EXPERIMENTAL

Plant material Poison sumac [*T vernix* L (Kuntze)] was collected in May 1978 near Hattiesburg, Mississippi and used immediately after collection The plant was authenticated by Professors Maynard Quimby and Thomas M Pullen and herbarium specimens are stored in the Drug Plant Herbarium, Department of Pharmacognosy, School of Pharmacy, University of Mississippi

General procedures Mps are uncorr. ^{1}H NMR spectra were recorded on a Varian EM-390 90 MHz instrument ^{13}C NMR spectra were obtained on a JEOL NJM-FX-60 Fourier transform instrument Chemical shifts were measured in δ-values (ppm) with TMS as int standard $CDCl_3$ was used as solvent in all cases A Finnigan 3200 GC/MS/DS instrument was used for GC/MS analysis at 70 eV The TMSi derivatives were prepared using BSTFA–pyridine and chromatographed using a 3% OV-225 column at 210° A Beckman GC-65 instrument was used for the GC analysis following lit procedures [2]

A Waters Associates Prep LC/system 500A liquid chromatograph with Prep PAK-500/C_{18} cartridge and RI detector was used for preparative separations For analytical studies, a Waters Associates chromatograph, equipped with U6K injector, a model 6000 pump and a model 440 UV detector at 254 nm, was used A 30 cm × 3 9 mm i d reversed phase column (μBondapak C_{18}) with a 10 μm particle size was used and analysis was done as previously reported [3]

Extraction Poison sumac (*T vernix*) leaves (141 5 g) were extracted by percolation with 95% EtOH (2 l × 6) at room temp After removal of the solvent, 28 5 g of residue was obtained Purification and other procedures have been described earlier [1–5]

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ACETYLENIC COMPOUNDS FROM *BIDENS GRAVEOLENS**

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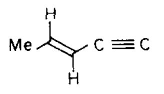
Key Word Index—*Bidens graveolens*, *Bidens* sp., Compositae; acetylenic compounds, C_{14}-acetylene, C_{17}-acetylene, monoterpene.

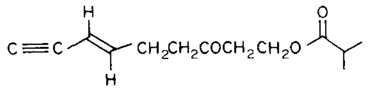
Abstract—*Bidens graveolens* afforded, in addition to known compounds, two new acetylenic esters and a monoterpene diol Other species only gave known compounds.

The roots of *Bidens graveolens* Mart. afforded germacrene D, bicyclogermacrene, cinnamyl alcohol and its acetate, **1a** [1], **2** [1] and **10** as well as the keto ester, **6**, the structure of which followed from its UV spectrum, molecular formula and ^{1}H NMR spectral data (Table 1). The presence of an isobutyrate group was deduced from the typical ^{1}H NMR signals, while the positions and the stereochemistry of the double bonds and the position of the keto group followed from spin decouplings, which clearly showed the sequences **A** and **B**.

As the UV spectrum required the presence of an enediynene chromophore [2], the structure of **6** was settled. The aerial parts afforded germacrene D, bicyclogermacrene, spathulenol, caryophylleneepoxide (**3**), the hydroxy germacradiene, **4**, the diynenes, **7** and **8** [2], as well as the isobutyrate, **9**, the structure of which followed from its ^{1}H NMR spectrum (Table 1), which was close to that of the known acetate [2]. Again, the nature of the ester group followed from the typical ^{1}H NMR signals. Furthermore, a small amount of **5a** was isolated. The



A



B

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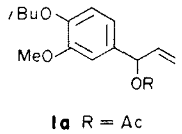
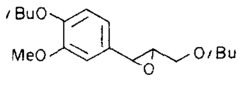
*Part 262 in the series "Polyacetylenic Compounds". For Part 261 see Greger, H, Grenz, M and Bohlmann, F (1982) *Phytochemistry* **21**, 1071



1a R = Ac
1b R = iBu



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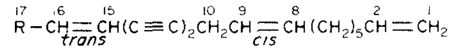
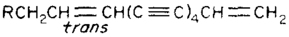


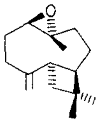
$R-\underset{trans}{CH=CH}(C\equiv C)_2CH_2\underset{cis}{CH=CH}(CH_2)_5CH=CH_2$

7 R = CH_2OH
8 R = CHO
9 R = CH_2OiBu



$RCH_2\underset{trans}{CH=CH}(C\equiv C)_4CH=CH_2$

10 R = H
11 R = OH
12 R = OAc
13 R = H, *cis*



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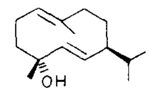

