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THE VOLATILE ESSENTIAL OILS OF FIVE *BOTHRIOCHLOA* SPECIES

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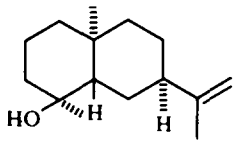
Key Word Index—*Bothriochloa*; Gramineae; essential oils; sesquiterpenes.

INTRODUCTION

Bothriochloa species [1, 2] (tribe Andropogoneae, Gramineae) are native to many parts of the world but not to the American subcontinent. They form part of a group of forage grasses referred to in N. America as 'Old World Bluestems', some of which are particularly attractive to cattle as fodder. Many are rich in essential oils, which impart to the grasses a pleasant smell and taste, believed to by responsible in part for animal-grazing selectivity. There is also evidence that the grasses are resistant to the ravages of some insect pests, such as the fall army worm (*Spodoptera frugiperda*), towards which some of the oils have antifeedant properties (Zalkow, L. H., personal communication). Finally, they are of special interest because of their forage production potential during the summer and the winter hardiness of many of them [3, 4].

A large collection of these and related grasses has been assembled and grown at the Oklahoma Agricultural Experiment Station [3–5]. The only contributions to their chemistry are those of Zalkow and co-workers, who have isolated a number of secondary plant metabolites from several strains of *Bothriochloa intermedia*, one of the species [6–10]. Compounds identified as components of the oils include intermedeol (**1**), neointermedeol (**2**), acorenone-B (**3**), kessane (**4**), β-eudesmol (**5**), elemol (**6**) and 7-hydroxycalamene (**7**). The gas chromatography of some *Bothriochloa* oils has been investigated in connection with a biosystematic study [11].



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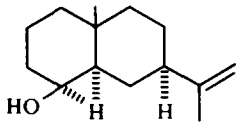

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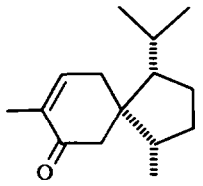

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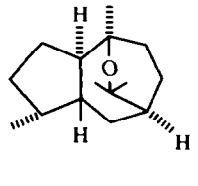

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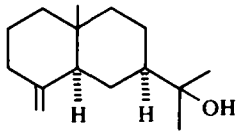

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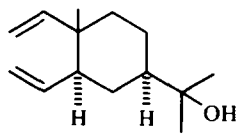

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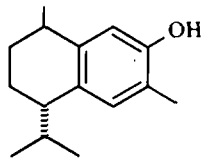

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RESULTS AND DISCUSSION

The results reported here are of a study of the steam-volatile essential oils of 20 accessions representing five *Bothriochloa* spp. (Table 1). Seventeen of the accessions proved to contain large amounts of steam volatile oil, two contained trace amounts only, and one was devoid of oil. Some of the major components of the oils have been identified, intermedeol (**1**), neointermedeol (**2**) and acorenone-B (**3**) being especially prominent.

EXPERIMENTAL

Plant material. Seed of the Old World Bluestem accessions, originating in various parts of the world, were germinated in a greenhouse at the Department of Agronomy, Oklahoma State University, then transplanted to the field in spring 1977 at the Agronomy Field Research Station at Stillwater, OK, and at the Southern Great Plains Field Research Station, Woodward, OK. Forage samples of the mature grasses were harvested at the boot to heading stage of growth in June or July of the same year, then used immediately after a short period of air drying.

Steam distillation. A weighed amount of each grass was packed into a specially designed stainless-steel steam distillation apparatus. A rapid current of steam was admitted at the base of the unit, and the vapors emerging at the top were conducted into an efficient downward condenser, and the distillate collected. Steam distillation was continued until no further oily droplets were noted in the distillate. The latter was cooled, saturated with NaCl, and extracted $\times 3$ with Et_2O. The combined extracts were dried and the ethereal extract was flash evapd via a 12 in. Vigreux fractionating column, last traces of solvent being removed by brief application of an aspirator pump (*ca* 30–35 mm Hg). The residual essential oil was weighed and examined as described below.

IR measurements. IR spectra of the oils were measured as thin films between rock salt plates.

GLC. Measurements were made on Et_2O solns of the oils, using a chromatograph with a flame ionization detector. SE-30 and 10%

Carbowax-20 M columns were used at temps. ranging from 160 to 200°. He (3 kg/cm^2) was carrier gas. Identification of components was effected by comparison of RR_t, IR, ^{1}H NMR, and MS with those of authentic samples (Table 1). Unidentified constituents will be investigated by GC–MS, and the results reported in forthcoming publications.

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Table 1. Composition of essential oils of *Bothriochloa* spp.

