
by Michael Moir, Peter Rüedi and Conrad Hans Eugster

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Zusammenfassung. Aus den Blättern und Stengeln von *Coleus somaliensis* (S. Moore) wurden die Diterpen-Hydrochinone H, I und K (Coleone H, I und K) isoliert und ihre Struktur aufgeklärt. Coleon H ist 3α-Acetoxy-6,11,12,14,16-(oder 17)-pentahydroxy-abieta-5,8,11,13-tetraen-7-on (2). Coleon I ist vermutlich das entsprechende A/B-trans-6,7-Diketon 5. Coleon K ist 16,17-Diacetoxy-3α,11,12,14-tetrahydroxy-abieta-8,11,13-trien-6,7-dion (6). Es sind die höchst hydroxylierten Coleone, die bisher aufgefunden worden sind.

Continuing our investigation of the leaf-gland pigments of East African Labiatae (*Coleus, Fuerstia* and *Plectranthus* spp.)\(^1\) we have now isolated and characterised five new diterpenoids, three coloured, two colourless, from *Coleus somaliensis* (S. Moore)\(^2\). The leaf-glands of this species are rich sources of pigments (cf. [3]).

In this communication we present evidence for the structures of the pigments, coleons H, I, and K\(^3\), whilst in the following paper [4] we discuss the colourless compounds, coleons G and J.

Coleon H (yellow needles, m.p. 199°, M+ 420, C\(_{22}H_{33}O_9\)) shows almost identical UV./VIS. absorption to coleon C (1) \(^5\) (Table 1), and in IR. absorption differs chiefly in the presence of an aliphatic ester carbonyl band at 1725 cm\(^{-1}\) (Table 2). A singlet (3H) at \(\delta 2.14\), together with signals from a hydroxyisopropyl and three tertiary methyl groups in the NMR. spectrum indicate that coleon H is an acetoxy-coleon C having the acetoxyl substituent in ring A. The relatively narrow signal (\(\Delta v_{1/2} = 9 \text{ Hz}\)) for the methine proton (\(>\text{CHOAc}\)) at \(\delta 4.78\) precludes axial-axial coupling as well as an axial conformation for the acetoxyl at C(2) \(^6\).

Mild oxidation of coleon H with AgO\(_8\) in chloroform yielded an oily, orange quinone (\(\lambda_{\text{max}} 270, 410-420 \text{ nm}, \nu_{\text{max}} 1669 \text{ cm}^{-1}\)) whose NMR. spectrum shows no

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1) For our most recent paper on *Coleus* see [1].
2) The species is described in [2]. Plants from the location of the type-specimen (Ga-an Libah, Somalia) were collected by P. R. O. Bally, Nairobi, and kept in the Städtischen Sukkulentensammlung, Zürich. From cuttings of these, plants for extraction were grown in Zürich.
3) The compounds were named in order of elution from the initial column.
shift of the methine proton resonance at $\delta 4.78$, but displays a new broad signal ($\omega_{1/2} = 20$ Hz) at $\delta 2.70$ typical of a deshielded equatorial proton at C(1)$^4$. We therefore conclude that coleon H-quinone is 3 and coleon H is 3\alpha-acetoxy-coleon C (2). CD. spectra (Fig. 1 and Table 3) indicate that coleon H possesses the same stereochemistry as coleon C (1) at C(10).

Coleon H is accompanied by a small amount of a more polar orange pigment ($M^+ 420, C_{22}H_{38}O_8$) which could not be purified to give satisfactory spectra. UV./VIS. absorption, however, is similar to that of coleon D (4) [7] and we consider that the compound (coleon I) is 3\alpha-acetoxy-coleon D (5), although evidence is not yet conclusive.

Coleon K (orange needles, m.p. 174–175°C, $M^+ 478, C_{24}H_{30}O_{10}$) shows typical UV./VIS. absorption of coleon D (4) (Table 1), but in the IR. spectrum (Table 2) there is an intense broad band at 1730 cm$^{-1}$ (aliphatic ester and C(6) carbonyl group). The NMR. spectrum, although similar to that of coleon D (4), lacks the secondary methyl signal (CH$_3$(16 or 17)), but shows a five proton AA'BB'X multiplet between $\delta$ 3.5 and 4.6, and, in addition, displays two sharp singlets (each 3H) at $\delta$ 1.96 and 2.02 from two acetoxy groups.

