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# CORDIACHROMES FROM *AUXEMMA ONCOCALYX*

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**Key Word Index**—*Auxemma oncocalyx*; Boraginaceae; wood; cordiachromes; spectral data.

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**Abstract**—Further cordiachromes, *rel*-10α,11β-epoxy-11α-ethoxy-8α-hydroxy-2-methoxy-8aβ-methyl-5,6,7,8,8a,9,10aβ-octahydro-1,4-anthracendione, 6-formyl-2-methoxy-9-methyl-7,8-dihydro-1,4-phenanthrendione, *rel*-8α,11α; 9α,11α-diepoxy-1,4-dihydroxy-2-methoxy-8aβ-methyl-5,6,7,8,8a,9,10,10aβ-octahydro-10-anthracenone, *rel*-9α,11α-epoxy-1,4,8α-trihydroxy-2-methoxy-8aβ-methyl-5,6,7,8,8a,9,10,10aβ-octahydro-10-anthracenone, *rel*-2″-methoxy-7″-methyl-1″,4″-naphtalendione-(6″ → 5)-tetrahydropyran-(2-eq → *O* → 2ax)-tetrahydropyran-(5′ → 6‴)-2‴-methoxy-7‴-methyl-1‴,4‴-naphthalendione, together with the known, allantoin, sitosterol and 3β-*O*-D-glucopyranosylsitosterol, have been isolated from *Auxemma oncocalyx*. Their structures were determined from spectral data, including 2D NMR experiments.

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## INTRODUCTION

In an earlier paper, we reported the isolation of the two new cordiachromes, **1** and **2** [1]. In this paper, we describe the isolation of a further five new cordiachromes from the same ethanolic extract of the wood of *Auxemma oncocalyx*. The structures of these natural products were deduced on the basis of spectral data, including 2D NMR experiments: $^1$H–$^1$H-COSY and $^1$H–$^{13}$C-COSY-$^nJ_{CH}$ ($n = 1$; $n = 2$ and 3, COLOC), and NOE difference spectra.

## RESULTS AND DISCUSSION

The known natural products, allantoin (**16**), sitosterol (**17**) and 3β-*O*-β-D-glucopyranosylsitosterol (**18**), were identified mainly by their $^1$H and $^{13}$C NMR spectral data, including the acetyl derivative **18a**, and comparison with literature data (**17** and **18**) [2].

The heteronuclear $^1$H–$^{13}$C-COSY-$^nJ_{CH}$ ($n = 2$ and 3, COLOC) 2D shift-correlated NMR spectra [3] of the cordiachrome **1**, and its derivative **1a**, were used to re-examine the assignments of the chemical shifts of the carbon atoms [1]. These experiments allowed to assign unambiguously the chemical shifts of C-5 ($\delta_C$ 146.4) and C-10a ($\delta_C$ 135.1) of **1** along with C-4a ($\delta_C$ 135.7), C-5 ($\delta_C$ 130.4), C-9a ($\delta_C$ 132.7 and C-10a ($\delta_C$ 144.1) of **1a**. Thus, our attributions described in the literature, **1**: $\delta_C$ 135.1 (C-5) and 146.4 (C-10a); **1a**: $\delta_C$ 132.7 (C-4a), 144.1 (C-5), 130.4 (C-9a) and 135.7 (C-10a) [1], were corrected.

Comparative analysis of the proton noise-decoupled (PND) and distortionless enhancement by polarization transfer (DEPT) [3] $^{13}$C NMR spectra, in combination with the $^1$H NMR (one- and two-dimensional $^1$H–$^1$H-COSY), IR [$\nu$ 3500 (OH), 1640, 1600 (conjugated carbonyl) cm$^{-1}$] and mass spectra ([M$^+$] absent $m/z$ 348) and peak at $m/z$ 303 (8%, [M − OCH$_2$CH$_3$]$^+$), allowed the deduction of the molecular formula $C_4O(C=O)_2(CH)_6(CH_2)_3(CH_3)(OMe)(OEt)(OH)$ for compound **3**. This molecular formula ($C_{19}H_{24}O_6$) requires eight degrees of unsaturation: two carbonyl groups [$\delta_C$ 182.7 (C-1) and 186.6 (C-4)], one C=CH [$\delta_C$ 158.3 (C-2) and 107.7 (C-3)], one C=C [$\delta_C$ 138.7 (C-4a) and 138.0 (C-9a)] and four cyclic systems (Table 1). The presence of a 2-methoxy-*para*-quinone moiety was revealed by the chemical shifts for H-3 [$\delta_H$ 5.85 (*s*)] and for the carbon atoms C-1 to C-4a [$\delta_C$ 182.7 (*s*, C-1), 158.3 (*s*, C-2), 107.7 (*d*, C-3), 186.6 (*s*, C-4), 138.7 (*s*, C-4a)] and C-9a [$\delta_C$ 138.0 (*s*)] by comparison with the values for the analogous cordiachrome **2** [1]. This deduction, the characterization of an ethoxy group [$\delta_C$ 63.0 (*t*, OCH$_2$) and 15.0 (*q*, CH$_3$); $\delta_H$ 3.78, 3.34 (*m*, *m*, OCH$_2$) and 1.08 (*t*, $J = 7.0$ Hz, CH$_3$), confirmed by homonuclear 2D $^1$H–$^1$H-COSY which clearly showed both the couplings between the methylene hydrogens and of these with the methyl group], and additional comparison of the remaining signals of **3** with the corresponding values of **2** (Table 1), allowed us establish the constitution of compound **3**, which may be an artifact formed probably from **4** during the extraction of

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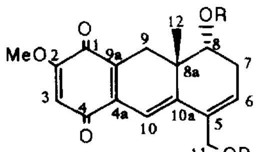
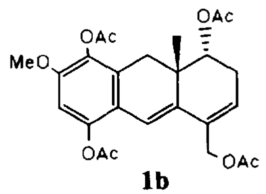


**1** R=H
**1a** R=Ac



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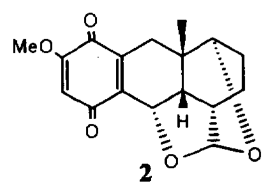

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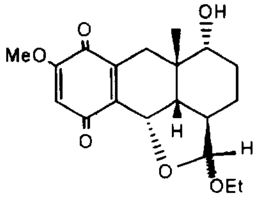

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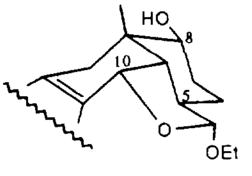
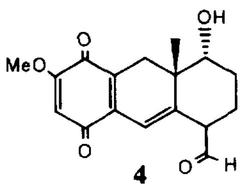


**3a**



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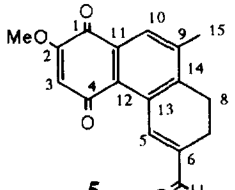

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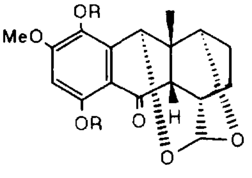
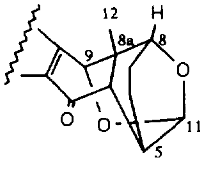
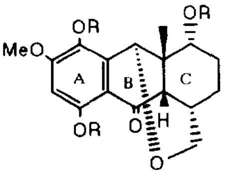


