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SHORT COMMUNICATION

OSAGE ORANGE PIGMENTS—XVII.[1]

1,3,6,7-TETRAHYDROXYXANTHONE FROM THE HEARTWOOD

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Abstract—1,3,6,7-Tetrahydroxyxanthone has been isolated from the heartwood of the osage orange (*Maclura pomifera* Raf.). The occurrence in this wood of morin and of 2,3',4,5'-tetrahydroxystilbene has been confirmed. Certain biogenetic relationships among the eight known pigments of this tree are discussed.

Two isoflavone pigments, osajin (II) pomiferin (IV), have been isolated from the fruit of the osage orange (*Maclura pomifera* Raf.) and their structures determined.[2] These structures were confirmed by the synthesis[3] of dihydroiso-osajin and dihydroisopomiferin. Three new xanthone pigments were later isolated[4] from the highly pigmented root bark of this tree and were designated alvaxanthone, macluraxanthone, and osajaxanthone. Structures (III, V, and I, respectively) were assigned to these pigments[1,5,6] and dihydro-osajaxanthone monomethyl ether was synthesized.[6] The heartwood of this tree is yellow and from this source Barnes and Gerber[7] isolated the yellow pigments morin (2',4',5,7-tetrahydroxyflavonol, VI) and 2,3',4,5'-tetrahydroxystilbene (VIII). We have also investigated this heartwood and, employing a considerably improved and simplified procedure, we have confirmed the presence therein of these two substances. The amount of the flavonol found was 0·05 per cent and that of the stilbene was 0·08 per cent of the heartwood. In addition a third light-yellow, crystalline pigment (0·09 per cent) was isolated.

The third pigment showed an extremely high melting point, a high stability toward alkali, and exhibited a positive reaction in the general color test for unsubstituted hydroxyxanthones (alcohol, magnesium, and hydrochloric acid). Especially significant was the finding that its u.v. spectrum was suggestive of a hydroxyxanthone. It formed a tetraacetate and a trimethyl ether and exhibited a strong coloration with alcoholic ferric chloride, all indicative of a chelated hydroxyl group *peri* to the carbonyl of a γ-pyrone ring. The hydroxyl pattern of the tetrahydroxyxanthone was established as 1,3,6,7 by identity with a synthetic sample. 1,3,6,7-Tetrahydroxyxanthone is the hydroxyxanthone whose 2-*C*-glucoside is mangiferin. Treatment of mangiferin with hydriodic acid in phenol was shown by Iseda[8] and later workers[9] to

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[1] Previous communication in this series: M. L. Wolfrom, F. Komitsky, Jr., and P. M. Mundell, *J. Org. Chem.* **30**, 1088 (1965).

[2] M. L. Wolfrom, W. D. Harris, G. F. Johnson, J. E. Mahan, S. M. Moffett and B. Wildi, *J. Am. Chem. Soc.* **68**, 406 (1946) and earlier publications cited therein.

[3] M. L. Wolfrom and B. Wildi, *J. Am. Chem. Soc.* **73**, 235 (1951).

[4] M. L. Wolfrom, E. E. Dickey, P. McWain, A. Thompson, J. H. Looker, O. M. Windrath and F. Komitsky, Jr., *J. Org. Chem.* **29**, 689 (1964).

[5] M. L. Wolfrom, F. Komitsky, Jr., G. Fraenkel, J. H. Looker, E. E. Dickey, P. McWain, A. Thompson, P. M. Mundell and O. M. Windrath, *J. Org. Chem.* **29**, 692 (1964).

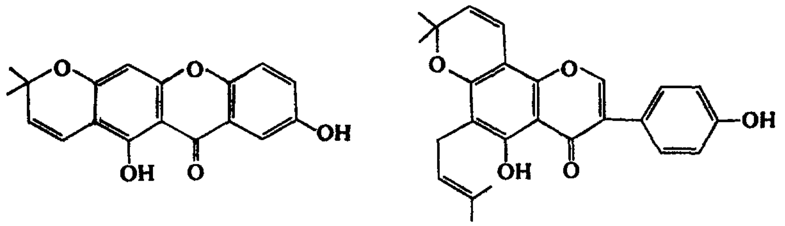
[6] M. L. Wolfrom, F. Komitsky, Jr., and J. H. Looker, *J. Org. Chem.* **30**, 144 (1965).

[7] R. A. Barnes and N. N. Gerber, *J. Am. Chem. Soc.* **77**, 3259 (1955).

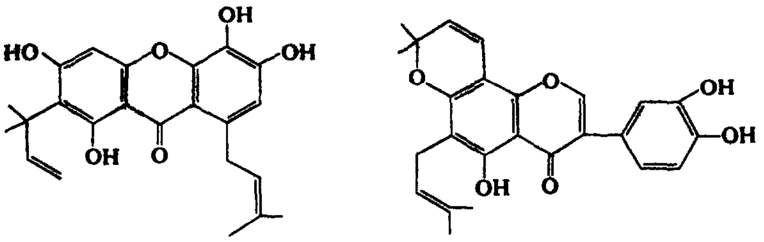
[8] S. Iseda, *Bull. Chem. Soc. Japan* **30**, 625 (1957); *Chem. Abstr.* **52**, 6329 (1958).

