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, *1785*, *1732*, 1635, 1374, 1181 cm^{-1}.

The *hepta-acetate* **8** crystallised from acetone/cyclohexane in colourless needles (20 mg), m.p. 79–80°. – MS.: M^+ 688 ($C_{34}H_{40}O_{15}$). – UV./VIS. (CH_3OH) (qual.): 265, *285*. – IR. ($CHCl_3$): 3020, 2960, *1788*, *1735*, *1670*, 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, $-CH\langle^{CH_2OAc}_{CH_2OAc}$); 2.12 (*s*, 3H, $\rangle$CHO*Ac* at C(3)); 2.33 (*s*, 9H, 3 × Ar—OAc); 2.42 (*s*, 3H, enolic OAc at C(6)); 3.75 (*m*, *X*-part, 1H, $-C\mathit{H}\langle^{CH_2OAc}_{CH_2OAc}$); 4,83 (*m*, $w_{1/2}$ = 9 Hz, 1H, $\rangle$C*H*OAc at C(3)).

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

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(3. IX. 73)

Zusammenfassung. Aus den Blättern und Stengeln von *Coleus somaliensis* (S. Moore) wurden die farblosen, tetracyclischen Diterpene Coleon G ($C_{22}H_{28}O_6$) und Coleon J ($C_{20}H_{26}O_5$) isoliert und vor allem aus Spektren (einschliesslich 270-MHz-^{1}H- und ^{13}C-NMR.) für sie die Strukturen **2** und **1** abgeleitet. Wir fassen sie als Abietanderivate auf mit einer aus der oxydierten 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) (*Labiatae*). 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-^{1}H- and ^{13}C-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.), $C_{22}H_{28}O_6$, absorbs strongly in the UV. at 240 nm (log ε = 4.09) (enedione chromophore [2]), and in strong acids instantaneously develops an intense purple colouration (λ_{max} 500, 605 nm) which

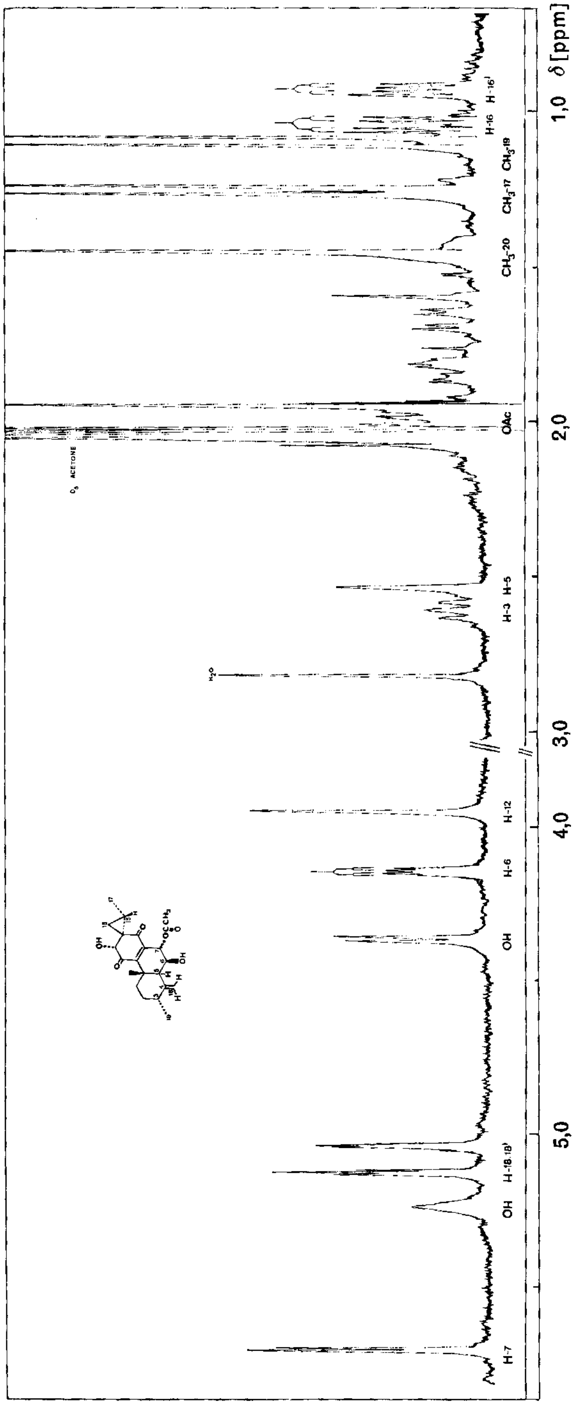
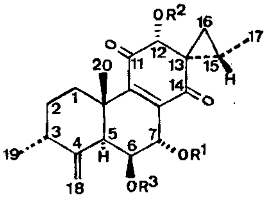


