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VOLATILE OIL CONSTITUENTS OF SAGEBRUSH

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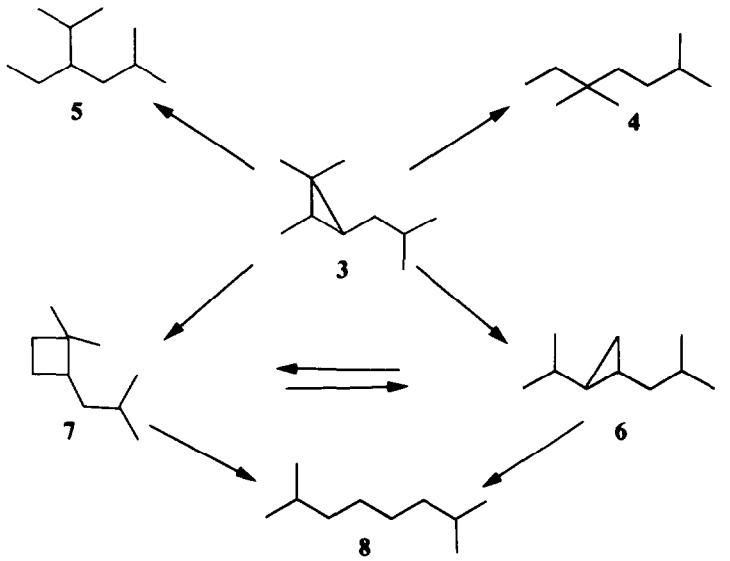
Key Word Index—*Artemisia arbuscula arbuscula*, Asteraceae (Compositae), volatile oil, monoterpenes, irregular monoterpenes

Abstract—The volatile oil of *Artemisia arbuscula arbuscula* contained a new irregular monoterpene, 2,5-dimethyl-4-vinyl-1,5-hexadiene-3-ol (isolyratol), which was isolated and identified by spectral means The optically pure furanoid (2*S*,5*S*)-*trans*-5-methyl-5-vinyltetrahydrofur-2-yl methyl ketone (arbusculone), was also characterized by transformation to known (2*S*,5*S*)-*trans*-linalyl oxide The former component has never been isolated from natural sources prior to this study The neutral pentane extract also contained several previously characterized non-head-to-tail monoterpenes including artemiseole, artemisia ketone, artemisyl acetate, methyl santolinate, and santolina triene, as well as the regular monoterpenes 1,8-cineole, camphor, *p*-cymene, camphene and the C_6 fragment, terelactone

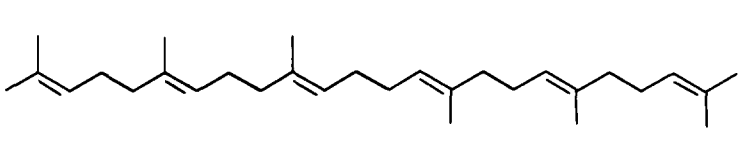
INTRODUCTION

The irregular, non-head-to-tail monoterpenes form a biosynthetically interesting class of natural products in that they disobey the biogenetic isoprene rule [1, 2] The formation of these compounds is not well understood at this time although several schemes have been proposed in the past One of these [3] suggests that irregular monoterpene biogenesis in plants may be related to that proposed [4] for the formation of the important steroid precursor squalene (**1**) in mammals

According to this theory, the biosynthesis of these terpenes involves ionization of chrysanthemyl pyrophosphate **2a**, the C_{10} analog of presqualene pyrophosphate **2b** [5–7], with subsequent rearrangement to generate the various carbon skeletons **4–8** shown in Scheme 1



Scheme 1



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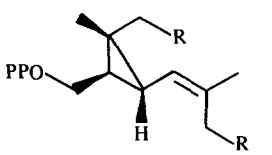


2a R = H
2b R = geranyl

This stereochemically consistent approach accounted for the known irregular monoterpenes possessing the chrysanthemyl (**3**), artemisyl (**4**) and santolinyl (**5**) skeletons, and predicted the biological occurrence of three additional C_{10} systems (**6–8**) as a result of the analogy with squalene biosynthesis The isolation of monoterpenes with these carbon skeletons would provide support for both of these schemes

The non-head-to-tail monoterpenes appear to be genetically related and of botanical interest [8] since they have been reported to occur only in the tribe Anthemideae of the Asteraceae [3] We have been screening species of *Artemisia* (sagebrush), the largest group in this tribe, for irregular monoterpenes and have characterized several new compounds during our investigations including the first example of the rothrockyl skeletal system (**6**) [9–14] We now wish to report our results concerning the volatile oil constituents of *A arbuscula arbuscula*

RESULTS AND DISCUSSION

A arbuscula arbuscula is commonly known as dark, little, low and scabland sagebrush This grey-green plant has narrow tridentate leaves and grows *ca* 50 cm tall at elevations of 7000–9000 feet in dry zlkaline soils of the western United States [15, 16]

