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SURVEY OF THE ESSENTIAL OIL IN *SPARTINA CYNOSUROIDES**

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Key Word Index—*Spartina cynosuroides*; Gramineae; giant cordgrass; essential oils; phenyl acetaldehyde; *p*-tolualdehyde; *o*-methylstyrene; terpenoids; phenols; indole.

Abstract—The essential oil of the giant cordgrass, *Spartina cynosuroides*, was isolated in 0·02% yield by steam distillation. Analysis by GLC–MS showed the presence of 60 compounds, including 12 aliphatic hydrocarbons, 18 aromatic hydrocarbons, 14 carbonyl compounds, 4 alcohols, 9 phenols and 3 other compounds. In all, these compounds represented 82·2% of the oil. Phenylacetaldehyde, *p*-tolualdehyde, carvacrol, benzyl alcohol and 2,4-di-*tert*-butylphenol are the major components of the oil. As expected, 2-furaldehyde is present. Benzothiazole was found, but no other related compound was present. The occurrence of phenolic alkaloids is anticipated from the presence of indole and phenols in this plant.

INTRODUCTION

THE MISSISSIPPI salt marsh is an irregularly flooded estuary dominated by the needlerush, *Juncus romerianus* (Juncaceae) and the giant cordgrass *Spartina cynosuroides* (Gramineae). Preliminary studies by De La Cruz[2,3] include primary production and decomposition of *S. cynosuroides* and the food value of this species to marsh and estuarine organism. Although there have been some superficial studies reported[4] on *S. cynosuroides*, to our knowledge there is no report of a detailed study on the organic constituents of this species. This communication on the essential oil of *S. cynosuroides* is a part[1] of a continuing chemoecological study of the Mississippi salt marsh.

RESULTS

From the GLC–MS analysis, 98 maxima were observed and usable scans were obtained on 82 maxima. Structural assignments were proposed for 60 compounds. These accounted for 82·2% of the oil which was amenable to GLC analysis. The compounds with their retention times expressed as Kovats indices[5] (I_k), MS fragmentation, and percentage com-

* Part II in the series "Constituents of Marsh Grass". For Part I see Ref. 1.

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[5] KOVATS, E. (1961) *Anal. Chem.* **181**, 351.

positions were grouped by classes and are presented in Table 1. These include 12 aliphatic hydrocarbons, 18 aromatic hydrocarbons, 14 carbonyl compounds, 13 alcohols and phenols and 3 miscellaneous compounds.

Among the most noteworthy features of this oil are the presence of indole, *o*-methylstyrene and benzothiazole and a rather large quantity of phenolic compounds. The aliphatic hydrocarbons consisted of six normal C_{10}–C_{16}, 3 branched and 3 unsaturated compounds.

TABLE 1. VOLATILE CONSTITUENTS OF *Spartina cynosuroides*

I_K^*	Compound	MS fragmentator or Ref.†	%‡
Aliphatic hydrocarbons			
1040	C_9H_{18}	41, 55, 43, 57, 69; 126	0·2
910	C_9H_{20}	43, 57, 41, 71, 85; 128	T§
1055	$C_{10}H_{20}$	43, 57, 41, 55, 71; 140	0·1
1010	*n*-Decane	6, 7	T§
1050	$C_{10}H_{22}$	43, 57, 41, 71, 85; 142	0·1
1300	*n*-Tridecane	6,7	0·1
1520	$C_{14}H_{22}$	69, 93, 91, 105, 133; 190	0·2
1400	*n*-Tetradecane	6, 7	0·1
1505	*n*-Pentadecane	6, 7	0·2
1600	*n*-Hexadecane	6, 7	0·3
1700	*n*-Heptadecane	6, 7	0·5
1790	2-Methylheptadecane	6, 7	0·5
Aromatic hydrocarbons			
978	Toluene	6, 7	T§
1040	*m*-Xylene	6, 7	0·2
1055	*p*-Xylene	6, 7	0·1
1190	*o*-Methylstyrene	6, 7	0·1
1070	1-Methyl-2-ethyltoluene	6, 7	T§
1090	Propylbenzene	6, 7	0·2
1105	1-Methyl-4-ethyltoluene	6, 7	0·1
1120	Cumene	6, 7	0·3
1130	Trimethylbenzene	6, 7	3·8
1390	Naphthalene	7	0·1
1180	*m*-Diethylbenzene	6, 7	0·3
1210	3-Ethyl-*o*-xylene	6	0·3
1240	Tetramethylbenzene	6	T§
1480	2-Methylnaphthalene	6, 7	0·1
1180	1-Ethylindan	6, 7	0·3
1595	Dimethylnaphthalene	9	T§
1490	1,1,4,5-Tetramethylindan	6, 7	0·1
Carbonyl compounds			
1062	2-Furaldehyde	6, 7	0·2
1160	Benzaldehyde	6, 7	0·4
1030	C_7H_6O	41, 43, 56, 55, 42; 106	T§
1193	Methylcyclohexan-1-one	6, 7	0·4
1250	Phenylacetaldehyde	6, 7	7·2
1515	*p*-Tolualdehyde	6, 7	20·3
1070	$C_8H_{12}O$ cyclic ketone	41, 43, 55, 67, 81; 124	T§
1396	Methyl 2-hexenoate	6, 7	0·1
1480	Pulegone	6, 7	1·2
1400	Undecanone	6, 7	0·1
1610	1,1-Dimethoxyacetophenone	6, 7	1·0
1540	4-Methyl-3-pentenycyclohexadiene-1-carboxaldehyde	1	0·3
1600	2-Tridecanone	6, 7	0·2
1605	$C_{13}H_{26}O$	43, 41, 55, 59, 83; 198	1·3

