(γ-lactone), 1725 (acetate), 1665 (C=C), 1245, 1145, 960 and 860, MS *m/e* (rel. int.): 290 (M^+, 1.5), 248 ($M^+ - 42$, 3.6), 230 ($M^+ - 60$, 38.6), 43 (100). (Found: C, 70.29; H, 7.70; O, 21.98. $C_{17}H_{22}O_4$ requires: C, 70.32; H, 7.64; O, 22.04%).

Dihydrohaageanolide acetate (**4**). To a soln of **1** (150 mg) in 2 ml MeOH, 200 mg $NaBH_4$ in 10 ml MeOH was added. After 30 min the reaction mixture was diluted with H_2O, acidified and extracted with $CHCl_3$. The washed and dried $CHCl_3$ soln was evapd to dryness and the residue acetylated in the usual way. The purified product, after recrystallization from EtOH, was shown to be identical with herbolide A (mp, mmp and IR spectrum).

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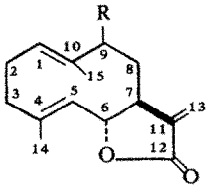

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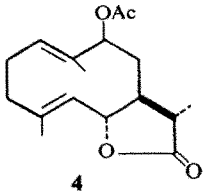
2 R = OAc
3 R = H



4

Table 1. ^{1}H-NMR data for **1** and **2** (ppm, δ-scale, TMS as internal standard, 100 MHz)

	1	**2** (Py-D_5)	**2** ($CDCl_3$)	*J*(Hz)
1-H	5.07 (*m*)	5.15 (*m*)	5.20*	5α 6β = 10
5-H	4.70*	4.69*	4.72 (*d*)	6β 7α = 8.5
6-H	4.70*	4.69*	4.60 (*dd*)	7α 13 = 3.1
7-H	2.70 (*m*)	2.77 (*m*)	2.70 (*m*)	7α 13′ = 3.1
9-H	4.40 (*dd*)	5.36 (*dd*)	5.20*	9α 8β = 10
13-H	5.53 (*d*)	5.53 (*d*)	5.54 (*d*)	9α 8α = 3
13′-H	6.32 (*d*)	6.29 (*d*)	6.24 (*d*)	
14-H	1.68 (*s*)	1.67 (*s*)	1.71 (*s*)	
15-H	1.40 (*br s*)	1.51 (*br s*)	1.46 (*br s*)	
OAc		2.07 (*s*)	2.03 (*s*)	

* The exact chemical shift and coupling constants cannot be determined because of overlap of the signals.

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THE DITERPENE DARUTIGENOL FROM *PALAFOXIA ARIDA**

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(*Received* 12 *January* 1978)

Key Word Index—*Palafoxia arida*; Compositae; darutigenol; diterpene.

INTRODUCTION

A number of years ago we isolated from *Palafoxia arida* B. L. Turner and M. I. Morris (Compositae)† a substance $C_{20}H_{34}O_3$ whose structure could not be established satisfactorily. Re-examination of a still extant very small sample has now permitted its identification as darutigenol (**1a**), the aglycone of the glycoside darutoside from *Siegesbeckia orientalis* L. (Compositae) [2, 3]‡. To our knowledge the aglycone itself has not been reported previously as a natural product.

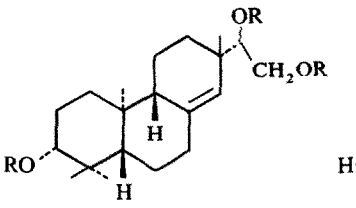
RESULTS

Elemental analysis of our material, mp 168–170°, lit. 168–170° [2], consistently showed retention of one molecule of water of solvation, but that the peak of

* Work supported in part by a grant (CA-13121) from the U.S. Public Health Service through the National Cancer Institute.

† The collection was originally identified as *P. linearis* by the collector. Because of its provenance (Sonora desert region of Southern Arizona) we deduced that it represents *P. arida* var. *arida* as Turner and Morris [1] point out that the binomial *P. linearis* properly belongs to a taxon which occurs only in Southern Baja, California, and has been misapplied by nearly all recent taxonomists working in the desert Southwest to the relatively common and widespread species named by them *P arida*

‡The stereochemistry of darutigenol at C-15 has not been established.



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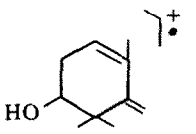
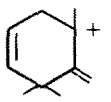
b R = Ac
c R = Bz



