Anal. Calcd for $C_{22}H_{26}O_8$: C, 63.15; H, 6.26. Found: C, 63.18; H, 6.37.

3,4′,5,5′-Tetramethoxy-2,2′-biphenyldiethanol (**7**).—A solution of 59.4 g (0.152 mole) of the diacetic acid in 610 ml of tetrahydrofuran was added dropwise to a stirred suspension of 22.8 g (0.608 mole) of lithium aluminum hydride in 610 ml of tetrahydrofuran. The mixture was refluxed for 2 hr, decomposed in the usual way with water, and then filtered (Filter Aid). From the filtrate, after removal of the solvent, 20 g of an oil was obtained that was dissolved in ethyl acetate. Chilling yielded 18.7 g (35%) of **7**, mp 127–128°. The cake of oxides was dissolved in 10% hydrochloric acid, the Filter Aid was removed, the filtrate was shaken with chloroform, and the aqueous layer was discarded. The chloroform layer was washed successively with water, saturated bicarbonate solution, and water and dried. Removal of the solvent gave 8 g of oil that on crystallization from ethyl acetate yielded an additional 6.2 g of **7**, mp 127–128°; total yield was 24.9 g (45%). An analytical sample was obtained by recrystallization from ethyl acetate–petroleum ether (bp 60–90°), mp 126–127°;[11] infrared ($CHCl_3$) at 3590, 3500–3300, 3000, 2940, 2820, 2440, 2400, 1600, and 1515 cm^{-1}; nmr ($CDCl_3$) at δ 1.93 (2 OH) 2.64 (2 CH_2), 3.63 (2 CH_2O), 3.78, 3.81, 3.84, and 3.91 (4 CH_3O), and 6.34, 6.50, 6.68, and 6.85 (4 aromatic). The mass spectrum showed a molecular weight of 326.

Anal. Calcd for $C_{20}H_{26}O_6$: C, 66.28; H, 7.23. Found: C, 66.57; H, 7.02.

From the bicarbonate washes starting material was recovered.

2,2′-Bis(2-bromoethyl)-3,4′,5,5′-tetramethoxybiphenyl (**8**).—One gram (0.00276 mole) of **7** was suspended in 28 ml of dry ether and at 0°, 0.75 g (0.00276 moles) of phosphorus tribromide was added dropwise. After 10–15 min a viscous material separated. Addition of an equal volume of benzene rendered the mixture homogeneous. The mixture was poured into 50 ml of ice water; the organic layer washed with cold water and dried. Distillation of the solvent gave 190 mg of an oil which was dissolved in 3 ml of benzene and the solution was passed through a bed of 5 g of Woelm alumina (grade I). The alumina was washed with 150 ml of benzene and after removal of the solvent from the combined eluates 100 mg of a colorless oil was obtained. The oil solidified, mp 89–91°; recrystallization from petroleum ether (bp 60–90°) raised the melting point to 91–92°; infrared (KBr) at 3000, 2940, 2830, 1605, 1580, and 1515 cm^{-1}; nmr ($CDCl_3$) at δ ~2.90 (2 CH_2), ~3.35 (2 CH_2Br), 3.80, 3.85, 3.87, and 3.95 (4 CH_3O), and 6.32, 6.50, 6.68, and 6.83 (4 aromatic).

Anal. Calcd for $C_{20}H_{24}Br_2O_4$: C, 49.20; H, 4.95; Br, 32.75. Found: C, 48.99; H, 5.01; Br, 32.85.

Protostephanine. 6,7,8,9-Tetrahydro-2,3,10,12-tetramethoxy-7-methyl-5H-dibenz[*d,f*]azonine (**9**).—Two hundred and fifty milligrams of **8** was heated for 2 hr at 140–150° with a solution of 0.5 g of methylamine in 10 ml of benzene under 200 psi of nitrogen. The product was washed with water. The bases were extracted into 10% hydrochloric acid, liberated with excess potassium hydroxide, and taken up in ether. The ethereal solution was dried and the solvent was distilled to leave 170 mg of a pale-colored syrup which crystallized on standing overnight. The solid was dissolved in 3 ml of benzene and passed over 10 g of Woelm alumina (grade II). Elution with 150 ml of benzene gave 61.8 mg of a white, crystalline solid, mp 84–86°,[12] identical (mass spectrum, nmr, infrared, and tlc) with a natural sample.

