye is discussed by Tisdale (21). Kisser (9) has reported a number of histochemical studies on several flavone-bearing heartwoods including that of Osage orange.

The wood of *Maclura pomifera* is the heaviest, toughest, and hardest of all the native hardwoods (12). It is extremely resistant to oxidative and bacterial decay and to insect erosion. It is, therefore, a popular material for fence posts, foundation piles for buildings, paving blocks, etc. To a limited extent, Osage orange wood is used for fellies (wheel rims), insulator pins, tree nails, and woodenware.

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Description of Fruit

Physical appearance and structure of the Osage orange fruit is described by McHargue (12) as follows: "At maturity the fruit has a greenish yellow color and averages 3.5 inches in diameter and 1 to 2.5 pounds in weight. The fruit consists of a dense, pear-shaped core at the center, from which radiates long, irregularly sized cells that terminate in an enlarged or club form, making an irregular surface. The cells are made up of two parts, the milk sacs and the seed sacs. The milk sacs form about two-thirds of the entire length of the cell and extend to the surface. The seed sacs lie beneath the milk sacs and are attached to the core at their base. The milk sacs contain a milky, mucilaginous fluid which in the ripe fruit is neutral to litmus, reacts only slightly with a tincture of guaiacum for oxidases, has an insipid taste and an odor similar to that emitted by the crushed twigs of cedar. The oranges contain a rather large amount of oval-shaped seeds, the kernels of which are approximately three-eighths inch long and one-eighth inch thick. They are easily separated from the hulls when dry."

Composition of Fruit

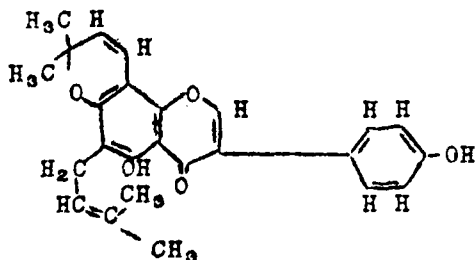
While considerable attention has been devoted to the utilization of Osage orange wood and the dye contained therein, there have been no industrial uses developed for the fruit and its constituents. In view of the fact that tremendous yields of Osage orange fruit are attainable and because the fruit may be harvested each year without destruction of the tree, as is the case when the wood or dye is obtained, investigations have been carried out to determine the composition of the fruit with a view to its use as a source of industrial raw materials.

So far as is known, the only reported work on the detailed chemical analysis of Osage orange fruit is that reported by McHargue (12) in 1915. The data presented in his reports have been verified for the most part by the results obtained by the authors. While present work lacks much of being completed, enough information has been gained to warrant a preliminary report on the promising potentialities of the Osage orange as a source of valuable industrial raw materials. They will be described later in this paper.

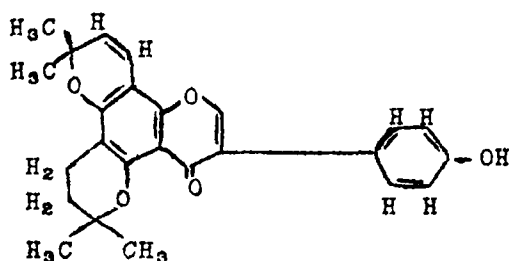
Table I shows the results of analyses obtained in this laboratory as compared with those reported by McHargue (12).

About 1912 considerable public interest was aroused over reports emanating from the University of Kansas to the effect that the Osage orange is a source of India rubber. This prompted an investigation (5) which showed no significant amount of rubber present. Analyses of this laboratory show the presence of 2.24% of material extracted by benzene and precipitated by acetone which may be rubber or a rubber-like substance.

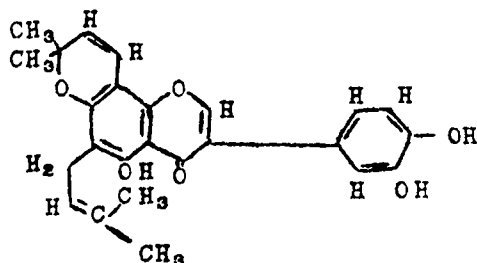
A considerable amount of work has been done on the pigments of the Osage orange fruit by Wolfrom and associates (23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33) at the Ohio State University. Through these studies the compounds, osajin, iso-osajin, pomiferin, and iso-pomiferin have been characterized and their chemical structures determined. They are isoflavones with the following structures:



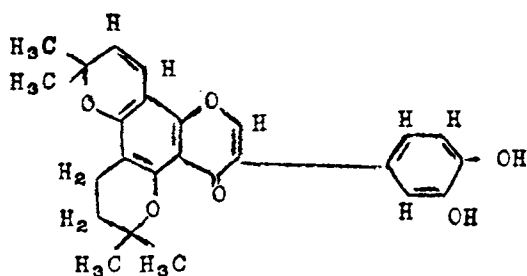
OSAJIN



ISO-OSAJIN



POMIFERIN



ISO-POMIFERIN

The two pigments, osajin and pomiferin, are present in approximately equal amounts and comprise about 10% of the dry weight of Osage orange fruit.