[9] J. P. Ramanathan and T. R. Seshadri, *Current Sci.* (*India*) **29**, 131 (1960).

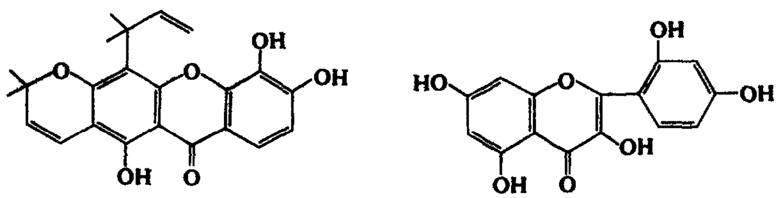
give 1,3,6,7-tetrahydroxyxanthone. Iseda[8] identified the xanthone by synthesis from 2,4,5-trihydroxybenzaldehyde and phloroglucinol according to the general method of Tanase.[10] The same xanthone was isolated,[11] together with mangiferin, from the leaves of *Athyrium*


(I) Osajaxanthone

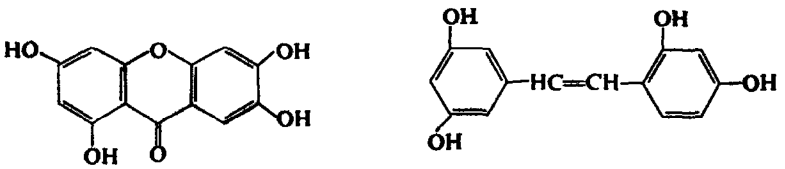
(II) Osajin


(III) Alvaxanthone

(IV) Pomiferin


(V) Macluraxanthone

(VI) Morin


(VII) 1,3,6,7-Tetrahydroxyxanthone

(VIII) 2,3′,4,5′-Tetrahydroxystilbene

FIG. 1 PIGMENTS OF THE OSAGE ORANGE (*Maclura pomifera* Raf.)

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[10] Y. TANASE, *J. Pharm. Soc. Japan* 61, 341 (1941).

[11] A. UENO, *Yakugaku Zasshi* 82, 1479 (1962); *Chem. Abstr.* 59, 737 (1963).

mesosorum, identity being established by synthesis[11] from 2,4,5-trihydroxybenzoic acid and phloroglucinol according to the general method of Grover, Shah and Shah.[12]

Figure 1 illustrates the structures of the compounds so far isolated from the pigmented parts of *Maclura pomifera* Raf. Some relationships may be noted among the members of this family of compounds. All those possessing the γ-pyrone ring carry a phloroglucinol nucleus in one ring and upon this there may be condensed one or more isoprene units in various ways. With the exception of morin (VI) and osajaxanthope (I), the other ring may be considered as being derived from a *p*-hydroxybenzoic acid or a 3,4-dihydroxybenzoic acid entity. In a previous publication[5] it has been suggested that a possible biosynthetic intermediate might be maclurin (IX) which has been isolated from a closely related species, *Maclura tinctoria*. If this be accepted, then cyclization of maclurin at the one position *ortho* to the carbonyl group could form the basic unit (X) of macluraxanthone and closure at the alternative *ortho* position could lead to 1,3,6,7-tetrahydroxyxanthone (VII) (Fig. 2).

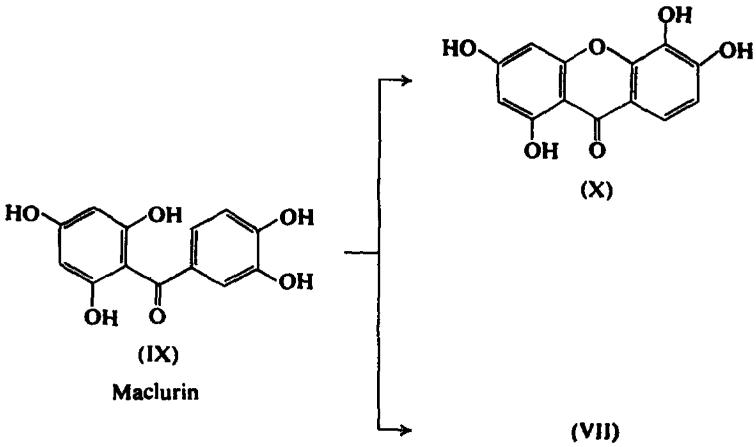

FIG. 2

EXPERIMENTAL

Extraction of the heartwood and Fractionation of the Extract

The wood of the osage orange tree (*Maclura pomifera* Raf.) was chipped mechanically (see *Acknowledgement*) and the 2·5-cm pieces from the yellow heartwood were separated by hand and reduced to a powder in a Wiley mill. The powder (1·2 kg) was extracted in a Soxhlet apparatus with petroleum ether (b.p. 40–60°) for 24 hr and then with methanol until the extract was colorless. The solvent was removed under reduced pressure from the deep orange methanolic extract to leave a dark-colored, resinous residue. Alternatively, acetone could replace methanol in this extraction. The residue was taken up in ether and the ethereal extract was washed successively with aqueous solutions of saturated sodium bicarbonate, 5 % sodium carbonate, and 1 % sodium hydroxide. These alkaline extracts will be denoted as Solution A (sodium bicarbonate), B (sodium carbonate), and C (sodium hydroxide).