Anal. Calcd for $C_{21}H_{27}NO_4$: C, 70.56; H, 7.61; N, 3.92. Found: C, 70.66; H, 7.84; N, 4.19.

The **sulfate** had mp 130–132° (dried for 4 hr at 100°).

Anal. Calcd for $C_{21}H_{27}NO_4 . H_2SO_4$: C, 55.02; H, 6.74; N, 2.80. Found: C, 55.38; H, 6.42; N, 3.07.

The infrared and nmr spectra of the free base were identical with those reported by Takeda.[2] The high-resolution mass spectrum showed a molecular ion at *m/e* 357.1950 corresponding to the formula $C_{21}H_{27}NO_3$ and in general was very similar to the mass spectrum of natural protestephanine except for some peaks which are attributed to impurities in the natural product. Thin layer chromatography also confirmed the presence of these impurities.

Registry No.—**9**, 549-28-0; **2**, 7732-73-2; **3**, 7732-74-3; **4**, 7732-75-4; **4c**, 7775-85-1; **5**, 7771-31-5; **5** (5-cyano-), 7732-76-5; **5a**, 7732-77-6; **5a** (5-cyano-); 7732-78-7; **6a**, 7732-79-8; **6b**, 7732-80-1; **7**, 10026-45-6; **8**, 7732-81-2.

Acknowledgment.—We wish to thank Mr. M. D. Rosenberg and Mr. R. C. Sunbury for very capable assistance. The microanalyses were performed by Dr. A. Steyermark and his staff. Drs. P. Bommer, F. Vane, and T. Williams, and Mr. S. Traiman provided the mass spectral, nmr, and infrared data.

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[11] Takeda[2] reported mp 123–125°.

[12] Takeda[2] reported mp 65–68°.

The Stucture of Two Isoflavones from the Abyssinian Berebera Tree

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Received November 18, 1966

The structures of two isoflavones, apparently earlier isolated by Clark, have been shown to be I and V by spectral and degradative studies.

In the course of his investigations of rotenone-bearing plants, Clark examined the seeds of the Abyssinian Berebera tree, *Millettia ferruginea* (Hochst.) Baker, isolating rotenone and deguelin[1] and artifacts resulting from alkaline treatment and aerial oxidation of the extracts.[2] Alumina chromatography of the filtrates provided two new compounds of mp 164–165° and 189–190°, respectively. Analysis of the lower melting material suggested the formula $C_{21}H_{20}O_6$, with two methoxyl groups, while the higher melting corresponded to $C_{23}H_{20}O_6$, with one methoxyl.

Recently we have been able to examine the seeds of this plant, and have encountered two isoflavones with properties which approximate those of Clark's unknowns.[3] Crystallization of ethyl acetate extracts of these seeds provided a material melting at 182.5–185°, which corresponded in combustion analysis and mass spectrum to $C_{22}H_{18}O_6$. As the nmr spectrum showed a single methoxyl group, it seemed likely that this material was Clark's higher melting compound.[4]

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[1] E. P. Clark, *J. Am. Chem. Soc.*, **65**, 27 (1943).

[2] Clark isolated dehydrorotenone, tephrosin, and isotephrosin, which are not now regarded as natural materials; *cf.* F. M. Dean, "Naturally Occurring Oxygen Ring Compounds," Butterworth and Co. (Publishers) Ltd., London, 1963, p 501.

[3] We are indebted to Dr. William Burger of the Chicago Museum of Natural History for the gift of these seeds.

[4] The compositions required by the two different formulas differ by C, 0.57, and H, 0.34; Clark's analyses and ours, fall between the two values, and do not provide a basis for choice. Clark reported a molecular weight determination by an unspecified method which corresponds to the higher formula, but the mass spectrum obviously is a more certain datum. Because Dr. Clark's samples are not available, and no further properties of these materials are reported, the identity of his materials must remain somewhat uncertain.

