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New Natural Products Isolated from One-Seeded *Juniperus* of the Southwestern United States: Isolation and Occurrence of 2-Ethenyl-3-Methyl Phenol and Its Derivatives

Robert P. Adams*
Biology Department, Baylor University, Box 727, Gruver, TX, 79040, USA
Philip S. Beauchamp, Vasu Dev and Stephen M. Dutz
Department of Chemistry, California State Polytechnic University, Pomona, CA, 91768, USA

Abstract

Re-examination of the leaf essential oils of the one-seeded, serrate leaf junipers of the Southwestern United States and northern Mexico, by GC, GC/MS and NMR, has yielded 2-ethenyl-3-methyl phenol (coahuilensol), 2-ethenyl-3-methyl anisole (coahuilensol, methyl ether), and 2-(1'-acetoxyethyl)-3-methyl anisole (pinchotene acetate) as new natural products. A survey of *Juniperus* oils revealed that these compounds were found in: three serrate leaf junipers (*J. angosturana,* two varieties of *J. coahuilensis*, and *J. pinchotii*). Coahuilensol was also found in the oils of two smooth leaf junipers of the western hemisphere (*J. virginiana* var. *virginiana* and J. v. var. *silicicola*); three multiple seeded, smooth leaf junipers of the eastern hemisphere (*J. semiglobosa, J. semiglobosa* var. *talassica*, and J. *thurifera*). The phenolic compounds were not found in section *Juniperus*, section *Caryocedrus* or in the one seeded, smooth leaf junipers of the eastern hemisphere. Coahuilensol has been previously reported as 2-(2-propenyl)-phenol (tentative). The leaf oils of *J. angosturana J. coahuilensis*, *J. coahuilensis* var. *coahuilensis, J. monosperma* and *J. pinchotii* were re-examined based on fresh oil collections and the compositions are reported. NMR data and mass spectra of the three 3-methyl phenols are presented to aid in future identification.

Key Word Index

Juniperus pinchotii, Juniperus coahuilensis, var. *coahuilensis,* Juniperus coahuilensis var. *arizonica, Juniperus angosturana, Juniperus monosperma*, Cupessaceae, essential oil composition, 2-ethenyl-3-methyl phenol (coahuilensol), 2-ethenyl-3-methyl anisole (coahuilensol, methyl ether), 2-(1'-acetoxyethyl)-3-methyl anisole (pinchotene acetate).

Introduction

The compositions of the leaf essential oils of the one-seeded, serrate leaf junipers of the Southwestern United States and northern Mexico were first reported by Adams et al. in 1981 (1). Several phenolic components were unidentified. The major unidentified phenolic compound was tentatively identified as 2-(2-propenyl)-phenol. In one of the subsequent reports on the composition of the leaf oils of serrate leaf junipers (2,3), these phenolic compounds were still unidentified. A re-examination of the leaf oil of *J. coahuilensis* var. *arizonica* from Rock Round State Park, NM, showed a considerable amount of these phenolic compounds in these plants. It was possible to do preparative work to isolate these compounds for NMR structural determination.

The group of serrate leaf margined *Juniperus* species of the western hemisphere appears to be a natural division of *Juniperus*, section *Sabina* (4). These junipers are characterized by having microscopic (40 X) serrations (teeth) on the scale leaves and these taxa are generally xerophytes, occurring in the great North American deserts and arid mountains adjacent to the deserts (4). The serrate leaf junipers range from northern Guatemala, into Mexico, thence northward into the southwestern United States, as far north as Oregon (*J. occidentalis*) and eastward to Arkansas (*J. ashei*). The group is thought to had been a part of the Madro-Tertiary flora dating from pre-Eocene (5). As the neotropical tertiary geoflora expanded into the drying conditions that created the southwestern deserts, Axlerod (5) hypothesized that there was a rapid evolution of new species. In this paper, we report a re-examination of the leaf essential oils of *J. angosturana J. coahuilensis* var. *coahuilensis*, *J. coahuilensis* var. *coahuilensis, J. monosperma* and *J. pinchotii*, junipers of the southwestern US and northern Mexico.

