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XANTHONOLIGNOIDS FROM *KIELMEYERA* AND *CARAIPA* SPECIES—^{13}C NMR SPECTROSCOPY OF XANTHONES

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Key Word Index—*Caraipa densiflora*; *Kielmeyera coriacea*; Guttiferae; xanthonolignoids; (5*S*,6*S*)-6(or 5)-hydroxymethyl-5(or 6)-(4″-hydroxy-3″-methoxyphenyl)-2,3:3′,4′-(2′-ethoxyxanthono)-1,4-dioxane; kielcorin; ca-densin-A, -B; toxyloxanthone-C; 2,3,4-trioxyxanthones; ^{13}C NMR.

Abstract—Kielcorin and the cadensins *A* and *B*, isolated respectively from *Kielmeyera coriacea* and *Caraipa densiflora* (Guttiferae), were shown to be xanthonolignoids. The structure of (5S,6S)-6(or 5)-hydroxymethyl-5(or 6)-(4″-hydroxy-3″-methoxyphenyl)-2,3:3′,4′-(2′-methoxyxanthono)-1,4-dioxane was proposed for kielcorin by analysis of high resolution MS and PMR spectra. The carbon shifts of xanthone were assigned and used in the ^{13}C NMR spectral confirmation of the proposed structure.

RESULTS AND DISCUSSION

Structural determination of xanthonolignoids

The genera *Kielmeyera* and *Caraipa* belong to the subfamily Kielmeyeroideae [3]. Chemically they are also closely related, containing 2,3,4-trioxygenated xanthones. In addition to the representatives listed in Table 1, only celebixanthone and 2,3,4-trihydroxyxanthone, respectively *ex Cratoxylon celebicum* Blume [11] and *Ochrocarpus odoratus* (Rafin) Merrill [12], two further Guttiferae, have been described.

Table 1. 2,3,4-Trioxyxanthones from *Kielmeyera* and *Caraipa* species

	Substituents at C				Occurrence
	2	3	4	8	
1	OMe	OH	OH	H	*K. corymbosa* [4]
2	OMe	OMe	OH	H	*K.* spp. [4–8], *C. grandifolia* [9]
3	OMe	OH	OMe	H	*K.* spp. [7, 8]
4	OCH_2	O	OH	H	*K.* spp. [4, 7, 8]
5	OCH_2	O	OMe	H	*K.* spp. [4, 6, 8]
6*	OMe	OMe	OH	OH	*C. grandifolia* [9], *C. densiflora* [10]

*Numbering used for convenience of structural comparison. The correct name is 1,5-dihydroxy-6,7-dimethoxyxanthone.

We wish to report on three additional derivatives of this xanthone series: kielcorin, $C_{24}H_{20}O_8$, whose isolation from *Kielmeyera coriacea* Mart., *K. corymbosa* (Spr.) Mart., *K. speciosa* St. Hil., *K. ferruginosa* A.P. Duarte [5] and *K. rubriflora* Camb. [8] was described previously, cadensin-A, $C_{24}H_{20}O_9$, and cadensin-B, $C_{25}H_{22}O_{10}$, from *Caraipa densiflora* Mart. The molecular formulae, expandable respectively to $C_{22}H_{12}O_4(OH)_2(OMe)_2$, $C_{22}H_{11}O_4(OH)_3(OMe)_2$ and $C_{22}H_{10}O_4(OH)_3(OMe)_3$ by PMR and ^{13}C NMR analysis, strongly suggest that the compounds possess identical skeletons. Indeed, the UV spectra of all three are compatible with xanthone nuclei, and the MS (Table 2) show series of peaks at *m/e* values corresponding in the case of kielcorin to di-OH-OMe- and in the case of the cadensins to tri-OH-OMe-xanthones.