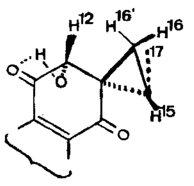
Fig. 1. *270 MHz-^{1}H-NMR. spectrum of coleon G* (**2**) *in d_6-acetone*

persists for several hours, even after dilution with water or methanol. The IR. spectrum of **2** exhibits broad OH absorption (3480 cm^{-1}) and three carbonyl bands at 1733 (acetate), 1695 (enedione) and 1675 cm^{-1} (hydrogen bonded enedione carbonyl at C(11)).

The 270-MHz-^{1}H-NMR. spectrum[1]) is very informative (Fig. 1 and Table 1). Singlets from the acetate and only one tertiary methyl group ($CH_3(20)$) appear at δ 1,97 and 1,47, respectively, and two methyl doublets are displayed at δ 1,27 (J = 6 Hz), $CH_3(17)$) and δ 1,12 (J = 7 Hz, $CH_3(19)$). Two narrow triplets (J = 1,5 Hz) at δ 5,16 and 5,07 can be assigned to the exocyclic methylene protons. The methine proton adjacent to the C(7) acetate group resonates as a doublet ($J_{6,7}$ = 2 Hz) at δ 5,84 whilst the signal for H(6) is a double doublet (J = 2 and 4 Hz) at δ 4,13. The larger coupling in the latter multiplet was shown to be due to the hydroxyl proton at δ 4,35 (d, J = 4 Hz) (removed by D_2O exchange) and hence $J_{5,6} \approx 0$ Hz. These low couplings are consistent with the stereochemical sequence C(5)-αH, C(6)-αH and C(7)-βH as depicted in **2** (see also Table 2). The sharp singlet at δ 3,93 is assigned to the proton at C(12).



1 R¹ = R² = R³ = H
2 R¹ = Ac, R² = R³ = H
3 R¹ = R² = Ac, R³ = H
4 R¹ = R² = R³ = Ac



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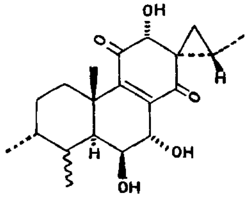

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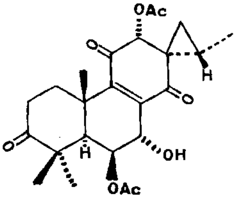

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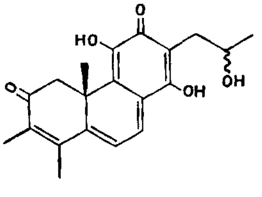

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Irradiation of the broad H(5) singlet (δ 2,55) collapses the exocyclic methylene signals to narrow doublets (J_{gem} = 1,5 Hz) showing that the bond between C(3) and H(3) lies between 0° and 30° to the plane of the double bond [3] (Table 2).

By far the most useful feature of the 270-MHz spectrum is that it clearly displays the signals from the cyclopropane protons H(16) and H(16') (see partial structure **5**). Both are double doublets, H(16) at δ 1,06 ($J_{15,16}$ = 9,0 Hz, $J_{16,16'}$ = 3,8 Hz) and H(16')

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[1] Measured on a *Bruker* AX-270 instrument. We thank Mr. *W. Schittenhelm*, *Spectrospin AG*, Fällanden ZH, for kindly running these spectra.

at δ 0,95 ($J_{15,16'}$ = 6,8 Hz). These assignments were made on the basis that J_{cis} is always larger than J_{trans} in cyclopropane systems [3].