Some discussion is needed to facilitate recent nomenclature changes (4). *Juniperus erythrocarpa*, the taxon in trans-Pecos, Texas and Mexico is now treated as *J. coahuilensis* var. coahui-

*Address for correspondence

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lensis in trans-Pecos, Texas and Mexico and as *J. coahuilensis* var. *arizonica* in Arizona and New Mexico ; *J. monosperma* var. *gracilis* Mart., from north-central Mexico, is now *J. angosturana* R. P. Adams (4). *Juniperus monsperma*, previously reported from Mexico, is now thought to be confined to the United States (4).

Experimental

Plant material: Specimens used in this study : *J. angosturana*, Adams 6881-6885, Angostura, San Luis Potosi, Mexico; *J. coahuilensis* var. *coahuilensis* Adams 6829-31, La Zarca Jct., Durango, Mexico; *J. coahuilensis* var. *arizonica* Adams 7635-7637, 7641-2, Rock Hound State Park, New Mexico; *J. monosperma*, Adams 7638-40, Santa Rosa, New Mexico, USA 8592-94, Oregon, USA; *J. pinchotii*, Adams 7483-87, 8736-45, Clarendon, Texas, USA. Voucher specimens have been deposited at the Herbarium, Baylor University (BAYLU).

Isolation of oils: Fresh leaves (200 g) were water distilled for 2 h using a circulatory Clevenger type apparatus (6). The oil samples were concentrated (diethyl ether trap removed) with nitrogen and the samples stored at -20°C until analyzed. The extracted leaves were oven dried (48 h, 100°C) for determination of oil yields.

Analyses: Oil from three to five trees of each of the taxa were analyzed and average values are reported. The oils were analyzed on a HP5971 MSD mass spectrometer, directly coupled to a HP 5890 gas chromatograph, using a J & W DB-5, 0.26 mm x 30 m, 0.25 µm coating thickness, fused silica capillary column (see 7 for operating details). Identifications were made by library searches of our volatile oil library (7), using the HP Chemstation library search routines, coupled with retention time data of authentic reference compounds. Quantitation was by FID on an HP 5890 gas chromatograph using the HP Chemstation software.

Additional GC/MS data were acquired at 70eV under EI conditions with AGILENT 5973 Network Mass Selective Detector interfaced with AGILENT 6950 GC system fitted with a 30 m x 0.25 mm (film thickness 0.25 µm) HP5MS capillary column. The GC was programmed at initial temperature of 50°C for 10 min followed by 3°C/min to 230°C and then isothermal at 230°C for 10 min.

NMR spectral data were acquired with a Varian Mercury 300 or with Varian iNOVA 400 spectrometer using $CDCl_3$ orC_6D_6 as the solvents.

Preparative HPLC: A Waters 3800 HPLC with a Knauer 2300 RI detector and a 25 cm x 1.0cm semi preparative 10µm Si gel column was used under isochratic conditions.

Isolation of oil components: Two vials of each oil were separately applied on a 200-400 mesh silica gel column packed as a slurry of 80 g silica gel in hexane. The column was eluted with 100 mL portions of hexane: Et_2O, ranging from 99:1 to 30:70 ratio. The eluent was collected in 72 test tubes, approximately 8 mL each. The chromatography fractions were spotted on a TLC plate, and developed in 80:20 hexane:Et_2O. After visualization under UV and then under I_2 vapors every fifth fraction was analyzed by GC and GC/MS. Fractions 45 through 55 seemed to contain one of the desired compounds. In order to get a better profile of the content of these fractions (45-55), every other fraction was also analyzed by GC and GC/MS. It was determined that fraction 50 contained one of the desired component in better than 95% purity. The analysis of its NMR data (Table I) indicated it to be 2-ethenyl-3-methyl anisole II; MS m/z (relative intensity) 148 M^+(93), 138(99), 115(29), 105(100), 77(22), 91(12).