TABLE I

CHEMICAL SHIFTS (δ) OF DURMILLONE, FERRUGONE, AND RELATED COMPOUNDS

		Proton position (TMS = 0)											
Compd	Solvent	2-H	5-H	6-H	2′-H	3′-H	5′-H	6′-H	2″-C(CH_3)$_2$	3″-H	4″-H	OCH_2O	CH_3O
Durmillone	$CDCl_3$	7.93	7.56		7.12		6.85	6.97	1.55	5.72	6.80	5.97	3.95
							(J = 8 cps)			(J = 10 cps)			
	$(CH_3)_2SO$	8.36	7.43		7.18		7.00	7.10		5.95	6.80	6.10	
							(J = 8 cps)			(J = 10 cps)			
	C_6H_6								1.29			5.36	3.33
Ichtynone[a]	$CDCl_3$	7.89	7.53			6.61		6.80	1.56	5.71	6.79	5.93	3.94
Ferrugone	$CDCl_3$	7.92	8.06	6.84				6.54	1.50	5.72	6.83	6.03	3.88
			(J = 8.5 cps)							(J = 10 cps)			3.85
	$(CH_3)_2SO$	8.26	7.90	6.95				6.58	1.50	5.95	6.83	6.10	3.83
			(J = 8.5 cps)							(J = 10 cps)			3.78
	C_6H_6								1.23			5.36	3.84
													3.56
Jamaicin[a]	$CDCl_3$	7.92	8.03	6.85		6.62		6.85	1.49	5.72	6.80	5.95	3.72

[a] Reference 8.

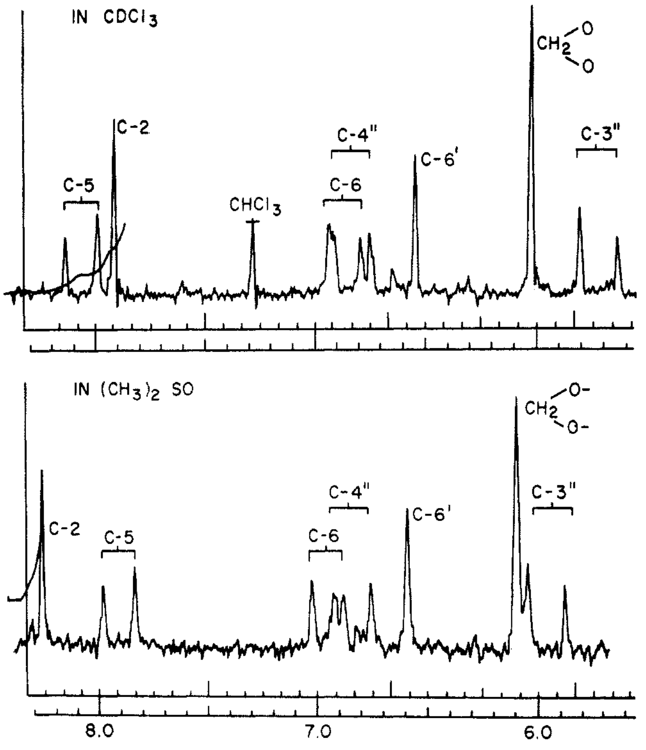

Figure 1.—Nmr spectra of the aromatic protons of ferrugone.

Filtrates from the crystallization of the higher melting compound could be concentrated to provide a second compound, which, after purification by thin layer chromatography and recrystallization, possessed mp 167–169°. Evidently this material is Clark's lower melting unknown, for the mass and nmr spectra show the composition $C_{23}H_{20}O_7$, with two methoxyl groups.[5]

Highly unsaturated CHO compounds isolated from rotenone-bearing plants may reasonably be supposed to possess structures elaborated from the C_{15} nucleus of flavone. In the present instance, this supposition is amply substantiated by the ultraviolet and infrared spectra of the material (see the Experimental Section). Within this context, examination of the nmr spectra readily reveals the structures.

The nmr data of the material of mp 167–169°, here named ferrugone, are listed in Table I. The two peaks of three protons each near 3.8 ppm and one two-proton peak at 6.03 ppm reveal the oxygen substituents as two methoxyl groups and a methylenedioxy group. The six-proton singlet at 1.50 can be assigned to a *gem*-dimethyl group which is shifted downfield by negative substitution. The singlet which occurs at 7.92 in $CDCl_3$ and 8.26 ppm in dimethyl sulfoxide reveals the compound to be an isoflavone, the downfield position being characteristic of a proton on an unsaturated carbon bearing an oxygen substituent.[6]