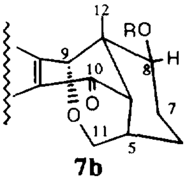
**6** R=H
**6a** R=Ac



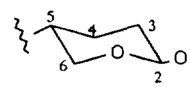
**6b**



**7** R=H
**7a** R=Ac



**7b**



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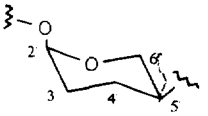

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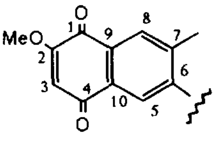
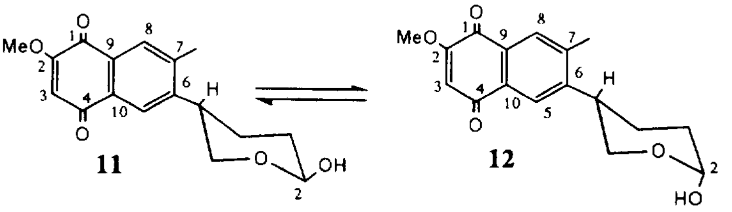


**10**

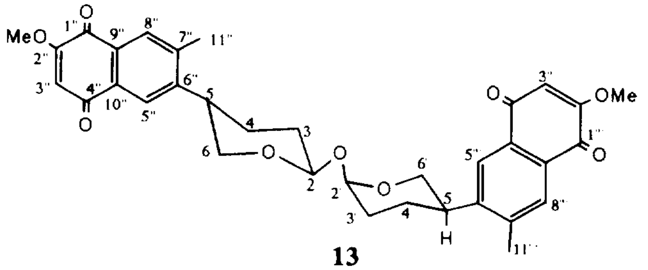
the material with ethanol. This constitution was confirmed by homonuclear $^1H$–$^1H$-COSY (spin–spin couplings) and heteronuclear $^1H$–$^{13}C$-COSY-$^nJ_{CH}$ ($n = 1$, coupling between C-13 and hydrogen atoms via one bond; $n = 2$ and 3, COLOC = correlation via long-range couplings) 2D shift-correlated NMR spectra [3], which were also used for the assignments together with the application of the usual parameters and the observed multiplicities of the signals of the carbon atoms deduced by comparative analysis of the PND- and DEPT-$^{13}C$ NMR spectra (Table 1).

The relative configuration at the chiral carbon atoms, C-5, C-8, C-8a, C-10, C-10a and C-11 of **3**, were deduced on the basis of the coupling constant data of H-8 ($J = 11.0$ Hz) signal which is consistent with the existence of an axial–axial (HO-8 equatorial) interaction of this hydrogen atom; resulting signal enhancements obtained by $^1H\{^1H\}$-NOE difference spectra are shown in Table 2. Thus, the structure of the new cordiachrome derivative was established as *rel*-10α,11β-epoxy-11α-ethoxy-8α-hydroxy-2-methoxy-8aβ-methyl-5α,6,7,8,8a,9,10aβ-octahydro-1,4-anthracendione (**3**).

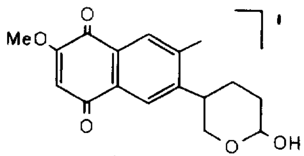
The molecular formula $C_7(C=O)_2(HC=O)(CH)_3(CH_2)_2(CH_3)(OMe)$ $[M]^+$ at $m/z$ 282 (23%) in the EI mass spectrum of **5** was deduced by a procedure (Table 3) analogous to that used for compound **3** (Table 1). This molecular formula ($C_{17}H_{14}O_4$) requires 11 ($C_{17}H_{36}O_4$-$C_{17}H_{14}O_4$ = $H_{22}$) degrees of unsaturation: two carbonyl ketone groups [$\delta_C$ 180.1 (C-1) and 187.4 (C-4), attributed to a *para*-quinone moiety], one aldehyde function [$\delta_C$ 193.6 (C-16)], three C=CH [$\delta_C$ 159.0 (C-2) and 111.7 (C-3); 125.4 (C-6) and 143.1 (C-5); 141.7 (C-9) and 130.5 (C-10)], two C=C [$\delta_C$ 130.3 (C-11) and 145.1 (C-12); 132.4 (C-13) and 141.4 (C-4)] and three cyclic systems of a formyl-methoxyanthracendione or formyl-methoxy-methylphenanthrendione (Table 3). The chemical shift of



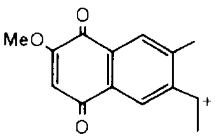
**11** **12**



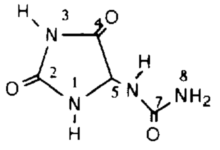
**13**



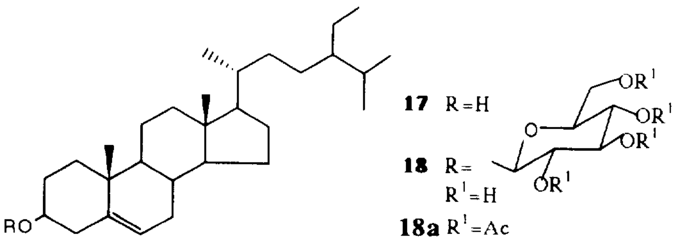
**13, m/z** 302(33 %)



**15, m/z** 229(100 %)



**16**



**17** R=H

**18** R= R'=H

**18a** R'=Ac

the methyl group [$\delta_H$ 2.42 (*s*, 3H-15)] observed in the $^1$H NMR spectrum implies that this substituent is bound to the aromatic ring. Homonuclear $^1$H {$^1$H}-NOE difference spectra performed with specific resonance at this methyl group showed enhancements (Table 3) in the signals corresponding to 2H-8 ($\delta_H$ 2.83, NOE = 7%) and H-10 ($\delta_H$ 7.99, NOE = 6%). These data, in combination with the presence of four singlet signals ($\delta_H$ 9.78 (H-16), 8.78 (H-5), 7.99 (H-10) and 6.09 (H-3)) and two methylene groups spin–spin coupled ($\delta_H$ 2.83 (*t*, *J* = 8.2 Hz, 2H-8) and 2.52 (*t*, *J* = 8.2 Hz, 2H-7) in the $^1$H NMR spectrum, were only justified by the presence of a phenanthrendione skeleton; thus, the anthracendione skeleton alternative was ruled out. This deduction was confirmed by the observed multiplicities of the signals of the carbon atoms (PND- and DEPT-$^{13}$C NMR), homonuclear $^1$H–$^1$H-COSY (spin–spin couplings) and heteronuclear $^1$H–$^{13}$C-COSY-$^nJ_{CH}$ ($n = 1$; $n = 2$ and 3, COLOC) 2D shift-correlated NMR spectra and additional data from the $^1$H {$^1$H}-NOE difference spectra (Table 3). Thus, the structure was defined as 6-formyl-2-methoxy-9-methyl-1,4-phenanthrendione (**5**), a new natural product with a phenanthrene skeleton.

