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CONSTITUENTS OF MARSH GRASS: SURVEY OF THE ESSENTIAL OILS IN *JUNCUS ROEMERIANUS*

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Key Word Index—*Juncus roemerianus*; Juncaceae; needlerush; essential oils; naphthalenes; benzyl cyanide; terpenoids; tetrachlorobenzene.

Abstract—The essential oil of *Juncus roemerianus* was isolated by steam distillation with a yield of 0·01% of the fresh grass. Analysis by combined GLC-MS gave evidence for the presence of 78 compounds. They included 13 benzene derivatives, 11 polycyclic (mostly naphthalene type) compounds, 8 cyclohexyl compounds, 32 acyclic compounds, 9 terpenoids, and 6 furan derivatives. In total, these compounds accounted for 46·6% of the oil. Due to the presence of tetrachlorobenzene and benzyl cyanide, other halogenated compounds and alkaloids can be anticipated.

INTRODUCTION

THE MISSISSIPPI salt marsh is an irregularly flooded estuary dominated by the needlerush *Juncus roemerianus* (Juncaceae). Preliminary studies by De La Cruz[1] include primary production and decomposition of *J. roemerianus* and the food value of this species to marsh and estuarine organisms. These studies have shown that 90–5% of the organic material produced in the marsh dies, falls to the mud, decomposes and enters the detritus food chain. It has long been recognized[2] that particulate organic matter, or organic detritus, may be a primary source of food for organisms as well as an important structural or conditions-of-existence factor in ecosystems. Although there have been some superficial studies reported[3] on related species, to our knowledge there is no report of a detailed study on the organic constituents of *J. roemerianus*. This communication on the essential oils is part of a wider study on the role of *J. roemerianus* and related species in the ecosystem of the Mississippi Gulf Coast.

RESULTS

After Florisil chromatography, all subfractions of the neat oil were combined into 7 fractions, and each was subjected to GLC–MS. Over 150 maxima were observed, and MS scans were obtained on 120.

Structural assignments were proposed for 78 compounds, 10 of which appeared in more than one fraction. They accounted for 46·6% of the oil which was amenable to GLC. The compounds with their MS fragmentations and percentage compositions were grouped by classes and are presented in Tables 1–6. They include 13 benzene derivatives, 11 polycyclic (mostly naphthalene type) compounds, 8 cyclohexyl compounds, 32 acyclic compounds, 9

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[1] DE LA CRUZ, A. A. (1972) Private Communication, Zoology Department, Mississippi State University.

[2] ODUM, E. P. and DE LA CRUZ, A. A. (1963) *AIBS Bull.* **13**, 39.

[3] BROWN, L. R. (1963) *Bull. Georgia Acad. Sci.* **21**, 20.

terpenoids, and 6 furan derivatives. Two indans, benzyl cyanide, and tetrachlorobenzene were among the more unexpected compounds.

TABLE 1. BENZENE DERIVATIVES

Fraction	I_K*	Compound	MS fragmentation†	Ref.	%‡
1	860	Dimethylbenzene	91,106,105,39,51; 106	10	1·3
4, 5	950	Benzaldehyde	77,106,105,51,50; 106	10, 11	0·7
6, 7	1855	Benzyl cyanide	117,90,116,89,51; 117	10, 11	1·2
1	955	1-Methyl-4-ethylbenzene	105,120,77,39,91; 120	10	0·8
4, 5	1190	*o*-Tolualdehyde	91,120,119,65,63; 120	10, 11	0·6
7	1230	*o*-Methoxyphenol	109,124,81,53,27; 124	11	0·4
1	1020	2-Methylpropenylbenzene	117,132,91,115,39; 132	10	0·4
5	1530	Vinylbenzaldehyde	132,131,103,77,104; 132	10, 11	0·2
1	1060	1,3-Diethylbenzene	119,105,134,91,27, 134	10	0·4
1	1260	1,3-Dimethyl-2-ethylbenzene	119,134,91,39,120; 134	10	0·7
1	1265	1,2-Dimethyl-3-ethylbenzene	119,134,91,105,39; 134	10	0·5
4	1390	Propoxyanisole	41,107,81,151,95; 166	10	0·5
1	1650	1,2,3,4-Tetrachlorobenzene	216,214,218,179,181, 214	10, 11	1·2

* 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.

