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): $\delta$ 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 ($CDCl_3$). $\delta$ 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 ($CDCl_3$): $\delta$ 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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# 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 $\mu m$ (shoulder),

Table 1. Analyses of *Garrya* species

| Genus and species | % Ash | %* Crude protein† | %* Polyphenol‡ | %* Oil§ | %* Hydrocarbon‖ |
|---|---|---|---|---|---|
| *Garrya flavescens* S. Wats. | 13.2 | 2.9 | 11.1 | 2.7 | 1.2 |
| *Garrya wrightii* Torr. | 3.2 | 1.8 | 4.8 | 2.7 | 0.4 |

*Per cent on a moisture- and ash-free sample weight basis.

†Crude protein: Per cent Kjeldahl nitrogen of whole-plant sample × 6.25.

‡Polyphenol: aqueous ethanol solubles of the acetone extract (see Experimental).

§Oil: hexane solubles of the acetone extract.

‖Hydrocarbon: hexane extract from the acetone marc.

whereas hydrocarbon of *G. flavescens* was crystalline gutta with distinctive sharp peaks at 11.4, 11.6 and 12.5 μm. The spectrum of amorphous gutta was similar to that of guayule rubber, which was used for comparison. The major differences between the spectra of amorphous and crystalline gutta were in the region from *ca* 11 to 14 μm. The crystallinity of gutta is influenced by several factors such as the type of solvent used in preparing films for IR, MW and temperature [5]. Spectral analyses by $^{13}C$ NMR showed that hydrocarbon from both species was essentially all *trans*-1,4-polyisoprene with chemical shifts similar to those previously reported [6, 7].

Weight average MWs for gutta were 142 000 for *G. flavescens* and 10 000 for *G. wrightii* (1 627 000 for guayule rubber) as determined by GPC [8]. Table 1 shows that the yields of hydrocarbon from *G. flavescens* and *G. wrightii* were 1.2 and 0.4%, respectively (dry, ash-free sample basis). These species also yielded moderate amounts of 'oil' and 'polyphenol' fractions. Protein content was low.

## EXPERIMENTAL*

Mature whole plants (above-ground) of the *Garrya* species were air-dried, milled to pass a screen with 1-mm holes and Soxhlet-extracted sequentially with $Me_2CO$ and hexane [2, 9]. $Me_2CO$ extracts were partitioned between hexane and 87.5% aq. EtOH to obtain 'oil' and 'polyphenol' extracts, respectively [10]. Procedures for extracting guayule rubber have been reported previously [11]. IR spectra of 'hydrocarbon' cast on an NaCl disk, were obtained with a Model 137 Perkin–Elmer spectrophotometer. $^{13}C$ NMR spectra of hydrocarbon fractions were obtained with a Bruker WH-90 spectrometer at 22.63 MHz. $^{13}C$ NMR analysis of guayule rubber was done with a Bruker WM-300 spectrometer at 75 MHz. $CDCl_3$ was the solvent for gutta and rubber, and TMS was the internal standard for both NMR instruments. Voucher specimens of the two *Garrya* species have been retained at the Arizona State University Herbarium.

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