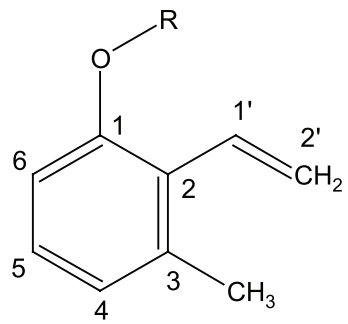

Figure 1. Structures for 2-ethenyl-3-methyl phenol (**I**, R=H) and 2-ethenyl-3-methyl anisole (**II**, R=CH3); see Table I for NMR data

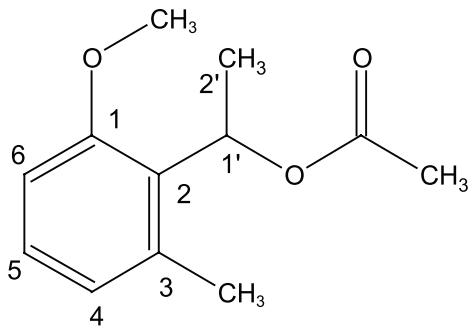

Figure 2. Structure for 2-(1'-acetoxy ethyl)-3-methyl anisole (**III**); see table II for NMR data

The GC and GC/MS of fraction 59 (~200 mg) indicated it to consist primarily of 63% camphor and 30% component of interest. The M^+ at m/z 134 and the m/z of several fragments of this component matched with those of II**,** which indicated it to be a phenol. A 3 mL portion of fraction 59 in 5 mL of hexane was vigorously stirred with 3 mL of 1.0 M NaOH. The aqueous phase was then stirred separately with 3 mL hexane and 300 mg $NaHCO_3$. A GC/MS of the hexane solution showed better than 95% purity of the component. The oily material left after the evaporation of hexane under N_2 and further drying under vacuum when subjected to NMR analysis (Table I) indicated it to be 2-ethenyl-3-methyl phenol I; MS m/z (relative intensity) 134 (100), 115(21), 105 (22), 91 (60), 77 (20), 65 (12), 51 (20).

Table I. ^{1}H- and ^{13}C-NMR data for 2-ethenyl-3-methyl phenol (I, R=H) and 2-ethenyl-3-methyl anisole (II, R=CH_3) in solvent shown in parenthesis

Atom	δ ^{1}H		Multiplicity J=Hz		δ ^{13}C	
	I(C_6D_6)	II(C_6D_6)	I(C_6D_6)	II(C_6D_6)	I(C_6D_6)	II($CDCl_3$)
1	--	--	--	--	153.6	157.5
2	--	--	--	--	124.1	125.8
3	--	--	--	--	137.1	137.2
4	6.73	6.74	d 7.9	d 7.7	122.1	122.8
5	6.92	6.99	dd 7.9, 7.6	dd 7.9, 7.9	128.4	127.4
6	6.61	6.47	d 7.3	d 8.2	113.5	108.2
1'	6.35	6.92	dd 18.1, 11.7	dd 18.2,12.0	132.2	131.1
2'	5.18	5.50	dd 11.7, 1.7(*cis*)	dd 12.0, 2.3(*cis*)		
	5.24	5.78	dd 18.1, 1.7(*trans*)	dd 18.2, 2.3(*trans*)	119.8	119.1
CH_3	2.03	2.24	s	s	20.1	22.6
OH	5.12	--	bs	--	--	--
OCH_3	--	3.31	--	s	-	55.5

Table II. ^{1}H- and ^{13}C- NMR data for 2-(1'-acetoxy ethyl)-3-methyl anisole (III) in $CDCl_3$

