Unusual Rearranged Abietanoic Diterpenoids from *Solenostemon* Species

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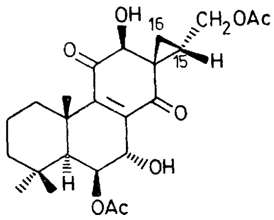
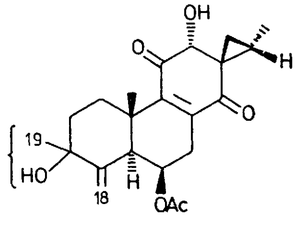
Summary From the leaf-glands of *Solenostemon monostachys* and *S. sylvaticus* (Labiatae) highly modified diterpenoids of the abietane series have been isolated and their structures established.

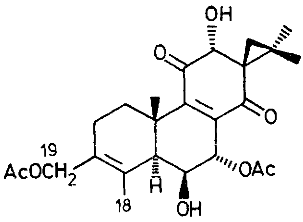
Coleus, Plectranthus, and related species accumulate in their coloured leaf-glands modified diterpenoids of the abietane group in a surprisingly high concentration.[1] We report herein the structures of seven minor constituents 'Syl-A, B, C, and D' (I), (II), (III), and (IVa) from *Solenostemon sylvaticus* (Gürke) Agnew comb. nov. and 'Mon-A, B, and C' (IVb), (IVc), and (IVd) from *S. monostachys* (P. Beauv.) Briq.† They were established mainly from n.m.r. analyses‡ and correlations with previously isolated compounds of similar structures.



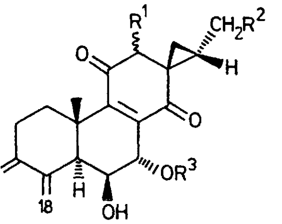
(I) 'Syl-A'



(II) 'Syl-B'



(III) 'Syl-C'



(IV)

a; $R^1 = \alpha$-OH, $R^2 = H$, $R^3 = Ac$: 'Syl-D'
b; $R^1 = \beta$-OAc, $R^2 = H$, $R^3 = Ac$: 'Mon-A'
c; $R^1 = \beta$-OAc, $R^2 = H$, $R^3 = CHO$: 'Mon-B'
d; $R^1 = \left\{\begin{array}{l}\beta\text{-OAc}\\ \beta\text{-OCHO}\end{array}\right.$, $R^2 = OAc$, $R^3 = Ac$: 'Mon-C'

'Syl-A' (I): amorphous; $C_{24}H_{26}O_8$; *m/e* 470 (M^+), is a diacetate [δ ($CDCl_3$) 1·88 and 2·03 (each 3 H, s)], showing three tertiary Me-groups [δ 1·04 and 1·06 (each 3 H, s, 4-Me), 1·51 (3 H, s, 10-Me)], the usual[2,3] pattern for 5-H_α [δ 1·72 (1 H, d-like, $J < 1$ Hz)], 6-H_α [δ 5·52 (1 H, dd, J 2·0 and < 1 Hz)], and 7-H_β [δ 4·42 (1 H, d, J 2·0 Hz)] and, like coleon P,[3] has a β-oxygen substituent [δ 2·90 (1 H, br. d, ^2J 13·0 Hz, 1-H_β) and 4·65 (1 H, s, 12-H)]. A novel feature is the acetoxylated C-17 [δ 1·9 (br, m, hidden, 15-H), and 3·67 and 4·31 (each 1 H, dd, J_{AB} 12·0 Hz, J_{AX} *ca.* 6 Hz, J_{BX} *ca.* 10 Hz)].

'Syl-B' (II): amorphous; $C_{22}H_{28}O_6$; *m/e* 388 (M^+) is a monoacetate [δ ($CDCl_3$) 2·08 (3 H, s)], showing three Me-signals [δ 1·27 (3 H, d, J 6·0 Hz, 15-Me), 1·47 (3 H, s, 10-Me), and 1·59 (3 H, s, 3-Me)] and an exocyclic methylene group similar to that in coleons G, J,[2] and N[3] [δ 5·22 and 5·36 (each 1 H, t-like, $^2J < 1$ Hz, $^4J_{5,18}$ 2·0 Hz, 18-H)]. It lacks a 7-substituent [δ 2·26 (1 H, d-like, J 2·0 Hz, 5-H), 4·55 (1 H, m, $w_{1/2}$ 10·0 Hz, 6-H), and 2·54 and 2·88 (each 1 H, dd, J_{AB} 20·0 Hz, J_{AX} *ca.* 2 Hz, J_{BX} *ca.* 4 Hz, 7-H)]. The α-OH substitution at C-12 follows from the chemical shifts of both 15-Me (see above) and 12-H [δ 4·29 (1 H, s)].

