Table 1. PMR data for dihydrochalcones

Compound	$H_{2,6}$	$H_{3,5}$	H_α	H_β	$H_{3'}$	$H_{5'}$	$H_{6'}$	OMe	$H_{1''}$
1	7.09	6.73	3.28	2.87	6.80	6.56	7.64	—	5.01
2	7.22	6.83	3.21	2.95	6.39	6.47	7.79	—	—
3	7.06	6.72	3.34	2.84	6.89	6.67	7.66	3.84	5.13
4	7.26	7.00	3.17	3.01	6.60	6.64	7.78	3.85	—
5	7.12	6.76	3.26	2.90	6.44	6.49	7.92	3.85	—
6	7.33	7.09	3.24	2.94	6.76	6.82	7.99	3.89	—

Solvent: d_6-acetone (except for 4 ($CDCl_3$)); standard TMS; shift values in ppm ±.02.

Table 2. ^{13}C-NMR data of dihydrochalcones and model compounds*

Compound	C_1	C_2	C_3	C_4	C_β	C_α	$C_{C=O}$	$C_{1'}$	$C_{2'}$	$C_{3'}$	$C_{4'}$	$C_{5'}$	$C_{6'}$	$C_{1''}$	$C_{2''}$	$C_{3''}$	$C_{4''}$	$C_{5''}$	$C_{6''}$	OMe
1	133.8	130.4	116.1	154.4	30.2	44 7	204.7	121.2	158.7	104.0	162.6	111.0	133.3	101 3	73.8	76.7†	70.3	77.1†	61.6	
2	132.1	129.6	115.4	155.8	29.5	39.7	200.7	113.3	165.6†	103.0	164.7†	108.1	133.0							
3	133.0	129.5	115.4	154.8	29.9	45.1	203.1	121.9	158.7	102.1	165.1	108.7	132.1	101.5	73.9	77.3	70.4	77 3	61.6	55.5
5	131 7	129 3	115 1	155.6	29.2	39.5	200.1	114 6	165.3†	100.7	166.1†	107.1	132.2							55.1
7						26.2	203 5	114.4	165.8†	101.3	166.8†	107.7	133.4							55.7
8						31.8	203.0	121.5	159.2	102.3†	165 3	109.3	133.2	101.1†	73.8	76.9†	70.4	77.2†	61.6	56.5
9	126.9	131.2	116.1	160.4	144.8	117 6	201 0	114.3	166.4†	101.1	166.9†	107.4	132.0							
salidro side	131.1	131.1	116.2	154 8	35.2	71.8								103 1	74.0	76 7	70.5	76.7	61.6	

*Solvent/standard: D_2O/dioxan, (glucosides); d_6-acetone/TMS.
†Numbers intechangeable in same horizontal row.

Hydrolysis of **3** (40 mg) in 2N HCl (5 ml) gave, after extraction with Et_2O, **5**, mp 70–72°, identical to the sample above.

Synthesis of **5**. 2',4-Dihydroxy-4'-methoxychalcone (**9**) was prepared as described [6]. Hydrogenation (atm. pres.) of **9** (160 mg) in EtOH with 5% Pd/C (20 mg) gave **5**, identical (mp, mmp. PMR) to the other samples.

Acetylation of **5** afforded the diacetate **6**, which was crystallized from EtOH, mp 81–82°. (Found C, 67.36; H, 5.60. $C_{20}H_{20}O_6$ requires C, 67.40; H, 5.66).

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1,3,6-TRIHYDROXY-7-METHOXY-8-(3,7-DIMETHYL-2,6-OCTADIENYL)XANTHONE FROM *GARCINIA COWA*

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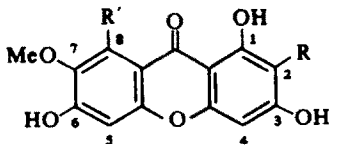
Key Word Index—*Garcinia cowa*; Guttiferae; 1,3,6-trihydroxy-7-methoxy-8-(3,7-dimethyl-2,6-octadienyl)xanthone; structural determination.

Abstract—1,3,6-Trihydroxy-7-methoxy-8-(3,7-dimethyl-2,6-octadienylxanthone has been isolated from the stems of *Garcinia cowa*.

Although a 3-methyl-2-butenyl (prenyl) substituent has been found in a number of xanthones from the families *Guttiferae* and *Moraceae*, xanthones containing an unmodified 3,7-dimethyl-2,6-octadienyl (geranyl) side-chain



(1) R = H, R′ = geranyl
(2) R = geranyl, R′ = H
(3) R = R′ = geranyl
(4) R = R′ = prenyl

are relatively few [1] and have been reported in only two species of the genus *Garcinia*, viz, rubraxanthone (1) from *Garcinia rubra*, cowaxanthone (2) and cowanin (3) from *Garcinia cowa*, respectively [2].

