Terpenes in the Essential Oil of Sagebrush (*Artemisia tridentata*)

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Essential oil from the leaves and young shoots of sagebrush growing in the Okanagan Valley of British Columbia was obtained by steam distillation and was then fractionated by distillations at 730, 15, and 0.65 mmHg and temperatures up to 180 °C. The distilled fractions were further separated by chromatography on alumina (AlO₃) columns. Depending on the purity of the eluates, samples were submitted to infrared (IR), nuclear magnetic resonance (NMR), and mass spectral (MS) analyses or to the analysis of a GC–MS coupled system. Identifications were based on comparison with spectra and retention times of authentic samples. Out of a total of 28 terpenes reported, one partly characterized compound is apparently unknown and four were tentatively identified by GC–MS data system only. The most predominant compounds present in the oil were camphor (40–45%), an unknown terpene ether (14%), and 1,8-cineole (12%).

American sagebrush (*Artemisia tridentata*) is also referred to in the literature as big sagebrush (*Artemisia tridentata* Nutt.) or often simply as sagebrush (*Artemisia tridentata*). The general chemical composition of its leaves in terms of fat, carbohydrate, protein, fiber, and ash as well as successful feeding trials on cattle with the pelleted plant material have been reported (Kinney and Sugihara, 1943; Furbush et al., 1961).

Various chemical constituents from sagebrush such as sesquiterpene lactones (Irwin and Geissman, 1969), coumarins (Shafizadeh and Melnikoff, 1970), and methoxylated flavonoids (Rodriguez et al., 1972) have been isolated. The principal terpenes in the essential oil of sagebrush from the Utah and Nevada regions were identified as cineole, camphor, and α-pinene (Kinney et al., 1941), the presence of which was later confirmed by GC analysis (Nagy, 1966). More recent work on the essential oils of 25 different *Artemisia* species was carried out by Banthorpe et al. (1971); however, the oil from *A. tridentata* was not included in the investigation.

The present study was undertaken to identify the major components of the essential oil in the leaves and young shoots of sagebrush, growing on range land of the central interior region of British Columbia to assess its potential commercial value and to survey techniques suitable for the preparation of the oil or its components by a small, seasonally operated industry.

EXPERIMENTAL SECTION

Distillations. Leaves (6.7 kg) including the young shoots of last season's growth were collected Nov 15–18, 1974, and steam distilled after 2 days of storage at 0 °C. The steam injected into the load was obtained from a vessel kept at 15 lb/in.². Total yield, including the recovered water oil, was 80 g (1.2%) of steam distillable, Na₂SO₄ dried oil. For further analysis 25 g of the oil was redistilled at pressures of 730 (atmospheric), 15, and 0.65 mmHg. At each pressure three fractions were collected with the following boiling point ranges: 64–84 °C (730 cut 1), 0.5 g; 164–174 °C (730 cut 2), 2.6 g; 178–184 °C (730

cut 3), 7.0 g; 62–68 °C (15 cut 1), 2.1 g; 75–80 °C (15 cut 2), 3.8 g; 85–95 °C (15 cut 3), 2.1 g; 70–78 °C (0.65 cut 1), 1.5 g; 80–90 °C (0.65 cut 2), 2.5 g; 90–100 °C (0.65 cut 3), 1.5 g. After the distillation a residue of 1.2 g with a distinct smell of pine resin, best soluble only in polar solvents such as ethanol, remained. Hereafter, cut 1 of the fractions obtained by distillation at 730 mmHg is designated as 730-1, for example, and others are coded similarly.