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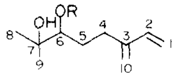
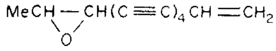
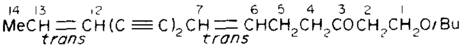


5a R = H
5b R = Ac



$MeCH-CH(C\equiv C)_4CH=CH_2$ (epoxide O)

14



$\underset{trans}{MeCH=CH}(C\equiv C)_2CH_2\underset{trans}{CH=CH}CH_2CH_2COCH_2CH_2OiBu$

6

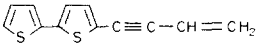
Table 1 ${}^1H$ NMR spectral data of **6** and **9** (400 MHz, $CDCl_3$, TMS as int standard)

	6		**9**
H-1	4 33 *t*	H-1 *c*	4 93 *br d*
H-2	2 72 *t*	H-1 *t*	4 99 *br d*
H-4	2 55 *t*	H-2	5 81 *dd*
H-5	2 42 *br dt*	H-3, H-7	2 04 *m*
H-6	6 24 *dt*	H-4–H-6	1 58 *m*
H-7	5 58 *br d*	H-8	5 38 *m*
H-12	5 56 *dq*	H-9	5 51 *m*
H-13	6 31 *dq*	H-10	3 07 *br d*
H-14	1 82 *dd*	H-15	5 75 *br d*
OCOR	2 52 *qq*	H-16	6 27 *dt*
	1 13 *d*	H-17	4 61 *dd*
		OCOR	2.57 *qq*
			1 17 *d*

J (Hz) Compound **6** 1, 2 = 6, 4, 5 = 7 5, 5, 6 = 7, 6, 7 = 12, 13 = 15, 12, 14 = 1 5, 13, 14 = 7, compound **9** 1*c*, 2 = 10, 1*t*, 2 = 17, 9, 10 = 6, 15, 16 = 15, 15, 17 = 1 5, 16, 17 = 6, O*i*Bu 2′, 3′ = 2′, 4′ = 7

$RCH_2CH=CH(C\equiv C)_3(CH=CH)_2H$

15a R = H
15b R = OAc



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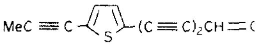

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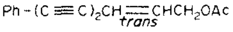
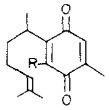
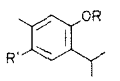


$Ph-(C\equiv C)_2\underset{trans}{CH=CH}CH_2OAc$

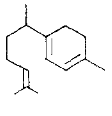
18



19 R = H
20 R = OH



	21	**22**	**23**
R	Me	iBu	Me
R'	H	H	OMe



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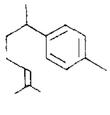

25

Table 2 Constituents of further *Bidens* species

Species (voucher)	Roots		Leaves	
	Air-dried wt (g)	Wt (mg) of compound	Air-dried wt (g)	Wt (mg) of compound
B andicola HBK (RMK 6876/7607)	280	10 **2**, 10 **10** and **13** (2 1), 30 **19**, 14 **20**, 18 **21**, 54 **22**, 3 5 **23**, 2 **24**, 2 **25**	240	3 **11**, 8 **14**, 6 **15b**
B connatus Willd (RMK 7572)	30	2 **10**, 1 **17**	165	2 **10**, 1 **12**, 1 **15a**, 1 **16**
B nitis (Michx) Sherff (RMK 7152)	100	34 **10**, 40 **11**, 5 **1b**, 40 **2**	500	400 Germacrene D, 42 **2**
B rubifolia HBK (RMK 8057)	40	3 **1a**, 2 **1b**, 100 **2**, 1 **10**, 1 **12**	20	6 Squalene, 5 methylcoumarate
B squarrosa HBK (RMK 7176)	100	22 **2**, 10 **10**, 8 **11**	190	5 **11**
B cynapiifolia HBK (RMK 8190)	5	4 **1a**, 5 **2**	200	5 Germacrene D, 5 bicyclogermacrene, 5 spathulenol

^{1}H NMR spectral data of the corresponding monoacetate clearly showed that a dihydroxy derivative of dihydromyrcene was present (see Experimental). Several other South American *Bidens* species only gave known compounds (see Table 2). The new results again showed that tetraynes, like **10**–**12**, eugenol and isoeugenol derivatives, may be characteristic for this genus.