Acetylation of coleon G (**2**) afforded the ***diacetate*** **3** (m.p. 233°, $C_{24}H_{30}O_7$, λ_{max} 234 nm, ν_{max} 1755 cm^{-1}, δ 2,06 and 2,11 (each *s*, 3H)) and the ***triacetate*** **4** (m.p. 173°, $C_{26}H_{32}O_8$, λ_{max} 234 nm, ν_{max} 1750 cm^{-1}, δ 1,99, 2,06 and 2,11 (each *s*, 3H)).

The IR. spectrum of **3** shows only one enedione carbonyl band (1682 cm^{-1}) indicating acetylation of the OH group at C(12). This is confirmed by the observed downfield shift from δ 3,39 to 4,91 of the H(12) singlet in the NMR. spectrum. Significantly, the cyclopropane methyl doublet (CH_3(17)) concurrently experiences an upfield shift of 0,11 ppm, a measure of the deshielding by the neighbouring hydroxyl group at C(12) in **2**. The IR. spectrum of the triacetate **4** also shows only one enedione carbonyl band (1680 cm^{-1}). As a result of acetylation at the C(6) hydroxyl, the signal for H(6) in the NMR. spectrum is a triplet (J = 2 Hz) shifted downfield to δ 5,35, and simultaneously, the adjacent exocyclic methylene proton experiences increased shielding of *ca.* 0,5 ppm with respect to **2** and **3**. By irradiation at the C(17) methyl doublet (δ 1,12) the third cyclopropane signal (H(15)) was located at δ 2,25. To account for this unusually high degree of deshielding we must invoke coplanarity of the C(15)–H(15) bond and the C(14) carbonyl ('pseudo-peri').

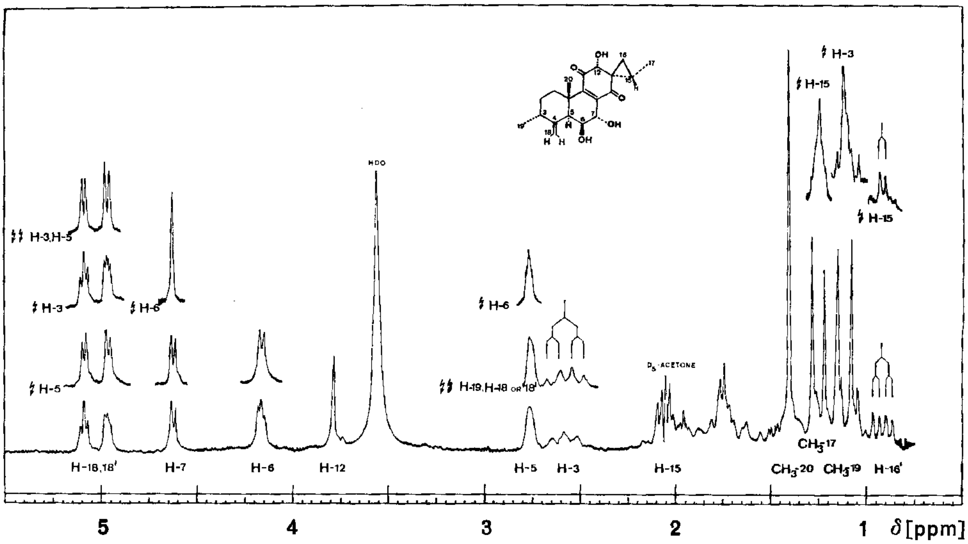

Fig. 2. *100 MHz-¹H- NMR. spectrum and decouplings of coleon J* (**1**)

Coleon J (**1**) (colourless needles, m.p. 194° (dec.), M^+346, $C_{20}H_{26}O_5$) also has the typical UV. and IR. absorptions of a hydroxylated molecule (ν_{max} 3488, 3420 cm^{-1} (OH)) possessing an enedione chromophore (λ_{max} 234 nm (log ε = 3,96), ν_{max} 1695, 1672 cm^{-1}). Acetylation of **1** afforded a small amount of coleon G(**2**) and the acetates **3** and **4**.