Spectral comparison of **6**, [M]$^+$ *m/z* 318 (100%), $C_{17}H_{18}O_6$ with nine degrees of unsaturation) and **7**, [M]$^+$ *m/z* 320 (17%), $C_{17}H_{20}O_6$ with eight degrees of unsaturation, in combination with their acetyl derivatives **6a** [two acetyl groups: $\delta_H$ 2.36 (*s*) and 2.32 (*s*); $\delta_C$ 169.2 (*s*), 168.7 (*s*), 21.2 (*q*) and 20.4 (*q*)] and **7a** [three acetyl groups: $\delta_H$ 2.35 (*s*, AcO + AcO) and (2.01 (*s*); $\delta_C$ 170.5 (*s*), 169.4 (*s*), 168.4 (*s*), 21.1 (*q*, Me + Me), 20.4 (*q*)], allowed us to deduce that the major distinction between the two natural products was the presence of an additional epoxy function in **6**, localized between CH-8 [$\delta_H$ 3.92 (*d*, *J* = 5.2 Hz); $\delta_C$ 74.2 (*d*)] and CH-11 [$\delta_H$ 5.03 (*d*, *J* = 4.8 Hz); $\delta_C$ 95.3 (*d*)] (Table 4). The $^1$H–$^1$H-COSY showed the respective coupling of H-5 [$\delta_H$ 2.52 (**6**) and 1.95 (**7**)] to *n*H-11 [$\delta_H$ 5.03 (**6**, $n = 1$) and to 3.69 and 3.55 (**7**, $n = 2$, methylene group)] and of H-8 [$\delta_H$ 3.92 (**6**) and 3.58 (**7**, shift downfield in **7a** by 1.55 ppm as anticipated)]

Table 1. $^1H$ (200 MHz) and $^{13}C$ (50 MHz) spectral data for compound **3**, compared with values described for **2** [1], in $CDCl_3$

| | **3** | | | | **2** | |
|---|---|---|---|---|---|---|
| | $^1H$–$^{13}C$-COSY-$^1J_{CH}$ | | $^1H$–$^{13}C$-COSY-$^nJ_{CH}$ | | | |
| | $\delta_C$ | $\delta_H$ | $^2J_{CH}$ | $^3J_{CH}$ | $\delta_C$ | $\delta_H$ |
| C | | | | | | |
| 1 | 182.7 | | | H-3, H-9 | 181.2 | |
| 2 | 158.3 | - | H-3 | MeO-2 | 158.7 | |
| 4 | 186.6 | — | H-3 | | 185.1 | |
| 4a | 138.7 | — | H-10 | H-3, H-9, H-10a | 143.1 | |
| 8a | 37.3 | — | H-9, 3H-12 | | 37.0 | |
| 9a | 138.0 | — | H-9 | | 137.3 | |
| CH | | | | | | |
| 3 | 107.7 | 5.85 (*s*) | | | 106.9 | 5.90 (*s*) |
| 5 | 43.0 | 1.4 (*m*) | | | 37.8 | 2.2 (*m*) |
| 8 | 76.9 | 3.46 (*dd*, *J* = 11.0, 5.6) | | | 74.2 | 3.49 (*br s*) |
| 10 | 70.6 | 5.06 (*d*, *J* = 7.8) | H-10a | H-11 | 68.5 | 4.96 (*d*, *J* = 3.0) |
| 10a | 46.0 | 2.12 (*dd*, *J* = 12.2, 7.8) | H-6 | H-9, 3H-12 | 46.4 | 1.8 (*m*) |
| 11 | 102.9 | 4.78 (*d*, J = 4.0) | | | 100.5 | 5.34 (*d*, *J* = 3.6) |
| $CH_2$ | | | | | | |
| 6 | 22.1 | 1.7 (*m*, H-6e)<br>1.4 (*m*, H-6a) | | | 20.4 | 1.8 (*m*) |
| 7 | 30.6 | 1.9 (*m*, H-7e)<br>1.5 (*m*, H-7a) | | | 15.5 | 1.8 (*m*) |
| 9 | 23.7 | 2.41 (*d*, *J* = 19.6, H-9e)<br>2.27 (*d*, *J* = 19.6, H-9a) | | | 31.4 | 2.70 (*d*, *J* = 17.6, H-9a)<br>2.60 (*d*, *J* = 17.6, H-9e) |
| $CH_3$ | | | | | | |
| 12 | 23.7 | 0.97 (*s*) | | | 28.3 | 1.02 (*s*) |
| MeO-2 | 56.1 | 3.7 (*s*) | | | 56.2 | 3.80 (*s*) |
| EtO-11 | 63.0 | 3.78 (*m*)<br>3.34 (*m*) | | | — | — |
| | 15.0 | 1.08 (*t*, *J* = 7.0) | | | — | — |

*Multiplicity of signals of carbon atoms deduced by comparative analysis of PND- and DEPT-$^{13}C$ NMR. Homonuclear $^1H \times {}^1H$-COSY 2D NMR was also used for these assignments. Chemical shifts and coupling constants (*J*) of the hydrogen atoms were obtained from the $^1H$ NMR spectrum. Chemical shifts with one decimal correspond to approximate values obtained by $^1H$–$^{13}C$-COSY-$^1J_{CH}$.

Table. 2. Data of $^1H\{^1H\}$-NOE difference spectra for compound **3**

| $^1H$ (Irradiated) | | NOE enhancements | | |
|---|---|---|---|---|
| H | $\delta_H$ | H | $\delta_H$ | % |
| MeO-2 | 3.72 | 3 | 5.85 | 9 |
| 12 | 0.97 | 8ax | 3.46 | 5 |
| | | 9eq | 2.41 | 4 |
| | | 10 | 5.06 | 2 |
| | | 10aax | 2.12 | 7 |
| 11 | 4.78 | 13b | 3.34 | 8 |
| 13a | 3.78 | 13b | 3.34 | 15 |
| | | 11 | 4.78 | 3 |
| 13b | 3.34 | 13a | 3.78 | 18 |
| | | 11 | 4.78 | 11 |
| | | 14 | 1.08 | 12 |
| 10 | 5.06 | 10a | 2.12 | 8 |

to 2H-7 [$\delta_H$ 2.1–1.7 (**6**) and 2.50, 2.10 (**7**)]. The chemical shifts of the hydrogen and carbon atoms of the oxymethine group at CH-9 are practically identical: $\delta_H$ 5.42 (**6**) and 5.40 (**7**); $\delta_C$ 67.5 (**6**) and 67.5 (**7**) (Tables 4 and 5). These data were used to confirm the presence of one epoxy function between the carbon atoms C-9 and C-11 (**6** and **7**) and of one hydroxyl group at C-8 of **7**, which was shifted downfield by 1.15 ppm ($\Delta\delta_H$ = 4.73–3.58) in the triacetate **7a** (Table 5). The five remaining degrees of unsaturation (**6** and **7**) were ascribed to one carbonyl group [$\nu$ 1625 (**6**) and 1620 cm$^{-1}$ (**7**); $\delta_C$ 204.1 (**6**) and 204.1 (**7**)] and one aromatic ring [$\nu$ 1600, 1495 cm$^{-1}$ (**6**) and 1600, 1495 cm$^{-1}$ (**7**); $\delta_C$ 158.3 (*s*), C-4), 154.3 (*s*, C-2), 135.8 (*s*, C-1), 123.6 (*s*, C-9a), 107.6 (*s*, C-4a) and 99.0 (*d*, C-3) of **6**; 157.4 (*s*, C-4), 155.2 (*s*, C-2), 136.5 (*s*, C-1), 121.1 (*s*, C-9a), 110.4 (*s*, C-4a) and 99.2 (*d*, C-3) of **7**]. The localization of the carbonyl group at C-10, involved in a chelatogenic system with a hydroxyl function at C-4 [$\delta_H$ 11.92 (*s*, **6**) and 12.30 (*s*, **7**)], was based on the