Atom	δ^{1} H	Multiplicity J=Hz	δ^{13} C
1	--	--	157.5
2	--	--	127.5
3	--	--	137.6
4	6.73	d 7.6	123.8
5	7.10	dd 7.9, 8.2	128.2
6	6.71	d 8.2	109.1
1'	6.42	q 6.8	67.9
2'	1.54	d 6.7	19.3
CH3	2.44	s	20.2
OCH3	3.80	s	55.8
O=C-CH3	2.02	s	21.2
C=O	--	--	170.3

Structural correlation of I and II was further confirmed when a 0.5 mL portion of the hexane solution of fraction 59 was evaporated and the residue stirred overnight with 2 mL acetone, 100 mg anhydrous K2 CO3 and 50 µL CH3I. The GC/MS of the solution showed complete conversion of I to II.

Fraction 62 had the highest concentration (29%) of the third component. Two cycles of HPLC using 80:20 hexane: ether as the mobile phase yielded the component in better than 80% purity. It was judged suitable for the acquisition of its NMR data. Analysis of the NMR data showed it to be consistent with 2-(1'-acetoxy ethyl)-3-methyl anisole III, MS m/z (relative intensity) 208 (32), 165 (8), 149 (48), 133 (100), 121 (18), 105 (40), 91 (32), 77 (18), 65 (9), 43 (64).

Results and Discussion

In order to separate the three components, the oil of *J. coahuilensis* var. *arizonica* was first subjected to column chromatography over Si gel using hexane with increasing concentrations of ether. The 76 fractions, approximately 8 mL each, collected from the chromatography of the oil were spotted on Si gel TLC plates. The plates were developed with 80:20 hexane: ether and visualized first with UV and then with I_2 vapors. A profile of the composition of the fractions was also obtained by analyzing every fifth fraction by GC and GC/MS. The three compounds of interest were observed to be present among fraction nos. 48-64 eluting with hexane mixtures containing 15-30% ether and each was analyzed by GC and GC/MS. The appropriate fraction containing 30% of I, 2-ethenyl-3-methyl phenol was partitioned between hexane and 1.0 M NaOH to remove the 63% camphor in this fraction. The NaOH solution was separately treated with $NaHCO_3$ and the resulting phenol extracted with hexane to give **I** having better than 95% purity. Compound **II**, 2-ethenyl-3-methyl anisole, with better than 95% purity was observed in one of the column chromatography fractions. From one of the more polar column chromatography fractions containing 29% **III**, 2-(1'-acetoxyethyl)-3-methyl anisole was isolated by HPLC using 80:20 hexane ether as the mobile phase. The structures of **I**, **II** and **III** were derived from their ^{1}H- ^{13}C- ^{1}H-^{1}H COSY, ^{1}H-^{13}C-COSY and DEPT, NMR spectral data. The ^{1}H-chemical shift assignments for **II** were further supported from its NOE data. The NMR spectral data in support of the assigned structures are summarized in Table I for **I** and **II**, and Table II for **III**.

It should be pointed out that although both **I** (8) and **II** (9) have been reported as synthetic products, the current report represents the first examples of their isolation as natural products. The reported ^{1}H- and ^{13}C- chemical shifts for **I** matched very closely with the observed values. However, the previous reports listed only the chemical shift values without listing specific assignments for several of the protons. Additionally, the ^{13}C assignments were completely lacking for both **I** and **II**. The 2D NMR data acquired by us and as summarized in Table I, satisfies this deficiency in the reported values. Interestingly, the reported ^{1}H- chemical shifts for **II** were quite ambiguous (9) and did not support the structure. The acquisition of the detailed 2D NMR spectral data for **II** as presented in Table I confirmed the assigned structure. The close structural relationship between **I** and **II** could be further established by the formation of **II** by reacting **I** with CH_3I in acetone with added K_2CO_3.