The noise-decoupled PFT-^{13}C-NMR. spectrum clearly displays twenty signals. On the basis of chemical shift values [4] the following assignments were made:

Table 1. *NMR. spectral data*

Proton(s)	Coleon J (**1**) 100-MHz d_6-acetone	Coleon G (**2**) 270-MHz d_6-acetone	Diacetate **3** 270-MHz $CDCl_3$	Triacetate **4** 100-MHz $CDCl_3$
H(3)	2.59 (*d*×*d*×*q*, 7, 13, 7)	2.63 (*d*×*d*×*q*, 7, 13, 7)	2.66 (*d*×*d*×*q*, 7, 13, 7)	2.65 (*d*×*d*×*q*, 7, 13, 7)
H(5)	2.77 (*m*)	2.55 (*m*)	2.49 (*m*)	2.67 (*m*)
H(6)	4.17 (*t*, 2)	4.13 (*d*×*d*, 2, 4)	4.24 (*m*)	5.35 (*t*, 2)
H(7)	4.63 (*d*, 2)	5.84 (*d*, 2)	5.73 (*d*, 2)	5.72 (*d*, 2)
H(12)	3.79 (*s*)	3.93 (*s*)	4.91 (*s*)	4.89 (*s*)
H(15)	ca. 2.06 (*m*)			2.25 (*m*)
H(16)	1.10 (*d*×*d*, 3.5, 8.5)	1.06 (*d*×*d*, 3.8, 7.0)		
H(16′)	0.92 (*d*×*d*, 3.5, 7.0)	0.95 (*d*×*d*, 3.8, 6.8)		
$CH_3(17)$	1.26 (*d*, 6.5)	1.27 (*d*, 6)	1.16 (*d*, 6)	1.14 (*d*, 6)
H(18)	4.97	5.07	4.99	4.52
H(18′)	(*m*) 5.09 (*t*, 2)	(*t*, 1.5) 5.16 (*t*, 1,5)	(*t*, 2) 5.06 (*t*, 2)	(*m*) 4.95 (*m*)
$CH_3(19)$	1.12 (*d*, 7)	1.12 (*d*, 7)	1.12 (*d*, 7)	1.12 (*d*, 7)
$CH_3(20)$	1.41 (*s*)	1.47 (*s*)	1.45 (*s*)	1.41 (*s*)
OAc	–	1.97 (*s*)	2.06/2.11 (each *s*)	1.99/2.06/2.11 (each *s*)

δ 199[2]) and 197, two unsaturated carbonyl C-atoms; δ 156, 153 and 142, three tertiary olefinic carbons; δ 109, primary olefinic carbon; δ 78,0, 73,4 and 72,0, three carbons adjacent to oxygen; δ 22,0, 21,6, 21,4 and 13,9, methylcyclopropane carbons.

The 100-MHz-^{1}H-NMR. spectrum only became meaningful after suppression of the CH–OH coupling by deuterium exchange (Fig. 2 and Table 1). Where possible, couplings already established in the preceding spectra were confirmed. As before, irradiation at the H(5) multiplet (δ 2,77) simplified the exocyclic methylene signals (δ 5,09 and 4,97) to double doublets (J = 2,0 Hz). However, the higher field signal of the latter pair collapsed to a double doublet (J = 1,0 and 2,0 Hz) on irradiation at δ 2,59 (H(3)) whereas the lower field partner was scarcely affected. Hence $J_{18,18'}$ =

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[2]) Spectrum run in $CDCl_3$. δ-values (ppm) are downfield from TMS = 0.