Table 3. $^1H$ (200 MHz) and $^{13}C$ (50 MHz) NMR spectral data for compound **5** in $CDCl_3$*

| | $^1H$–$^{13}C$-COSY-$^1J_{CH}$ | | $^1H$–$^{13}C$-COSY-$^nJ_{CH}(n = 2,3)$ | | $^1H\{^1H\}$-NOE† |
|---|---|---|---|---|---|
| | $\delta_C$ | $\delta_H$ | $^2J_{CH}$ | $^3J_{CH}$ | Enhancements (%) |
| C | | | | | |
| 1 | 180.1 | — | | H-3 | |
| 2 | 159.0 | — | | MeO-2 | |
| 4 | 187.4 | — | | | |
| 6 | 125.4 | — | | | |
| 9 | 141.7 | — | 3H-15 | | |
| 11 | 130.3 | — | | | |
| 12 | 145.1 | — | | | |
| 13 | 132.4 | | | | |
| 14 | 141.4 | — | | 2H-7 | |
| CH | | | | | |
| 3 | 111.7 | 6.09 (*s*) | | | |
| 5 | 143.1 | 8.78 (*s*) | | | H-16 (20) |
| 10 | 130.5 | 7.99 (*s*) | | 3H-15 | 3H-15 (9) |
| 16 | 193.6 | 9.78 (*s*) | | | H-5 (22) |
| $CH_2$ | | | | | |
| 7 | 17.6 | 2.52 (*t*, $J = 8.2$) | | | 2H-8 (6), H-16 (1) |
| 8 | 24.5 | 2.83 (*t*, $J = 8.2$) | | | 2H-7 (10), H-15 (8) |
| $CH_3$ | | | | | |
| 15 | 20.5 | 2.42 (*s*) | | | 2H-8 (7), H-10 (6) |
| MeO-2 | 56.4 | 3.88 (*s*) | | | H-3 (9) |

*Multiplicity of signals of carbon atoms deduced by comparative analysis of PND- and DEPT-$^{13}$C NMR. Homonuclear $^1H$–$^1H$-COSY 2D NMR was also used for these assignments. Chemical shifts and coupling constants (*J*) of hydrogen atoms obtained from $^1$H NMR.

†Results obtained by $^1$H NMR difference spectra with specific irradiation of the hydrogens which appear in the same line.

spin–spin interaction of this carbon atom ($\delta_C$ 204.1) with hydrogen H-10a [$\delta_H$ 2.21 (**6**)] and C-9 ($\delta_C$ 67.5) with H-10a ($\delta_H$ 2.21) and 3H-12 ($\delta_H$ 0.82) observed in 2D-$^1H$–$^{13}C$-COSY-$^nJ_{CH}$ ($n = 2$ and 3) NMR spectrum (Table 4), which was also used in the assignments of the chemical shifts of the hydrogen and carbon atoms and to define the presence of a hydrogen atom at C-3 (*ortho*-position) by long-range coupling ($^3J_{CH}$) between C-4a ($\delta_C$ 107.6) and H-3 ($\delta_H$ 6.34), H-9 ($\delta_H$ 5.42) and HO-4 ($\delta_H$ 11.92) and, consequently, to establish the constitutions of **6** and **7** and their acetyl derivatives (**6a** and **7a**). The modifications observed in the comparative analysis of the $^1$H and $^{13}$C NMR spectra of **6** and **6a**, restricted to the aromatic ring and carbonyl group due to the disappearance of the chelatogenic system by acetylation of the hydroxyl group at C-4, (for **6** and **7** plus at C-8 for **7**), are in accordance with the prediction based on the electronic-[C-1 to C-4a, C-9a and C-10 and H-3 (**6** → **6a** and **7** → **7a**), *β*-(carbonyl carbon atom of the acetoxyl group at C-8 (**7** → **7a**), mesomeric and inductive effects of the carbonyl of the acetoxyl group (by greater electronegativity of the oxygen atom)) and *γ*-effects (methyl and oxygen atom of the carbonyl function of the acetoxyl group at C-8a [$\Delta\delta_C = 37.3$ (**7a**) $- 38.9$ (**7**) $= -1.6$ ppm] and C-7 [$\Delta\delta_C = 27.1$ (**7a**) $-31.0$ (**7**) $= -3.9$ ppm] (Tables 4 and 5) [4, 5].

The relative configurations at the chiral carbon atoms, C-5, C-8, C-8a, C-9, C-10a and C-11, of **6** were assigned on the basis of $^1H\{^1H\}$-NOE difference spectra: (a) irradiation at $\delta$2.52 (H-5) resulted in 3% NOE at $\delta$2.21 (H-10a) and 12% NOE at $\delta$5.03 (H-11); (b) irradiation at $\delta$3.92 (H-8) showed 8% NOE at $\delta$5.42 (H-9) and 6% NOE at $\delta$0.82 (3H-12); (c) irradiation at $\delta$5.42 (H-9) revealed 5% NOE at $\delta$3.92 (H-8) and 2% NOE $\delta$0.82 (3H-12); (d) irradiation at $\delta$5.03 (H-11) resulted in 9% NOE at $\delta$2.52 (H-5); (e) irradiation at $\delta$0.82 (3H-12) furnished 4% NOE at 3.92 (H-8), 3% NOE at $\delta$5.42 (H-9) and 4% NOE at $\delta$2.21 (H-10a); (f) irradiation at $\delta$3.88 (MeO-2) induced 7% NOE at $\delta$6.34 (H-3) (Table 4). These data are consistent with the stereochemistry shown in **6b** and the structure of this new cordiachrome was established as *rel*-1,4-dihydroxy-9α,11α;8α,11α-diepoxy-2-methoxy-8a*β*-methyl-5,6,7,8,8a,9,10,10a-octahydro-10-anthracenone (**6**).

