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BISABOLENE DERIVATIVES AND OTHER CONSTITUENTS FROM *COREOPSIS* SPECIES

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Key Word Index—*Coreopsis fasciculata*; *C. mitica*; *C. longipes*; *C. capillacea*; *C. nodosa*; Compositae; sesquiterpenes; bisabolene derivatives; phenylpropane derivatives; 1,3-diacetoxy tetradeca-6,12-dien-8,10-diin.

Abstract—The investigation of five *Coreopsis* species afforded in addition to typical compounds isolated previously two new perezone derivatives, a coniferyl alcohol derivative and a diacetylenic compound.

So far the investigations of *Coreopsis* species (Compositae, tribe Heliantheae, subtribe Coreopsidinae) have shown that special acetylenic compounds [1], flavonoids, chalcones and aurones [2] as well as a large variety of phenylpropane derivatives [3] are characteristic. We have now studied a few further species which gave some new compounds in addition to ones isolated previously.

The aerial parts of *Coreopsis fasciculata* Wedd. afforded phenyl heptatriyne [1], heptadeca-1,8-dien-11,13,15-triyne, eugenol methyl ether, 2-hydroxy-α-curcumene and two quinones (**2** and **4**); their structures followed from the molecular formulae and the ^{1}H NMR spectra (Table 1). Compound **2** was obviously perezone methyl ether. Accordingly, all signals were nearly identical with those of perezone and the relative position of the methoxy group followed from the coupling $J_{2,15}$. The latter was absent in the spectrum of **4**, the signal of H-15 being a sharp singlet. The methoxy group was replaced by an acetoxy group (δ2.35, *s*) and its relative position could be deduced from the presence of a coupling $J_{5,7}$ as followed from spin decoupling.

The roots of *C. mitica* DC. afforded trideca-1,11-dien-3,5,7,9-tetrayne, the corresponding acetoxy derivative and the aldehyde [1], perezone (**1**) and the isovalerate **3** [4], bornylferulate [5] and parvifolin (**10**) [5]. The roots of *C. capillacea* HBK. also contain trideca-1,11-dien-3,5,7,9-tetrayne, phenyl hepta-1,3-diin-5-ene and the corresponding 7-hydroxy and acetoxy derivative [1], the isoeugenol derivative **7** [3] and the diacetate **11**. The structure followed from the UV maxima, which indicated the presence of an endiynene [1], the molecular formula and the ^{1}H NMR spectrum (see Experimental). The position of the acetoxy groups was indicated by spin decoupling which led to the sequence $AcOCH_2CH_2CH(OAc)CH_2$ while the position of the chromophoric system directly followed from the ^{1}H NMR spectral data. Compound **11** is the 4,5-dihydro derivative of the more widespread corresponding endiynediene [1].

The aerial parts of *C. longipes* Hook. gave similar compounds as other *Coreopsis* species (see Experimental) and in addition to the isoeugenol derivatives **6** and **7** the corresponding alcohol **5**, its structure being easily deduced from the ^{1}H NMR spectrum (see Experimental) which was close to that of **6**, only the H-9 signals being shifted up field. The roots gave only known compounds (see Experimental). The aerial parts of *C. nodosa* Sherff. gave in addition to **7** some further typical compounds (see Experimental).

The present results agree nicely with those of *Coreopsis* species investigated previously.

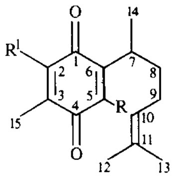
EXPERIMENTAL

The air dried plant material was worked-up in the usual fashion. The aerial parts of *Coreopsis fasciculata* (160 g, voucher RMK 9003) gave CC fractions (100 ml) as follows: 1 (petrol), 2 (Et_2O–petrol, 20:1) and 3 (Et_2O–petrol, 3:1). TLC (silica gel, petrol) of fraction 1 gave 2 mg heptadeca-1,8-dien-11,13,15-triyne and 15 mg phenylhepta-1,3,5-triyne. TLC of fraction 2 (Et_2O–petrol, 20:1) gave 10 mg eugenol methyl ether and 5 mg **2**, while TLC of fraction 3 (Et_2O–petrol, 1:3) afforded 10 mg 2-hydroxy-α-curcumene and 5 mg **4**.

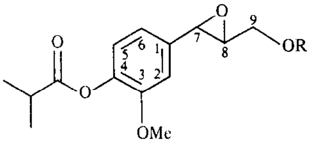
Table 1. ^{1}H NMR spectral data of compounds **2** and **4** (400 MHz, $CDCl_3$, TMS as int. standard)

	2	**4**
H-2	6.47 *q*	—
H-5	—	6.52 *d*
H-7	3.09 *br tq*	2.92 *br tq*
H-9	1.93 *m*	1.96 *m*
H-10	5.06 *tqq*	5.04 *tqq*
H-12	1.68 *br s*	1.65 *dt*
H-13	1.58 *br s*	1.55 *br s*
H-14	1.23 *d*	1.10 *d*
H-15	2.04 *d*	1.93 *s*
OAc	—	2.35 *s*
OMe	3.95 *s*	—

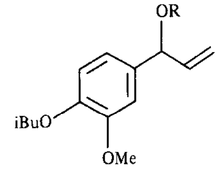
J (Hz): 7, 8 = 7, 14 = 9, 10 = 7; 10, 12 = 10, 13 ~ 1; compound **2**: 2, 15 = 1.7; compound **4**: 5, 7 = 1.