Among the benzene derivatives (Table 1), six were alkyl-substituted, three were aldehydes, two were ethers, and one each was chlorinated and cyanide containing. They accounted for 8·9 % of the total oil. Eleven polycyclic compounds which accounted for 6·1 % of the total oil are listed in Table 2. They included naphthalene and decahydronaphthalene, 4 alkylated and 2 acetylated naphthalenes, 2 alkyl indans, and phenanthrene. No new compounds

TABLE 2. POLYCYCLIC COMPOUNDS

Fraction	I_K*	Compound	MS fragmentation†	Ref.	%‡
1, 2	1370	Naphthalene	128,51,129,64,127; 128	10	1·4
3	1030	Decahydronaphthalene	138,67,96,81,82; 138	10	0·3
1, 2	1560	2-Methylnaphthalene	142,141,115,143,71; 142	10, 11	1·1
2	1610	1-Methylnapthalene	142,141,115,71,57; 142	10, 11	0·6
1	1220	1-Ethylindan	117,28,27,146,115, 146	10, 11	0·3
1	1250	1,1-Dimethylindan	137,91,146,115,132; 146	11	0·3
1, 2	1810	Dimethylnaphthalene	156,141,155,153,157; 156	11	0·9
2	1860	2,6-Dimethylnapththalene	156,141,155,157,128; 156	10, 11	0·3
2	1980	Acetylnapththalene	170,155,169,153,152, 170	10	0·3
2	2050	Acetylnaphthalene	170,155,169,161,69; 170	10	0·1
3	2280	Phenanthrene	178,179,176,89,76; 178	10, 11	0·5

* Footnotes as in Table 1.

appeared in this group. Table 3 lists 8 cyclohexyl compounds that accounted for 4·6% of the total oil. They included an alkyl cyclohexane, 4 cyclohexyl carboxaldehydes, 2 cyclohexanones and an acetylated cyclohexane.

TABLE 3. CYCLOHEXYL COMPOUNDS

Fraction	I_K*	Compound	MS fragmentation†	Ref.	%‡
4	820	4-Methylcyclohexanone	55,41,56,27,57; 112	10, 11	0·2
5	805	Cyclohexane carboxaldehyde	55,83,41,68,39; 112	11	0·1
4	900	Methylcyclohexyl ketone	55,43,83,41,71; 126	11	0·5
4	1020	2,2,6-Trimethylcyclohexanone	82,56,41,69,55; 140	12	0·2
4	1335	2-Cyclohexylcyclohexanone	98,83,55,70,41; 180	10	0·1
5	1395	(4-Methyl-pent-3-enyl) cyclohexadiene-1-carboxaldehyde	69,121,41,105,91; 190	—	1·3
4	1350	(4-Methyl-pent-3-enyl) cyclohexane carboxaldehyde	69,123,109,91,81; 192	—	0·2
5	1310	(4-Methyl-pent-3-enyl) cyclohexane carboxaldehyde	69,125,43,109,93; 194	—	2·0

* Footnotes as in Table 1.

The structures (4-methyl-pent-3-enyl) cyclohexadiene-1-carboxaldehyde m/e 190 (M^+), (4-methyl-pent-3-enyl) cyclohexene-1-carboxaldehyde m/e 192 (M^+), and (4-methyl-pent-3-enyl) cyclohexane carboxaldehyde m/e 194 (M^+) gave similar and characteristic fragmentations. The base peak in each was m/e 69. The second or third strongest fragment in these structures was m/e 121, 123 or 125, depending on the degree of unsaturation in the ring. These could also be attributed to allylic fission. Other fragments, m/e 93, 91 and 81, indicate the ring structure of the molecules. The position of the double bonds in the rings, as well as the point of attachment of the side chains on the rings, can only be speculative, at best.

Table 4 lists 32 acyclic compounds which accounted for 16·1% of the total oil. They included 6 hydrocarbons (C_{11}–C_{20}), 3 unidentified ethers (C_{12}-C_{15}), 7 aldehydes (C_6–C_9), 9 ketones (C_5–C_{18}), and 7 alcohols (C_6–C_{18}). There were apparently no new compounds in this group although complete structures could not be deduced from the data in several instances. Table 5 lists 9 terpenoids that accounted for 5·4% of the total oil. They included 3 ketones, 1 aldehyde, and 5 alcohols, all known compounds. Table 6 lists 6 furan derivatives that accounted for 5·5% of the total oil. They included 3 aldehydes, 1 ketone, 1 primary and 1 tertiary alcohol. There may be other furans present since several additional spectra were obtained with the characteristic m/e 81 fragment. The structure 3-(2-furyl)-propionaldehyde was proposed by the following analysis. The β-cleavage process[4] in this molecule gave m/e 81 and 43 fragmentations. Elimination of a ketene from the furfuryl ion is responsible for the m/e 39 peak ($C_3H_3^+$) in the spectrum and m/e 29 indicates the presence of CHO^+ ion.