The location of the hydroxyl group at C-8 of **7** in the equatorial position was deduced on the basis of the *J*-value (11.8 Hz) observed for the signal of the H-8 [$\delta_H$ 4.73 (*dd*, $J = 11.8$ and $J = 6.5$ Hz), shifted downfield $\Delta\delta_H = 4.73$ (**7a**) $-3.58$ (**7**) $= 1.15$ ppm] in the $^1$H NMR spectrum of the triacetate **7a** (Table 5). Thus, the stereochemistry shown in **7b** was defined and the structure of this new natural product was characterized as *rel*-1,4,8α-

Table 4. $^1H$ (200 MHz) and $^{13}C$ (50 MHz) NMR spectral data for compound **6**, and its acetate derivative **6a**, in $CDCl_3$*

| | 6 | | | | | | |
|---|---|---|---|---|---|---|---|
| | $^1H$–$^{13}C$-COSY-$^1J_{CH}$ | | $^1H$–$^{13}C$-COSY-$^nJ_{CH}$($n$ = 2,3) | | $^1H\{^1H\}$-NOE† | **6a** | |
| | $\delta_C$ | $\delta_H$ | $^2J_{CH}$ | $^3J_{CH}$ | Enhancements (%) | $\delta_C$ | $\delta_H$ |
| C | | | | | | | |
| 1 | 135.8 | — | HO-1 | H-3 | | 134.3 | — |
| 2 | 154.3 | — | H-3 | MeO-2, HO-1 | | 155.7 | — |
| 4 | 158.3 | — | H-3, HO-4 | | | 148.5 | — |
| 4a | 107.6 | — | | H-3, H-9, HO-4 | | 116.0 | — |
| 8a | 39.5 | — | 3H-12 | | | 39.6 | — |
| 9a | 123.6 | — | | HO-1 | | 135.1 | — |
| 10 | 204.1 | — | H-10a | | | 198.0 | — |
| CH | | | | | | | |
| 3 | 99.0 | 6.34 (*s*) | | HO-4 | | 107.2 | 6.61 (*s*) |
| 5 | 38.6 | 2.52 (*t*, *J* = 3.9) | | | H-10a (3), H-11 (12) | 39.8 | 2.58 (*t*, *J* = 3.9) |
| 8 | 74.2 | 3.92 (*d*, *J* = 5.2) | | 3H-12 | H-9 (8), 3H-12 (6) | 74.3 | 3.88 (*d*, *J* = 5.3) |
| 9 | 67.5 | 5.42 (*d*, *J* = 1.6) | | 3H-12, H-10a | H-8 (5), 3H-12 (2) | 68.5 | 5.04 (*d*, *J* = 1.7) |
| 10a | 48.6 | 2.21 (*d*, *J* = 1.2) | | 3H-12 | | 48.3 | 2.09 (*d*, *J* = 1.2) |
| 11 | 95.3 | 5.03 (*d*, *J* = 4.8) | | | H-5 (9) | 95.9 | 5.02 (*d*, *J* = 5.2) |
| $CH_2$ | | | | | | | |
| 6 | 20.2 | 2.1–1.7 (*m*) | | | | 20.3 | 2.0–1.5 (*m*) |
| 7 | 21.8 | 2.1–1.7 (*m*) | | | | 21.3 | 2.0–1.5 (*m*) |
| $CH_3$ | | | | | | | |
| 12 | 17.7 | 0.82 (*s*) | | | H-8 (4), H-9 (3), H-10a (4) | 17.7 | 0.77 (*s*) |
| MeO-2 | 56.3 | 3.88 (*s*) | | | H-3 (7) | 56.4 | 3.84 (*s*) |
| OR | — | | | | | 169.2 | |
| | | | | | | 168.7 | |
| | | 5.52 (*s*, HO-1) | | | | 21.2 | 2.36 (*s*, OAc) |
| | — | 11.92 (*s*, HO-4) | | | | 20.4 | 2.32 (*s*, OAc) |

*Multiplicity of signals of carbon atoms deduced by comparative analysis of PND- and DEPT-$^{13}C$ NMR. $^1H \times {}^1H$-COSY 2D NMR also used for these assignments. Chemical shifts and coupling constants ($J$) of hydrogen atoms obtained from $^1H$ NMR. Chemical shifts with one decimal correspond to approximate values obtained by $^1H$–$^{13}C$-COSY-$^1J_{CH}$.

†Results obtained by $^1H$ NMR difference spectra with specific irradiations of the hydrogens which appear in the same line.

trihydroxy-9α,11α-epoxy-2-methoxy-8a*β*-methyl-5,6,7,8,8a,9,10,10a-octahydro-1-anthracenone (**7**). As can be observed in the comparison between **6** and **7**, the hydroxyl group at C-8 of **7** has the same configuration as in **6** but the corresponding ring adopts a different conformation (boat in **6** and chair in **7**).

The IR spectrum of **13** showed absorption bands for a conjugated carbonyl (1680 cm$^{-1}$) group and an aromatic ring (1600, 1560 cm$^{-1}$). The 2D-$^1H$–$^1H$-COSY spectra, including one obtained on a 400 MHz spectrometer which allowed us to observe all *vicinal* and *geminal* spin–spin interactions of the hydrogen atoms of the heterocyclic rings, combined with the $^{13}C$ NMR (PND and DEPT) and heteronuclear 2D-$^1H$–$^{13}C$-COSY-$^1J_{CH}$ (coupling via one bond) spectra, were used to recognize the presence of two heterocyclic moieties containing carbon atoms directly bound to two oxygen atoms [**8**: $\delta_C$ 96.0 (*d*, C-2) and 69.4 (*t*, C-6); $\delta_H$ 4.89 (*br d*, *J* = 8.4 Hz, H-2 axial), 4.00 (*br d*, *J* = 12.8 Hz, H-6 equatorial) and 3.70 (*t*, *J* = 12.8 Hz, H-6 axial); **9**: $\delta_C$ 90.7 (*d*, C-2′) and 63.1 (*t*, C-6′); $\delta_H$ 5.31 (*br s*, H-2′ equatorial), 4.10 (*br d*, *J* = 10.7 Hz, H-6′ equatorial), 3.60 (*t*, *J* = 10.7 Hz, H-6′ axial)]. Thus, the attribution of the chemical shifts of the additional carbon and hydrogen atoms of these moieties was also carried out (Table 6). The possibility of a mixture of the epimers **11** and **12** was definitively ruled out by reaction with $Ac_2O$ in the presence of pyridine, which showed no formation of an acetyl derivative. The minor chemical shifts of the carbon atoms C-4′ ($\delta_C$ 23.4) and C-6′ ($\delta_C$ 63.1) of **9** when compared with the corresponding C-4 ($\delta_C$ 28.1) and C-6 ($\delta_C$ 69.4) of **8** revealed a γ-effect [$\Delta\delta_C$ = 23.4 (**9**) − 28.1 (**8**) = −4.7 ppm and $\Delta\delta_C$ = 63.1 (**9**) − 69.4 (**8**) = −6.3 ppm] attributed to an axial oxygen atom located at C-2′ (**9**). Obviously, the connection of these two moieties, **8** and **9**, can only be made through one oxygen atom (**13**).