The formulae can, thus, be again expanded; this time respectively to $[C_{13}H_5O_4.OMe].[C_9H_7(OH)_2OMe]$, $[C_{13}H_4O_4.OH.OMe]$. $[C_9H_7(OH)_2OMe]$ and $[C_{13}H_4O_4.OH.OMe].[C_9H_6(OH)_2(OMe)_2]$. Fragmentation features, attributable to the C_9-units, reveal the presence of a primary OH and locate the additional OH and the OMe on an Ar moiety (Table 2). Indeed, methylation of kielcorin with Me_2SO_4/K_2CO_3 led to a monoMe ether which sustains an acetylatable OH. This clearly belongs to a primary alcohol function, as shown by comparison of the PMR spectra of kielcorin or its Me ether on one hand and the Me ether acetate or the diacetate on the other (Table 3). The 220 MHz PMR of the Me ether acetate, furthermore, establishes the link of this CH_2OH-group to an $ArCHCH_2$-unit in which both carbons are connected to ether functions.

The determination of the substitution patterns of this aryl, and also of the xanthone moiety of kielcorin [13] is trivial. Considering the data of Table 1, the resulting

Part 35 in the series 'The Chemistry of Brazilian Guttiferae'. For Part 34 see ref. [1]. Part 50 in the series '^{13}C NMR of Naturally Occurring Substances', For Part 49 see ref. [2].

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Table 2. Interpreted MS of kielcorin (**a**), O-methylkielcorin (**b**), cadensin*A* (**e**) and cadensin*B* (**f**)

Structures **7** or **8**	**a**		**b**		**e**		**f**	
	m/e	%	*m/e*	%	*m/e*	%	*m/e*	%
M^+	436	3	450	29	452	39	482	8
M^+-H_2O	418	5	432	9	434	7	464	2
M^+-MeOH	404	2	418	6	420	24	450	10
M^+-$ArCH_2$	299	23	299	20	315	13	315	17
M^+-$ArC{\equiv}CCH_2OH{=}X$	258	78	258	26	274	100	274	100
X^+-Me	243	42	243	14	259	36	259	38
X^+-H_2CO	228	5	228	12	245	5	245	6
X^+-Me-H_2O	225	8	225	11	241	5	241	4
X^+-Me-CO	215	14	215	4	231	15	231	17
X^+-Me-CO-CO	187	15	187	12	203	9	203	12
$ArCH{=}CHCH_2OH{=}Y$	180	86	194	100	180	68	210	48
Y^+-H_2O	162	37	176	30	162	11	192	—
Y^+-HCO or H_2CO	151	15	165	45	151	6	180	29
$ArCH_2$	137	100	151	100	137	71	167	42
ArH	124	100	138	100	124	32	154	19

Table 3. PMR spectra (shifts in τ values) of kielcorin (**a**), its derivatives (**b**, **c**, **d**) and tri-O-acetylcadensin*B* (**g**)

7 or **8** MHz Solvent	**a** 100 DMSO	**b** 100 $CDCl_3$ + DMSO	**c** 220 $CDCl_3$	**d** 60 $CDCl_3$	**g** 60 $CDCl_3$
H-8′	1.83 *dd*, *J* = 8, 2	1.75 *dd*, *J* = 8, 2	1.64 *dd*, *J* = 8, 1.7	1.64 *dd*, *J* = 8, 2	—
H-6′	2.26 *td*, *J* = 7, 2	2.39 *t*, *J* = 7	2.27 *ddd*, *J* = 8.5, 7, 1.7	2.26 *ddd*, *J* = 8.7, 2	2.32 *t*, *J* = 8
H-5′	2.39 *dd*, *J* = 8, 2	2.49 *dd*, *J* = 8, 2	2.39 *dd*, *J* = 8.5, 1.2	2.4–2.7 *m*	2.52 *dd*, *J* = 8, 2
H-7′	2.57 *td*, *J* = 7, 2	2.68 *t*, *J* = 7	2.60 *ddd*, *J* = 8, 7, 1.2		3.00 *dd*, *J* = 8, 2
H-1′	2.85 *s*	3.01 *s*	2.61 *s*	2.60 *s*	2.69 *s*
H-2″	2.92 *s*(broad)	2.96 *dd*, part. cov.	3.01 *dd*, *J* = 8, 1.5		3.31 *s*
H-5″	3.12 *s*(broad)	3.10	3.07 *d*, *J* = 1.5	2.85–3.05 *m*	2.93 *s*
H-6″		3.14 *d*, *J* = 8	3.09 *d*, *J* = 8		— —
H-5	4.94 *d*, *J* = 8	4.86 *d*, *J* = 7.8	4.90 *d*, *J* = 7.8		
H-6	5.63 *dm*, *J* = 8	5.87 *m*, width 15	5.57 *ddd*, *J* = 7.8, 4.5, 3	5.4–5.9 *m*	5.4–5.9 *m*
HC-6	6.15 *m*, part. cov.	6.1 *m*, part. cov.	5.52 *dd*, *J* = 12.5, 3		
HC-6	6.42 *dd*, *J* = 12.5, 3	6.49 *dd*, *J* = 12.5, 4	5.89 *dd*, *J* = 12.5, 4.5		
MeO-2′	6.15 *s*	6.15 *s*	6.02 *s*	6.13 *s*	6.16 *s*
MeO-3″	6.19 *s*	6.20 *s*	6.08 *s*	6.02 *s*	—
MeO-4″	—	6.20 *s*	6.08 *s*	—	6.06 *s*
MeO-6″	—	—	—	—	6.16 *s*
AcO-8′	—	—	—	—	7.52 *s*
AcO-3″	—	—	—	—	7.67 *s*
AcO-4″	—	—	—	7.67 *s*	—
AcO-6	—	—	7.86 *s*	7.90 *s*	7.92 *s*