2,0 Hz, and the allylic couplings can be summarised: $J_{5,18} = 2{,}0$ Hz, $J_{5,18'} = 1{,}0$ Hz, and $J_{3,18} = J_{3,18'} \approx 0$ Hz (see also Fig. 3 and Table 2). A triple resonance experiment, by simultaneous irradiation at δ 2,59 and 2,77 produced very sharp doublets from the exocyclic methylenes. Irradiation at δ 2,77 (H(5)) also simplified the H(6) triplet to a doublet (δ 4,17, $J = 2$ Hz), whilst irradiation at δ 4,17 itself sharpened the H(5) signal and collapsed the H(7) doublet (δ 4,63, $J = 2$ Hz) to a sharp singlet. These experiments confirm again the stereochemistry at C(6) and C(7). The H(15) multiplet was located under the solvent peaks (d_6-acetone, δ *ca.* 2,06) by irradiation at the centre of the CH_3(17) doublet (δ 1,26, $J = 6{,}5$ Hz). Furthermore, irradiation at δ 2,06 reciprocally collapsed the CH_3(17) doublet and partially decoupled the H(16′) signal (δ 0,92, $d \times d$, $J = 3{,}5$ and 7,0 Hz) to a doublet ($J_{gem} = 3{,}5$ Hz). Irradiation at δ 2,59 (H(3)) collapsed the CH_3(19) doublet (δ 1,12, $J = 7$ Hz), partly revealing the H(16) multiplet, the outer components of which are separated by 12 Hz. In the cyclopropane ring the respective values of J_{gem}, J_{cis}, and J_{trans} are therefore seen to be 3,5, 8,5 and 7,0 Hz (Fig. 4 and Table 2).

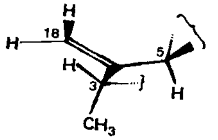

Fig. 3. *Part of coleons G and J seen from the α-side*

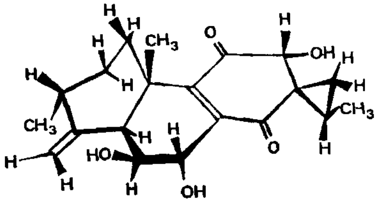

Fig. 4. *Coleon J*

Finally, simultaneous irradiation at the centre of the CH_3(19) doublet (δ 1,12) and at δ 4,97 (H(18) or H(18′)) simplified the H(3) multiplet to a double doublet $J = 7$ and 13 Hz).

Hydrogenation of coleon J (**1**) over *Adams'* catalyst in acetic acid gave a mixture of epimers **6** (m.p. 177–178°, M^+348, $C_{20}H_{28}O_5$). The IR. spectrum of **6** differs from that of **1** only in the absence of the band with ν_{max} 902 cm^{-1} (exocyclic methylene). The NMR. spectrum lacks the signals from these exocyclic methylene protons, but

Table 2. *Approximate dihedral angles in Ring A predicted from* J_{vic} (Φ) *and* $J_{allylic}$ (Θ)

$J_{a,b}$	$J_{2,3}$	$J_{2',3}$	$J_{3,18}$	$J_{3,18'}$	$J_{5,18}$	$J_{5,18'}$
Hz	7	13	0	0	2.0	1.0
$\Phi_{a,b}$	30°	150°	–	–	–	–
$\Theta_{a,b}$	–	–	<20°	<20°	>30°	>30°

a double doublet at δ 0,92 (J = 4,0 and 7,5 Hz, 1H) confirms that the cyclopropane ring has survived reduction. A singlet at δ 1,71 from the CH_3(20), *i.e.* 0,3 ppm downfield relative to coleon J (**1**), demonstrates the degree of shielding by the exocyclic double bond, and is consistent with a 1,3-diaxial deshielding interaction with the hydroxyl at C(6) [5]. Hydrogenation of coleon J over 10% palladium on charcoal in 2-propanol gave a complex mixture of products from which three pale yellow compounds were isolated by preparative TLC. in trace amounts. All three have UV./VIS. curves characteristic of hydroxybenzoquinones (λ_{max} 275, 400 nm, λ_{max} (in base) 282, 515 nm [6], purple spot on TLC. with ammonia vapour [7]) from which it is clear that hydrogenolysis of the cyclopropane ring has occurred.

The mass spectra of coleon G (**2**), coleon J (**1**), the diacetate **3**, and the triacetate **4** show very little fragmentation and are practically identical. The parent ions are extremely weak, the base peak at m/e 328 in **1**, **2**, and **3** being produced by facile loss of R–OH (R = H, Ac).