The presence of two 2-methoxy-7-methyl-1,4-naphthalendione moieties, with an additional substituent at C-6 (**10**), was recognized by comparative analysis of the $^1H$ and $^{13}C$ NMR spectra of **13** (Table 6) and other cordiachromes described in this paper containing a *para*-quinone system with a methoxyl group at C-2 (e.g. **5**, Table 3) in combination with the following data: (a) two singlets corresponding to six isolated hydrogens bound to $sp^2$ carbon atoms [$\delta_H$ 7.92 (H-5‴), 7.82 (H-5″, H-8″ and H-8‴) and 6.07 (H-3″ and H-3‴)] when com-

Table 5. $^{1}H$ (200 MHz) and $^{13}C$ (50 MHz) NMR spectral data for compound **7**, and its derivative **7a**, in $CDCl_3$*

| | **7** | | **7a** | |
|---|---|---|---|---|
| | $\delta_C$ | $\delta_H$ | $\delta_C$ | $\delta_H$ |
| C | | | | |
| 1 | 136.5 | — | 132.2 | — |
| 2 | 155.2 | — | 156.9 | — |
| 4 | 157.4 | — | 148.6 | — |
| 4a | 110.4 | — | 117.6 | — |
| 8a | 38.9 | — | 37.3 | — |
| 9a | 121.1 | — | 135.6 | — |
| 10 | 204.1 | — | 196.2 | — |
| CH | | | | |
| 3 | 99.2 | 6.42 (*s*) | 107.7 | 6.66 (*s*) |
| 5 | 34.2 | 1.95 (*br s*) | 34.2 | 1.88 (*br s*) |
| 8 | 77.2 | 3.58† | 77.7 | 4.73 (*dd*, *J* = 11.8, 6.5) |
| 9 | 67.3 | 5.40 (d, *J* = 1.6) | 69.0 | 5.07 (*d*, *J* = 1.7) |
| 10a | 53.1 | 2.31 (*br s*) | 53.9 | 2.33 (*br s*) |
| $CH_2$ | | | | |
| 6 | 31.2 | 1.98 (*m*, H-6eq) | 30.4 | 2.0–1.6 (*m*) |
| | — | 1.82 (*m*, H-6ax) | — | 2.0–1.6 (*m*) |
| 7 | 31.0 | 2.50 (*m*, H-7eq) | 27.1 | 2.35 (*m*, H-7eq) |
| | — | 2.10 (*m*, H-7ax) | — | 1.95 (*m*, H-7ax) |
| 11 | 63.3 | 3.69 (*dd*, *J* = 12.2, 2.5) | 63.3 | 3.64 (*td*, *J* = 12.4, 2.8) |
| | — | 3.55 (*br d*, *J* = 12.2) | — | 3.50 (*br d*, *J* = 12.4) |
| $CH_3$ | | | | |
| 12 | 22.7 | 0.90 (*s*) | 22.5 | 0.76 (*s*) |
| MeO-2 | 56.3 | 3.93 (*s*) | 56.4 | 3.86 (*s*) |
| RO | — | | 170.5 | |
| | — | | 169.4 | |
| | | | 168.4 | |
| | — | 5.47 (*s*, HO-1) | 21.1 | 2.35 [*s*, $(OAc)_2$] |
| | — | 12.30 (*s*, HO-4) | 20.4 | 2.01 (*s*, OAc) |

*Multiplicity of signals of carbon atoms deduced by comparative analysis of PND- and DEPT-$^{13}C$ NMR $^{1}H$–$^{1}H$-COSY 2D NMR also used for these assignments. Chemical shifts of hydrogen atoms obtained from $^{1}H$ NMR. Chemical shifts with one decimal correspond to approximate values obtained by $^{1}H$–$^{13}C$-COSY-$^{1}J_{CH}$.

†Superimposed on signals of 2H-11.

pared with the intensities of the signals of H-2 [$\delta_H$ 4.89 (*d*, *J* = 8.4 Hz)] and H-2′ [$\delta_H$ 5.31 (*br s*)], which indicated the existence of substituents at C-6″, C-6‴, C-7″ and C-7‴; (b) pairs of signals attributed to carbon atoms C-5″ [$\delta_C$ 123.5 (*d*)] and C-5‴ [$\delta_C$ 123.9 (*d*)], C-6″ [$\delta_C$ 147.9 (*s*)] and C-6‴ [$\delta_C$ 147.0 (*s*)], C-7″ [$\delta_C$ 142.7 (*s*)] and C-7‴ [$\delta_C$ 142.4 (*s*)], C-9″ [$\delta_C$ 128.8 (*s*)] and C-9‴ [$\delta_C$128.9 (*s*)] on the basis of 2D-$^{1}H$–$^{13}C$ heteronuclear correlation via one bond ($^{1}H$–$^{13}C$-COSY-$^{1}J_{CH}$) and long-range coupling ($^{1}H$–$^{13}C$-COSY-$^{n}J_{CH}$, $n = 2$ and 3) spectra (Table 6), along with the intensities of the signals corresponding to C-3″ and C-3‴ [$\delta_C$ 109.5 (*d*)], C-11″ and C-11‴ [$\delta_C$ 19.6 (*q*)] and MeO-2″ and MeO-2‴ [$\delta_C$ 56.3 (*q*)] and H-3″ and H-3‴ [$\delta_H$ 6.07 (*s*, 2H)], 3H-11″ and 3H-11‴ [$\delta_H$ 2.44 (*s*, 6H)] and MeO-3″ and MeO-3‴ [$\delta_H$ 3.84 (*s*, 6H)]; (c) results obtained from NOE difference spectra performed with specific resonance at the 3H-11″/3H-11‴ [$\delta_H$ 2.44 (*s*)] revealing signal enhancements at $\delta_H$ 7.82 (*s*, H-8″ and H-8‴, NOE = 7%) and 3.3–3.1 (*m*, H-5 and H-5′, NOE = 6%), which were also used to define the location of the methyl groups at C-7″ and C-7‴ and the tetrahydropyran moieties at C-6″ and C-6‴. Thus, all these data were used to establish the relative configuration of the new dimer cordiachrome as 2″-methoxy-7″-methyl-1″,4″-naphthalendione-(6″ → 5)-tetrahydropyran-(2eq → *O* → 2′ax)-tetrahydropyran-(5′ → 6‴)-2‴-methoxy-7‴-methyl-1‴,4‴-naphthalendione (**13**). The EI mass spectrum of this natural product (*m/z* 586 $[M]^+$, absent) revealed ions at *m/z* 302 (33%, **14**) and 229 (100%, **15**).

## EXPERIMENTAL

Mps: uncorr. $^{1}H$ (200 MHz) and $^{13}C$ (50.3 MHz) NMR: $CDCl_3$, TMS as int. standard. EIMS: direct inlet at 70 eV, CC: silica gel (Carlo Erba, 0.05–0.02 mm). TLC: silica gel 60 (Carlo Erba), spots visualized by UV (254 and 366 nm), exposure to $I_2$ vapour and spraying with vanillin–perchloric acid–EtOH soln. TLC was used to analyse frs collected from CC.