Table 1. UV./VIS. data

<table>
<thead>
<tr>
<th>Compound Nr.</th>
<th>Solvent</th>
<th>$\lambda_{\text{max}}$ (log $e_{\text{max}}$) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ethanol</td>
<td>266 (4.05), 280–286 (3.87), 327 (3.67), 395 (3.77)</td>
</tr>
<tr>
<td>2</td>
<td>Methanol</td>
<td>268 (4.14), ~ 280 (4.05), 333 (3.63), 398 (3.77)</td>
</tr>
<tr>
<td>3</td>
<td>Ether</td>
<td>270, 410–420 (qual.)</td>
</tr>
<tr>
<td>4</td>
<td>Ethanol</td>
<td>283 (3.74), 346 (3.76), 421 (3.88)</td>
</tr>
<tr>
<td>6</td>
<td>Methanol</td>
<td>270 (3.83), 333 (3.79), 395 (3.66)</td>
</tr>
</tbody>
</table>

Table 2. IR. data

<table>
<thead>
<tr>
<th>Compound Nr.</th>
<th>Solvent</th>
<th>$v_{\text{max}}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CHCl$_3$</td>
<td>3515, 3390, 1626, 1597, 1455</td>
</tr>
<tr>
<td>2</td>
<td>CHCl$_3$</td>
<td>3515, 3380, 1725, 1627, 1601, 1455</td>
</tr>
<tr>
<td>3</td>
<td>CHCl$_3$</td>
<td>3400, 1730, 1669, ~1625, 1460</td>
</tr>
<tr>
<td>4</td>
<td>KBr</td>
<td>3475, 3370, 1725, 1622, 1594, 1452</td>
</tr>
<tr>
<td>6</td>
<td>CHCl$_3$</td>
<td>3518, 3360, 1731, 1619, 1430</td>
</tr>
<tr>
<td>7</td>
<td>CHCl$_3$</td>
<td>1785, 1732, 1635, 1181</td>
</tr>
<tr>
<td>8</td>
<td>CHCl$_3$</td>
<td>1788, 1735, 1670, 1603, 1180</td>
</tr>
</tbody>
</table>

~ Means shoulder

Acetylation of coleon K afforded a penta-O-acetyl derivative ($M^+ 688, C_{34}H_{46}O_{15}$) and a small amount of a tetra-O-acetyl derivative ($M^+ 646, C_{32}H_{38}O_{14}$). The C(7) carbonyl absorption in the IR. spectra of these derivatives (Table 2) is in accord with enolisation of the C(6) carbonyl [7], and the absence of a signal at ca. 13 ppm in the NMR. spectrum of the hepta-acetate confirms that the chelated hydroxyl at C(14) has been acetylated [7]. Furthermore, the NMR. of the hepta-acetate displays

4) We have observed this pronounced deshielding of equatorial protons at C(1) ($\delta$ 2.7–3.0; $J_{gem} = 16–20$ Hz) in all abietane derivatives having a $p$-quinonoid ring C (e.g. royleanones, isoroyleanone [3], coleon C-quinone [5]).
Fig. 1. CD spectra of coleon C (1) (---), coleon H (2) (----) (above) and coleon D (4) (----),
coleon K (6) (-----) (below) in Dioxane.

Table 3. CD data (in Dioxan)

<table>
<thead>
<tr>
<th>Compound Nr.</th>
<th>λ in nm (Δε)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>235 (+0.3), 271 (+7.05), 275 (+6.8), 281 (+7.62), 295 (0), 302 (−3.45), 340 (0), 385 (−0.91), 440 (0)</td>
</tr>
<tr>
<td>2</td>
<td>234 (+3.80), 269 (+14.1), 278 (+12.2), 282 (+12.7), 302 (0), 331 (−2.96), 360 (0), 374 (+0.09), 405 (0)</td>
</tr>
<tr>
<td>4</td>
<td>228 (+4.75), 250 (+0.83), 279 (+4.33), 286 (+3.92), 297 (+4.75), 314 (0), 326 (−1.73), 343 (0), 356 (+0.83), 374 (0), 399 (−0.83), 413 (0), 442 (+3.33), 510 (0)</td>
</tr>
<tr>
<td>6</td>
<td>235 (+2.89), 246 (+1.23), 279 (+4.73), 292 (+3.65), 295 (+3.74), 315 (0), 326 (−0.78), 338 (0), 355 (+0.90), 383 (0), 397 (−0.24), 408 (0), 441 (+2.41), 510 (0)</td>
</tr>
</tbody>
</table>
only one low field methine proton signal (δ 4.83, 1 H, >CHOAc), and, from the band width (w1/2 = 9 Hz) and chemical shift compared to those of the corresponding signal in the coleon H spectrum, we deduce that the hepta-acetate possesses a 3α-acetoxy group, and that coleon K has a 3α-hydroxyl. Coleon K can thus be represented by 6 and the hexa- and hepta-acetates by 7 and 8 respectively. Since the CD. curves for coleon D (4) and coleon K (6) are almost superimposable (Fig. 1 and Table 3), the stereochemistry at the A/B ring junction must be trans as depicted.