Dihedral angles Φ and θ [3], predicted from the observed vicinal and allylic coupling constants are tabulated below (Table 2). These dictate that ring A in coleon G and J adopts a distorted boat conformation in which, by virtue of the magnitudes of $J_{2',3}$ (13 Hz) and $J_{3,18}$ ($\approx$ 0 Hz) (*cf.* $J_{5,18}$ = 2 Hz!), the methyl group at C(3) must occupy the pseudoequatorial position, *i.e.* 3α. The β-configuration at C(10) is anticipated on biogenetic grounds as *C. somaliensis* contains the abietane derivatives coleon H and coleon K [1]. The stereochemistry of rings A and B can then only be as depicted in **1** and **2**. A study of molecular models shows that *no other* structure can accommodate *all* the observed facts (coupling constants, influence of OH at C(6) on H(18) or H(18′), and shielding of the CH_3(20) by the exocyclic double bond). Although we have no direct proof of configuration at C(12), we consider that **1** and **2** possess 12α-hydroxyl groups as the chemical shift of H(12) in **3** and **4** is almost the same as that of barbatusin (**7**), a similar diterpenoid recently isolated from *Coleus barbat(h)us* [8]. Moreover, since acetylation in **1** and **2** of the OH at C(12) shifts the CH_3(17) doublets upfield to *exactly* the same position as that of the barbatusin CH_3(17) doublet, we conclude that the C(15) methyl and the C(12) hydroxyl groups have the same relative stereochemical arrangement in **1**–**4** and **7**. In support of this assignment of *S*-chirality at C(15), the tertiary proton at this centre is found to lie in the deshielding zone of the C(14) carbonyl group as required by the observed lowfield chemical shift. The *R*-chirality at C(15) is not excluded, however, since stereochemical inversion of the chiral centres C(12), C(13), and C(15) would have very little effect on the rest of the molecule. It is worthy of note that no conclusions can be drawn from the CD. spectrum of coleon G (**2**) (Fig. 5) in the absence of suitable models.

Remarks on the structure of coleons G and J. – Rationalising the structure of coleon E (**8**) we postulated the intermediacy of a cyclohexadienonespiro-methylcyclopropane during the biogenesis of this diterpenoid [9]. A short time later, the structure of barbatusin (**7**) from *Coleus barbat(h)us* was elucidated by X-ray analysis. Obvious similarities exist between **8**, the first diterpenoid having a spiro[2,5]octane system, and coleons G (**2**) and J (**1**), especially the stereochemistry at C(5), C(6), C(7), and C(10). However, the exocyclic $\Delta^{4(18)}$-bond and the secondary methyl group at

C(3) are novel, features which permit subsequent conjugated unsaturation in rings A, B, and C to furnish the coleon E series.

Besides coleons G and J, the only abietanes known to possess the 4 → 3 *abeo* structure are triptolide, tripdiolide [10], coleon E [9], and coleon F [7].

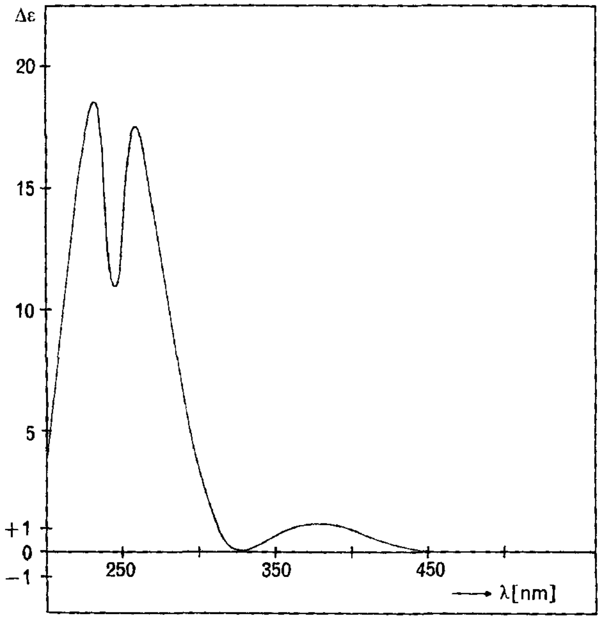

Fig. 5. *CD. spectrum of Coleon G* (**2**) *in dioxane*

This work was supported by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung* (grant No. 2.434.71). One of us (*M. M.*) is grateful to the *Royal Society*, London for a European Exchange Programme Fellowship.