While **I** and **II** have been previously reported as synthetic products (8,9), there are no reports of the isolation of **III** as a synthetic or a natural product. Aside from its M^+ value of m/z 208, its mass spectrum was very similar to **II** indicating it to be a CH3COOH (m/z 60) addition product of **II** whose M^+ appeared at m/z 148. The NMR data presented in Table II supports this observation and the assigned structure for **III**.

In order to verify that these isolated products were not artifacts of the essential oil isolation process, a sample of the leaf oil was obtained directly by inserting a syringe needle into an oil gland of *J. coahuilensis var. arizonica*. Direct injection into the inlet of the GC/MS resulted in the presence of **I**, **II** and **III** in the RIC in the same ratios as previously found in the water distilled leaf oil.

The compositions of the leaf oils of the southwestern-northern Mexico, one-seeded junipers are shown in Table III. Several compounds not previously identified have now been identified. The three phenolic compounds (coahuilensol; coahuilensol, methyl ether; and pinchotene acetate) are highlighted (Table III). *Juniperus coahuilensis* var. *arizonica* was highest in these phenolics (2.5, 13.8, 2.6%). All of these phenolics were missing in *Juniperus monosperma*. The oil of *J. pinchotii* was dominated by camphor (28.4%), and sabinene (18.4%). *Juniperus coahuilensis* var. *coahuilensis* oil had the largest concentration of sabinene (35.5%) with a very small amount of camphor (0.4%). The oil of *J. coahuilensis* var. *arizonica*, contained large amounts of α-pinene (13.9%), coahuilensol, methyl ether (13.8%), sabinene (12.3%) and camphor (9.9%).

Table III. Comparisons of the per cent total oil for leaf essential oil components of *J. pinchotii* (PN), *J. coahuilensis* var. *coahuilensis* (CC), *J. coahuilensis* var. *arizonica* (CA), *J. angosturana* (AN), and *J. monosperma* (MN)

KI	Compound	PN	CC	CA	AN	MN
855	(2,E)-hexenal	0.1	t	-	0.3	-
926	tricyclene	0.4	-	0.4	t	t
931	α-thujene	0.6	1.6	0.8	-	-
939	α-pinene	1.9	2.6	13.9	36.4	56.6
953	α-fenchene	t	t	t	0.6	t
953	camphene	0.6	t	0.5	0.3	0.6
957	thuja-2,4(10)-diene	-	-	-	-	0.1
967	verbenene	-	-	0.3	2.0	0.3
976	sabinene	18.4	35.5	12.3	0.2	t
980	β-pinene	0.1	0.3	0.9	1.2	1.1
991	myrcene	2.3	2.6	2.1	2.9	1.6
1001	δ-2-carene	-	-	-	-	t
1005	α-phellandrene	0.1	0.3	0.2	0.2	0.5
1011	δ-3-carene	0.8	-	1.6	12.9	1.0
1018	α-terpinene	1.7	3.6	1.1	0.2	0.1
1026	p-cymene	0.2	0.3	0.8	0.4	0.7
1027	sylvestrene	-	-	-	0.1	-
1031	limonene	4.4	1.8	2.6	0.6	1.9
1031	β-phellandrene	-	1.9	2.6	1.0	5.0
1032	1,8-cineole	t	0.3	-	0.3	-
1050	(E)-β-ocimene	-	0.2	0.4	0.2	t
1062	γ-terpinene	2.8	5.6	1.8	0.6	0.5
1065	*cis*-sabinene hydrate	1.4	1.5	0.8	-	t
1067	*cis*-linalool oxide (furanoid)	-	0.1	t	t	t
1088	fenchone	-	-	-	-	0.5
1088	terpinolene	1.2	1.9	1.0	2.8	0.5
1095	terpene alcohol, FW152, 96,109,137	-	-	-	1.1	0.8
1098	*trans*-sabinene hydrate	1.4	2.2	0.9	-	t
1098	linalool	-	-	-	0.3	-
1102	nonanal	-	-	-	0.3	0.1
1114	*trans*-thujone(=β-thujone)	-	0.1	t	-	-
1116	3-methyl butanoate, 3-methyl-3-butenyl-	-	-	-	-	0.3
1121	*cis*-p-menth-2-en-1-ol	-	0.9	-	0.1	0.3
1125	α-campholenal	-	-	-	0.1	0.1
1132	*cis*-limonene oxide	-	-	-	t	-
1134	*cis*-p-mentha-2,8-dien-1-ol	0.5	-	-	t	-
1139	*cis*-pinene hydrate	-	-	0.4	-	-
1139	*trans*-pinocarveol	-	-	-	0.2	0.8
1140	*trans*-p-menth-2-en-1-ol	0.1	0.6	0.3	-	-
1141	*cis*-verbenol	-	-	-	0.2	t
1143	camphor	28.4	0.4	9.9	0.9	0.8
1146	neoisopulegol	-	0.4	-	-	0.7