The peaks in the aromatic region are confused and obscure in the deuteriochloroform solution, but are fortuitously shifted in dimethyl sulfoxide solution and allow a reasonable interpretation. (See Figure 1.) The doublet centered at 5.95 and that at 6.83 ppm (J = 10 cps) correspond to the AB system of a *cis*-styrene. With the peculiar *gem*-dimethyl group, this group suggests that the seventh oxygen atom occurs in the dimethylpyran system which has previously been demonstrated in several isoflavones. Of the remaining quartet at 7.90 and 6.95 ppm (J = 8.5 cps) the downfield proton must be situated adjacent to the carbonyl group to occur so far downfield in a highly oxygenated aromatic system; as the coupling constant is characteristic of *ortho* protons, the upfield proton must lie at C-6; that the chemical shift is less than 7.0 suggests that the remaining oxygen is at C-7. These observations may be assembled into the A and C ring systems of structure I. As this is identical with the AC moiety of jamaicin[7] (II), it is possible to compare the published spectral data,[8] as in Table I. The close correspondence of spectral properties leaves little doubt of the correctness of this partial structure.

The two methoxyl groups, the methylenedioxy group, and the proton which occurs as a singlet at 6.54 in deuteriochloroform solution remain to be placed on

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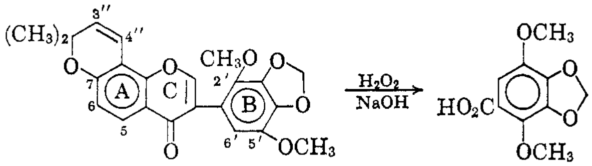
[5] The analyses reported correspond better to the lower of the two formulas for this material, which differ in C, 0.83, and H, 0.53; in particular the reported molecular weight (350) is far from that of the higher formula (408). As analytical difficulties are not uncommon in this series, the present material may still be tentatively identified with Clark's material of mp 164–165°.

[6] T. J. Batterham and R. J. Highet, *Australian J. Chem.*, **17**, 428 (1964); J. Massicot and J. R. Marthe, *Bull. Soc. Chim. France*, 1962 (1962); A. Grouiller, *ibid.*, 2404 (1966). This peak is a great aid in the characterization of isoflavones, which are otherwise easily confused with other flavonoids; *cf.* F. M. Dean, ref 2, p 336; L. Jurd in "The Chemistry of Flavonoid Compounds," T. A. Geissman, Ed., The Macmillan Co., New York, N. Y., 1962, p 147.

[7] O. A. Stamm, H. Schmid, and J. Büchi, *Helv. Chim. Acta*, **41**, 2006 (1958).

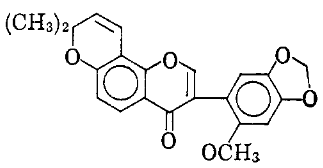
[8] J. S. P. Schwarz, A. I. Cohen, W. D. Ollis, E. A. Kaczka, and L. M. Jackman, *Tetrahedron*, **20**, 1317 (1964).

ring B. The orientation of these groups is partially revealed by the chemical shift of the methoxyl groups in benzene solution, for only that group of which the resonance is altered from 3.78 to 3.56 ppm can lie next to the proton.[9] It is unlikely that the proton lies in the 4′ position, for this is the position most commonly substituted in the B rings of isoflavones.[10] The two remaining positions for the proton can be distinguished by the following argument. Substitution of a methoxyl at C-6′ of jamaicin, which would produce one of the alternative structures, should alter the chemical shift of the C-3′ proton from 6.61 to *ca.* 6.3 ppm;[11] that the observed chemical shift is 6.54 ppm suggests that the proton is at C-6′ and, indeed, substituting a methoxyl at C-3′ of jamaicin to produce the oxygenation pattern required could reasonably be expected to shift the C-6′ proton from 6.80 to *ca.* 6.5 ppm. The resulting alternative structures[12] were differentiated and all uncertainty was removed by the peroxide oxidation[7,8] of ferrugone to apiolic acid (III), demonstrating the structure of the parent isoflavone to be I.