![Chemical structures](image)

Coleon L (9), the hypothetical parent of coleon K acetates, was not detected in C. somaliensis. Coleons H and K are the most highly oxidised diterpenoids isolated so far from Coleus spp. Pododacric acid (10) was the first example of an abietane derivative having a bis-hydroxylated isopropyl side chain [8].

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Experimental Part

Instrumentation and chromatographic adsorbents have been described previously [5] [7]. The UV./VIS. spectra recorded as follows: (Solvent) $\lambda_{\text{max}}$ in nm ($\log \varepsilon_{\text{max}}$).

Isolation of coleons H, I, and K. - Dried shoots and leaves of *Coleus somalensis* (100 g) were extracted with cold ether (2 x 1 l) overnight, and the evaporated extract was partitioned between hexane/benzene 1:1 and methanol/water 4:1. Evaporation of the hypophase yielded an orange resin (2.4 g) which was chromatographed on a column of silicic acid in benzene/acetonitrile 15:1. Three orange zones separated (in decreasing order of Rf):

Zone 1: This zone consisted chiefly of colourless coleon G and traces of orange pigments.

Zone 2: The orange foam (240 mg) from this zone was chromatographed on a column of polyamide. Elution with methanol/water 1:1 gave a further quantity of coleon G and the orange (methanol) eluate was concentrated and rechromatographed on a column of silicic acid in benzene/ether 9:1 to yield a yellow band and a slower moving orange band. The yellow band afforded coleon H (40 mg) which was crystallised from ether/cyclohexane in yellow needles, m.p. 199°. The orange band yielded an oil (60 mg) containing coleon I (5). Efforts to purify this material further have so far resulted in decomposition.

Zone 3: Chromatography of the orange foam (600 mg) from this zone over a column of polyamide in methanol gave colourless coleon J. Elution with methanol/acetonitrile 1:1 gave an orange fraction which was passed through a column of silicic acid in benzene/ether 9:1 to yield coleon K (130 mg). This pigment crystallised from acetonitrile/cyclohexane in orange needles, m.p. 174-175° (dec.).

Spectral data. - *Coleon H* (2): MS.: $M^+$ 420 ($C_{24}H_{28}O_8$); m/e 360 ($M^+-\text{HOAc}$), 345 ($M^+-\text{HOAc} \rightarrow \text{CH}_3$), 327 ($M^+-\text{HOAc} \rightarrow \text{CH}_3, \text{H}_2\text{O}$). - UV./VIS. (CH$_3$OH): 268 (4.14), ~280 (4.05), 333 (3.65), 398 (3.77). - CD. (Dioxan) ($\Delta$e): 234 (+3.80), 269 (+14.1), 278 (+12.2), 282 (+12.7), 302 (0), 374 (+0.09), 405 (0) ($c = 0.030$ mg/ml, $d = 0.3$ cm, $T = 22^\circ$). - IR. (CHCl$_3$): 3155, 3380, 2940, 1725, 1627, 1601, 1455 cm$^{-1}$. - NMR. (CDCl$_3$): 1.38 (d, $J = 7$ Hz, 3H, $>\text{CH}_3$H); 1.41 and 1.52 (each 3H, $-\text{CH}_3$); 1.72 (s, 3H, CH$_3$(18) and CH$_3$(19)); 1.78 (s, 3H, CH$_3$(20)); 2.14 (s, 3H, OAc); 3.2 (m, X-part, 1H, $-\text{CH}<\text{CH}_3$OH); 3.7-4.2 (m, $AB$-part, 2H, $-\text{CH}_2\text{OH}$); 4.78 (m, $w_{1/2} = 9$ Hz, 1H, $>\text{CH}_3$OH).

*Coleon I* (5): MS.: $M^+$ 420 ($C_{24}H_{28}O_8$). - UV./VIS. (CH$_3$OH) (qual.): 325, 400. *Coleon K* (6): MS.: $M^+$ 478 ($C_{24}H_{28}O_{18}$); m/e 460 ($M^+-\text{H}_2\text{O}$), 418 ($M^+-\text{HOAc}$), 358 ($M^+-\text{HOAc} \rightarrow \text{CH}_3, \text{C}=\text{O}, \text{H}_2\text{O}$), 343 (m/e 328 $<\text{CH}_3$). - UV./VIS. (CH$_3$OH): 270 (3.83), 333 (3.79), 395 (3.66). - CD. (Dioxan) ($\Delta$e): 325 (+2.89), 246 (+1.23), 279 (+4.73), 292 (+3.65), 295 (+3.74), 315 (0), 326 (+0.78), 338 (0), 355 (+0.90), 383 (0), 397 (-0.24), 408 (0), 441 (+2.41), 510 (0) ($c = 0.105$ mg/ml, $d = 0.5$ cm, $T = 22^\circ$). - IR. (CHCl$_3$): 3518, 3360, 2970, 2960, 1731, 1619, 1430, 1378, 1255, 1040 cm$^{-1}$. - NMR. ($d_6$-acetone): 1.05 (s, 3H, CH$_3$ at C(4)); 1.43 (s, 6H, CH$_3$ at C(4)) and C(3)-H(β)); 1.35 (s, 1H, chel. OH at C(14)).

