^1H 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 ^1H 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), ^1H 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-6t,12t-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 $[M - COCH_2CH_2O iBu]^+$ (38), 129 $[C_{10}H_9]^+$ (33), 128 $[C_{10}H_8$, McLafferty$]^+$ (55), 71 $[C_3H_7CO]^+$ (100)

Heptadeca-1,8c-15t-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

Table 1 Composition of wax fractions from *Colletia paradoxa* (wt % determined by GC)

		Esters				
Carbon No	Hydrocarbons	*n*-Acids	Alcohols	Ketones	Free alcohols	Free acids
14	—	2	—	—	TR	TR
16	—	26	11	—	2	5
18	—	14	3	—	1	1
18 1	—	13	—	—	—	TR
20	TR	2	TR	—	TR	TR
21	TR	—	—	—	—	—
22	TR	5	4	—	TR	TR
23	TR	—	—	—	—	1
24	1	4	—	—	—	2
25	2	1	—	—	—	—
26	2	3	—	—	—	1
27	3	3	—	—	—	2
28	5	26	—	—	—	86
29	11	—	—	—	—	—
30	4	TR	—	—	—	1
31	49	—	—	—	—	—
32	3	—	—	—	—	—
33	5	—	—	—	—	—
Taraxerol	—	—	47	—	23	—
Germanicol	—	—	32	—	24	—
Lupeol	—	—	3	—	46	—
Taraxerone	—	—	—	87	—	—
Unidentified	13 (1)	—	—	13(4)	—	—

Figures in parentheses indicate number of unknown components
TR, Components below 1 % concentration

being high [3]. There was extensive overlapping of fractions on CC, so this method was used for isolation but not for quantitation [3] A previously described [7] combination of TLC and GC methods gave good quantitative results, indicating the presence of hydrocarbons (27 %), esters (12 %), ketones (22 %), free alkanols (16 %) and free acids (17 %) as the main fractions The composition of the different fractions was determined by GC (Table 1)

Triterpenoid components are known to be minor constituents in many plant waxes [8, 9] They are important in certain fruit waxes [8, 10], cotton [11], young peach leaves [12], *Cirsium* [13] and *Dudleya* [14]. In *C paradoxa* wax, almost half of the wt is formed by triterpenic ketones and alcohols Taraxerone, the major triterpene in *C paradoxa* wax, has also been found in Gramineae [9], Ouricouri [15] and *Dudleya* [14] waxes Taraxerol and lupeol are present in many waxes, either free [9, 15], as ethers [8, 9, 16] or as esters [13, 15]. Germanicol [17] has not been described in other waxes Ceanothic acid, a triterpenic acid, however, has been isolated from *C. paradoxa* roots [18], but could not be identified in the wax in the present work.

The acid constituents have similarities with those identified in *Cereus peruvianus* wax [3], having a bimodal distribution, one at low MW (C_{16}–C_{18}), the other at high MW (with C_{28} as main component) In both waxes there are mono-unsaturated acids [3]

EXPERIMENTAL

Wax collection Samples of plant material were collected in Santa Victoria, San José (Uruguay), in March 1979 Herbarium voucher samples are kept at the Herbario José Arechavaleta (Facultad de Química, Montevideo), as MVFQ No 3090 The wax (5 9 g, 2 4 % dry wt) was extracted by immersion (15 sec) of the stems (250 g) in $CHCl_3$ It was recovered by evaporation of solvent

Chromatography CC was carried out as described in ref [3] Quantitative TLC–GC was carried out as described in ref [7], using $CHCl_3$-Me_2CO (19 1) as first solvent and petrol (60–70°)–C_6H_6 (4 1) as second solvent system *n*-Tetracosane was used as int standard GC was carried out using the conditions described previously [3] Ketones were chromatographed on a 5 % OV-1 column Taraxerone, lupeol, germanicol and taraxerol were identified by co-chromatography against authentic samples, and by NMR and mass spectrometry of the isolated products

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A MONOTERPENE FROM *ASTER BAKERANUS**

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Key Word Index—*Aster bakeranus*, Compositae, monoterpene.

Abstract—The aerial parts of *Aster bakeranus* afforded 6,7-dihydroxy-6,7-dihydro-*cis*-ocimene.

So far chemical investigations of representatives of the large genus *Aster* (Compositae, tribe Astereae) have shown that, in addition to acetylenic compounds [1], umbelliferone derivatives [2] and a variety of other constituents are present We now have studied a South African species, *Aster bakeranus* Burtt Davy ex C A Smith The roots afforded only *ent*-kaurenic acid and the corresponding aldehyde, γ-humulene, friedelin, euphone and some further triterpenes which have not been identified. The aerial parts contained squalene and a monoterpene diol; its structure followed from the spectroscopic data, especially from the ^{1}H NMR spectrum which displayed signals for an olefinic methyl (δ1.87 *dt*, $J = 1$, 1 Hz), two tertiary methyls (1.23 *s* and 1.18 *s*), a vinylic end group (6.75 *ddd*, 5 26 *br d* and 5.14 *ddd*) and an olefinic proton (5.48 *br t*). Furthermore, a lowfield double doublet at δ 3.43 and a broadened triplet at 2.35 were visible. These data indicated the presence of a monoterpene with two conjugated double bonds. The chemical shifts of the olefinic signals corresponded to those of *cis*-ocimene. In agreement with the IR spectrum, the double doublet at δ 3.43 was assigned as a proton adjacent to a hydroxyl group. As the chemical shifts of the singlets at δ 1.23 and 1.18 required an oxygen function, the presence of the diol, **1**, was very likely Accordingly, reaction with acetone and

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

	1	**2**
H-1*t*	5 26 *br d*	5 25 *br d*
H-1*c*	5 14 *ddd*	5 14 *ddd*
H-2	6 75 *ddd*	6.75 *ddd*
H-4	5 48 *br t*	5.48 *br t*
H-5	2 35 *br t*	2 43 *br dt* 2.37 *br dt*
H-6	3 43 *dd*	3 75 *dd*
H-8	1.18 *s*	1 10 *s*
H-9	1 23 *s*	1.22 *s*
H-10	1 87 *dt*	1 84 *dt*
Acetonide	—	1 32 *s*
Me	—	1 41 *s*

J(Hz) 1*t*, 2 = 17, 1*c*, 2 = 11, 1*t*, 1*c* = 1*c*, 4 = 2, 4 = 4, 10 = 5, 10 ~ 1, 4, 5 = 5, 6 = 7 5, 5′, 6 = 6 (compound **2** 4, 5 = 8, 4, 5′ = 6)

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*Part 468 in the series "Naturally Occurring Terpene Derivatives" For Part 467 see Omar, A A., Sarg, T. M, Khafagy, S. M, Ibrahim, Y E, Zdero, C. and Bohlmann, F (1983) *Phytochemistry* **22**, 779