Column Chromatography. A glass column was packed with a 1.8 × 45 cm bed (~60 g) of neutral alumina, Brockman activity 1, 80–200 mesh, in petroleum ether, bp 35.5–49.7 °C. Up to 2.0 g of a particular essential oil fraction was applied to the column with petroleum ether and eluted with the solvents listed below, where each consecutive 40 ml of eluate from the column was designated as fr1, 2, 3, 4, 5, etc.: petroleum ether, 100 ml; petroleum ether–benzene, 30:10 ml; 20:20 ml; 10:30 ml. Benzene, 40 ml; benzene–ethyl ether, 30:10 ml; 20:20 ml; 10:30 ml. Ethyl ether, 40 ml; ethyl ether–methanol, 30:10 ml; 20:20 ml; 10:30 ml. Methanol, 40 ml. The solvent from each fraction was flash evaporated and the products, mostly oils, except in the case of camphor were transferred to small vials for further purification by microdistillation, sublimation, and TLC.

TLC Chromatography. Initial analysis for the purity of the fractions was carried out on 5 × 20 cm glass or plastic plates, precoated with a 0.250-mm layer of silica gel GF₂₅₄, activated at 100 °C for 1 h. The solvent system consisted of 15% v/v ethyl acetate in hexane and chromatography was carried out in a solvent saturated chamber at −30 °C for about 40 min. Components were detected with UV light (~260 nm) and with antimony(III) chloride spray reagent consisting of 25 g of antimony trichloride in 75 g of chloroform. For full color development the plates were heated up to 10 min at 100 °C.

Instrument Analysis. NMR spectra of purified fractions were recorded in deuterated chloroform relative to reference tetramethylsilane with a Varian HA-100 or T60 instrument. MS data were obtained from a Nuclide 12-90-G mass spectrometer or a Finnigan coupled GC-quadrupole mass spectrometer equipped with a data acquisition–search system. Columns available for this instrument were 5 ft long (glass columns), 0.25 in. (o.d.) packed with 3% OV 17 or OV 225 on Chromosorb WHP, 80–100 mesh for nonpolar and polar compounds, respectively. Temperature programs varied for different applications and are described later. Flow rate was generally 35 ml of He/min. For mass spectrometry the separator and transfer line temperature was 250 °C. The mass spectra were obtained with an accelerating voltage of 3000 V with 70 eV of energy and a scanning time of 1

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Table I. Terpenes in the Essential Oil of Sagebrush (*Artemisia tridentata*)[b]

Component	Identification	Fraction	Approx. %
Camphor	MS, NMR, mp	730-2, 3 fr 6-8; 15-1, 2, 3	40-45
Unknown terpene ether	GC-MS, IR	730-2, 3 fr 4, 5	14
1,8-Cineole (eucalyptol)	MS, NMR, IR	730-2, 3 fr 3; 15-2 fr 2	12
δ-3-Carene	GC-MS, NMR, IR	730-2, 3 fr 2	4
Santolinyl ester	GC-MS, NMR	730-3 fr 5, 6, 7; 15-2 fr 2	3
α-Pinene	GC-MS, NMR, IR	730-2, 3 fr 2	3
Camphene	GC-MS	730-2, 3 fr 2	3
Thujone	GC-MS	0.65-1 fr 7	1.5
β-Pinene	GC-MS	730-2, 3 fr 2	1.5
α-Terpineol	GC-MS	730-2, 3 fr 10	1
Thujyl alcohol	GC-MS	15-2 fr 12; 730-3 fr 11	1
α-Phellandrene	GC-MS	730-3 fr 2	1
Borneol	GC-MS	0.65-1 fr 7; 15-2 fr 12	0.5
β-Ocimene	GC-MS	730-3 fr 2	0.5
Terpinen-4-ol	GC-MS	730-2 fr 10	0.4
Myrcene	GC-MS	730-3 fr 2	0.3
Methyl isopimarate[a]	GC-MS	15-3 fr 11; 0.65-3 fr 1	0.3
β-Caryophyllene	GC-MS	0.65-1 fr 12	0.2
Fenchyl alcohol	GC-MS	730-2 fr 11	0.2
Fenchone	GC-MS	730-1, 2 fr 9	0.1
Neral	GC-MS	0.65-3 fr 1	0.1
Nerolidol	GC-MS	0.65-3 fr 1	0.1
Methyl levopimarate[a]	GC-MS	15-3 fr 11; 0.65-2 fr 6	0.1
Carvacrol	GC-MS	730-3 fr 11	0.1
Isopulegol	GC-MS	0.65-3 fr 1	0.1
α-Ionone	GC-MS	0.65-3 fr 1	0.1
Methyl palustrate[a]	GC-MS	15-2 fr 12	0.1
Methyl *trans*-communate[a]	GC-MS	730-2 fr 7-8; 0.65-3 fr 15	Tr