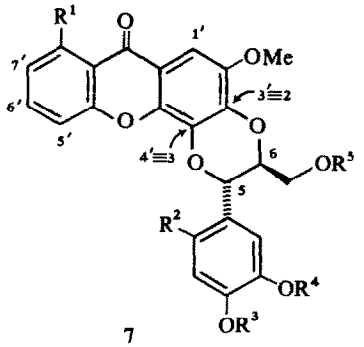
2,3,4-oxygenation is reasonable, and was confirmed by de-etherification of the compound to 2,3,4-trihydroxyxanthone, identified by direct comparison of its triacetate and tri-Me ether with authentic samples [4]. The stability of the OMes, expressed in terms of relative stability of the M^+, M^+-15 and M^+-30 peaks in the MS [10], excludes OMe from the 4-position, and kielcorin may consequently be represented by one of the alternative structures **7a** or **8a**. The *trans*-relation of the dioxane protons was deduced from their axial–axial coupling constant, and the *para*-relation of the phenolic OH with respect to the side chain by a negative Gibbs test [14].

The xanthone OH of the cadensins must occupy the 8–position (UV $AlCl_3$-shifts), and this immediately suggests the alternative structures **7e** or **8e** for cadensin*A* and **7f** or **8f** for cadensin*B* in view of their co-occurrence with **6** (Table 1). Indeed, the UV spectra of **6** (λ_{max} 236, 260, 315, 379 nm [10]) and of the cadensins (λ_{max} 236, 256, 321, 374 nm) are closely comparable and, by the argument expounded above, the xanthone OMe cannot be located at C-4.

No PMR spectra of cadensin*A* are available and the assignment of the OH and OMe groups respectively to positions 3″ and 4″ of the aryl unit is speculative. It may explain the introduction of an additional oxy–group into the 2″–position of cadensin*B*.

The choice between the alternatives **7** and **8** is as difficult [15] in the case of the three xanthonolignoids, as it was in the case of the three previously reported natural benzodioxanes silybin (**9**) [16], where the problem was solved by synthesis [17], eusiderin (**10a**) [18] and eusiderin*B* (**10b**), where the problem was solved by lanthanide induced PMR shifts [19].

The negative contribution of C-3 to the optical rotation of silybin (**9**) was interpreted in terms of the 3R-configuration, following, in view of the *trans*-arrangement of the hydrogens ($J_{Hax\text{-}2,Hax\text{-}3}$ 8 Hz), the 2R-configuration [16]. By the same arguments, dextrorotatory kielcorin should possess the 5S,6S-configuration and thus becomes (5S,6S)-6(or 5)-hydroxymethyl-5(or 6)-(4″-hydroxy-3″-methoxyphenyl)-2,3:3′,4′-(2′-methoxyxanthone)-1,4-dioxane.