Table 6. $^1$H (200 MHz) and $^{13}$C (50 MHz) NMR spectral data for compound **13**, in $CDCl_3$*

| | $^1$H-$^{13}$C-COSY-$^1J_{CH}$ | | $^1$H-$^{13}$C-COSY-$^nJ_{CH}$ | |
|---|---|---|---|---|
| | $\delta_C$ | $\delta_H$ | $^2J_{CH}$ | $^3J_{CH}$ |
| C | | | | |
| 1″,1‴ | 179.7 | — | | H-3″, H-3‴ |
| 2″,2‴ | 160.2 | — | H-3″,H-3‴ | MeO-2″, MeO-2‴ |
| 4″,4‴ | 184.9 | — | H-3″, H-3‴ | H-5″, H-5‴ |
| 6″ | 147.9 | — | | H-8″, 3H-11″ |
| 6‴ | 147.0 | — | | H-8‴, 3H-11‴ |
| 7″ | 142.7 | — | 3H-11″ | H-5″ |
| 7‴ | 142.4 | — | 3H-11‴ | H-5‴ |
| 9″ | 128.8 | — | | H-5″ |
| 9‴ | 128.9 | — | | H-5‴ |
| 10″,10‴ | 130.0 | — | | H-3″, H-3‴, H-8″, H-8‴ |
| CH | | | | |
| 3″,3‴ | 109.5 | 6.07 (*s*) | | |
| 2 | 96.0 | 4.89 (*d*, $J = 8.4$) | | |
| 2′ | 90.7 | 5.31 (*br s*) | | |
| 5 | 38.0 | 3.09 (*m*) | | H-5″ |
| 5′ | 38.6 | 3.10 (*m*) | | H-5‴ |
| 5″ | 123.5 | 7.82 (*s*) | | |
| 5‴ | 123.9 | 7.92 (*s*) | | |
| 8″ | 128.5 | 7.82 (*s*) | | 3H-11″ |
| 8‴ | 128.4 | 7.82 (*s*) | | 3H-11‴ |
| $CH_2$ | | | | |
| 3 | 32.2 | 2.10 (*m*) | | |
| | — | 1.65 (*m*) | | |
| 3′ | 30.0 | 1.95 (*m*) | | |
| | — | 1.85 (*m*) | | |
| 4 | 28.1 | 2.1–1.9 (*m*, 2H) | | |
| 4′ | 23.4 | 2.30 (*dq*, $J = 13.5, 5.7$) | | |
| | — | 1.80 (*m*) | | |
| 6 | 69.4 | 4.00 (*br d*, $J = 12.8$) | | |
| | — | 3.70 (*t*, $J = 12.8$) | | |
| 6′ | 63.1 | 4.10 (*br d*, $J = 10.7$) | | |
| | — | 3.60 (*t*, $J = 10.7$) | | |
| $CH_3$ | | | | |
| 11″, 11‴ | 19.6 | 2.44 (*s*) | | H-8″, H-8‴ |
| $(MeO)_2$-2″, 2‴ | 56.3 | 3.84 (*s*) | | |

*Multiplicity of signals of carbon atoms deduced by comparative analysis of PND- and DEPT-$^{13}$C NMR. Homonuclear 2D-$^1$H–$^1$H-COSY, including one taken on a 400 MHz spectrometer, also used for these assignments. Chemical shifts ($\delta$) and coupling constants ($J$) of the hydrogen atoms obtained from $^1$H NMR.

*Plant material.* *Auxemma oncocalyx* Taub was collected in Pentecoste, Ceará State, Brazil, in September 1990 and identified by Professor Afrânio Gomes Fernandes (Universidade Federal do Ceará, Fortaleza). A voucher specimen (no 18459) is deposited at the Herbarium Prisco Bezerra of the Departamento de Biologia of the Universidade Federal do Ceará.

*Extraction and isolation constituents from branches.* Dried and powdered wood (7.4 kg, bark removed) was successively extracted with hexane and EtOH at room temp. and the solvents removed under vacuum to yield 12.3 and 168.2 g of residues, respectively. Part of the residue obtained from the EtOH extract (150 g) was dissolved in $H_2O$ and the aq. soln extracted with $CHCl_3$. The residue (40 g) of the $CHCl_3$ extract was chromatographed on a column of silica gel and eluted with hexane, $CHCl_3$, EtOAc and MeOH. The fr. eluted with EtOAc (23.5 g) was chromatographed on a silica gel (100 g) column. Elution with $CHCl_3$ gave frs A (0.9 g) and B (1.8 g), $CHCl_3$–EtOAc (1:1) frs C (2.0 g), D (1.8 g) and E (3.8 g), EtOAc frs F (5.6 g) and G (4.3 g) and MeOH fr. H (2.4 g). Fr. C (2.0 g) was rechromatographed on a silica gel (20 g) column and eluted with hexane (frs 1–6, 0.5 g) and hexane–$CHCl_3$ [1:1, frs 7–11 (0.35 g) and 12–18 (0.5 g)]. TLC ($CHCl_3$–EtOAc, 4:1) of frs 12–18 yielded **2** (14 mg) and **6** (21 mg). Silica gel (20 g) CC (eluent indicated in parentheses) of fr. D (1.8 g): frs 1–7 ($CHCl_3$), 8–16 ($CHCl_3$–EtOAc, 3:1) and 17–28 ($CHCl_3$–EtOAc, 1:1). Repeated silica gel CC of frs 17–28 eluted with $CHCl_3$–EtOAc (7:3) afforded **7** (25 mg) after recrystallization from hexane–$Me_2CO$. Fr. F (5.6 g) was rechromatographed on a silica gel (30 g) column and eluted with $CHCl_3$ (frs 1–3), $CHCl_3$–EtOAc (3:1, frs 4–9), $CHCl_3$–EtOAc (1:1, frs to 10–34), EtOAc (frs 35–40) and MeOH (frs 41–43). The ppt. obtained from frs 35–40 was washed with a small quantity of $Me_2CO$ to furnish **18** (18 mg). Frs 10–34 (2.8 g) were rechromatographed on a silica gel (20 g) column and eluted with $CHCl_3$ (frs 1–9) and $CHCl_3$–EtOAc (1:1, frs 10–39); frs 10–39 (1.85 g) was washed with a small quantity of $Me_2CO$ to yield **1** (650 mg).

Dried powdered bark (5.8 kg) was successively extracted with hexane and EtOH at room temp. to afford 21.1 g and 110.2 g of residues, respectively, after evapn of solvents under vacuum. Partial evapn of the EtOH soln produced a ppt which was separated into an EtOH-insol. and an EtOH-sol. portion. This ppt was washed successively with small quantities of $Me_2CO$ and MeOH to furnish **16** (4.6 g).