Oxidation of coleon H. - Coleon H (11 mg) was shaken with an excess of silver oxide in chloroform at room temp. for 10 min [5]. The filtered solution was evaporated to give an orange oil which was immediately chromatographed on a short column of silicic acid in cyclohexane/acetone 5:2. The major orange band yielded coleon H-quinone (3) (8 mg) as an unstable orange oil. UV./VIS. (ether) (qual.): 270, 410-420. - IR. (CHCl$_3$): 3400, 2930, 1730, 1609, ~1625, 1460, 1380, 860 cm$^{-1}$. - NMR. (CDCl$_3$): 1.25 (d, $J = 7$ Hz, 3H, $>\text{CH}_3$H); 1.44 and 1.52 (each 3H, CH$_3$(18) and CH$_3$(19)); 1.79 (s, 3H, CH$_3$(20)); 2.14 (s, 3H, OAc); 2.70 (br. m, $w_{1/2} = 20$ Hz, 1H, C(1)-H(β)). - 3.38 (m, X-part, 1H, $-\text{CH}<\text{CH}_3$); 3.6-4.2 (m, $AB$-part, 2H, $-\text{CH}<\text{CH}_2$); 4.82 (m, $w_{1/2} = 9$ Hz, 1H, $>\text{CH}_3$OH).

Acetylation of coleon K. - Coleon K (39 mg) was dissolved in pyridine (1 ml) and acetic anhydride (1 ml) and kept at room temp. for 60 h. The mixture was poured into ice-water, extract-
ed with ether, and the acetates separated by preparative TLC on silica gel in chloroform/methanol (2%). The hexa-acetate 7 (higher Rf) was obtained as an oil (5 mg). – MS.: M+ 646 (C$_{32}$H$_{38}$O$_{14}$). – IR. (CHCl$_3$): 2940, 7785, 7732, 1635, 1374, 1181 cm$^{-1}$.

The hepta-acetate 8 crystallized from acetone/cyclohexane in colourless needles (20 mg), m.p. 79-80°. – MS.: M+ 688 (C$_{34}$H$_{40}$O$_{15}$). – UV./VIS. (CH$_3$OH) (qual.): 265, 285. – IR. (CHCl$_3$): 3020, 2960, 7788, 7735, 7670, 1603, 1374, 1180 cm$^{-1}$. – NMR. (CDCl$_3$): 1.35 and 1.42 (each s, 3H, CH$_3$(18) and CH$_3$(19)); 1.77 (s, 3H, CH$_3$(20)); 1.99 (s, 6H, CHOAc at C(3)); 2.12 (s, 3H, CH$_3$OAc); 2.33 (s, 9H, 3 x Ar-OAc); 3.75 (m, X-part, 1H, CH$_2$OAc); 4.83 (m, w$_{1/2}$ = 9 Hz, 1H, CHOAc at C(3)).

REFERENCES


262. Diterpenoids from Coleus somaliensis (S. Moore): Coleons G, and J

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Zusammenfassung. Aus den Blättern und Stengeln von Coleus somaliensis (S. Moore) wurden die farblosen, tetracyclischen Diterpene Coleon G (C$_{22}$H$_{29}$O$_5$) und Coleon J (C$_{20}$H$_{28}$O$_5$) isoliert und vor allem aus Spektren (einschließlich 270-MHz-1H- und 13C-NMR.) für sie die Strukturen 2 und 1 abgeleitet. Wir fassen sie als Abietanderivate auf mit einer aus der oxydierter Isopropylgruppe entstandenen spiro-Methylcyclopropan-cyclohexendion-Struktur. Sie enthalten zudem anstelle der geminalen Methylgruppen an C(4) eine α-ständige Methyl- an C(3) und eine exocyclische Methylengruppe an C(4).

In the preceding paper [1] we reported the structures of coleons H, I, and K, three pigments from Coleus somaliensis (S. Moore) (Labiateae). From the same plant we have isolated two colourless diterpenoids, coleon G and coleon J, and from chemical evidence and detailed NMR. studies (including 270-MHz-1H- and 13C-NMR. spectra) of these compounds and their derivatives, we have deduced that their structures are 2 and 1, respectively.

Coleon G (2) (colourless needles, m.p. 195–196° (dec.), C$_{22}$H$_{29}$O$_5$, absorbs strongly in the UV. at 240 nm (log $\varepsilon$ = 4.09) (enedione chromophore [2]), and in strong acids instantaneously develops an intense purple colouration ($\lambda_{\text{max}}$ 500, 605 nm) which