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MACLURAXANTHONE AND TWO ACCOMPANYING PIGMENTS FROM THE ROOT BARK OF THE OSAGE ORANGE

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THE isolation of three crystalline, yellow, optically inactive pigments from the root bark of the osage orange (Maclura pomifera Raf.) has been reported briefly.[1] These are isolable from ether extractives of the root bark in a total yield of 0.6%. The one found in major amount and now designated macluraxanthone is dimorphous, m.p. 181-182° and 204-205° [Found: mol. wt., 372 (Rast); C, 69.97; H, 5.42; Calc. for $C_{23}H_{22}O_6$: mol. wt., 394; C, 70.04; H, 5.62%]. Methylation with dimethyl sulfate and sodium hydroxide at room temperature gave a light yellow dimethyl ether, m.p. 162-163° [Found: C, 71.00; H, 6.27; OCH_3, 14.54. Calc. for $C_{23}H_{20}O_4(OCH_3)_2$: C, 71.07; H, 6.20; OCH_3, 14.69%]. The NMR spectrum[2] of macluraxanthone

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[1] M. L. Wolfrom, J. H. Looker, E. E. Dickey, P. McWain, and A. Thompson, Abstr. Papers Am. Chem. Soc. 119, 16M (1951).

[2] All NMR spectra were taken in deuterochloroform solution with a tetramethylsilane internal reference standard (τ = 10.00). A Varian 60 megacycle A-60 nuclear magnetic resonance spectrophotometer was used.

dimethyl ether included a singlet at τ = -3.78, corresponding to a phenolic proton chelated with a carbonyl group. Methylation with dimethyl sulfate and potassium carbonate in refluxing acetone yielded a colorless trimethyl ether, m.p. 98° [Found: C, 71.48; H, 6.35; OCH_3, 21.14. Calc. for $C_{23}H_{19}O_3(OCH_3)_3$: C, 71.54; H, 6.47; OCH_3, 21.33%]. Hydrogenation of macluraxanthone, with platinic oxide catalyst in absolute ethanol proceeded stepwise to yield a dihydro derivative, m.p. 181-182° [Found: C, 69.92; H, 6.08. Calc. for $C_{23}H_{24}O_6$: C, 69.68; H, 6.10%] and a tetrahydro derivative, which X-ray powder diffraction data showed to exist in two dimorphous forms, m.p. 204-205° and 206-207° [Found: C, 69.28; H, 6.73. Calc. for $C_{23}H_{26}O_6$: C, 69.33; H, 6.58%]. The NMR spectrum of tetrahydromacluraxanthone showed no signals characteristic of aliphatic unsaturation.

The similarity of the U.V. and I.R. spectra of macluraxanthone and its derivatives with those of known xanthones,[3-5] left no doubt of the ring system present. Especially striking is the correspondence of the U.V. spectrum of jacareubin (I)[5] with that of macluraxanthone (Table I). Furthermore the infrared spectra of jacareubin trimethyl ether (II) and macluraxanthone trimethyl ether (IV) were nearly superposable between 2 μ and 7 μ. The NMR spectrum of macluraxanthone trimethyl ether (Table II) showed the presence of two doublets in the

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

[4] J. C. Roberts, Chem. Revs. 61, 591 (1961).

[5] F. E. King, T. J. King, and L. C. Manning, J. Chem. Soc. 3931 (1953).

Table I

U.V. Data for Macluraxanthone and Other Xanthones

Compound	λ_{max}^{EtOH} (mμ) (log ε)			
Macluraxanthone	242 (4.31)	278 (4.64)	338 (4.28)	-
Jacareubin[5]	240 (4.09)	279 (4.60)	334 (4.26)	-
Mangostin[3]	243 (4.54)	259 (4.44)	318 (4.38)	351 (3.86)
Mangiferin[4,6]	242 (4.44)	260 (4.50)	320 (4.22)	368 (4.10)

aromatic region. The doublet at τ = 1.99 can only be due to a proton ortho to the xanthone carbonyl group, in the 8 position of the xanthone nucleus. The adjacent 7 position must also bear a hydrogen atom to account for the magnitude of the coupling (J = 9.4 cps) between the two aromatic hydrogens. Since, as mentioned above, the NMR spectrum of macluraxanthone dimethyl ether includes a signal attributed to a chelated phenolic hydrogen, C-1 must bear a hydroxyl group. Further examination of the NMR spectrum of IV revealed the presence of a 2,2-dimethylchromene ring.[7,8] Except for the AB system, no signals due to aromatic protons could be detected. Thus the presence of a xanthone nucelus, a 2,2-dimethylchromene ring, three hydroxyl groups, and two aromatic left only a C_5H_9 fragment unaccounted for in macluraxanthone (III). The portion of the spectrum of IV corresponding to the

[6] S. Iseda, Bull. Chem. Soc. Japan 30, 625 (1957).

[7] B. F. Burrows and W. D. Ollis, Proc. Chem. Soc. 177 (1960).