[a] No reference samples available. Identification made by computer data match with unknown spectrum (one mismatch).
[b] The fractions indicated in Table I are an approximate guide and varied slightly during different repeat experiments.

s over a mass range of m/e 35-500. The Nuclide 12-90-G mass spectrometer with a direct insertion probe was operated at 70 eV.

Retention times were also obtained with Varian Aerograph 1700 and Hewlett Packard 5700 A instruments using the above columns or a 10 ft × $^1/_8$ in. Carbowax 20M column for the more polar compounds. Carrier gas was 15 ml/min nitrogen and the instruments were temperature programmed at 60 °C for 8 min and 60 to 180 °C at 2 °C/min while detection was by FID. Commercially available samples of compounds were used as reference standards which in some instances were purified by sublimation, distillation, or column chromatography before use. In the case of the iso- and levopimarates and related diterpenes no reference standards were available and identification was based on a computer match with the reference mass spectra. Infrared analyses were carried out with a Beckman 20A or a Unicam SP 200 spectrophotometer.

RESULTS AND DISCUSSION

Camphor, the major constituent in the essential oil of sagebrush (*Artemisia tridentata*) harvested in British Columbia, ranged from 40 to 45% with eucalyptol (1,8-cineole) and a yet unidentified terpene ether making up the next most abundant compounds at 12 and 14%, respectively (Table I). Eucalyptol and the ether appeared invariably as mixtures of each other. The possibility that the unknown terpene is an epoxide formed by oxidation during steam distillation has not yet been sufficiently investigated. One compound, presumably santolinyl ester (4-hexenoic acid methyl ester 2,5-dimethyl-3-ethenyl) previously reported by Epstein and Shaw (1973), was present at a level of about 3%. Other compounds are listed in an approximate order of their content in the oil and are generally known terpenoid structures (Devon and Scott, 1972). The individual fractions in Table I are only a general guide to the position of compounds in the eluates since some variations, possibly due to different activities

of the adsorbent and moisture conditions of solvents and the oil, were observed during repeat experiments.

Capillary GC columns, molecular stills, preparative GC, or HPLC, which would have provided superior separation and led to faster identification of components, were not available and therefore prefractionation of the essential oil prior to GC analysis was most effectively carried out on AlO₃ columns by conventional elution chromatography. Although apparent changes of some sagebrush oil constituents were observed by an increasing yellowness when the oil came in contact with the chromatographic adsorbent, satisfactory separation of some of the major classes of compounds was possible. The hydrocarbons, mostly of the $C_{10}H_{16}$ type from the distillation cuts 730-2 and 3, were in the first fractions (turpentine smell) eluted with petroleum ether and were then followed by oxygenated compounds such as cineole, the unknown ether, santolinyl ester, and camphor on the application of eluents of increasing polarity. Alcohols such as borneol, thujol, and other esters were obtained in the fractions eluted with polar solvents, i.e. 730-2, 3 frs 11 and 12. These fractions which emitted a very pleasant odor could be separated from a high boiling, yellow, polar residue (~3%) by a short-path distillation. However, as the yellow residue was difficult to analyze, i.e. severe streaking on AlO₃ plates, etc., it was assumed that it probably represented resins or degradation products and only the distillates of these fractions were subjected to further analysis.