EXPERIMENTAL

Air-dried plant material was extracted with Et_2O–petrol (1 2) and the extracts obtained were separated by CC (Si gel) and further by repeated TLC (SiO_2) Known compounds were identified by their ^{1}H NMR and UV spectra Voucher specimens were deposited in the U.S National Herbarium

Bidens graveolens (*voucher RMK* 8221) The roots (150 g) gave 10 mg germacrene D, 5 mg bicyclogermacrene, 10 mg cinnamyl alcohol, 30 mg of its acetate, 30 mg **1a**, 10 mg **2**, 2 mg **6** (Et_2O–petrol, 1 4) and 1 mg **10**, while the aerial parts (300 g) afforded 10 mg germacrene D, 5 mg bicyclogermacrene, 10 mg spathulenol, 10 mg **3**, 8 mg **4**, 2 mg **5** (Et_2O) and 10 mg **7**, 2 mg **8** and 2 mg **9** (Et_2O–petrol, 1 10)

6,7-*Dihydroxy*-6,7-*dihydromyrcene* (**5a**). Colourless oil, IR $\nu_{\max}^{CCl_4}$ cm^{-1}. 3600 (OH). Acetylation (Ac_2O, 1 hr, 70°) afforded **5b**, colourless oil, MS (CI, isobutane) *m/z* (rel int) 195 $[M - H_2O + 1]^+$ (100) ($C_{12}H_{18}O_2 + 1$), 135 $[195 - HOAc]^+$ (20), ^{1}H NMR ($CDCl_3$) δ 5 07 (*br d*, H-1*c*), 5.20 (*br d*, H-1*t*), 6 36 (*dd*, H-2), 2.0 (*m*, H-4), 1 6 (*m*, H-5), 4 26 (*dd*, H-6), 1 18 (*s*) and 1 19 (*s*, H-8 and H-9), 5.00 (*br s*) and 5 04 (*br s*, H-10) [*J* (Hz) 1*c*, 2 = 11, 1*t*, 2 = 17, 5, 6 = 10, 5′, 6 = 3]

3-*Oxo-tetradeca*-6*t*,12*t*-*diene*-8,10-*diyn*-1-*ol isobutyrate* (**6**) Colourless gum, IR $\nu_{\max}^{CCl_4}$ cm^{-1} 1735 (CO_2R), 1725 (C–O), UV $\lambda_{\max}^{Et_2O}$ nm 312, 290, 274, MS *m/z* (rel int) 286 157 $[M]^+$ (1) ($C_{18}H_{22}O_3$), 198 $[M - RCO_2H]^+$ (20), 143 $[M - COCH_2CH_2OiBu]^+$ (38), 129 $[C_{10}H_9]^+$ (33), 128 $[C_{10}H_8$, McLafferty$]^+$ (55), 71 $[C_3H_7CO]^+$ (100)

Heptadeca-1,8*c*-15*t*-*triene*-11,13-*diyn*-17-*ol isobutyrate* (**9**) Colourless gum, IR $\nu_{\max}^{CCl_4}$ cm^{-1} 1740 (CO_2R), UV $\lambda_{\max}^{Et_2O}$ nm 280, 266, 252, MS (CI, isobutane) *m/z* (rel int) 313 $[M + 1]^+$ (2) ($C_{21}H_{28}O_2$), 225 $[318 - RCO_2H]^+$ (14), 99 $[C_7H_{13}]^+$ (100)

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EPICUTICULAR WAX OF *COLLETIA PARADOXA*

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Key Word Index—*Colletia paradoxa*, Rhamnaceae, Espina de la Cruz, epicuticular wax, hydrocarbons, esters, ketones, alkanols, acids

Abstract—The composition of *Colletia paradoxa* epicuticular wax was determined. Hydrocarbons (27 %), ketones (22 %—mainly taraxerone), free acids (17 %), free alcohols (16 %—mainly lupeol, germanicol and taraxerol) and esters (12 %—mainly taraxeryl and germanicryl derivatives) were the main components.

INTRODUCTION

Epicuticular waxes control the evaporation of water from plant surfaces and, thus, are a basic element in plant water economy [1, 2]. Examples of xerophytic plants with thick wax layers are known [3] and there are results which indicate that water-stressed plants increase epicuticular wax production [1, 4] On the other hand, there seems to be no compositional pattern common to drought resistant plants [1], although *a priori* this biological approach would seem possible.

Colletia paradoxa (Spreng.) Escal. (= *C. cruciata* Gill et Hook), is a xerophytic member of the Rhamnaceae native to the Río de la Plata basin [5] When mature it stands as a spiny aphyllous shrub, which has found use in local folk medicine as a minor substitute for quina [6] It is sometimes used for building 'living corrals', as it grows into impassable hedges Our interest in the relationship of chemical composition to natural drought resistance led us to investigate its wax composition

RESULTS AND DISCUSSION

The wax extracted represents 2.4 % of the dry wt of the stems and has a melting range of 63–68°, both these figures