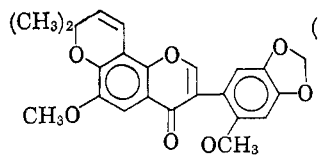
I, ferrugone

III, apiolic acid

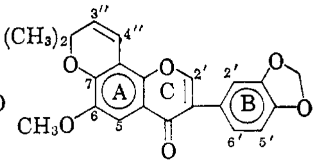


II, jamaicin

The structure of the higher melting material could similarly be deduced from its spectra. The infrared and nmr spectra revealed a dimethylpyranoisoflavone system bearing a methoxyl and methylenedioxy groups. (See Table I and the Experimental Section.) The singlet at 7.56 ppm showed the 5 position to be the only unsubstituted position of ring A, and placed the methoxyl at C-6. The methylenedioxy group must therefore be on the B ring and is shown to be in the 3′,4′ position by the characteristic nmr resonance of a 1,2,4-substituted aromatic ring. The postulated structure V is well supported by a comparison of chemical shifts with those reported for ichthynone (IV;[8] see Table I). Recently the isoflavone durmillone from *M. dura* (Dunn) has been shown[13] to possess this structure. Comparison of the two materials has shown them to be identical.



IV, ichthynone



V, durmillone

Mass Spectra.—The fragmentation patterns of these materials reflect the stability of the aromatic systems. The parent peaks are strong. The fragments formed by loss of a methyl group provide the base peaks, and also appear as doubly charged ions. The anticipated losses of methoxyl groups and formaldehyde can be detected in less important peaks of the spectra, as both singly and doubly charged ions.

Experimental Section[14]

Extraction.—A 70-g sample of the seeds of *Millettia ferruginea* (Hochst.) Baker was ground dry in a Waring blender, and extracted with three 300-ml portions of hexane and one 300-ml portion of benzene. Concentration of these extracts provided 19.9 g of a mobile, golden oil which has not been further examined. The seeds were now extracted with 300-ml portions, three times each, of benzene, ethyl acetate, and chloroform. The extracts were separated, evaporated to dryness, and crystallized from ethanol. No crystalline materials were obtained from the benzene or first ethyl acetate extracts. Crystallization of subsequent extracts provided 0.27 g of durmillone, mp 174–187°; concentration of the filtrates provided an additional 0.14 g, mp 164–181°. On standing the filtrates deposited 0.12 g of a solid melting over a wide range, which was crystallized from ethanol–chloroform to provide 87 mg of ferrugone, mp 153–164°.

Durmillone was recrystallized from chloroform–ethanol and from ethanol to provide colorless prisms: mp 182.5–185°, on several months standing the melting point became 167–185°; on silicic acid, R_f 0.37 (15% ethyl acetate in benzene); $[\alpha]_D$ ±0° (*c* 0.67, chloroform); λ_{max} 229 mμ (ε 31,000), 264 (33,000), 333 (10,800), and 347 (9600); ν_{max} (chloroform) 1630 (C=O), 1585 (aromatic), 1390, 1375 [$(CH_3)_2C$], 1035 (OCH_3), 933 (OCH_2O), 894 cm^{-1} (dimethylpyran). *Anal.* Calcd for $C_{22}H_{18}O_6$: C, 69.83; H, 4.80; mol wt, 378.4. Calcd for $C_{23}H_{20}O_6$: C, 70.40; H, 5.14; mol wt, 392.4. Found: C, 70.09; H, 5.17.

Ferrugone was purified by chromatography on a silicic acid plate (chloroform), and recrystallized from methanol to provide needles of mp 167–169°; on silicic acid, R_f 0.40 (15% ethyl acetate in benzene); λ_{max} 233 mμ (ε 36,000), 263 (42,700), 309 (7100), 322 sh (6700); ν_{max} (chloroform) 1630, 1590, 1568, 1390, 1365, 1270, 1035, 950, 888 cm^{-1}.

Oxidation of Ferrugone.[7,8]—A 13-mg sample of the isoflavone was dissolved in 1.25 ml of 5% ethanolic potassium hydroxide solution and stirred at 50° while treated with four 0.030-ml portions of 30% hydrogen peroxide at 10-min intervals. A yellow color developed on dissolution which disappeared during the peroxide treatment. The solution was diluted with water and extracted twice with chloroform. The aqueous raffinates were acidified with 6 *N* hydrochloric acid and extracted thrice with chloroform. The organic layer was washed with water and con-

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(9) Aromatic methoxyl groups between two *ortho* substituents possess the same chemical shift in benzene and deuteriochloroform solution, while the shift of a methoxyl adjacent to at least one proton lies at 0.3–0.5 ppm higher field in benzene solution than in deuteriochloroform; *cf.* H. M. Fales and K. S. Warren, *J. Org. Chem.*, **32**, 501 (1967). In the present case, this observation eliminates the two structures bearing the 2′,3′-dimethoxy-4′,5′-methylenedioxyphenyl group, and the 2′,4′-dimethoxy-5′,6′-methylenedioxyphenyl group.