'Syl-C' (III): amorphous, $C_{24}H_{30}O_8$, *m/e* 326 (M^+ − 2AcOH), exhibits Me-signals ($CDCl_3$) at δ 2·03 and 2·06 (each 3 H, s, Ac), 1·28 (3 H, d, J 6·0 Hz, 15-Me), 1·46 (3 H, s, 10-Me), and 1·88 (3 H, br. s, $w_{1/2}$ 5·0 Hz, 4-Me). Thus it has an endocyclic 3,4-double bond similar to coleon O.[3] The low field 7-H [δ 5·71 (1 H, d, J 2·0 Hz)], the AB-system centred at δ 4·64 (2 H, AB_q, J 12·0 Hz, 19-H), and the positive nuclear Overhauser effect of 6-H at δ 4·32 (1 H, dd, J 2·0 and <1 Hz) and the AB-system, upon irradiation at δ 1·88 (4-Me) localise the acetoxy groups as depicted in (III).

The novel structure of 'Syl-D' (IVa), m.p. 187—189 °C (dec.), $C_{22}H_{26}O_6$, *m/e* 326 (M^+ −AcOH), is fully supported by its ^{1}H- and ^{13}C-n.m.r. spectra:§ Me-signals at δ 1·26 (3 H, d, J 6·5 Hz, 15-Me), 1·49 (3H, s, 10-Me), and 1·91 (3H, s, Ac), two exocyclic CH_2 groups at δ_H 4·70 and 4·98 (each 1 H, t, J 1, 5 Hz, 19-H), δ_C 108·9 p.p.m. (1 C, t, C-19), and δ_H 5·15 and 5·28 (each 1 H, t, $^4J_{5,18}$ 2·0 Hz, 18-H), δ_C 109·6 p.p.m. (1 C, t, C-18), with quaternary carbon signals at δ_C 146·8 and 148·3 p.p.m. (each 1 C, s), *cf.* ref. 4. The familiar pattern for 5-, 6-, and 7-H [δ 2·35 (1 H, s-like, $w_{1/2}$ 4·0 Hz), 4·22 (1 H, t-like, J 2·0 Hz), and 5·73 (1 H, d, J 2·0 Hz), respectively], the lack of double allylic protons, and the intense positive Cotton effect ($\Delta\epsilon$ +18·01) establish structure (IVa).

The similar butadienes (IVb), (IVc), and (IVd), isolated from *S. monostachys*, have almost the same ^{1}H- and ^{13}C-n.m.r. features as (IVa).§

'Mon-A' (IVb): m.p. 164—168 °C, $C_{24}H_{28}O_7$, *m/e* 368 (M^+ −AcOH), differs from (IVa) only in having a β-acetoxy group at C-12 [δ 5·70 (1 H, s, 12-H)], whereas 'Mon-B' (IVc), m.p. 158—160 °C, $C_{23}H_{26}O_7$, *m/e* 414 (M^+), has a 7α-formyloxy group [δ 5·83 (1 H, d, J 2·0 Hz, 7-H) and 8·10 (1 H, s, formyl-H)].

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† A full account of further diterpenoids from these plants will be published elsewhere.

‡ Extensive multiple resonance experiments lead unequivocally to the assigned structures. For detailed arguments concerning 8-hydroxy-1-methylspiro[2·5]oct-5-ene-4,7-dione derivatives see reports on coleons G and J (ref. 2) as well as coleons M to Q (ref.3).

§ ^{1}H-n.m.r. spectra in $(CD_3)_2CO$; ^{13}C-n.m.r. spectra in $CDCl_3$.

'Mon-C' (IVd): amorphous, $C_{25}H_{28}O_9$–$C_{26}H_{30}O_9$, m/e 472–486 (each M^+) was obtained as an unseparable β-acetoxy–formyloxy mixture at C-12 in the ratio 3:2 [δ 5·84 (s, 12-H), 7·98 (s, formyl-H), and 5·87 (s, 12-H), 2·14 (s, Ac)]. To our knowledge (IVd) is the first abietane derivative having only one single skeletal Me-group [δ 1·36 (3 H, s, 10-Me)]. As in (I), the AB-part of the 15-CH_2O appears at δ_H 3·59 and 4·29 (each 1 H, J_{AB} 12·0 Hz, J_{AX} *ca.* 7 Hz, J_{BX} *ca.* 10 Hz), and δ_C 61·7 p.p.m. (1 C, t, C-17)]. The absolute configurations of all these diterpenoids were established by correlation of their c.d. curves with known compounds.[3]

The compounds reported here are very labile. We consider them to be active intermediates in the terpene-catabolism of these plants. The combination of several unusual structure elements such as butadienes, cyclopropylcarbinols *etc.* is interesting from the biogenetic point of view.[3]

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[1] For our most recent paper on leaf-gland pigments, see: S. Arihara, P. Rüedi, and C. H. Eugster, *Helv. Chim. Acta*, 1977, **60**, 1443.

[2] M. Moir, P. Rüedi, and C. H. Eugster, *Helv. Chim. Acta*, 1973, **56**, 2539.

[3] S. Arihara, P. Rüedi, and C. H. Eugster, *Helv. Chim. Acta*, 1975, **58**, 343.

[4] H. U. Pfeffer and M. Klessinger, *Org. Magnetic Resonance*, 1977, **9**, 121.