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[4] BUDZIKIEWICZ, H., DJERASSI, C. and WILLIAMS, D. H. (1967) *Mass-Spectrometry of Organic Compound,* Holden-Day, San Francisco.

TABLE 4. ACYCLIC COMPOUNDS

Fraction	I_K*	Compound	MS fragmentation†	Ref.	%‡
4, 5	630	Methyl-isopropenyl ketone	41,43,39,69,84; 84	10	0·2
6	780	2,4-Hexadienal	81,39,41,53,67; 96	10	0·2
6, 7	820	2,4-Hexadiene-1-ol	41,39,55,27,98; 98	10, 11	0 3
4	720	Hexanal	44,43,56,41,57; 100	10	0·2
7	760	2-Hexanol	45,43,27,41,29; 102	10	1·2
6	830	$C_7H_{12}O$ alcohol	43,45,41,55,39; 112	10	0·4
4	620	2,4-Dimethylpentanal	43,58,41,27,29; 114	10	0·2
5	810	2-Heptanone	43,58,27,71,29; 114	10, 11	0·1
7	930	$C_8H_{10}O$ alcohol	45,43,41,69,27; 122	—	0·2
4	950	4,4-Dimethyl-1-penten-2-al	57,41,29,39,27, 126	11	0·1
5	895	2-Methyl-2-hepten-6-one	43,41,69,55,108; 126	12	0·9
4	860	Octanol	43,29,41,44,57; 128	11, 12	0·5
5	875	6-Methyl-2-heptanone	43,58,41,27,71; 128	10, 11	0·3
7	915	1-Octen-3-ol	57,43,29,72,27; 128	12	0·2
6	1060	*n*-Nona-2-4-dienal	81,41,39,67,29; 138	10	0·5
6	1090	Nona-*trans*-*cis*-2,6-dienal	41,69,70,67,53; 138	15	0 3
1	1035	5-Methyldecane	57,43,41,29,27; 156	11	0·7
7	955	1-Octanol	41,43,69,28,55; 158	10, 11	0·6
2	1120	*n*-Dodecane	57,43,71,41,85; 170	10	0·5
3	1130	5-Undecanone	43,58,29,57,41; 170	11	T§
5	1135	2-Undecanone	58,43,59,71,41; 170	10, 11	0·5
4	1570	$CH_3COC_{10}H_{15}$	43,41,57,55,71; 178	10	0·6
1	1190	Tridecene	41,43,55,57,56; 182	11	1 1
3	1530	$C_{12}H_{22}O$ ether	43,57,41,71,55; 182	—	0 3
1	1195	2,6-Dimethylundecane	57,43,41,71,29, 184	11	1·1
4, 5	1310	2-Tridecanone	58,43,59,71,41; 198	10, 11	0·2
3	1680	$C_{15}H_{24}O$ ether	43,41,69,71,205; 220	—	T†
3	1700	$C_{15}H_{24}O$ ether	41,69,43,55,57; 220	—	0 1
1	1810	$C_{19}H_{40}$	57,43,71,41,85; 268	—	0 5
4	1980	Octadecen-ol	43,41,55,57,59, 268	—	3·4
5	2170	$C_{18}H_{36}O$ ketone	43,58,41,71,57, 278	10	0·3
1	1935	$C_{20}H_{42}$	57,43,71,41,85, 282	—	0·4

* Footnotes as in Table 1.
§ T—Trace.