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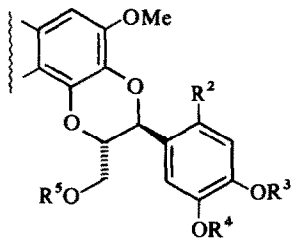
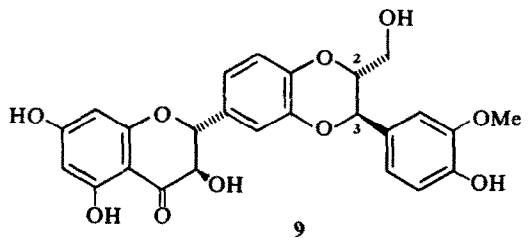


8

	R^1	R^2	R^3	R^4	R^5
a	H	H	H	Me	H
b	H	H	Me	Me	H
c	H	H	Me	Me	Ac
d	H	H	Ac	Me	Ac
e	OH	H	Me	H	H
f	OH	OMe	Me	H	H
g	OAc	OMe	Me	Ac	Ac



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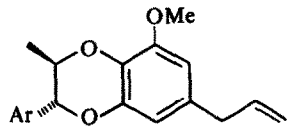
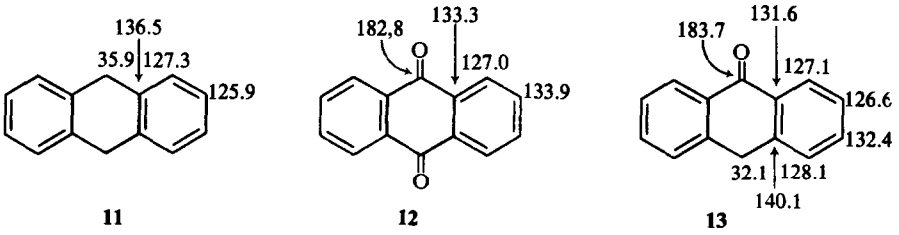


10a Ar = 3,4,5-trimethoxyphenyl
10b Ar = 3,4-methylenedioxyphenyl

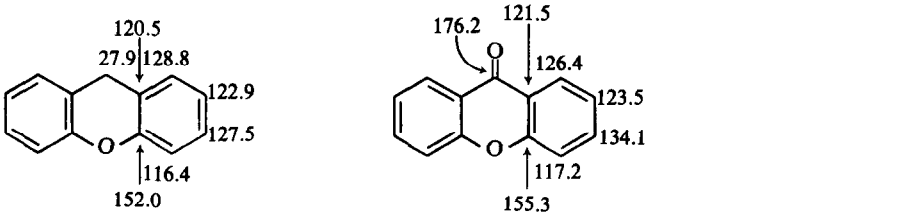
A 60 MHz PMR spectrum of cadensin*B* triacetate (Table 3), while confirming, in comparison with standard spectra [13], the postulated substitution pattern of the xanthone part, revealed an unexpected substitution pattern for the aryl group. Its two protons, giving rise to singlets, must keep the *para*-relationship. The values of the corresponding frequencies are in slightly better accord with calculated values for 5-acetoxy-2,4-methoxyphenyl than for the two additional isomeric forms.

^{13}C *NMR spectroscopy of xanthones*

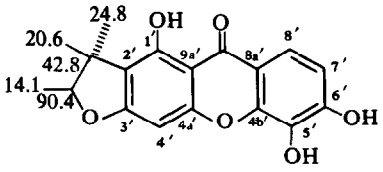
In order to facilitate the ^{13}C NMR analysis of xanthone containing natural products, it is useful to ascertain the carbon shifts of the parent compound. They are unknown, even though those of a few natural xanthones have been reported [20]. The interpretation of the spectra of xanthone (**15**) depends on the shift analysis of the structurally related tricycles anthrone (**13**) and xanthene (**14**) [21].