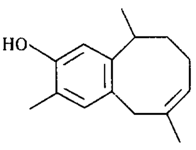
	1	2	3	4
R	OH	OMe	OiVal	H
R1	H	H	H	OAc



5 R=H
6 R=Ac
7 R=iBu



8 R=Ac
9 R=iBu



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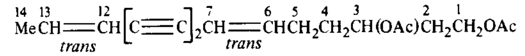

$\overset{14}{\mathrm{Me}}\overset{13}{\mathrm{CH}}\underset{trans}{=\!=}\overset{12}{\mathrm{CH}}[\mathrm{C}\equiv\mathrm{C}]_2\overset{7}{\mathrm{CH}}\underset{trans}{=\!=}\overset{6}{\mathrm{CH}}\overset{5}{\mathrm{CH_2}}\overset{4}{\mathrm{CH_2}}\overset{3}{\mathrm{CH}}(\mathrm{OAc})\overset{2}{\mathrm{CH_2}}\overset{1}{\mathrm{CH_2}}\mathrm{OAc}$ **11**

The roots of *Coreopsis mitica* (250 g, voucher RMK 7338) gave CC fractions as follows (100 ml): 1 (petrol), 2 (Et_2O–petrol, 1 : 10) and 3 (Et_2O–petrol, 1 : 1). TLC of fraction 1 (petrol) gave 2 mg trideca-1,11-diene-3,5,7,11-tetrayne, TLC of fraction 2 (Et_2O–petrol, 1 : 20) gave 10 mg 13-acetoxytrideca-1,11-diene-3,5,7,11-tetrayne and 8 mg trideca-1,11-diene-3,5,7,9-tetrayne-13-al. TLC of fraction 3 (Et_2O–petrol, 1 : 1) afforded 5 mg **3**, 80 mg **1**, 70 mg parvifolin and 100 mg bornyl ferulate.

The roots of *Coreopsis longipes* (180 g, grown from seeds, voucher 245/78) gave CC fractions (100 ml) as follows: 1 (petrol), 2 (Et_2O–petrol, 1 : 10), 3 (Et_2O–petrol, 1 : 3) and 4 (Et_2O–petrol, 1 : 1). TLC of fraction 1 (petrol) gave 0.1 mg tridecapentaynene, 5 mg trideca-1,11-diene-3,5,7,9-tetrayne and 30 mg phenylhepta-1,3,5-triyne. TLC of fraction 2 (Et_2O–petrol, 1 : 10) gave 10 mg phenyl-[7-acetoxyhept-5-en-1,3-diyne] and 10 mg 2-phenyl-5-[3-acetoxyprop-1-inyl]-thiophene. TLC of fraction 3 (Et_2O–petrol, 1 : 3) gave 25 mg **9**, 15 mg **8**, 80 mg **6**, 5 mg ferulyl aldehyde and 8 mg methyl ferulate. TLC of fraction 4 (Et_2O–petrol, 1 : 1) gave 5 mg **5**. The aerial parts (2 kg) gave CC fractions (100 mg) as follows: 1 (petrol), 2 (Et_2O–petrol, 1 : 10) and 3 (Et_2O–petrol, 1 : 3 and 1 : 1). TLC of fraction 1 (petrol) gave 70 mg germacrene D, 35 mg phenylhepta-1,3,5-triyne and 7 mg 2-phenyl-5-[hepta-1,3,5-triynyl (1)]-thiophene. TLC of fraction 2 (Et_2O–petrol, 1 : 10) gave 80 mg methyl linolenate and 30 mg bisabola-1,10-diene-3,6-endoperoxide, while TLC of fraction 3 (Et_2O–petrol, 1 : 3) afforded 15 mg **9**, 25 mg **7** and 50 mg **6**.

The roots of *Coreopsis capillacea* (180 g, voucher RMK 7863) gave CC fractions (100 mg) as follows: 1 (petrol), 2 (Et_2O–petrol, 1 : 10), 3 (Et_2O–petrol, 1 : 3) and 4 (Et_2O–petrol, 1 : 1). TLC of fraction 1 (petrol) gave 1 mg trideca-1,11-diene-3,5,7,9-tetrayne and 45 mg 1-phenylhept-5*E*-ene-1,3-diyne. TLC of fraction 2 (Et_2O–petrol, 1 : 10) afforded 20 mg 7-acetoxy-1-phenylhept-5E-ene-1,3-diyne and 25 mg **7**. TLC of fraction 3 (Et_2O–petrol, 1 : 3) gave 15 mg **11** and TLC of fraction 4 (Et_2O–petrol, 1 : 1) afforded 3 mg 7-hydroxy-1-phenyl-hept-5*E*-ene-1,3-diyne.