TABLE 5. TERPENES

Fraction	I_K*	Compound	MS fragmentation†	Ref.	%‡
7	1635	Thymol	135,150,91,117,136; 150	13	0 6
5	1380	Pulegone	81,67,152,109,43; 152	14	0 6
6	1520	Sabinol	91,43,41,108,55; 152	10, 11	0·4
6	1405	Camphor	95,81,108,69,152; 152	11, 14	0·5
5	1430	Geranial	69,41,84,94,109; 152	14	0·5
7	1620	α-Terpineol	59,93,121,43,136; 154	10, 11	0·4
6	1580	$C_{10}H_{20}O$ alcohol	43,41,55,58,71; 156	—	0·5
7	1760	Citronellol	41,69,55,67,82; 156	10, 12, 14	0·9
6, 7	1940	β-Ionone	177,43,41,123,91; 192	11	1·0

* Footnotes as in Table 1.

DISCUSSION

The only compound which has been reported[3] in marsh grass is 2-furaldehyde. It accounted for 7·2% of the dry wt of *Spartina alterniflora* which is a species that grows in proximity with *J. roemerianus*. Of interest is the large number of benzene and naphthalene compounds. There is ample evidence for the presence of benzene compounds in plants,[5–7] but naphthalene compounds may be more limited. Several naphthalenic derivatives have been found in the heartwood of *Zelkova serrata*.[8] Aromatic ethers also have been reported in a number of plants.[6,9] The terpenoids and acyclic compounds, products of lipid metabolism, are present in a wide variety of plants. Perhaps the most unusual compounds in *J. roemerianus* are benzyl cyanide, tetrachlorobenzene, 1-ethylindan and 1-1-dimethylindan. Halogenation of aromatic nuclei might be expected because of the growth of this plant in salt water and apparently does occur to some extent since tetrachlorobenzene was found in this oil.

TABLE 6. FURAN DERIVATIVES

Fraction	I_K*	Compound	MS fragmentation†	Ref.	%†
7	860	2-Furaldehyde	96,95,39,29,38; 96	10, 11	3·2
7	950	5-Methyl-2-furaldehyde	110,109,53,27,29; 110	10, 11	0·3
7	1040	3-(2-Furyl)-propionaldehyde	81,43,39,29,124; 124	—	0·2
7	1353	$C_9H_{12}O_2$ Ketone	81,41,39,67,121; 152	—	0·4
7	1510	$C_9H_{12}O_2$ 3° alcohol	59,41,81,79,43,134; 152	—	0·8
7	1595	$C_9H_{12}O_2$ 1° alcohol	81,41,39,67,55,134; 152	—	0·6

* Footnotes as in Table 1.

EXPERIMENTAL

Isolation of the essential oil. Fresh marsh grass (80 kg) was harvested from Bay St. Louis, Mississippi, and stored below 0° until it was steam distilled. Each time 10 kg of marsh grass was chopped and steam distilled in a brass–copper system for about 2·5 hr. The entire apparatus was thoroughly cleaned with several solvents and by distilling H_2O through it before use. The distillate was extracted with CH_2Cl_2, dried with anhyd. Na_2SO_4, and the solvent removed under vacuum at 40° to give 8 g of oil. Yield = 0·01% [calculated on the basis of fresh marsh grass].

Column chromatography. The marsh grass essential oil (2 g quantities) was chromatographed on 2 × 25 cm jacketed Florisil column which was cooled with ice water to prevent column cracking. The column was eluted successively with 100 ml portions of pentane, 2% Et_2O in pentane, 5% Et_2O in pentane, 10% Et_2O in pentane, 20% Et_2O in pentane and 100% Et_2O. Four 25 ml fractions were collected from each solvent system. The separations were monitored by Silica gel TLC and the original 24 fractions were recombined into the following seven fractions: 1 (1–6); 2 (7–8); 3 (9–11); 4 (12–15); 5 (16–18); 6 (19–20); 7 (21–24). Approximate material balances for all fractions were obtained by weighing or peak triangulation as appropriate.

Analytical GLC–MS. Each fraction (0·3 μl of the neat oil) was introduced via a Waston–Biemann separater from a 15·24 m × 0·25 mm open tubular SCOT silanized column coated with 20% Carbowax 20M. Carrier gas flow was 1·0 ml/min N_2, column temperature manually programmed from 100° to 155°. The mass spectrometer was a double focusing PE-270 unit interfaced with a PE-900 gas chromatograph. Fragment ion

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values were compared with those of Cornu and Massot,[10] A.M.S.D.,[11] Bondarovich *et al.*,[12] von Sydow,[13,14] and Buttery *et al.*[15] GLC retention times are presented as Kovats indices[16] (I_K).

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