11 12 13



14 15



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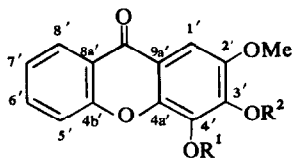
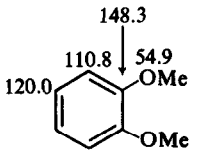


17a $R^1 = R^2 = Me$
17b $R^1 = H$, $R^2 = Me$
17c $R^1 = Me$, $R^2 = H$



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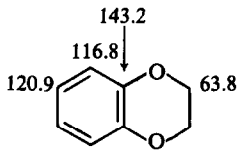

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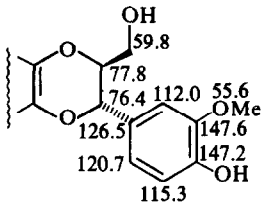

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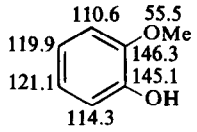

21

The chemical shifts of 9,10-dihydroanthracene (**11**) [21] and anthraquinone (**12**) and the expected shift invariance of an aromatic carbon on modification of its *meta*-substituent yield the shift assignment of anthrone (**13**). The designation of the methine shifts is confirmed by a correlation of carbon and hydrogen shifts [22] and the known low-field position of the aromatic proton *peri* to the carbonyl group. The 2 non-protonated aromatic carbon signals are differentiated by the weaker intensity of the α-keto carbon in view of fewer hydrogens two bonds removed causing slower relaxation and the observation of two-bond coupling with the methylene protons in the signal of the other non-protonated carbon.* All carbon shifts of tricycles **11**–**15** are portrayed on the formulae.

The shift assignment of toxyloxanthone*C* (**16**) [24] is based on the shifts of xanthone (**15**), signal multiplicities from a single-frequency off-resonance decoupled (sford) spectrum and standard chemical shift theory [25]. The signals for C-7′ and C-8′ are differentiated in the sford spectrum by the low-field position of H-8′ (*vide supra*). The two methine signals at *ca* 90 ppm are distinguished by their one-bond carbon–hydrogen coupling in a gated (fully coupled) spectrum, ie J values of 168 and 150 Hz for C-4′ and the non-aromatic oxymethine, respectively.

*This shift assignment is identical to one presented in a recent study utilizing carbon–carbon couplings for the $^{13}C{=}O$ enriched compound [23].

Table 4. Carbon shifts (in δ values) of xanthones*†

	16	17a	17b	17c	7a or 8a
C-9a′	116.1	116.3	116.7	111.6	113.7
C-1′	165.0	100.4	95.5	99.8	96.4
C-2′	102.7	149.5	149.8	146.7	145.6
C-3′	157.8	147.7	142.1	149.1	139.4‡
C-4′	89.3	140.9	139.5	135.0	132.3
C-4a′	157.2‡	144.8	141.6	146.1	141.1‡
C-4b′	146.1	154.9	155.3	155.1	155.1
C-5′	132.4	117.6	118.0	117.8	117.9
C-6′	151.7	134.3	134.6	134.0	134.5
C-7′	113.1	123.7	123.8	123.7	124.1
C-8′	115.9	125.3	125.7	125.6	125.7
C-8a′	113.1	120.2	120.4	120.7	120.6
C=O	180.1	174.3	174.5	174.1	174.5
MeO-2′		55.8	55.7	55.8	55.6
MeO-3′		60.6‡	60.5		
MeO-4′		61.2‡		60.8	

*δ(TMS) = δ(d_6-DMSO) + 39.5 ppm. †Here, as well as text, the carbons of the xanthone systems of **16**, **17a**, **b**, **c** are numbered as for kielcorin (**7a** or **8b**) for the sake of consistency. ‡Signals in any vertical column may be interchanged.

The latter signal also shows unresolved interactions with the Me hydrogens. The gated spectrum is helpful in separating the oxyaromatic carbon signals into three groups. Carbons 4b′, 5′ and 6′ have one *meta*-hydrogen ($^3J_{CH}$ = 6–10 Hz), C-3′ and C-4a′ have an *ortho*-hydrogen ($^2J_{CH}$ = *ca* 4 Hz) and C-1′ is unmeasurably split by a *para*-hydrogen. As noted earlier [20], the carbonyl group is deshielded relative to that of xanthone due to the hydrogen bond with the 1-OH group. The shifts of the non-aromatic carbons of toxyloxanthone*C* are presented on formula **16** and those of the aromatic carbons in Table 4.