The distillate from 730-3 fr 11, for instance, was resolved on a 10 ft × 1/8 in. Carbowax 20M column (0.5 μl of sample; other details as described in the Experimental Section) into 32 major and about 30 medium sized peaks. Retention times of some of these components corresponded to the following reference alcohols and esters: 2-propanol, propanol, 2-butanol, butanol, hexanol, heptanol, octanol, methyl acetate, methyl propionate, propyl acetate, isobutyl acetate, propyl butyrate, isobutyl butyrate, amyl propionate, isoamyl propionate, heptyl acetate. Butanol, methyl acetate, octanol, and diethylene glycol monoethyl

ether of the nonterpene compounds were later also confirmed by mass spectrometry. The more polar terpene compounds such as thujyl alcohol, α-terpineol, and others listed in Table I were identified by GC–MS where, however, circumstances dictated the use of shorter columns and analysis of all of the components in these interesting fractions could not be fully completed.

Analyses of the various distillation cuts showed that fractionation of the essential oil with the small Quickfit apparatus was relatively inefficient and certain compounds could be found distributed throughout. Camphor, for instance, was still present although in small amounts in the high boiling fractions which were distilled at 0.65 mmHg and 100 °C, although it was found most abundantly in cuts 2 and 3 from the distillation at atmospheric pressure, 730 mmHg (730-2,3), as well as in cuts 1, 2, and 3 from the distillation carried out at 15 mmHg (15-1, 2, 3). A similar distribution, although less pronounced, was evident for the unknown terpene ether and santolinyl ester as well as for cineole. However, the methyl pimarates and related diterpenes were found distributed primarily in the medium and higher boiling fractions.

Following the analytical work, reconstitution of the original aroma of the sagebrush with the major oil components in Table I was attempted. Although initially the odor only vaguely resembled that of sagebrush oil it seemed to "improve" upon standing at room temperature for several weeks. Missing most of all was the strong, somewhat pungent, slightly lachrymatic effect associated with sagebrush odor which was still present in the first distillation cuts. This note was not regenerated even after the addition of methacrolein previously reported as a constituent of the oil (Kinney et al., 1941).

The mass spectrum of the unknown ether was similar to that of 1,8-cineole with the exception that its molecular ion (M^+) occurred at m/e 152 rather than 154 and the corresponding $M^+ - 15$ ion at m/e 137 instead of at 139. The base peaks for both molecules were at m/e 43 and the relative abundance for the m/e 55 ion peaks was 35%. The IR spectrum for the unknown ether showed a strong absorption at 1635 cm^{-1} indicative of a double bond, but no evidence for alcohol or ketone functional groups was present. On reduction of the double bond with H_2/PtO_2 the unknown compound consumed 1 mol of hydrogen but was not converted to cineole. Evidence for the C–O–C ether stretch came from absorptions at 1030, 1070, 1110, 1150 cm^{-1}. A peak at 1460 cm^{-1} was due to a single methyl group and two geminal methyls exhibited the characteristic strong doublet at 1360 and 1380 cm^{-1}.

On TLC plates coated with silica gel and run under conditions described in the Experimental Section, the unknown ether had an R_f value of 38.1 and reacted on heating with the antimony(III) chloride reagent to form at first a grey to dark brown spot which changed to red brown and then to mauve and remained a blue-violet color 20 h after spraying. When reduced, this compound had an R_f of 39.6 and its final color was a dark brown-grey, while 1,8-cineole (R_f 34) after spraying and heating with the antimony reagent changed colors from an orangy-brown to purple, red to grey, and brown being the final color after standing for 20 h at room temperature.

The GC retention time, on a 5 ft × 0.25 in. (o.d.) 3% OV 17 column, 130 °C isothermal, 35 ml/min He, for the unknown ether (730-3 fr 6) was 1.0 min and it was 1.75 min for 1,8-cineole, which often accompanied this compound as a contaminant. Under identical experimental conditions, the GC retention time for the santolinyl ester (15-2 fr 3) was 3.50 min while that for camphor was 5.20 min.

