REFERENCES

1. Bertelli, D. J. and Crabtree, J. H. (1968) *Tetrahedron* **24**, 2079.
2. Vokac, K., Samek, Z. and Herout, V. (1970) *Collect. Czech. Chem. Commun.* **35**, 1296.
3. Daniewski, W. M., Kocor, M. and Krol, J. (1975) *Bull. Acad. Pol. Sci. Ser. Sci. Chem.* **23**, 637.
4. Widen, K. G. and Seppa, E. L. (1979) *Phytochemistry* **18**, 1226.
5. Daniewski, W. M., Kroszczynski, W., Warzun, A., and Rymkiewicz, A. (1983) *10th Conf. on Isoprenoids*, Vol. 21. Czechoslovak Academy of Sciences, Czechoslovakia
6. Kohara, K. (1969) *Bull. Chem. Soc.* (*Jpn.*) **42**, 3229.

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AN ACETYLENIC EPOXIDE AND A FERULATE FROM *COREOPSIS LONGULA*

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Key Word Index—*Coreopsis longula*; Compositae; acetylenes; hepta-decatetraendiyne derivative; ferulic acid ester.

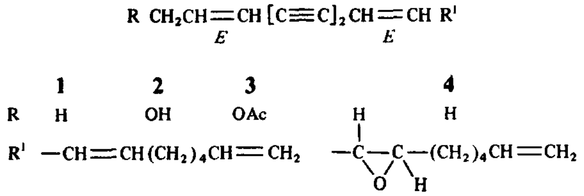
Abstract—The aerial parts of *Coreopsis longula* gave, in addition to known compounds, a new acetylenic epoxide, hepta-deca-1,9*E*,15*E*-trien-11,13-diyn-7,8-epoxide, while the roots afforded a new ferulate, coniferyl ferulate.

Many species from the large genus *Coreopsis* (tribe Heliantheae) have been studied chemically. In addition to acetylenic compounds, flavonoids and phenyl propane derivatives [1] may be characteristic of the genus. We have now studied *Coreopsis longula* Blake from Peru. The aerial parts of this plant gave the epoxide **5** [1], the acetylenic compounds **1–3** [1] and the new epoxide **4**. The molecular formula of **4**, $C_{17}H_{20}O$, was deduced from the chemical ionization mass spectrum while the UV spectrum indicated the presence of an endiyne [1]. The ^1H NMR spectrum showed the presence of a vinyl end group and a propenyl end group. As all the signals were assigned by spin decoupling, the position and the configuration of the double bonds and the epoxide were determined. Thus **4** was the epoxide of **1**.

The roots also contained **1**, **4** and **5** as well as **6** [1] and the ferulate **7**, the structure of which followed from the ^1H NMR spectra of **7** and its acetate **8**.

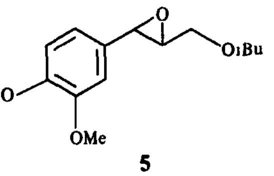
EXPERIMENTAL

The air-dried plant material (voucher RMK 9189, collected in January 1983 in Peru) was worked-up in the usual fashion [2]. The extract of the aerial parts (300 g) was separated by CC and gave the following fractions: 1 (petrol), 2 (Et_2O–petrol, 1 : 9), 3 (Et_2O–petrol, 1 : 3) and 4 (Et_2O and Et_2O–MeOH, 8 : 1). TLC (petrol) of fraction 1 gave 50 mg **1** and TLC (Et_2O–petrol, 1 : 5) of fraction 2 afforded 2 mg **4** (R_f 0.70), 2 mg **3** and 3 mg **5**. TLC of fraction 3 (Et_2O–petrol, 1 : 1) gave 2 mg **2**, while fraction 4 gave nothing of interest. CC of the extract of the roots (100 g) gave the following fractions: 1 (petrol and Et_2O–petrol, 1 : 20), 2 (Et_2O–petrol, 1 : 3) and 3 (Et_2O–petrol, 1 : 1 and Et_2O). TLC of fraction 1 (petrol) gave 2 mg **1** and 2 mg **4**. TLC (Et_2O–petrol,



$$\underset{E}{\text{R CH}_2\text{CH}=\text{CH}}[\text{C}\equiv\text{C}]_2\underset{E}{\text{CH}=\text{CH}}\text{ R}'$$

	1	2	3	4
R	H	OH	OAc	H
R'	$-CH=CH(CH_2)_4CH=CH_2$			$-\overset{H}{C}-\underset{H}{C}-(CH_2)_4CH=CH_2$ (O)



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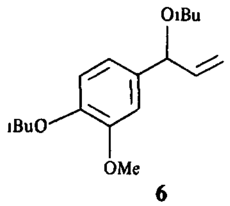

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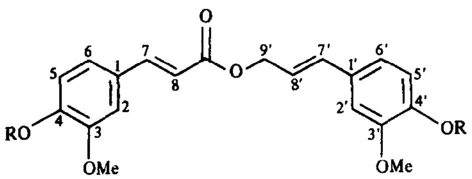

7 R = H
8 R = Ac

1:3) of fraction 2 afforded 5 mg **6** and TLC of fraction 3 (Et_2O–petrol, 1:1) gave 5 mg **5**, 5 mg **6**, 10 mg **7** (R_f 0.45) and 2 mg **2**. Known compounds were identified by comparison of their 400 MHz ^1H NMR spectra and mass spectra with those of authentic material.