In this work, we report the isolation of a yellow pigment, $C_{24}H_{26}O_6$, from the stems of *Garcinia cowa*, which, based on the following evidence is assigned structure (1). The compound formed a triacetate, and a diMe derivative on reaction with Et_2O–CH_2N_2. Its UV spectrum is similar to that of cowaxanthone (2) [2] and mangostin (4) [3] but is different from that of 1,3,7,8-oxygenated xanthone [4]. No change in the spectrum was observed when H_3BO_3–NaOAc was added. However, a bathchromic shift of the 310 nm peak occurred on addition of NaOAc alone, confirming the absence of *ortho* OH groups and the presence of C-3 and/or C-6 OH groups in the xanthone nucleus. The oxygenation pattern of the xanthone is further indicated by the PMR spectrum which shows (i) peaks at δ 13.4 corresponding to the proton of a chelated OH at C-1 and (ii) 3 aromatic protons at δ 6.18 (J = 2 Hz), 6.29 (J = 2 Hz) and 6.81, consistent with expected chemical shifts [5] for protons at C-2, C-4 and C-5 respectively. The observed J value is also in accordance with that recorded for $J_{2,4}$ in 1,3-oxygenated xanthones [5]. The attachment of a geranyl side-chain is readily deduced from the PMR spectrum of the diMe derivative and is corroborated by the appearance of fragment ions at *m/e* 341 (M^+-69) and 287 (M^+-123) in the MS of the parent xanthone [2, 6]. The presence of a peak at *m/e* 299 (M^+-68-43) allows the assignment of the OMe group to C-7, *ortho* to the geranyl side-chain at C-8, as it has been established from MS studies of model compounds [2] that a geranyl substituent with an *O*-Me group undergoes characteristic cleavage as shown below.

EXPERIMENTAL

Extraction and isolation. Powdered stem (0.75 kg) of *G. cowa* was continuously extracted with C_6H_6 for 3 days. After removal of solvent, the residue was redissolved in Et_2O and extracted with freshly prepared 2% aq. NaOH. Acidification of the alkaline soln and isolation with Et_2O gave a dark brown gum from which crude 1,3,6-trihydroxy-7-methoxy-8-(3,7-dimethyl-2,6-octadienyl)xanthone (0.7 g) was obtained by extraction with boiling petrol (8 × 50 ml). The product (R_f 0.53) was purified by PLC (precoated Si gel 60 F_{254}, 2 mm) developed with C_6H_6–EtOAc (3:1) and crystallized from C_6H_6 as yellow needles, mp 205–206°, (Found: C, 70.3; H, 6.3. $C_{24}H_{26}O_6$ requires: C, 70.2; H, 6.4%). λ_{max}^{MeOH} nm (log ε): 242 (4.50), 253 (4.44), 310(4.32), 348 (3.95); $\lambda_{max}^{MeOH-NaOAc}$ nm: 239, 254, 355. ν_{max}^{Nujol} cm^{-1}: 3410, 1640, 1600, 1570, 1160. PMR (60 MHz, Me_2CO-d_6, TMS): δ 1.55 (6H, *br s*, CMe_2), 1.85 (3H, *br s*, CMe), 3.8 (3H, *s*, OMe), 4.11 (2H, *br d*, J = 7 Hz, Ar-$\underline{CH_2}$), 5.1 (2H, *m*, —$C\underline{H}$=C), 6.18 (1H, *d*, J ≒ 2 Hz, C-2), 6.29 (1H, *d*, J = 2 Hz, C-4), 6.81 (1H, *s*, C-5), 9.46 (2H, *br s*, 3 and 6-OH), 13.40 (1H, *s*, 1-OH). MS (70 ev) *m/e* (rel. int.): 411 (7), 410 M^+ (25), 395 (M^+-15; 2), 367 (M^+-43; 3), 342 (M^+-68; 22), 341 (M^+-69; 100), 311 (15), 309 (10), 299 (M^+-68-43; 27), 295 (6), 288 (22), 287 (M^+-68-55; 7), 285 (M^+-68-57; 10), 273 (12), 271 (M^+-68-71; 8), 153 (6), 141 (5), 123 (5), 69 (12), 41 (16).

Triacetate derivative. Needles from aq. MeOH, mp 118–120° (Found: C, 67.2; H, 6.4. $C_{30}H_{32}O_9$ requires: C, 67.2; H, 6.0%). ν_{max}^{Nujol} cm^{-1}: 1770, 1660, 1180.