The aerial parts of *Coreopsis nodosa* (310 g, voucher RMK 9032) gave CC fractions (100 mg) as follows: 1 (petrol), 2 (Et_2O–petrol, 1 : 10), 3 (Et_2O–petrol, 1 : 3) and 4 (Et_2O). TLC (petrol) of fraction 1 gave 30 mg α-selinene, TLC (Et_2O–petrol, 1 : 10) of fraction 2 gave 10 mg 7-acetoxy-1-phenyl-hept-5*E*-ene-1,3-diyne and 10 mg 1-acetoxy-2-chloro-trideca-3*E*,11*E*-diene-5,7,9-triyne, TLC of fraction 3 (Et_2O–petrol, 1 : 3) gave 50 mg coniferyl cinnamate and TLC of fraction 4 (Et_2O) gave 20 mg 4,2′-dihydroxy-4′-methoxychalcone.

5-O-Methylperezone (**2**). Yellow oil; IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 1665, 1650, 1600 (quinone); MS *m/z* (rel. int.): 262.157 $[M]^+$ (18) ($C_{16}H_{22}O_3$), 247 $[M-Me]^+$ (4), 219 $[247-CO]^+$ (22), 180 $[M-C_6H_{10}$, McLafferty$]^+$ (100).

2-Acetoxy-5-desoxyperezone (**4**). Yellow oil; IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 1785 (OAc), 1670, 1655, 1610 (quinone); MS *m/z* (rel. int.): 290.152 $[M]^+$ (2.5) ($C_{17}H_{22}O_4$), 248 $[M-\text{ketene}]^+$ (17), 209 $[M-C_6H_9]^+$ (44), 166 $[248-C_6H_{10}$, McLafferty$]^+$ (100).

4-O-Isobutyryl-3-O-methyl-7,8-epoxyconiferyl alcohol (**5**). Colourless oil; IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 3620 (OH), 1770 (PhOCOR); MS *m/z* (rel. int.): 266.115 $[M]^+$ (8) ($C_{14}H_{18}O_5$), 248 $[M-H_2O]^+$ (2), 196 $[M-O{=}C{=}C(Me)_2]^+$ (70), 166 $[196-CH_2O]^+$ (52), 137 $[166-CHO]^+$ (100); ^{1}H NMR ($CDCl_3$): δ 6.92 (*br s*, H-2), 7.01 (*d*, H-5, *J* = 8 Hz), 6.90 (*br d*, H-6, *J* = 8 Hz), 4.17 (*d*, H-7, *J* = 4 Hz), 3.45 (*m*, H-8), 3.55 (*m*, H-9), 2.83 (*qq*, *J* = 7, 7 Hz) and 1.32 (*d*, *J* = 7 Hz) (*iso*-butyrate), 3.82 (*s*, OMe).

1,3-Diacetoxy-tetradeca-6E,12E-diene-8,10-diyne (**11**). Unstable colourless oil; IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 2240 (C≡C), 1745 (OAc), 955 (*trans* CH=CH); MS *m/z* (rel. int.): 302.152 $[M]^+$ (5) ($C_{18}H_{22}O_4$), 242 $[M-HOAc]^+$ (24), 199 $[243-COMe]^+$ (45), 129 $[C_{10}H_9]^+$ (42), 43 $[MeCO]^+$ (100); UV $\lambda_{\max}^{\mathrm{Et_2O}}$ nm: 312, 292, 275; ^{1}H NMR ($CDCl_3$): δ 4.10 (*t*, H-1, *J* = 6.5 Hz), 1.89 (*dt*, H-2, *J* = 6.5, 6.5 Hz), 5.00 (*tt*, H-3, *J* = 7, 6.5 Hz), 1.70 (*m*, H-4), 2.09 (*br dt*, H-5, *J* = 7, 7 Hz), 6.25 (*dt*, H-6, *J* = 15, 7 Hz), 5.57 (*br d*, H-7 and H-12, *J* = 15 Hz) 6.33 (*dq*, H-13, *J* = 15, 7 Hz), 1.84 (*dd*, H-14, *J* = 7, 1.5 Hz), 2.06 (*s*, OAc, 6H).

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REFERENCES

1. Bohlmann, F., Burkhardt, T. and Zdero, C. (1973) *Naturally Occurring Acetylenes*. Academic Press, London.
2. Swain, T. and Williams, C. A. (1977) *The Biology and Chemistry of the Compositae* (Heywood, V. H., Harborne, J. B. and Turner, B. L., eds.) p. 685. Academic Press, London.
3. Bohlmann, F. and Zdero, C. (1968) *Chem. Ber.* **101**, 3242.
4. Nathan, P. J., Garcia, E. and Mendoza, V. (1977) *Phytochemistry* **16**, 1086.
5. Bohlmann, F. and Zdero, C. (1977) *Chem. Ber.* **110**, 468.