Hepta-deca 1,9E,15E-*trien*-11,13-*diyn*-7,8-*epoxide* (**4**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2200 (C≡C), 1640 (*trans* CH=CH); UV $\lambda_{max}^{Et_2O}$ nm: 315, 295, 278, 263, 250, 237, 230; CIMS (isobutane) *m/z* (rel. int.): 241 $[M+1]^+$ (5); ^1H NMR ($CDCl_3$, 400 MHz, TMS as internal standard): δ 4.99 (*d* (*br*), H-1*t*), 4.95 (*d*(*br*), H-1*c*), 5.73 (*ddt*, H-2), 2.05 (*t*(*br*), H-3), 2.82 (*dt*, H-7), 3.11 (*dd*, H-8), 5.93 (*dd*, H-9), 5.89 (*d*, H-10), 5.55 (*d*(*br*), H-15), 6.33 (*dq*, H-16), 1.82 (*dd*, H-17); *J* (Hz): 1*t*, 2 = 17; 1*c*, 2 = 10; 2, 3 = 7; 6, 7 = 6; 7, 8 = 2; 8, 9 = 7; 9, 10 = 15, 16 = 16; 15, 17 = 2; 16, 17 = 7.

Coniferyl ferulate (**7**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3540 (OH), 1715 (CO_2R), 1635 (Ph), 1590 (C=C); MS *m/z* (rel. int.): 356.126 $[M]^+$ (32) (calc. for $C_{20}H_{20}O_6$: 356.126), 177 $[RCO]^+$ (100), 131 (51); ^1H NMR ($CDCl_3$). δ 7.03 (*d*, H-2), 6.81 (*d*, H-5), 7.07 (*dd*, H-6), 7 65 (*d*, H-7), 6.31 (*d*, H-8), 6.94 (*d*, H-2′), 6.91 (*d*, H-5′), 6.90 (*dd*, H-6′), 6.62 (*d* (*br*), H-7′), 6.19 (*dt*, H-8′), 4.82 (*dd*, H-9′), 3.90 and 3.91 (each *s*, OMe); *J* (Hz): 2.6 = 2′, 6′ = 2; 5, 6 = 5′, 6′ = 8; 7, 8 = 7′, 8′ = 16; 7′, 9′ = 1.5; 8′, 9′ = 7.

Acetylation (Ac_2O, 70°) of **7** gave **8**; colourless crystals, mp 115°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1770 (PhOAc), 1720 (CO_2R), 1640 (Ph), 1605 (C=C); MS *m/z* (rel. int.): 440.147 $[M]^+$ (8) (calc. for $C_{24}H_{24}O_8$: 440.147), 398 $[M-\text{ketene}]^+$ (22), 356 $[398-\text{ketene}]^+$ (23), 219 $[RCO]^+$ (28), 177 $[219-\text{ketene}]^+$ (100); ^1H NMR ($CDCl_3$): δ 7.12 (*s*(*br*), H-2), 7.06 (*d*, H-5), 7.14 (*dd*, H-6), 7.69 (*d*, H-7), 6.43 (*d*, H-8), 7.00 (*m*, H-2′, H-5′, H-6′), 6.68 (*d* (*br*), H-7′), 6.31 (*dt*, H-8′), 4.87 (*dd*, H-9′), 3.87 and 3.86 (*s*, OMe), 2.33 and 2 32 (*s*, OAc); *J* (Hz): 2, 6 = 2; 5, 6 = 8; 7, 8 = 7′, 8′ = 16; 7′, 9′ = 1.5; 8′, 9′ = 7.

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REFERENCES

1. Bohlmann, F., Ahmed, M., Grenz, M., King, R. M. and Robinson, H. (1983) *Phytochemistry* **22**, 2858.
2. Bohlmann, F., Zdero, C., King, R. M. and Robinson, H. (1984) *Phytochemistry* **23**, 1979.

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NEW SOURCES OF GUTTA-PERCHA IN *GARRYA FLAVESCENS* AND *G. WRIGHTII*

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Key Word Index—*Garrya flavescens*; *Garrya wrightii*; Garryaceae; polyisoprene; gutta-percha.

Abstract—Analyses of extracts from whole-plant samples revealed that *Garrya flavescens* and *Garrya wrightii* produced gutta (*trans*-1,4-polyisoprene) as the major hydrocarbon in yields of 1.2 and 0.4 %, respectively. The average MWs of gutta were 142 000 for *G. flavescens* and 10 000 for *G. wrightii*. These species also yielded moderate amounts of 'oil' and 'polyphenol'. To our knowledge, these are the first species of Garryaceae reported to produce gutta.

Currently, we are analysing U.S. plants for their fiber, protein, 'oil', 'polyphenol' and 'hydrocarbon' contents to identify species that are promising commercial alternate crops [1, 2]. Many dicotyledonous hydrocarbon-producing plants native to the U.S. produce rubber (*cis*-1,4-polyisoprene) but few produce gutta (*trans*-1,4-polyisoprene) [3]. We are interested in such species because of U.S. dependency on foreign sources of natural polyisoprenes.

In analysing plants native to Arizona, we discovered that *Garrya flavescens* S. Wats. and *Garrya wrightii* Torr. of Garryaceae contained gutta in whole-plant extracts. Previously, the seed oils of several species of Garryaceae have been reported to be rich in petroselinic acid [4]. However, to our knowledge *Garrya* species have not been reported to be gutta producers.

'Hydrocarbon' fractions of plant samples were extracted with hexane and analysed by IR and ^{13}C NMR spectroscopy and by gel permeation chromatography (GPC). IR spectra indicated that hydrocarbon of *G. wrightii* was amorphous gutta with characteristic absorptions centred at 8.7, 11.9 and 12.4 μm (shoulder),