Dimethyl derivative. Prepared by reaction with Et_2O–CH_2N_2 methane at room temp., mp 92.5–94° from MeOH, (Found: C, 71.0; H, 6.8. $C_{27}H_{32}O_6$ requires; C, 71.2; H, 6.9%). ν_{max}^{Nujol} cm^{-1}: 1650. PMR (60 MHz, $CDCl_3$, TMS): δ1.56 (6H, *br d*, J = 4 Hz, CMe_2), 1.83 (3H, *br s*, CMe), 2.01 (4H, *br s*, —$C\underline{H_2}$—), 3.78, 3.83, 3.93 (9H, *s*, OMe), 4.1 (2H, *br d*, J = 7 Hz, Ar-$\underline{CH_2}$), 4.9–5.4 (2H, *m*, —$C\underline{H}$=C), 6.24 (2H, *s*, C-3 and C-4), 6.69 (1 H, *s*, C-5), 13.36 (1H, *br s*, 1-OH).

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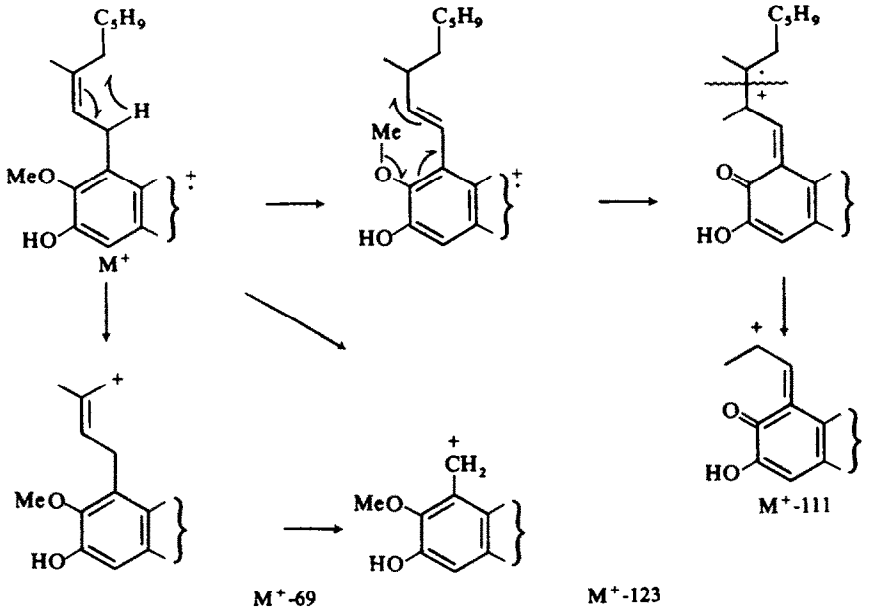

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PRELIMINARY INVESTIGATION OF *CROTON CALIFORNICUS* VAR. *TENUIS* AND *UVARIA KIRKII*: A XANTHONE AND A BENZYLDIHYDROCHALCONE

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Key Word Index—*Croton californicus* var. *tenuis*; Euphorbiaceae; *Uvaria kirkii*; Annonaceae; xanthone; 1,2,3,4,6,7-hexamethoxyxanthone; benzyldihydrochalcone; uvaretin; 1-[2,4-dihydroxy-3(2-hydroxybenzyl)-6-methoxyphenyl]-3-phenyl-1-propanone.

Whole plants of *Croton californicus* Muell.—Arg. var. *tenuis* (Wats.) Ferg. (Euphorbiaceae) were collected in California in November, 1974. *Uvaria kirkii* Hook. f. (Annonaceae) roots were collected in Tanzania in January, 1975. Identification of both plants was confirmed by Dr. Robert E. Perdue, Chief, Medicinal Plant Resources Laboratory, U.S.D.A., Beltsville, MD. Reference specimens are maintained by the U.S.D.A.

Previous work on *Croton californicus*, pharmacological activity [1]; *Uvaria kirkii*, none. *C. californicus* var. *tenius* (whole plants) was extracted exhaustively with petrol (bp 30–60°). The petrol extract was then fractionated. *U. kirkii* (defatted roots) was extracted exhaustively with EtOH. The EtOH extract was partitioned between $CHCl_3$ and H_2O, and the $CHCl_3$ phase further fractionated.

In the case of both plants the additional fractionation consisted of column chromatography (Si gel) followed by preparative-TLC (Si gel G, PF 254). This led to the isolation of 1,2,3,4,6,7-hexamethoxyxanthone [2] from both *C. californicus* var. *tenuis* and *U. kirkii*. In addition, *U. kirkii* yielded the benzyldihydrochalcone uvaretin [3] {1-[2,4-dihydroxy-3-(2-hydroxybenzyl)-6-methoxyphenyl]-3-phenyl-1-propanone}. Identification of these two compounds was accomplished by spectral (IR, PMR) analysis, mp, and comparison with authentic specimens (undepressed mmp, identical TLC R_f values and IR spectra).

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