Experimental Part

Materials and instrumentation have been described elsewhere [9] [11] [12]. The UV./VIS.-spectra are recorded as follows: λ_{max} in nm (log ε_{max}).

Extraction of dried plant material (100 g) and separation of coleons G and J are detailed in [1].

Coleon G (**2**): crystallised from acetone/cyclohexane in colourless needles (200 mg), m.p. 195–96° (dec.), M (osmometric) 386, $C_{22}H_{28}O_6$ requires M 388. – MS.: M^+ not visible; m/e *328* (M^+ – HOAc), 313 (M^+ – HOAc, – CH_3), 310 (M^+ – HOAc, – H_2O). – UV./VIS. (CH_3OH): 240 (4,09). – CD. (Dioxan) ($\Delta\varepsilon$): 232 (+18,8), 245 (+10,6), 258 (+17,4), 325 (0), 378 (+1,13), 460 (0) (c = 0,055 mg/ml, d = 0,5 cm, T = 22°). – IR. ($CHCl_3$): *3480*, 2980, 2940, 2895, *1733*, *1695*, *1675*, 1384, 1251. – NMR. (see Table 1).

Coleon J (**1**): crystallised from 2-propanol/water in colourless needles (200 mg), m.p. 194° (dec.), M (osmometric) 346. MS.: M^+ 346 ($C_{20}H_{26}O_5$); *m/e 328* (M^+ – H_2O), 313 (M^+ – H_2O, – CH_3). – UV./VIS. (CH_3OH): 234 (3,96). – IR. (KBr): *3488*, 3420, 3362, 2968, *1695*, *1672*, *1045*, *902* cm^{-1}. – NMR. (see Table 1).

Coleons G and J are both revealed as bluish-purple spots on a TLC. plate sprayed with sulfuric acid (see Fig. 6).

Acetylation of coleon J. Coleon J (40 mg) was acetylated in pyridine (1 ml) and acetic anhydride (1 ml) at room temp. overnight. Coleon G (**2**) was identified in the mixture by TLC. only (SiO_2, chloroform and SiO_2, hexane/acetone 2:1), but the two major products were separated by preparative TLC. on silica gel in chloroform.

Tri-O-acetyl-coleon J (**4**) (higher Rf) was obtained as colourless crystals (20 mg), m.p. 173° from acetone/hexane. – MS.: M^+ not visible; *m/e* 370 (M^+ – HOAc, $-CH_2=C=O$), 352 (M^+ – 2 HOAc), *310* (M^+ – 2HOAc, $-CH_2=C=O$), *295* (*m/e* 310 $-CH_3$). – UV./VIS. (CH_3OH) (qual.): 239. – IR. (2965, *1750*, 1681, 1374, 1200, 1025, 905. – NMR. (see Table 1).

Di-O-acetyl-coleon J (**3**) crystallised from acetone/hexane in colourless crystals (8 mg), m.p. 233°. – MS.: M^+ not visible; *m/e* 370 (M^+ – HOAc), *328* (M^+ – HOAc, $-CH_2=C=O$), *310* (M^+ – 2HOAc), 295 (M^+ – 2HOAc, $-CH_3$). λ_{max} (CH_3OH) (qual.): 238 nm. – IR. ($CHCl_3$): *1755*, 1716, *1682*, 1600, 1376, *1262* cm^{-1}. – NMR. (see Table 1).

Acetylation of coleon G. Coleon G (25 mg) was acetylated as described for coleon J. Preparative TLC. in chloroform gave *mono-O-acetyl-coleon G* (**3**) (9 mg) identical (NMR., mixed m.p., TLC.) to *di-O-acetyl-coleon J* and *di-O-acetyl-coleon G* (**4**) (15 mg) identical (NMR., mixed m.p., TLC.) to *tri-O-acetyl-coleon J*.