Table III. continued

KI	Compound	PN	CC	CA	AN	MN
1148	camphene hydrate	1.2	t	0.4	0.1	0.1
1153	citronellal	1.0	4.1	-	-	t
1156	iso-(iso)pulegol	-	0.2	-	-	-
1159	p-mentha-1,5-dien-8-ol	-	-	-	0.1	t
1160	*trans*-pinocamphone	-	-	-	-	t
1162	pinocarvone	-	-	-	-	t
1165	borneol	1.8	t	0.5	0.1	0.1
1177	coahuilensol	0.2	t	2.5	0.3	-
1177	pinocamphone	-	-	-	0.1	t
1177	terpinen-4-ol	7.4	12.4	4.6	0.3	0.4
1183	p-cymen-8-ol	-	-	t	0.1	-
1189	α-terpineol	0.4	0.6	0.2	0.3	0.2
1191	myrtenol	-	t	-	t	-
1193	(Z)-4-decenal	-	-	t	0.5	-
1193	*cis*-piperitol	t	0.2	t	-	-
1195	methyl chavicol	-	-	-	0.1	-
1204	verbenone	-	-	-	0.7	0.2
1205	*trans*-piperitol	t	0.3	0.2	-	0.2
1217	*trans*-carveol	-	-	-	t	
1222	coahuilensol, methyl ether	0.1	-	13.8	1.0	-
1228	citronellol	3.2	4.9		-	-
1233	unknown, FW194, 119, 43, 109, 152	-	-	-	1.1	-
1241	carvacrol, melhyl	-	-	-	0.1	-
1242	carvone	-	-	-	-	0.1
1252	piperitone	-	-	0.2	0.6	0.3
1258	(Z)-4-decenol	-	-	0.2	-	-
1262	terpene alcohol, FW152, 123,91	-	-	0.6	-	0.5
1274	pregeijerene B	0.1	0.4	0.2	t	2.7
1274	isopulegol acetate	-	-	-	0.1	-
1283	isobornyl acetate	-	-	-	-	0.8
1283	iso-(iso)pulegol acetate	-	-	-	0.2	-
1285	bornyl acetate	5.5	-	2.2	0.5	-
1286	safrole	-	-	-	0.5	-
1290	thymol	-	-	-	0.1	0.1
1297	*trans*-pinocarvyl acetate	-	-	-	-	t
1298	carvacrol	t	-	0.3	0.2	t
1312	citronellic acid	-	0.6	-	-	t
1314	(E, E)-2,4-decadienal	-	-	-	-	0.2
1350	α-terpinyl acetate	-	-	-	0.1	-
1351	α-cubebene	0.1	-	0.2	0.1	-
1356	eugenol	-	-	-	t	-
1372	unknown, FW166, 151,121	-	-	0.6	-	-
1376	α-copaene	0.1	-	0.1	t	-
1387	β-cubebene	-	t	0.2	t	-
1389	β-elemene	-	0.1	-	0.4	-
1403	methyl eugenol	-	-	-	t	-
1418	β-caryophyllene	0.1	0.1	0.2	0.1	0.1
1429	*cis*-thujopsene	-	-	t	-	-
1434	γ-elemene	-	-	-	0.1	-
1444	*cis*-murrola-3,5-diene		0.2	0.7	0.8	-
1450	*trans*-muurola-3,5-diene	0.2	-	-	-	-
1454	α-humulene	t	t	0.2	t	t
1470	pinchotene acetate	t	t	2.6	0.2	-
1473	*trans*-cadina-1(6),4-diene	0.2	0.2	0.7	0.8	-
1477	γ-muurolene	-	-	-	0.1	-
1485	β-selinene	-	0.2	-	0.2	-
1491	*trans*-muuola-4(14),5-diene	-	0.4	1.8	1.7	-
1491	valencene	-	0.2	-	-	-
1493	*cis*-cadina-1,4-diene	0.4	-	-	-	-
1494	epi-cubebol	0.2	0.1	0.7	0.8	-
1499	α-muurolene	t	t	0.1	0.2	0.2
1513	γ-cadinene	-	0.2	1.8	-	-
1513	cubebol	0.8	-	-	1.9	-