Since kielcorin (**7a** or **8a**) contains a 2,3,4-trioxyxanthone moiety, models **17** were investigated. The assignments of the aromatic carbon signals are based on xanthone (**15**) and are helped greatly by the use of long-range carbon–hydrogen coupling information, through decoupling of regions of the hydrogen spectrum [26]. The large *meta*-coupling, $^3J_{CH}$, and the interaction of a ring carbon with its OMe substituent can be observed and the signal of a methine *ortho* to another methine can be recognized by the appearance of second-order lines in the sford spectrum [26, 27]. The carbon shifts of models **17** are presented in Table 4.

Comparison of models **17** with each other shows that replacement of OMe substituent at C-3′ or C-4′ by a OH group causes shielding of the carbons *ortho* and *para* to the carbon under consideration, while the carbons *meta* to it change only slightly. This is due to steric inhibition to resonance of the OMe group by its two *ortho* substituents [28]. However the latter do not affect the conjugation of a OH group with the aromatic ring [29], eg the **17a** to **17b** transformation leaves C-9a′ unaffected, but causes shielding of C-1′ by *ca* 5 ppm; the **17a** to **17c** conversion leaves C-1′ the same, but induces *ca* 5 ppm shielding of C-9a′. The OMe carbon shifts constitute another useful diagnosis. The 2′-OMe group resonates at *ca* 56 ppm, while the signals of the 3′- and 4′-OMe functions, being *ortho*-disubstituted, appear at *ca* 61 ppm [28].

The carbon shift assignment of kielcorin (**7a** or **8a**) is based on models **17** and the use of coupling information (*vide supra*). The two oxymethines are distinguished in the sford spectrum by the shift positions of their hydrogen resonances (see Table 3). The carbon shifts are presented in Table 4 and on formula **20**.

Comparison of the ^{13}C NMR data for kielcorin with those of models **17** indicates the presence of the 2,3,4-trioxyxanthone moiety. Since both methoxycarbons resonate at 55.6 ppm, only C-2′ of the xanthone unit in **7** can be methoxylated, thus showing the linkage of the dioxane ring to be at C-3′ and C-4′. This result is confirmed by the C-1′ and C-9a′ shifts. *Both* are shielded relative to **17a**, indicating that substituents at both *para* positions, ie, C-3′ and C-4′, show no steric inhibition to resonance. This rules out a phenolic OH group at only one of the locations and is in accord with a heterocycle whose two oxygens are in full conjugation with the benzene ring. The closeness of the shifts of the carbons *para* to the oxygens in models **18** and **19** indicates that the dioxane ring introduces only minimal changes at the sterically unperturbed carbon sites.

Decoupling of the aromatic hydrogens leaves the signals of C-3′ and C-4′ as singlets, indicative of their only weak coupling with H-5 and H-6. Therefore the latter are perpendicular to the plane of the xanthone unit, ie, in a *trans*-diaxial relationship in accord with the above J_{HH} result. Further support of this argument comes from the shifts of C-5, C-6 and the 6-hydroxymethyl group. They are in good agreement with those of eusiderin (**10a**) [30] after addition of the expected effect of the OH group on the three carbons.

The gauche interaction between the hydroxymethyl unit and the aryl group is reflected also in the chemical shift of C-1″, which is only 6.6 ppm to lower field than the corresponding carbon in guaiacol (**21**) [31]. The α-effect of the dioxane ring would be expected to be considerably larger, eg the isopropyl group shielding *ipso* carbon of isopropylbenzene by 20.1 ppm [32]. The 3″-OH and 4″-OMe substitution pattern of the remaining aromatic ring is inferred by the similarity of the shifts with those of guaiacol (**21**) as well as by carbon–hydrogen coupling information, eg the methoxycarbon shows only one *meta*-hydrogen and therefore must be located *meta* to the dioxanyl substituent.

EXPERIMENTAL

^{13}C NMR spectra were obtained on a spectrometer operating at 25.2 MHz in the Fourier transform mode. The shifts denoted on formulae **12**, **13**, **15**, **18**, **19** and **21** are from $CDCl_3$ solns; δ(TMS) = δ($CDCl_3$) + 76.9 ppm.