The dry fruit contains 18% of a fixed oil with an iodine value of 130-135. On this basis, it would be

TABLE I
Composition of Osage Orange Fruit and Its Constituents

Values in Per Cent	Texas Research Foundation Laboratories	Reported in the literature (12)
Water (in ripe fruit).....	80.0	80.0
Fruit pulp as a whole (d.y wt.):		
Oil, resins, and pigments (acetone ext.).....	40.03	29.30
Oil (Petroleum ether ext.).....	18.34	
Resins and pigments.....	21.69	
Nitrogen.....	2.56	2.81
Crude protein.....	16.00	17.56
Total sugars.....	15.3	
Reducing sugars.....	10.8	
Hydrolyzable sugars.....	4.5	
Other hydrolyzable carbohydrates (by difference).....	7.0	
Crude fiber.....	12.0	
Total ash.....		6.60
Ashed at 900°C.		
(K ₂ O volatilized).....	4.07	
Rubber (benzene after acetone).....	2.24	
Amyrins (mostly β).....	0.91	
Seeds (dry wt.):		
Oil.....	42.0	42.04
Nitrogen.....	6.2	
(On oil-free basis).....		10.7
Crude protein.....	38.9	
(On oil-free basis).....		67.0
Other constituents.....	19.1	

classified as a semidrying oil. Investigations are now underway to determine the actual fatty acid composition of this oil.

Little is known, at present, regarding the resins occurring in the Osage orange fruit. The resin extracted by acetone contains a liquid and a solid portion. The solid portion consists of the two pigments, osajin and pomiferin, which can be polymerized to a hard resinous mass by heating. The properties of the liquid resin will be the subject of a future study. It makes up 10-15% of the Osage orange fruit.

Regarding the enzymes present in fresh Osage orange fruit, a carbohydrase and a proteinase have been reported present (7, 8). The proteinase is suggested as being useful as a meat tenderizer in a manner similar to papain and bromelin (19).

Swift and Walter (20) have reported the presence of .23% lupeol in the dried fruits. It is of interest to note that lupeol is chemically closely related to the amyryns (present as 0.91%) which are the principal constituents of chicle, the chewing gum base.

From a commercial standpoint the Osage orange fruit provides a rich source of several valuable industrial raw materials. The oil (semidrying) should be acceptable to the edible oil trade and may hold considerable promise in the field of drying oils, either when blended with drying oils or by having its drying properties enhanced by various modification treatments known to the trade. The resins should prove useful in the paint and varnish and other protective-coating and adhesive industries. The Osage orange fruit contains 15% of water-soluble sugars which consist mainly of a mixture of glucose, arabinose, and an unidentified disaccharide. These sugars should be useful either collectively or individually in the food and fermentation industries. Osajin and pomiferin, the pigments comprising 10% of the dry weight of the fruit, could be produced on a large scale. These pigments are of potential value as vegetable dyes and as chemical raw materials in the manufacture of numerous compounds on a commercial basis. After removal of the oil, sugars, resins, and pigments about 45% of the original dry weight of the Osage orange fruit is left in the form of a palatable and nutritious feed containing 30 to 35% protein.

A bulk analysis of Osage orange is shown in the following table:

I. Seed:			40%
A. Hulls			50%
B. Kernels			50
1. Oil		42%	
2. Meal		58	
a. Protein	67%		
b. Non-Protein	33		
II. Fruit Bulk			60%

McHargue (12) has reported a rather detailed analysis of the mineral constituents of the Osage orange fruit. He found CaO, 0.16; MgO, 0.20; K₂O, 3.82; Na₂O, 0.13; P₂O₅, 0.67; and total (crude) ash, 6.60% of the dry fruit. The dried fruit contains more nitrogen and more than twice as much potassium as wheat bran (12).

From the standpoint of commercial production the Osage orange holds some remarkable possibilities. The young trees grow rapidly under a great variety of soil and climatic conditions. Actual harvesting measurements have shown that the yield of fruit per tree may vary from nothing to as much as 1,000 pounds or more. The female of the species starts bearing fruit at 4 to 6 years of age. Thereafter the yield increases to a maximum and gradually decreases.

There are no definite indications that any toxic substances are present in dried Osage orange fruit (16, 19). The fresh fruit is said to cause dairy animals to "dry-up," and this is possibly due to the low molecular weight resins present in the latex, causing some inflammatory action in the digestive tract. The fruit has been successfully used as a feed for horses, mules, and steers. It is doubtful if any harmful effects could arise from feeding the dried fruit, for during the drying process the resins become polymerized and quite inert from a physiological standpoint. The boiled latex has been injected subcutaneously into pigeons without any visible effects (8). If the fresh latex is injected in the same manner, the proteolytic enzymes present cause sufficient digestion, *in vivo*, to kill the experimental animal. To our knowledge no cases of poisoning have occurred as the result of feeding Osage orange fruit.

The wide geographical distribution of the Osage orange tree, its adaptability to many types of soils and environmental conditions, its resistance to drought and plant diseases, and the tremendous yields of

fruit obtainable makes this tree worthy of consideration as a producer of industrial raw materials, especially in view of the several valuable materials (oil, resins, sugars, pigments, and feed-stuff) occurring in the fruit. In addition, there are several unidentified minor constituents of the fruit which may ultimately enhance its commercial value.

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Component Fatty Acids of Some Cruciferae Oils^{1,2,3}

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Brassica seed oils, like rape, mustard, ravison, etc., form a very important group of edible and industrial oils. Considerable investigation on the fatty acid composition of oils of this species has been reported recently by many workers (1, 2, 3). In view of some recent work by Hilditch (1, 2) in which he used low-

temperature fractional crystallization methods prior to distillation of the methyl esters, the earlier work of Foreman and Brown (3a) that eicosenoic acid was present in rape seed oil, and the indication by Hopkins (3) that eicosenoic acid was present in the seed fat of a wild species of a cruciferae plant (*Brassica orientalis*), here's ear mustard, the results of earlier investigations (4, 10) have been considerably revised.

The development of the method for the quantitative determination of highly unsaturated acids by ultraviolet absorption after alkali isomerization (5)

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³ This investigation had been completed prior to the publication of Baliga and Hilditch's paper, "The Component Acids of Rapeseed Oil" (J. Soc. Chem. Ind., **67**, 258-262 (1948)).