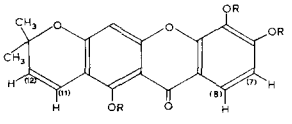
[8] N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, Varian High Resolution Nuclear Magnetic Resonance Spectra Catalog, p. 344, Varian Associates, Palo Alto, California.

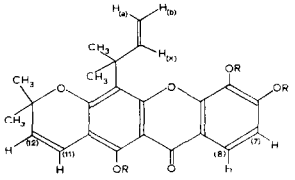
Table II

NMR Data for Jacareubin Trimethyl Ether (II) and

Macluraxanthone Trimethyl Ether (IV)

Compound



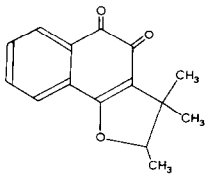


I, R=H; II, R=CH_3 III, R=H; IV, R=CH_3

Protons	τ (p.p.m.)	J loci	J c.p.s.	τ (p.p.m.)	J loci	J c.p.s.
Aromatic						
C-4	3.37					
C-7	3.15*	7,8	9.0	3.04*	7,8	9.4
C-8	2.09*			1.99*		
Methoxyl	6.06, 6.08			6.01, 6.06 6.07		
2,2-Dimethyl-chromene ring						
Methyl	8.55			8.54		
Olefinic	3.32, *4.41*	11,12	10.0	3.21, *4.30*	11,12	10.0
1,1-Dimethyl-2-propenyl group						
Methyl				8.28		
Vinyl (x)				3.54+	a,x	17.9
Vinyl (a)				5.09+	b,x	10.2
Vinyl (b)				5.18+	a,b	1.0

*Doublet.
+Quartet.

C_5H_9 residue consisted of an ABX system characteristic of a vinyl group linked to a carbon atom with no hydrogens on it[9,10] and a sharp singlet at τ = 8.28 of such relative area that it was attributed to two equivalent methyl groups. The only structure of the C_5H_9 residue consistent with the above is a 1,1-dimethyl-2-propenyl (α,α-dimethylallyl) group. It was found that macluraxanthone is recovered unchanged upon treatment with acid. Thus the 1,1-dimethyl-2-propenyl group is not ortho to a hydroxyl, since otherwise it would be expected to isomerize to a furan ring in a manner analogous to the reaction used in the synthesis of dunnione (V).[11] This fact, coupled with the above evidence, eliminates



V

all possible structures for macluraxanthone save III and VI. The structure of macluraxanthone is undoubtedly III since, as mentioned above, the I.R. spectra of macluraxanthone trimethyl ether (IV) and jacareubin trimethyl ether (II), with a 1,3,5,6 oxygenation pattern, are nearly superposable between 2 μ and 7 μ. If VI were the structure of

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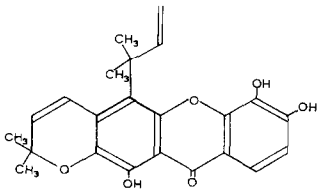
[9] Ibid., p. 155.

[10] J. A. Pople, W. G. Schneider, and H. J. Bernstein, High Resolution Nuclear Magnetic Resonance, p. 238, McGraw-Hill Book Company, Inc., New York (1959).

[11] R. G. Cooke, Austral. J. Sci. Res. 3, 481 (1950).



VI

macluraxanthone, wherein, in effect, an alkoxyl group has been moved from C-3 to C-2, the spectra of the trimethyl ether would be expected to be significantly different in the carbonyl region.[12] Neither would the U.V. spectra of VI be expected to correspond closely with that of jacareubin, as the U.V. spectra of macluraxanthone does (Table I). Xanthones with the same oxygenation pattern have quite similar U.V. spectra,[3,4] as is the case with mangostin[3] and mangiferin[6] (Table I), both of which are 1,3,6,7-tetraoxygenated xanthones.

To our knowledge, macluraxanthone (III) is the first example of a plant phenolic product with an isoprenoid residue occurring as a 1,1-dimethyl-2-propenyl group. The biogenetic considerations of this are of interest, for the presence of this group indicates that an aromatic precursor has attacked 2,2-dimethylallyl pyrophosphate in a manner analogous to an S_N2' nucleophilic substitution.[13]

The other two pigments are now designated osajaxanthone (VII),

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[12] W. E. Whitman and L. A. Wiles, J. Chem. Soc. 3016 (1956).

[13] W. D. Ollis and I. O. Sutherland, Recent Developments in the Chemistry of Natural Phenolic Compounds, p. 79, Pergamon Press, London (1961).

$C_{18}H_{14}O_5$, m.p. 265°, and alvaxanthone (VIII, isolated by the late Alva Thompson), $C_{23}H_{24}O_6$, m.p. 155°. These occur in the approximate ratio III:VIII:VII of 100:30:1. The analytical data on VII and VIII together with their U.V. and I.R. spectra indicate that these also are isoprenoid-substituted hydroxyxanthones for which, however, their NMR spectra do not afford a unique structural solution. Further work is in progress to elucidate their formulas. Full details of this work will be communicated elsewhere.

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