An additional quantity of branches was separated into bark, sapwood and heartwood. Dried powdered heartwood (5.0 kg) was extracted with EtOH at room temp. and solvent removed under vacuum to afford 222.5 g of residue. This residue was successively extracted with hexane and $CHCl_3$. The residue (114 g) obtained from the $CHCl_3$ soln after evapn of solvent under vacuum was submitted to CC on silica gel (60 g), using as eluents, $CHCl_3$ [frs 1–17 (67 g) and 18–27 (11.5 g)], $CHCl_3$–EtOAc [1:1, frs 28–37 (9.7 g) and 38–50 (0.8 g)], EtOAc [frs 51–65 (5.3 g)] and EtOH [frs 66–79 (12 g)]. Frs 1–17 (67 g) were rechromatographed on silica gel (96 g) eluted with petrol–$CHCl_3$ [1:1, frs I (2.3 g), II (6.4 g), III (5.1 g) and IV (15.8 g)], $CHCl_3$ [frs V (7.5 g) and VI (11.4 g)], $CHCl_3$–EtOH [1:1, fr. VII (12 g)], EtOAc [fr. VIII (3.6 g)] and EtOH [fr. IX (2 g)]. Frs 1–17 (67 g) and VII (12 g) were combined and repeated silica gel CC furnished an additional quantity of **1** (6.26 g). Fr. II (6.4 g) was rechromatographed on silica gel (75 g) using as eluents, hexane–EtOAc (9:1) [fr. IIa (0.3 g)], (4:1) [frs IIb (0.4 g), IIc (0.6 g) and IId (2.3 g)], (7:3) [fr. IIe (1.2 g)] and (1:1) [fr. IIf (0.9 g)] and EtOH [fr. IIg (0.5 g)]. Fr. IId (2.3 g) was recrystallized from hexane and MeOH to afford **17** (1.8 g). Fr. IIe (1.2 g) yielded **5** (19 mg), after being submitted to CC (silica gel, elution with hexane–EtOAc mixts of increasing polarity) and washing of the fraction eluted with hexane–EtOAc (4:1) with a small quantity of hexane–$Me_2CO$. Fr. IV (15.8 g) was chromatographed on a silica gel (100 g) column eluted with hexane–EtOAc [1:1, frs IVa (0.3 g) and IVb (1.4 g)], hexane–EtOAc [3:2, frs IVc (8 g) and IVd (4.1 g)], hexane–EtOAc [2:3, fr. IVe (0.8 g)], hexane–EtOAc [1:4, fr. IVf (0, 3 g)] and EtOH [fr. IVg (0.5 g)]. Prep. TLC [hexane–$CHCl_3$ (1:9)] of fr. IVb (1.4 g), and recrystallization from hexane–$Me_2CO$, yielded an additional quantity of **6** (65 mg). Repeated CC (silica gel) of fr. IVc (8 g) afforded **3** (474 mg). Fr. IVd (4.1 g) was also submitted to CC to furnish **13** (165 mg).

rel-8α-*Hydroxy-5-hydroxymethyl-2-methoxy-8aβ-methyl,7,8,8a,9-tetrahydro-1,4-anthracendione* (**1**). Mp and spectral data, including derivatives **1a** and **1b** as Ref. [1].

rel-8α,11α; 10α,11α-*Diepoxy-2-methoxy-8aβ-methyl-5,6,7,8,8a,9,10,10a-octahydro-1,4-anthracendione* (**2**). Mp and spectral data as Ref. [1].

rel-10α,11β-*Epoxy-11α-ethoxy-8α-hydroxy-2-methoxy-8aβ-methyl-5,6,7,8,8a,9,10,10aβ-octahydro-1,4-antracendione* (**3**). Mp 111–113°. IR $\nu_{max}^{KBr}$ cm$^{-1}$: 1640, 1600, 1220, 1080. $^1$H and $^{13}$C NMR: Table 1; NOE difference spectra: Table 2. EIMS 70 eV *m/z* (rel. int.): 348 ($[M]^{+1}$, absent), 303 ($[M - OEt]^+$, 8), 274 ($[M - HCO_2Et]^+$, 65), 256 ($[M - HCO_2Et–H_2O]^+$, 17), 241 ($[M - HCO_2Et–H_2O–Me]^+$, 27).

6-*Formyl-2-methoxy-9-methyl-7,8-dihydro-1,4-phenanthrendione* (**5**). Mp 268–270°. IR $\nu_{max}^{KBr}$ cm$^{-1}$: 1680, 1610, 1260, 1120. $^1$H and $^{13}$C NMR and NOE difference spectra: Table 3. EIMS 70 eV *m/z* (rel. int.): 282 ($[M]^+$, 23), 253 ($[M - HCO]^+$, 100).

rel-8α,11α;9α,11α-*Diepoxy-1,4-dihydroxy-2-methoxy-8aβ-methyl-5,6,8,8a,9,10,10aβ-octahydro-10-anthracenone* (**6**). Mp 234–237°. IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3400, 1620, 1490, 1220, 1020. $^1$H and $^{13}$C NMR and NOE difference spectra: Table 4. EIMS 70 eV *m/z* (rel. int.): 318 ($[M]^+$, 100), 272 ($[M - HCO_2H]^+$, 92), 257 ($[M - HCO_2H - Me]^+$, 87).

1,4-*Di-O-acetyl derivative* (**6a**). Treatment of **6** (100 mg) with $Ac_2O$ (2 ml) and pyridine (2 ml), and usual work-up, produced **6a** (102 mg). Mp 202–205°. IR $\nu_{max}^{KBr}$ cm$^{-1}$: 1750, 1600, 1240, 1200, 1180, 1120. $^1$H and $^{13}$C NMR: Table 4.

rel-9α,11α-*Epoxy-1,4,8α-trihydroxy-2-methoxy-8aβ-methyl-5,6,7,8,8a,9,10,10aβ-octahydro-10-anthracenone* (**7**). Mp 269–270°. IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3500, 1620, 1600, 1490, 1220, 1100. $^1$H and $^{13}$C NMR: Table 5. EIMS 70 eV *m/z* (rel. int.): 320 ($[M]^+$, 17), 302 ($[M - H_2O]^+$, 16), 220 ($[M - CH_2{=}CHOH–CH_2{=}CH–CHO]^+$, 13), 219 ($[M - CH_2 = CHOH - CH_2 = CH - CHO–H]^+$, 38).

1,4,8α-*Tri-O-acetyl derivative* (**7a**). Prepared in the way, **7** (20 mg) with $Ac_2O$ (1 mg) and pyridine (1 ml), to give **7a** (23 mg). Mp 240–243°. IR $\nu_{max}^{KBr}$ cm$^{-1}$: 1760, 1740, 1670, 1600, 1240, 1080. $^1$H and $^{13}$C NMR: Table 5.

rel-2″-*Methoxy-7″-methyl-1″,4″-naphthalendione-(6″ → 5)-tetrahydropyran-(2eq → 2′ax)-tetrahydropyran-(5′ → 6‴)-2‴-methoxy-7‴-methyl-1‴,4‴-naphthalendione* (**13**). Mp 131–144°. IR $\nu_{max}^{KBr}$ cm$^{-1}$: 1680, 1610, 1050, 1020. $^1$H and $^{13}$C NMR: Table 6. EIMS 70 eV *m/z* (rel. int.): 586 ($[M]^+$, absent), 302 (**14**, 33), 229 (**15**, 100).

*Allantoin* (**16**). Mp 227–230° (Ref. [6] mp 226.9° dec.). Spectral data, mainly $^1$H and $^{13}$C NMR [7] and EIMS, were used to confirm this structure.

*Sitosterol* (**17**). Mp 121–123°. Spectral data, mainly $^{13}$C NMR (50 MHz, $CDCl_3$), in agreement with lit. values [8].

3β-O-β-D-*Glucopyranosylsitosterol* (**18**). Mp 290–292°. Spectral data, mainly $^{13}$C NMR (50 MHz, MeOH-$d_4$) of the natural product and its peracetyl derivative **18a** (50 MHz, $CDCl_3$), in agreement with lit. values [2, 8].

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