tive spot (R_f 0.12). This was isolated by prep. TLC as before. Crystallization from Me_2CO yielded colourless needles, mp 176–178° (45 mg).

Benzylation of **4** (C_6H_5Cl–K_2CO_3 in Me_2CO) yielded 8-acetyl-5-benzyloxy-3-hydroxy-2,2-dimethylchroman as colourless needles from *n*-hexane–M_2CO, mp 110°, identified by comparison with an authentic sample prepared earlier [10] (mmp, co-TLC and IR).

(±) *Bakuchalcone* (**1**). A mixture of **2** (30 mg) and *p*-hydroxybenzaldehyde (15 mg) in EtOH (2 ml) was treated with aq. KOH (0.5 ml, 80%) dropwise at *ca* 0° and the reaction kept at room temp. for 4 days. It was diluted with ice-cold H_2O to 15 ml, neutralized with dil. HCl and extracted with $CHCl_3$ (4 × 15 ml). Bakuchalcone was separated from the reaction mixture by prep. TLC (C_6H_6–EtOAc, 17:3, R_f 0.25). Crystallized from *n*-hexane–Me_2CO, as pale-yellow needles (5 mg) mp 201–202°. It was identical with the natural compound (mmp, IR, co-TLC).

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^{13}C NMR SPECTRA OF 1, 3, 6 -TRIHYDROXY-7-METHOXY-8-(3, 7 -DIMETHYL-2,6-OCTADIENYL)XANTHONE AND ITS DIMETHYL DERIVATIVE

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Key Word Index—*Garcinia cowa*; Guttiferae; 1,3,6-trihydroxy-7-methoxy-8-(3,7-dimethyl-2,6-octadienyl)-xanthone; ^{13}C NMR spectra.

Abstract—The ^{13}C NMR spectra of 1, 3, 6-trihydroxy-7-methoxy-8-(3, 7-dimethyl-2, 6-octadienyl)xanthone and its dimethyl derivative are discussed. The data obtained confirmed the assigned structures. The geometrical configuration of the C_{10} dienyl side-chain has been deduced as *trans*.

A yellow pigment, $C_{24}H_{26}O_6$, isolated from the stem of *Garcinia cowa* (Guttiferae), has been assigned the xanthone structure, **1**, based on evidence from light absorption and ^{1}H NMR as well as from mass spectra [1]. The alternative structure, **2**, proposed for cowaxanthone [2], a pigment reported to have been isolated also from the same plant, was not rigorously excluded by the available data. In this paper, we describe a study of the ^{13}C NMR spectra of **1** and its dimethyl derivative, **3**, which unequivocally support the assigned structure.

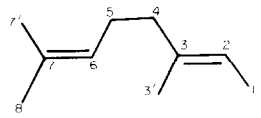
Several papers on the ^{13}C NMR spectra of naturally

Table 1. ^{13}C chemical shift data of xanthones

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-4a	C-9a	C-9a	C-10a	OMe
1*	162.9	97.7	164.5	92.9	101.7	156.9	143.3	136.4	181.1	156.3	109.8	102.0	154.5	60.0
4†	163.1	98.1	165.1	94.1	102.9	164.1	113.9	127.1	179.2	157.1	112.6	102.9	157.1	60.8 (C-7) 55.9 (C-3) 55.5 (C-6)
3‡	163.4	96.7	165.5	91.5	98.2	158.1	144.0	137.1	181.7	156.5	112.7	103.8	155.3	
5†	161.7	95.0	(164.3)	92.6	95.5	(164.0)	112.4	128.1	174.6	159.6	116.8	—§	156.4	55.6, 56.1

*Determined in Me_2SO-d_6.
†Data from ref. [5]. Assignments in parentheses may be interchanged.
‡Determined in $CDCl_3$.
§Signal unobserved.