*Isolation of cadensin*A *and* B. The mother-liquors of A_4 and B_4 [10] gave, by TLC (Si gel) 7 (or **8**)**e** and 7 (or **8**)**f**.

Kielcorin. 7 (or **8**)**e**, slightly yellow, mp 250–251° (EtOH) [Found: C, 66.05; H, 4.62. $C_{24}H_{20}O_8$ requires: C, 59.95; H, 4.67%]. λ_{max}^{EtOH} (nm): 239, 286, 318 (ε 42300, 10800, 16100); $\lambda_{max}^{EtOH+NaOH}$ (nm): 257, 292, 318 (ε 48600, 14100, 17100). ν_{max}^{Nujol} (cm^{-1}): 3320, 1636, 1611, 750. MS: Table 2. PMR: Table 3. $[\alpha]_{400}^{dioxan}$ +300°, $[\alpha]_{300}^{dioxan}$ +1200°. *Me ether*, 7 (or **8**)**b**, obtained by treatment of kielcorin with Me_2SO_4, K_2CO_3, Me_2CO under reflux, mp 269–270° (EtOH) [Found: C, 66.55; H, 4.85. $C_{25}H_{22}O_8$ requires: C, 66.66; H, 4.92%]. λ_{max}^{EtOH} (nm): 240, 285, 315 (ε 43200, 10800, 16200). MS: Table 2. PMR: Table 3. *Me ether acetate*, 7 (or **8**)**c**, obtained by treatment of the Me ether with

Ac_2O–C_5H_5N at 100°, mp 265–268°. ν_{max}^{Nujol} (cm^{-1}): 1748, 1639, 1623, 760. MS: Table 2. PMR: Table 3. *Diacetate*, **7** (or **8**)**d**, obtained by treatment of kielcorin with Ac_2O–C_5H_5N at 100°, mp 206–208° (EtOH). λ_{max}^{EtOH} (nm): 254, 280, 313 (ε 38000, 11000, 15800). ν_{max}^{Nujol} (cm^{-1}): 1765, 1725, 1635, 1610, 760. MS: Table 2. PMR: Table 3. *2,3,4-Trihydroxyxanthone*, obtained by refluxing kielcorin in C_6H_6 with $AlCl_3$, was partly acetylated and partly methylated. The triacetate and tri-Me ether were identified by direct comparison with authentic samples [4].

*Cadensin*A. **7** (or **8**)**e**, yellow needles, mp 264–267° (EtOH) [Found: C, 63.51, H, 4.42. $C_{24}H_{20}O_9$ requires: C, 63.72, H, 4.46%]. λ_{max}^{EtOH} (nm): 233, 256, 321, 374 (ε 39000, 43000, 17300, 9600), $\lambda_{max}^{EtOH+NaOH}$ (nm): 251, 285, 400 (ε 47400, 26900, 11800), $\lambda_{max}^{EtOH+AlCl_3}$ (nm): 234, 264, 336 (ε 42400, 31700, 22600, 17500). Gibbs test positive λ_{max} (nm): 680 (A 0.835). ν_{max}^{KBr} (cm^{-1}): 3570, 1639, 1587, 1449, 1399, 1282. MS: Table 2.

*Cadensin*B. **7** (or **8**)**f**, yellow, mp 236–238° (insol in common solvents) [Found: C, 62.39, H, 4.58. $C_{25}H_{22}O_{10}$ requires: C, 62.24; H, 4.60%]. λ_{max}^{EtOH} (nm): 256, 321, 371 (ε 39500, 15000, 7500), $\lambda_{max}^{EtOH+AlCl_3}$ (nm): 236, 264, 288, 336 (ε 36500, 27000, 16600, 14200). ν_{max}^{KBr} (cm^{-1}): 3450, 1639, 1587, 1515, 1471, 1449. MS: Table 2.

Triacetate. **7** (or **8**)**g**, obtained by treatment of cadesin*B* with Ac_2O–C_5H_5N at 100°. PMR: Table 3.

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