A



B

highest *m/e* ($C_{20}H_{34}O_3$) in the high resolution mass spectrum was not due to the loss of water but represented the molecular ion was evident from integration of the 270 MHz spectrum and conversion to a gummy triacetate (lit. gum [2]) and a crystalline tribenzoate: mp 81–82° (lit. 83° [2]). Analysis of the NMR spectrum (C_5D_5N) demonstrated the presence of the 1,2-dihydroxyethyl C-13 side chain of darutigenol and a number of similar diterpenes (A_2B system centered near 4 ppm), the somewhat broadened vinyl resonance of H-14 and the four methyl signals typical of 8(14)-pimarenes and an equatorial hydroxyl on carbon adjacent to one-CH_2-(broad singlet, $W_{\frac{1}{2}}$ = 8 Hz). The high resolution mass spectrum was rich in detail (see Experimental) and exhibited all significant peaks to be expected from fragmentation of an 8(14)-pimarene modified by a C-3 hydroxyl group [4]; in particular, although we did not observe the weak ion at *m/e* 153 referred to by Audier *et al.* [5], the significant ions of *m/e* 152 (7.5%, $C_{10}H_{16}O$, A) and *m/e* 135 (60.6% $C_{10}H_{15}$, B) indicating hydroxyl substitution in ring A and mentioned by the French workers were prominent§. Although we were unable to secure a sample of darutigenol for direct comparison, the coincidence of physical properties and the newly-reported data leave little question about the identity of our sample.

EXPERIMENTAL

Above ground parts of *Palafoxia arida* B. L. Turner and M. I. Morris (9 kg), collected by Mr. R. Barr (Barr 6389) near Gadsden, Yuma County, Arizona on March 26 1963, were extracted with $CHCl_3$ in the usual manner [6]. The crude gum (15 g) was chromatographed over 300 g of silicic acid (Mallinckrodt 100 mesh), 200 ml fraction being collected in the following order, 1–10, C_6H_6, 11–20, C_6H_6–$CHCl_3$ (1:1), 31–40, C_6H_6–$CHCl_3$ (1:3), 41–50, $CHCl_3$, 51–60, $CHCl_3$–MeOH (97:3), 61–70, $CHCl_3$–MeOH (19:1), 71–80, $CHCl_3$–MeOH (9:1). Fractions 52–58 were semicrystalline, combined and recrystallized from EtOAc, yield 0.45 g darutigenol, mp 168–179°, IR bands (KBr) 3360 (strong), 1670 cm^{-1}, NMR signals (270 MHz; C_5D_5N) at 5.40 *br* (H-8), 4.14 *ddbr* (11, 10.5, H-16), 3.94 *dbr* (11, H-15), 3.63 *br* (H-3), 2.50 *dd* (12, 3, 1*p*), 2.27 *ddbr* (15, 3, 2*p*), 1.86 *c* (10*p*), 1.74 *c* (2*p*), 1.52 *c* (2*p*), 1.16, 1.03, 0.93, 0.81 ppm (four methyl singlets). Calcd for $C_{20}H_{34}O_3 . H_2O$: C, 70.55; H, 10.66: O, 18.79. Found: C, 70.92; H, 1064; O, 18.68. Calcd for $C_{20}H_{34}O_3$: 322.2507 Found (MS): 322.2513 (6.1%). Other significant peaks in the high resolution MS were *m/e* (composition, %) 307 ($C_{19}H_{31}O_3$, M^+-Me, 8.9), 304 ($C_{20}H_{32}O_2$, M^+-H_2O. 27.8), 289 ($C_{19}H_{29}O_2$, M^+-Me-H_2O, 22.9), 273 ($C_{18}H_{29}O$, M^+-H_2O-MeO, 34.2), 271 ($C_{19}H_{29}O$, M^+-Me-2H_2O, 17.6), 261 ($C_{18}H_{29}O$, M^+-$C_2H_5O_2$, 5.1), 258 ($C_{19}H_{27}$, 16.4), 243 ($C_{18}H_{27}$, 24.2), 227 ($C_{17}H_{23}$, 13), 187 ($C_{14}H_{19}$, 9.8), 173 ($C_{13}H_{17}$, 14.8), 164 ($C_{11}H_{16}O$, 18.2), 161 ($C_{12}H_{17}$, 12.5), 159 ($C_{12}H_{15}$, 14.8), 157 ($C_{12}H_{13}$, 9), 152 ($C_{10}H_{16}O$, 7.5-A), 151 ($C_{10}H_{15}O$, 34.5), 147 ($C_{11}H_{15}$, 23.6), 145 ($C_{11}H_{13}$, 20.3), 143 ($C_{11}H_{11}$, 11.3), 135 ($C_{10}H_{15}$, 60.6-B), 134 ($C_{10}H_{14}$, 46.6), 131 ($C_{10}H_{11}$, 36.5), 123 (C_9H_{15}, 71.8), 121 (C_9H_{13}, 85.8), 120 (C_9H_{12}, 86.5), 119 (C_9H_{11}, 50.3), 109 (C_8H_{13}, 38.6), 107 (C_8H_{11}, 57.8), 105 (C_8H_9, 100). Acetylation gave a gummy triacetate (NMR spectrum). Benzoylation gave a solid tribenzoate (NMR spectrum) mp 81–82° after purification by prep-TLC (EtOAc–C_6H_6, 99:1).

§ Unfortunately, the mass spectrum of darutigenol is not reproduced in ref. 5 and no other details, other than the appearance of ions corresponding to loss of the two groups attached to C-13, are given.

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