Table 2. ^{13}C chemical shift data of geranyl substituent



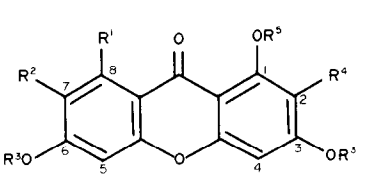
Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-3′	C-7′
1	25.4	123.5	133.7	*	25.9	124.0	130.4	25.3	16.0	17.4
3	25.9	123.2	135.2	39.8	26.7	124.4	131.1	25.6	16.4	17.6

*Signal obscured by solvent peaks.

occurring polyhydroxyxanthones with all chemical shifts assigned have recently been published [3–8]. A comparison of the reported ^{13}C NMR data of 1, 3, 6-trihydroxyxanthone (**4**) [5, 7] and the trimethyl derivative [5, 6] with those of **1** and **3** greatly facilitates the assignment of the ^{13}C chemical shifts in the latter (Table 1). Particularly useful are the methoxy and alkyl substituent effects on the ^{13}C shifts, [4–8] and the assumption that $^3J(CH)$ is greater than $^2J(CH)$, as is the case for several aromatic systems [9]. The signal for C-7 in **4** is at δ113.9. Considering that a methoxyl substituent at C-7 would shift the ipso carbon signal downfield by δ32–34 and that the *ortho* substituent effect of the geranyl group (see below) at C-8 can be assumed to be the same as that of a 3-methyl-2-butenyl group [5; Lee, H.-H. and Ng, S., unpublished], i.e. δ2–3 upfield, the signal at δ143.3 in **1** or 144.0 in **3** is easily assigned to C-7, with a methoxy group attached to it. In both **1** and **3** three signals appear close together in the range δ154.5–158.1, with the two higher field lines of lower intensity. In the proton-coupled spectrum the low field signal shows a multiplet structure while the other two are doublets with splittings at 3.7 and 4.2 Hz in **1** and 3.7 and 4.8 Hz in **3**. Like the signal at δ158.1, that at 165.5 in **3** shows a multiplet structure which could only arise from coupling to three methoxy protons and one or two other protons. If account is also taken of the upfield *ortho* substituent effect of the methoxy group at C-7, the signal at δ158.1 is assigned to C-6 and that at 165.5 to C-3 in **3**. The available data suggest that the signal at δ156.9 should be assigned to C-6 in **1**. The *para* substituent effect of the methoxyl group [5–8] at C-7 allows the signals at δ154.5 in **1** and 155.3 in **3** to be assigned to C-10a. The remaining signal in the group is assigned to C-4a.

The signal for C-8 in **4** is at δ127.1. Taking the ipso substituent effect of the 3, 7-dimethyl-2, 6-octadienyl (geranyl) substituent as δ11–13 downfield, and [5; Lee, H.-H. and Ng, S., unpublished] considering also the *ortho* substituent effect of the methoxyl group at C-7, the signals at δ136.4 in **1** and 137.1 in **3** are assigned to C-8. The geranyl group cannot be attached to C-2 since the signals at δ97.7 in **1** and 96.7 in **3** are unambiguously assigned to C-2 with a proton attached to it being confirmed by the proton coupled spectra.

The assignment of chemical shifts for the C_{10} side-chain, shown in Table 2, is based on the proton-coupled spectrum, and is found to be consistent with the literature data for geraniol [10]. Since the signal for the 3-methyl carbon (C-3′, Table 2) in the side-chain is at δ16.0 in **1** and 16.4 in **3**, it is deduced from the data for nerol and geraniol [10] that in both **1** and **3** the 3-methyl group is *cis* to the methylene group in position 1, as shown in Table 2.