GC retention times of the H_2/PtO_2 reduced, unknown terpene ether and standard cineole were 1.25 and 1.95 min, respectively, when chromatographed on the same column but with a temperature program from 60 to 250 °C at 6 °C/min. A search for this compound in standard reference works for terpenes (Devon and Scott, 1972) and of mass spectral data (Cornu and Massot, 1966a,b) did not, however, reveal any compounds with structural characteristics resembling or matching the analytical data. The unknown ether was not identical with compounds such as nerol oxide (Schreier et al., 1976), α-pinene 2,3-epoxide (Stadtler Research Laboratories, 1975), matata biether (Isoe et al., 1968), or hop ether (Naya and Kotake, 1968) although their molecular formulas, $C_{10}H_{16}O$, are identical.

The santolinyl ester was eluted off the AlO$_3$ columns following the terpenes containing ether type linkages and was often contaminated with camphor. A mass spectrum of the methyl ester could be obtained after separating the compounds by GC; however, the NMR spectrum contained significant camphor impurities. Despite this, all of the characteristic proton resonance peaks of the santolinyl methyl ester $(Me)_2C=CHCH(CH=CH_2)CH(Me)CO_2Me$ were recognizable in the spectrum. The methyl ester OMe grouping was inferred from the sharp (3 H) singlet at δ 3.58 ppm and the signals of the methyl protons $(Me)_2C=C$ were located at δ 1.60 (3 H) and 1.68 (3 H). At δ 1.12 was a sharp doublet (3 H), $J = 7.5$ Hz, from the Me group bonded to the carbon α to the carbonyl group $CH(Me)CO_2$. The respective methine proton signal of that grouping was a broad quartet at δ 3.14 (1 H), $J = 7.5$ Hz. The terminal protons of the vinyl group $C=CH_2$ and the olefinic proton of the grouping $(Me)_2C=CH$ resonated in a complex multiplet (3 H) at about δ 5.0 ppm. The signal from the single proton of the vinyl group $-CH=$ was located as a well-resolved multiplet (five major peaks) centered at δ 5.58 ppm (1 H). The splitting was due to coupling with the cis and trans vinylic protons, $J = 10$ and 17 Hz, respectively, and also with the adjacent methine proton ($J = 7$ Hz). The resonance signal of this methine proton was located at δ 2.42 ppm (1 H), $J = 7$ Hz, with some underlying camphor proton signals.

The mass spectrum of the santolinyl ester showed a molecular ion (M^+) at m/e 182 and corresponding $M^+ - 15$, $M^+ - 31$, and $M^+ - 59$ ion peaks due to loss of the Me, OMe, and carbomethoxyl groups, respectively. The base peak at m/e 95 is presumably generated by loss of the $CH(Me)CO_2Me$ group ($M^+ - 87$). Since fragmentation next to double bonds is not a favored reaction the above cleavage is the predominant mechanism. Other prominent ions in the spectrum were at m/e 67 (95 − 28), 55, and 41.

Since earlier measurements of the cineole (eucalyptol) content of the essential oil of Utah and Nevada sagebrush were based on the phosphoric acid and resorcinol addition production (Kinney et al., 1941), it is possible that their comparatively high values were due to the fact that they contained the unknown ether in their reported values. However, further work on variations of composition with season would also have to be carried out before differences can definitely be attributed to regional factors.

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A Three-Step Synthesis of Cadin-1(10)-en-11-ol

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Cadin-1(10)-en-11-ol has been synthesized in three steps from the readily available terpene alcohol l-isopulegol. Using tosyl chloride in pyridine, l-isopulegol was dehydrated to mentha-3,8-diene (4-methyl-1-isopropenylcyclohex-1-ene) in 21% yield. This terpene was then condensed with methyl acrylate (Diels–Alder condensation) to give 4,7-dimethyl-1,2,3,5,6,7,8,8a-octahydronaphthalene-1-carboxylic acid methyl ester in 75% yield. After treatment with sodium methoxide, the methyl ester was reacted with methylmagnesium iodide to give cadin-1(10)-en-11-ol in 47% yield. The structure was confirmed by ^{1}H NMR, mass, and IR spectra and by conversion to the known cadinane.