Species	Indentification No.	Wt of dry grass (g)	Wt of oil (g)	Composition of oil
B. glabra	239164	950	0.60	4 major, one a volatile hydrocarbon, 9 minor components
B. glabra	240833	260	0.75	neointermedeol (80%), and 4 minor components
B. glabra	301380	900	0.20	1 major, 4 minor components, major is a volatile hydrocarbon
B. glabra	364395	2350	4.00	acorenone-B (90%), and 7 minor components
B. insculpta	301396	290	0.20	acorenone-B (90%), and 2 minor components
B. hassele	309951	370	none	
B. intermedia	300754	282	2.24	intermedeol (90%), and 1 minor component
B. intermedia	300771	2320	4.05	acorenone-B (90%), and 10 minor components
B. intermedia	300857	773	1.80	acorenone-B (>90%), and 5 very minor components
B. intermedia	300858	1220	3.00	acorenone-B (>90%), and 12 very minor components
B. intermedia	300886	990	2.30	acorenone-B (>90%), and 11 very minor components
B. intermedia	300741	661	0.90	6 minor, 14 very minor components, unidentified
B. intermedia	301551	488	trace	not examined
B. intermedia	300848	446	1.31	intermedeol (70–75%), and 6 minor components, one a hydrocarbon
B. intermedia	300811	388	0.40	neointermedeol (60%), acorenone-B (10–15%), and 6 minor components
B. intermedia	301556	360	2.12	intermedeol (75%), and 2 minor components
B. intermedia	300877	350	1.17	acorenone-B (>90%), and 4 very minor components
B. intermedia	300853	270	1.40	intermedeol (80%), and 2 minor components
B. intermedia	300745	170	1.00	intermedeol (85%), and 1 minor component
B. edwardiana	337509	588	trace	not examined

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GUAIANOLIDES FROM *AGRIANTHUS PUNGENS**

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Key Word Index—*Agrianthus pungens*; Compositae; sesquiterpene lactones; guaianolides.

The Brazilian genus *Agrianthus* has not been investigated chemically. Therefore, we have studied the constituents of *A. pungens* Mattf. The roots only afforded the widespread pentaynene **1** [1], coumarin (**2**), and dammaradienyl acetate (**4**) [2] but the aerial parts yielded in addition to **2** and germacrene D (**3**) [3] a complex mixture of sesquiterpene lactones, which could be only partly separated. The main compound most probably had the structure **5**. The ^{1}H NMR data (Table 1) were very similar to those reported for graminiliatrin [4], which, however, has another ester function at C-8 and the additional hydroxyl group at C-9 is missing. The 9α-position of this hydroxyl in **5** was indicated by the observed coupling $J_{8,9}$ and the downfield shift of 1α-H. Models show that the latter should be deshielded by the 9α-hydroxy group. The assignments were established by double resonance experiments.

A second lactone, not separated completely from an unidentified lactone, most probably was the corresponding precursor of **5**, where the epoxy oxygen at C-3, C-4 is missing. The ^{1}H NMR data (Table 1) would be in agreement with the structure **6**, which we have named agriantholide. The structures of three further lactones

Table 1. ^{1}H NMR spectral data of compounds **5** and **6** (270 MHz, in $CDCl_3$ with TMS as internal standard)

	5	**6**
1-H	2.27 *dd*	2.1 *m*
2-H	3.91 *d*	4.75 *m*
3-H	3.42 *s*	5.68 *s(br)*
5-H	2.44 *dd*	2.35 *dd*
6-H	5.08 *dd*	5.18 *dd*
7-H	3.09 *dddd*	3.22 *dddd*
8-H	5.62 *dd*	5.46 *dd*
9-H	4.38 *d*	3.99 *d*
13-H	6.32 *d*	6.33 *d*
13′-H	5.52 *d*	5.48 *d*
14-H	3.04 *d*	3.08 *d*
14′-H	2.75 *d*	2.85 *d*
15-H	1.71 *s*	2.00 *s(br)*
OCOR	6.89 *q(br)*	6.89 *q(br)*
	1.80 *d(br)*	1.81 *d(br)*
	1.79 *s(br)*	1.80 *s(br)*

J(Hz): 1,2 = 5; 1,5 = 7.5; 5,6 = 10; 6,7 = 9; 7,8 = 2; 7,13 = 3.3; 7,13′ = 3; 8,9 = 4.5.

* Part 276 in the series "Naturally Occurring Terpene Derivatives". For Part 275 see Bohlmann, F., Zdero, C., King, R. M. and Robinson, H. (1980) *Phytochemistry* **19** (in press).