TABLE 1.—*cont.*

I_K^*	Compound	MS fragmentator or Ref.†	%‡
Alcohols and phenols			
1230	Phenol	6	1·2
1262	Benzyl alcohol	6, 7	6·9
1190	1-Ethylcyclohexanol	6, 7	1·7
1312	*o*-Cresol	6, 7	0·1
1480	$C_9H_{18}O$	41, 55, 57, 69, 83; 142	0·1
1370	Butylphenol	8	0·3
1475	*o*-*tert*-Butylphenol	6, 7	0·2
1555	Carvacrol	6, 7	17·7
1545	6-*tert*-Butyl-*o*-cresol	6, 7	0·2
1640	2,4-Diisopropylphenol	6, 7	0·4
1530	$C_{13}H_{20}O$ 2° alcohol	43, 45, 56, 55, 73; 192	0·1
1705	2,4-Di-*tert*-butylphenol	6, 7	9·7
1905	2,4,6-Tri-*tert*-butylphenol	6, 7	0·3
Miscellaneous compounds			
1590	Indole	6, 7	0·6
1475	Benzothiazole	6, 7	1·4
1525	*p*-*tert*-Butylphenetole	6	0·3

* KOVATS, E. (1961) *Anal. Chem.* **181,** 351.

† The five most intense fragment ion values (*m/e*) arranged in order of decreasing relative abundance with the proposed parent ion presented sixth.

‡ % of total oil.

§ T—Trace; less than 0·1%.

These represented only a small portion of the oil (2·3%). Eighteen aromatic hydrocarbons which included 12 alkylated benzenes, *o*-methylstyrene, naphthalene, 2 alkylated naphthalenes and two alkyl indans accounted for 6% of the total oil. *o*-Methylstyrene is the only unusual compound in this group.

Table 1 lists 14 carbonyl compounds that accounted for 32·7% of the total oil. Phenylacetaldehyde and *p*-tolualdehyde, are the major compounds in this class (27·5%). 2-Furaldehyde was the only heterocyclic carbonyl compound present. There were 4 alcohols and 9 phenols which accounted for 8·8% and 30·1% of the oil, respectively. The largest single component was carvacrol (17·7%) which along with pulegone (1·2%) were the only terpenoids found. There were also two nitrogenous compounds (indole and benzothiazole) and an ether (*p*-*tert*-butylphenetole). Together they represented only 2·3% of the oil.

Thus, the oil is comprised mostly of aromatic compounds (65·3%) with smaller quantities of several classes of acyclic compounds (40%), cyclic compounds (4·0%) and 3 heterocyclic compounds (2·2%).

DISCUSSION

The only compound which has been reported from the related species, *S. alternifiora* is 2-furaldehyde. Recently, Miles *et al.*[1] investigated the essential oils of another marsh grass, *J. roemerianus* (Juncaceae) which grows in close proximity to *S. cynosuroides*. The compounds identified included 13 benzene, 11 polycyclic (mostly naphthalene type), 8 cyclohexyl, 32 acyclic, 9 terpenoid and 6 furan derivatives. *S. cynosuroides* contains much higher quantities of aromatic compounds than *J. roemerianus* (19·6%). The presence of indole and phenols suggests that phenolic alkaloids may also be present in this plant. Whether the high aromatic content reflects an enhanced ability of this plant to biosynthesize aromatic compounds or a decreased ability to metabolize or excrete them is unknown.

EXPERIMENTAL

Isolation of the essential oil. Fresh marsh grass (1 kg) was harvested from Bay St. Louis, Mississippi, and stored at below 0° until it was chopped and steam distilled in an all glass system for *ca* 3 hr. The distillate was extracted with redistilled anhyd. Et_2O, the Et_2O was dried and the solvent removed under vacuum at 35° to give 0·2 g oil. Yield = 0·02% (calculated on the basis of fresh plant).

Column chromatography. The essential oil was chromatographed on a 2 × 25 cm jacketed Florisil column which was cooled with ice H_2O to prevent column cracking. The column was eluted successively with 200 ml pentane; 15% Et_2O in pentane and 100% Et_2O. The separations were monitored by TLC.

Analytical GLC–MS. The 3 fractions were introduced separately into a Hewlett–Packard 5930 quadrupole mass spectrometer interfaced with a 5700A gas chromatograph from a 250′ × 0·03″ capillary GC column coated with OV-17. Carrier gas flow was 8·0 ml/min N_2. The GLC Unit was programmed from 120° to 160° at 1°/min rate. The final temp. was maintained for 30 min. MS were obtained at 70 eV. Fragment ion values were compared with those of A.M.S.D.,[6] Cornu and Massot,[7] Occolowitz,[8] and Miles *et al.*[1] GLC retention times are presented as Kovats indices (I_k). Estimates of the per cent content of each component in the oil were made by peak triangulation of the maximae of the GLC profile trace.

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