1 R^1 = geranyl, R^2 = OMe, R^3 = R^4 = R^5 = H

2 R^1 = R^3 = R^5 = H, R^2 = OMe, R^4 = geranyl

3 R^1 = geranyl, R^2 = OMe, R^3 = Me, R^4 = R^5 = H

4 R^1 = R^2 = R^3 = R^4 = R^5 = H

5 R^1 = R^2 = R^4 = H, R^3 = R^5 = OMe

EXPERIMENTAL

The ^{13}C NMR spectra were recorded on a JEOL FX-100 FT-NMR spectrometer operating at 25.05 MHz. The probe temp. was 301 K. Solns in $CDCl_3$ or Me_2SO-d_6 were *ca* 0.015 mol/dm^3 and 10 mm o.d. high precision tubes were used. Spectral widths of 5000 Hz with 4096 plot data points were used for the noise-decoupled ^{13}C NMR spectra while 8192 plot data points were used for the proton-coupled ^{13}C spectra. A pulse width of 5.5 μsec (30°) and a pulse interval of 6.6 sec were used to obtain each spectrum. Chemical shifts were measured from the center peak of the solvent signal and corrected using the appropriate expression: $\delta_{TMS} = \delta_{Me_2SO\text{-}d_6} + 39.4$; or $\delta_{TMS} = \delta_{CDCl_3} + 77.1$. Values are reported as $\delta \pm 0.1$ downfield from $SiMe_4$.

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PHENOLICS FROM THE SEEDS OF *ARGEMONE MEXICANA*

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Key Word Index—*Argemone mexicana*; Papaveraceae; 5,7,2',6'-tetrahydroxyflavone; argemexitin; 5,7-dihydroxychromone 7-neohesperidoside.

Abstract—Two new phenolic compounds, 5, 7, 2', 6'-tetrahydroxyflavone and 5, 7-dihydroxychromone 7-neohesperidoside have been characterized from the seeds of *Argemone mexicana*.

Argemone mexicana (Papaveraceae) a spiny herbaceous annual is reported to possess a number of medicinal properties [1, 2]. Earlier chemical investigations [3–8] of various parts of this plant have revealed a number of alkaloids, fatty acids, amino acids and carbohydrates, but phenolic components [6] have been reported only from the flowers. The present communication reports the isolation and characterization of two new phenolic compounds, 5, 7, 2', 6'-tetrahydroxyflavone (argemexitin) (**1**) and 5, 7-dihydroxychromone 7-neohesperidoside (**2**), from the seeds.

The colour reactions and UV spectral data (λ_{max}^{MeOH} nm: 270, 343) of **1** suggested that it was a flavonoid. Strong IR absorptions at 3350 and 1640 cm^{-1} indicated the presence of –OH and chelated >CO functions, respectively. Its UV spectrum shifted bathochromically on addition of both sodium acetate and aluminium chloride indicating the presence of a free hydroxyl at C-7 and a chelated hydroxyl at the C-5 position, respectively. The solubility of **1** in 10% sodium carbonate also supported the presence of a hydroxyl at C-7. Negative Quastel [9] as well as Gossypetone [10] tests indicated the absence of *ortho*- and *para*-dihydroxy groupings, respectively. Methylation of **1** yielded a tetramethyl ether (**1a**). The ^1H NMR spectrum of **1a** in deuterochloroform showed the presence of four methoxyl functions (two of identical nature) along with the signals for six aromatic protons. The broad singlet at δ 6.6 integrating for two protons was attributed to the aromatic protons at C-3 and C-6 positions whereas the one proton *meta*-coupled doublet at δ 6.86 was considered to be due to a C-8 proton. The remaining two methoxyls in **1a** were therefore located in ring B. The most appropriate positions for these methoxyls appeared to be at the C-2' and C-6' positions because this explained the presence of two identical methoxyl functions and also the presence of two *ortho*-coupled doublets ($J = 9$ Hz) in the aromatic region. Thus the doublet at δ 6.75 integrating for two protons was assigned to the protons at C-3' and C-5' positions whereas the one at δ 7.05, integrating for one proton, to the proton at C-4'. **1a** was therefore identified as 5, 7, 2', 6'-tetramethoxyflavone.

The ^1H NMR spectrum of the acetate (**1b**) of **1**, showing signals for four acetoxyl functions and six aromatic protons, also supported the placements of the four oxygen functions, at the C-5, C-7, C-2' and C-6' positions. The signals attributed to protons at C-6, C-8, C-3' and C-5' were shifted markedly downfield compared to their relative values in **1a**, whereas the signals attributed to the C-3 and C-4' protons remained almost unchanged. The downfield shifts of the signals could be due to the deshielding effect of the acetoxyl functions on the adjacent aromatic protons. Hence **1** was identified as 5, 7, 2', 6'-tetrahydroxyflavone.

The colour reactions and UV spectrum of **2** showed