(10) W. D. Ollis in "The Chemistry of Flavonoid Compounds," ref 6, p 357.

(11) P. L. Corio and B. P. Daily, *J. Am. Chem. Soc.*, **78**, 3043 (1956).

(12) The alternative structure to I would bear the 2′,3′-methylenedioxy-4′,5′-dimethoxyphenyl group.

(13) W. D. Ollis, C. A. Rhodes, and I. O. Sutherland, *Tetrahedron*, in press. We are indebted to these authors for communicating these results to us prior to publication and for making this comparison.

(14) Melting points were observed on a Kofler microscope hot stage and are corrected. Thin layer chromatography was performed on Merck silica gel G. Infrared spectra of films or chloroform solutions were determined on a Perkin-Elmer Model 21 double-beam spectrophotometer; those of KBr pellets were determined on a Beckman IR-7 grating double-beam spectrophotometer; ultraviolet spectra were obtained in absolute ethanol solution on a Cary Model 11 MS recording spectrophotometer. Nmr spectra were recorded on a Varian A-60 spectrometer, using tetramethylsilane (δ = 0.0 ppm) as an internal standard. Relative intensities of peaks, integrated electronically, are listed parenthetically, and the peaks are described by the following abbreviations: s, singlet; m, multiplet. Mass spectra were determined on an Associated Electrical Industries MS-9 double-focussing mass spectrometer at 70 ev; accurate masses were determined at a resolution of 1/10,000 by comparing the peaks with those of slightly less mass from perfluorotributylamine.

centrated to dryness under reduced pressure. Chromatography on a silicic acid plate (R_f 0.72; 90 benzene, 25 dioxane, 4 acetic acid[15]) provided 1.5 mg of apiolic acid, mp 169–172°. The mass spectrum (see Table II) and infrared spectrum (KBr) were identical with those of authentic apiolic acid: ν_{max} (KBr) 2930, 2860, 1690, 1630, 1590, 1325, 1070, 1045, 965, 940 cm^{-1}.

Preparation of Authentic Apiolic Acid.—Parsley seed oil (Fritsche Brothers, New York, N. Y.) was distilled through a Podbielniak column at 19 mm to a temperature of 167°. Distillation of the residue at 124–127° (0.3 mm) and recrystallization from pentane provided apiole: mp 29–30.3° (lit.[16] mp 30°); λ_{max} 282 mμ (ϵ 904); ν_{max} (film) 1640, 1610, 1498 (aromatic), 1240, 1060 (CH_3O), 1045, 952 (OCH_2O), 990, 910 (vinyl) cm^{-1}; nmr (in $CDCl_3$) 6.33 (aromatic, s, 1), 5.95 (OCH_2O, s, 2), 3.90 (OCH_3, s, 3), 3.86 (OCH_3, s, 3), *ca.* 6.0 (vinyl, m, 1), *ca.* 5.2 (vinyl, m, 1), *ca.* 4.9 (vinyl, m, 1), *ca.* 3.4 (allyl, m, 1), *ca.* 3.3 ppm (allyl, m, 1); (in benzene) 5.45 (OCH_2O, s, 2), 3.75 (OCH_3, s, 3), 356 (OCH_3, s, 3); other resonances were unchanged. Oxidation of this material by alkaline permanganate and crystallization from water gave a small yield of apiolic acid: mp 175° (lit.[17] mp 175°); nmr ($CDCl_3$) *ca.* 10.5 (1, br), 7.45 (1, s), 6.17 (2, s), 4.18 (3, s), 3.93 ppm (3, s).