Hydrogenation of coleon J. (a) *Over Platinum.* Coleon J (30 mg) was hydrogenated in acetic acid (10 ml) over *Adams'* catalyst (40 mg) for 1 h after which time 1.1 mol-equ. of hydrogen had been absorbed.

The filtered solution was evaporated and the oily residue chromatographed on a silica gel plate in hexane/acetone 2:1. The major band was eluted and yielded a mixture of epimeric *dihydrocoleons J* (**6**) (7 mg), m.p. 177–178°. – MS.: M^+ 348 ($C_{20}H_{28}O_5$); *m/e* 330 (M^+ – H_2O), 315 (M^+ – H_2O, – CH_3). – UV./VIS. (CH_3OH) (qual.): 235. – IR. (KBr): 3490, 3300, *1698*, *1682*, 1605 cm^{-1}. – NMR. (d_6-acetone): 1,71 (*s*, 3H, CH_3 (20)).

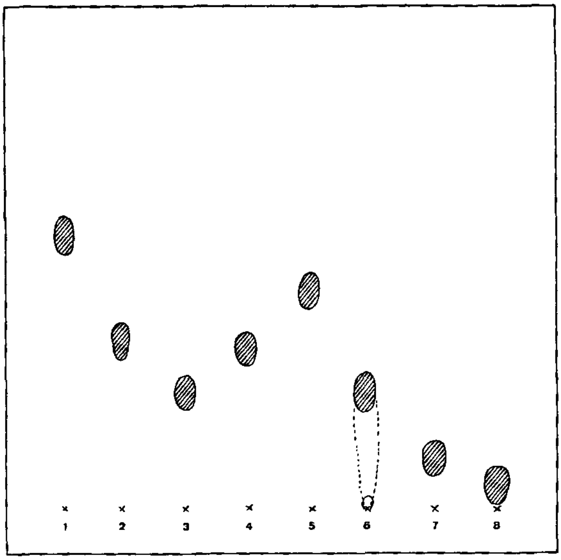

Fig. 6. *Thin layer chromatogram of some diterpenoids isolated from Coleus spp. on silica gel (di-isopropylether)*

1 Coleon C (yellow) [11].
2 Coleon D (orange) [12].
3 Coleon E (red) [9].
4 Coleon G (colourless, $UV._{254}$, purple with H_2SO_4).
5 Coleon H (yellow) [1].
6 Coleon I (orange, not pure) [1].
7 Coleon J (colourless, $UV._{254}$, purple with H_2SO_4).
8 Coleon K (orange) [1].

(b) *Over Palladium.* Coleon J (25 mg) was shaken in 2-propanol (5 ml) with 10% palladium on charcoal (30 mg) under hydrogen for 4 h. The filtered solution was evaporated to give a yellow oil which was shown to be a complex mixture (TLC. on silica gel in chloroform). Three pale yellow bands, separated by TLC. (each < 1 mg) had identical UV./VIS. (CH_3OH) (qual.): *275*, 400; ($CH_3OH/NaOH$) (qual.): *282*, 515, but were not investigated further.

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263. Absolute Konfiguration der enantiomeren α-Cyclogeraniumsäuren, α-Cyclogeraniale, α-Jonone, γ-Jonone, α- und ε-Carotine

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(27. VIII. 73)

Summary. By chemical correlation with manool and ambrein the absolute configurations of the enantiomeric α-cyclogeranic acids, α-cyclogeranials, α-ionones and α- and ε-carotenes have been elucidated.

Einleitung. – Die vorliegende Arbeit ergänzt und erweitert unsere vorläufige Mitteilung von 1969 [5].

Die Zahl der strukturell bekannten Carotinoide dürfte heute gegen 300 betragen. Von diesen sind mehr als 200 chiral. Zu Beginn dieser Arbeit war noch von keinem einzigen Carotin die absolute Konfiguration bekannt. 1957 [6] und 1958 [7] syntheti-

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1) Diplomarbeit, Zürich 1969 [1].
2) Diplomarbeit, Zürich 1970 [2].
3) Diplomarbeit, Zürich 1970 [3].
4) Dissertation, Zürich 1960 [4].