Table III. continued

KI	Compound	PN	CC	CA	AN	MN
1524	δ-cadinene	0.5	0.2	1.6	1.3	-
1526	zonarene	-	t	0.4	0.5	-
1532	*trans*-cadina-1(2),4-diene	-	-	0.1	0.2	-
1539	α-copaen-11-ol	-	-	0.2	-	0.2
1545	selina-3,7(11)-diene	-	0.2	-	0.1	-
1549	elemol	3.3	5.8	1.2	6.3	2.7
1554	elemicin	-	-	-	6.1	-
1556	germacrene B	0.2	-	-	-	0.3
1581	caryophyllene oxide	-	-	0.1	t	-
1606	humulene epoxide II	-	-	-	t	-
1627	1-epi-cubenol	0.5	0.5	1.6	2.2	-
1630	γ–eudesmol	0.6	1.0	0.2	0.9	1.9
1640	epi–α–muurolol	-	-	-	0.6	-
1642	cubenol	-	-	0.2	-	-
1645	α–muurolol (= torreyol)	-	-	t	t	-
1646	agarospirol	-	-	-	-	0.3
1649	β–eudesmol	0.6	1.2	0.6	1.1	1.6
1652	α–eudesmol	0.9	1.3	0.6	1.3	3.3
1666	bulnesol	0.2	0.5	-	0.4	0.2
1675	cadalene	-	-	t	-	-
1741	8α–11-elemenadiol	-	0.3	-	-	-
1789	8α–acetoxyelemol	-	0.7	0.3	0.1	1.7
1989	manoyl oxide	0.5	t	-	0.1	t
2054	abietatriene	t	t	-	0.1	t
2080	abietadiene	0.3	t	-	-	-
2288	4-epi-abietal	-	t	-	t	-
2313	abieta-7,13-dien-3-one	0.1	-	-	-	-
2314	abietal	0.2	t	-	-	-
2302	*trans*-totarol	-	-	-	0.1	-
2325	*trans*-ferruginol	-	t	-	0.1	-

KI = Kovat's index on DB-5(= SE54) column; compositional values less than 0.1% are denoted as traces (t); unidentified components less than 0.5% are not reported

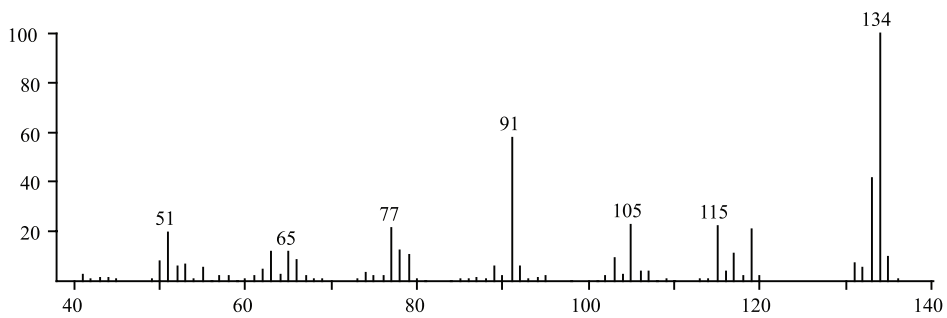

Figure 3. Mass spectrum of 2-ethenyl-3-methyl-phenol (coahuilensol); KI = 1177 on DB-5