TABLE II

MASS SPECTROMETRIC DATA

	Obsd	Calcd
	Ferrugone	
$C_9H_5O_3$	161.0245	161.0239
$(C_{20}H_{12}O_6)^{2+}$	174.0322	174.0317
$C_{11}H_{10}O_2$	174.0669	174.0681
$C_{11}H_7O_3$	187.0402	187.0395
$(C_{21}H_{14}O_7)^{2+}$	189.0376	189.0369
$(C_{22}H_{17}O_7)^{2+}$	196.5475	196.5487
$C_{20}H_{12}O_6$	348.0670	348.0634
$C_{20}H_{11}O_7$	363.0509	363.0505
$C_{22}H_{17}O_6$	377.1049	377.1025
$C_{22}H_{18}O_6$	378.1050	378.1103
$C_{22}H_{17}O_7$	393.0972	393.0974
$C_{23}H_{20}O_7$	408.1195	408.1209
	Durmillone	
$(C_{21}H_{14}O_6)^{2+}$	181.0377	181.0395
$(C_{21}H_{15}O_6)^{2+}$	181.5430	181.5434
$C_{21}H_{15}O_6$	363.0879	363.0869
$C_{22}H_{18}O_6$	378.1106	378.1103
	Apiolic Acid	
$C_7H_5O_4$	153.0172	153.0188
$C_8H_5O_5$	181.0123	181.0137
$C_9H_7O_6$	211.0226	211.0242
$C_{10}H_{10}O_6$	226.0457	226.0477

Registry No.—I, 7731-08-0; V, 7731-09-1; III, 7731-10-4; apiole, 523-80-8.

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(15) H. J. Petrowitz and G. Pastuska, *J. Chromatog.*, **7**, 128 (1962).

(16) E.v. Gerichten, *Ber. Dtsch. Chem. Ges.*, **9**, 1477 (1876).

(17) G. Ciamician and P. Silber, *ibid.*, **21**, 1621 (1888).

Osage Orange Pigments. XVIII.[1] Synthesis of Osajaxanthone

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The *p*-toluenesulfonate ester is established as an effective blocking group for the conversion of phenolic 2,2-dimethylchromanones to chromanols and chromenes. Attempts to prepare osajaxanthone (**8**) derivatives from 7-hydroxy-5-methoxy-2,2-dimethylchromene (**5**) failed. The previously synthesized dihydroosajaxanthone monomethyl ether (**6**) was converted into osajaxanthone monomethyl ether (**8**, 7 = OMe), dihydroosajaxanthone (**7**), and osajaxanthone (**8**), the last named being identical with the natural pigment.

The 2,2-dimethylchromene ring system is of common occurrence in plant pigments, where it is frequently found attached to coumarin, flavone, isoflavone, xanthone, and other heterocyclic ring systems containing the γ-pyrone nucleus.[2] Two isoflavone pigments, osajin and pomiferin, have been isolated in this laboratory from the fruit of the osage orange (*Maclura pomifera* Raf.)[3] and have been shown to contain the 2,2-dimethylchromene ring system.[4] Two xanthone pigments, macluraxanthone and osajaxanthone (**8**), isolated from the root bark of this same tree,[5] have likewise been demonstrated to possess this ring system.[6,7]

Several approaches to the synthesis of osajaxanthone (**8**), the simplest of these osage orange pigments, have been under investigation in this laboratory. Dihydroosajaxanthone monomethyl ether (**6**) was successfully synthesized.[7] One approach to the synthesis of the natural pigment was to build the xanthone ring onto 7-hydroxy-5-methoxy-2,2-dimethylchromene (**5**) with a suitably substituted *o*-hydroxybenzoic acid. To this end 5,7-dihydroxy-2,2-dimethylchromanone[7] (**1**) was converted into 5-methoxy-7-(*p*-tolylsulfonyloxy)-2,2-dimethylchromanone (**2**) in one step. Chromanone **2** was converted, in 82% yield, into chromanol **3** by reduction with lithium aluminum hydride and **3** was dehydrated (90% yield) with *p*-toluenesulfonic acid to form chromene **4**. The *p*-toluenesulfonate group in **4** was then removed to form the desired 5-(methyl ether) (**5**) of the 5,7-dihydroxy-2,2-dimethylchromene. Chromene **5** was, however, unsuitable for xanthone formation with the acidic reagents normally employed for this synthesis and only intractable red tars were obtained in the reaction. In view of the reported stability toward nitric acid of the chromene double bond in the closely related, naturally occurring chromene *allo*-evodionol,[8] such behavior was not anticipated.

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