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[12] P. K. GROVER, G. D. SHAH and R. C. SHAH, *J. Chem. Soc.* 3982 (1955).

Isolation of Morin (5,7,2′,4′-Tetrahydroxyflavonol, VI)

Solution A above was acidified carefully with dilute hydrochloric acid, with cooling. A pale yellow solid separated which was removed and crystallized from warm acetic acid by the addition of water; yield 600 mg of light yellow crystals, dec. 290° (reported[13] 289–290°). The substance gave a green color with alcoholic ferric chloride and a deep orange color with magnesium and hydrochloric acid. Methylation of this substance with methyl iodide and potassium carbonate in acetone yielded a colorless methyl ether which was purified by chromatography on a silica gel plate developed with ethyl acetate: benzene (1:1) with sideband indication with iodine vapor, m.p. 157° (reported[14] 156–157°).

Isolation of 1,3,6,7-*Tetrahydroxyxanthone* (*VII*)

Acidification of Solution B yielded an orange solid which was crystallized from methanol, yield 1·1 g, m.p. > 320°. The substance, which could be sublimed at 300°/0·1 mm, gave a deep orange color with ethanol magnesium, and hydrochloric acid[15] and was stable toward heating in a steam bath with 10% sodium hydroxide; $\lambda_{max}^{(KBr)}$ 3448, 3311, 1661, 1613, 1582, 1475, 1389, 1174, 1078, and 830 cm^{-1}.

The pale yellow trimethyl ether of the xanthone was prepared with diazomethane and was recrystallized from acetone-methanol, m.p. 218° (recorded[14] 218°), undepressed on admixture with an authentic synthetic[11] sample of 1-hydroxy-3,6,7-trimethoxyxanthone of like melting point. (Found: C, 64·10; H, 4·60; OCH_3, 29·7. Calc. for $C_{13}H_5O_3(OCH_3)_3$: C, 63·57; H, 4·60; OCH_3, 30·7%). The u.v. spectrum was in agreement with that reported for this compound by Yates and Stout.[16] The i.r. spectra of both samples of the trimethyl ether were superposable. The X-ray powder diffraction patterns[17] were likewise identical: 12·7 m, 9·35 vs (2), 7·18 s, 6·64 vs (3), 6·03 s, 5·74 m, 5·31 m, 4·27 m, 3·95 s, 3·80 s, 3·69 s, and 3·40 vs (1).

The colorless tetraacetate of the xanthone was prepared with acetic anhydride and pyridine and was recrystallized from hot methanol, m.p. 198° (recorded[11] 198°), undepressed on admixture with an authentic synthetic[11] sample. The i.r. spectra and X-ray powder diffraction patterns of the two samples were identical; X-ray powder diffraction data:[17] 12·9 s, 10·2 vs (2), 9·05 vs (1), 8·04 s, 6·51 m, 6·15 vs (3), 5·87 s, 5·35 m, 5·00 s, 4·51 m, 4·12 s, 3·79 s, 3·60 s, 3·33 m, 3·09 s, and 2·86 m.

Isolation of 2,3′,4,5′-*Tetrahydroxystilbene* (*VIII*)

Acidification of Solution C gave a semicrystalline solid which was crystallized readily from hot water, yield 1·0 g, m.p. 208° (recorded[7] 203–208°). The tetraacetate was prepared with acetic anhydride and pyridine and was recrystallized from hot methanol, m.p. 142–143° (recorded[18] 141–142°), $\lambda_{max}^{(KBr)}$ 1750, 1608, 1585, 1493, 1440, 1370, 1212, 1147, 1124, 1093, and 1021 cm^{-1}.

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[13] Q. L. Morris, T. B. Gage and S. H. Wender, *J. Am. Chem. Soc.* **73**, 3340 (1951).

[14] T. J. Haley and M. Bassin, *J. Am. Pharm. Assoc.* **40**, 111 (1951); *Chem. Abstr.* **45**, 4001 (1951).

[15] J. Shinoda, *J. Pharm. Soc. Japan* **48**, 214 (1928); *Chem. Abstr.* **22**, 2947 (1928).

[16] P. Yates and G. H. Stout, *J. Am. Chem. Soc.* **80**, 1691 (1958).

[17] Interplanar spacing, Å., Cu Kα radiation. Relative intensity, estimated visually: s, strong; m, medium; w, weak; v, very; three strongest lines numbered (1, strongest).

[18] M. Takaoka, *J. Faculty Sci. Hoddaido Imp. Univ. Ser III*, 3, 1 (1940); *J. Chem. Soc. Japan* **60**, 1261 (1939); *Chem. Abstr.* **36**, 5163 (1942).