Both *J. angosturana* and *J. monosperma* oils were dominated by α-pinene (36.4, 56.6%), but *J. angosturana* oil also had considerable amount of δ-3-carene (12.9%).

Examination of the oils of other junipers, revealed that these phenolic compounds occurred only in the section *Sabina* and appeared to be absent in sections *Caryocedrus* and *Juniperus*. In the section Sabina, the coahuilensol was found in *J. virginiana* var. *virginiana* (0.7%); *J. virginiane* var. *silicicola* (trace); *J. semiglobosa* var. *semiglobosa* (0.1%); *J. semiglobosa* var. *talassica* (trace); and *J. thurifera* (0.2%). It is likely that coahuilensol methyl ether and pinchotene acetate are also present in these taxa as trace amounts.

In order to assist colleagues in the identification of these phenolics in essential oils, their mass spectra are presented in Figures 3-5 along with KI (Kovat's Index) on DB-5. These phenolics are also included in the 4th edition of Adams' essential oil book and library (7).

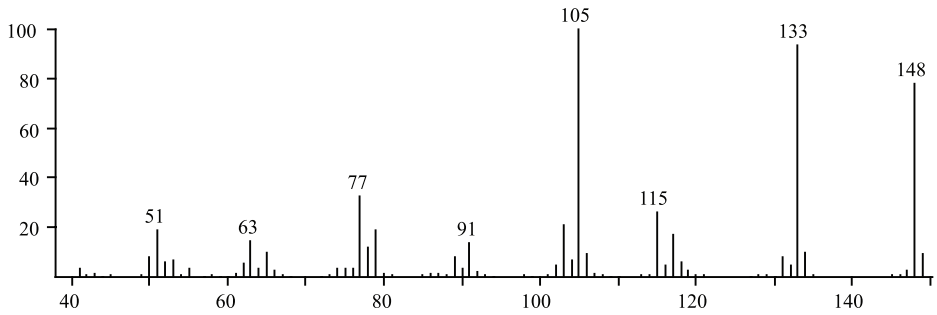

Figure 4. Mass spectrum of 2-ethenyl-3-methyl anisole (coahuilensol, methyl ether); KI = 1222 on DB-5

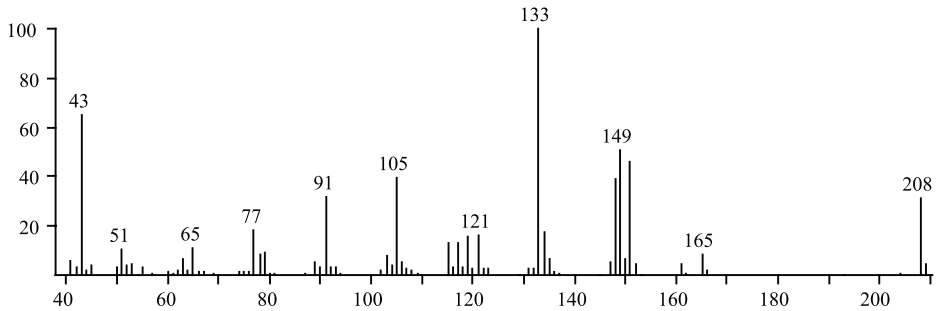

Figure 5. Mass spectrum of 2-(1'-acetoxy ethyl)-3-methyl anisole (pinchotene acetate); KI = 1470 on DB-5

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