The most commonly found, naturally occurring, cadinene and cadinol sesquiterpenes have the double bonds or hydroxyl group either in the decalin ring or in the methyl side chains leaving the isopropyl group completely saturated with no functional groups. Exceptions are veticadinol (cadin-10(15)-en-11-ol) and khusol (cadina-10(15),5-dien-12-ol) and some related hydrocarbons. In a study involving the volatile products of Streptomyces the authors isolated an unusual sesquiterpene alcohol different from those previously reported in Streptomyces (Gerber, 1971, 1972). One of the possible structures deduced from the spectral data was cadin-1(10)-en-11-ol. The synthesis of this compound was carried out to test this possibility. Although the synthetic cadin-1(10)-en-11-ol proved to be different from the Streptomyces sesquiterpene alcohol it was felt that the synthesis and spectral data of the synthetic compound were of interest because of its close structural relationship to veticadinol and the possibility that it may also occur naturally.

EXPERIMENTAL SECTION

The synthesis is outlined in Figure 1.

Synthesis of Mentha-3,8-diene (II). l-Isopulegol (I, Aldrich, 77 g) was dissolved in pyridine (200 ml) and p-toluenesulfonyl chloride (tosyl chloride, 96 g) was added gradually at room temperature over 1 h with vigorous stirring (cf. Wintersteiner and Moore, 1943). The mixture was allowed to stand overnight at room temperature. It was then gently refluxed for 3 h. Pyridine was distilled off under vacuum (20 mm). The residue was then extracted with pentane (400 ml) under reflux for 0.5 h. The pentane extract was then washed with water (100 ml) and

dried over anhydrous sodium sulfate. The residue was then further extracted with benzene (200 ml) by refluxing for 0.5 h and the benzene extract poured onto a column (200 × 34 mm) of activated alumina (Woelm No. 1). This was eluted with pentane (400 ml) and combined with the pentane extract from above. Removal of the solvent gave 54 g of crude terpene hydrocarbons which was found by gas–liquid chromatographic (GLC) analysis to contain 26% (21% yield) of mentha-3,8-diene (II).

Diels–Alder Condensation. A distilled fraction (bp 71–74 °C (15 mm)) of the above terpene hydrocarbons (17.9 g, 38% II) was mixed with methyl acrylate (4.75 g) and the mixture heated under nitrogen at 85 °C for 16 h. Distillation of the product under vacuum gave 9.7 g (75% yield) of 4,7-dimethyl-1,2,3,5,6,7,8,8a-octahydro-naphthalene-1-carboxylic acid methyl ester (III) (bp 100–105 °C (0.3 mm)). This material was treated with sodium methoxide (from 1 g of sodium) in methanol (50 ml) solution at room temperature for 24 h. The mixture was then poured into a saturated solution of sodium bicarbonate in water (200 ml) and extracted with pentane. After drying with sodium sulfate the pentane was removed on the steam bath to give III with the ester group in the more stable configuration.

Cadin-1(10)-en-11-ol (IV). III (7.4 g) in ether (20 ml) was added dropwise over 0.5 h to methylmagnesium iodide (prepared from 2.4 g of Mg, 14.2 g of MeI, and 100 ml of ether). The mixture was refluxed for 1 h and then water (50 ml) was added dropwise. The ether layer was then decanted and dried over sodium sulfate. Removal of the ether gave crude IV (6.9 g). Purification of the crude product by packed column GLC separated pure IV as a major peak forming 50% of the total. The overall yield of pure IV was thus 47%.

Dehydration and Hydrogenation to Cadinane. IV (10 mg) was mixed with 200 mg of activated alumina

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