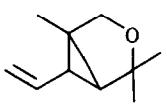
The neutral pentane extract of a sample* of this sagebrush collected near Paradise Valley, Nevada was initially analysed by GC/MS [15] The results indicated that the major constituents of the volatile oil were, (artemiseole (**9**, 28 8%), methyl santolinate (**10**, 15 4%), santolina triene (**11**, 14 7%), 1,8-cineole (**12**, 14 6%), camphor (**13**, 7 3%), *p*-cymene (**14**, 0 8%) and camphene (**15**, trace) The GC/MS data also revealed the presence of an unidentified component (17 9%) with a mass ion at *m/z* 112, and a GC retention time slightly longer than that of camphor on Carbowax 20 M For isolation purposes a second collection of plant material was made at the original site Attempts to purify the unknown component via column chromatography failed, since silica gel was found to catalyse the decomposition of the compound in question

The isolation of this material was accomplished by preparative GC of the crude volatile mixture yielding a colorless oil showing no optical activity Examination of the spectral data allowed the assignment of structure **16** to the unidentified component This compound, terelactone, was first isolated in 1881 [17] and is also present in the essential oils of hop [18], lavender [19] and tobacco plants [20] In addition, Thomas and Dubini [21] have reported terelactone to be a constituent of the essential oils of *A pallens*, presumably arising from the air oxidation of davanone (**17**) The biosynthesis of this compound will be discussed later

Several monoterpenes which had been previously identified by GC/MS were isolated from the essential oils and characterized by IR and ^{1}H NMR spectroscopy, as well as by GC coinjection studies with authentic samples The identification of artemiseole, methyl santolinate, 1,8-cineole and camphor, verifies the GC/MS evidence Artemisia ketone **19** was the major constituent of the oils, and artemisyl acetate **20** was also isolated although neither was detected in the former work These differences most likely involve a seasonal variation in the essential oil composition, rather than a problem of analysis

A third compound which had not been detected during the GC/MS survey was initially isolated by preparative GC from the essential oil mixture Analysis of the spectral data obtained from this material established it as an unknown component, to which we have given the trivial name, arbusculone, Silica gel chromatography of the essential oils obtained from the neutral pentane extract of the leaves and flower heads of *A arbuscula arbuscula* yielded a multi-component fraction with an R_f of 0 33 (EtOAc–petrol, 1 4) containing the desired compound The unknown was further purified by preparative GC to afford a colorless oil, $[\alpha]_D$ −48 1°, with a molecular formula of $C_9H_{14}O_2$ deduced from the mass spectrum $[M]^+$ (*m/z* 154) in conjunction with the ^{1}H and ^{13}C NMR spectra

*A voucher specimen is available at the University of Utah Herbarium



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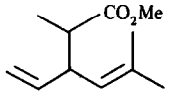

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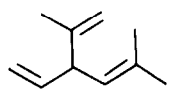

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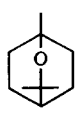

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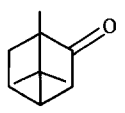

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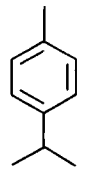

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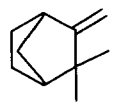

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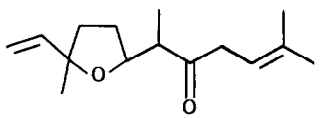

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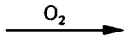

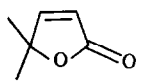

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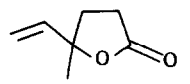

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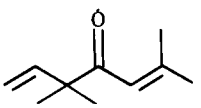

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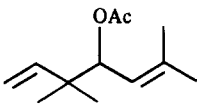

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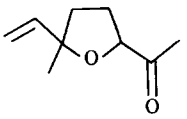

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The IR spectrum of this material contains absorptions at 1710 and 1370 cm^{-1} indicating the presence of a methyl ketone moiety and the three hydrogen singlet at δ2 22 in the ^{1}H NMR spectrum supports this assignment Absorption characteristic of a vinyl (–CH=CH_2) double bond system are present in the IR (3064, 1410, 1000 and 925 cm^{-1}), ^{1}H NMR (doublet of doublets at δ5 03, 5 17, and 5 83) and ^{13}C NMR (triplet at δ112 2 and a doublet at 142 9) spectra The absence of both hydroxyl and additional absorptions requires an ether linkage to explain the functionality of the second oxygen atom The IR band at 1020 cm^{-1} is consistent with this type of sub-structure

The three hydrogen singlet at δ1 39 in the ^{1}H NMR spectrum is characteristic of a methyl group bound to a carbon involved in an ether linkage ($C\underline{H}_3$–CR_2OR), while the one proton doublet of doublets at δ4 34 can be depicted as (–CH_2–$C\underline{H}$ORCO–) due to its downfield absorption The remaining four protons appear as a multiplet in the saturated methylene (–CH_2–) region of the spectrum Thus, the spectral evidence supports structure **21** for this compound

The fragmentation pattern exhibited by the mass spectrum of this material is also consistent with a furanoid system Ions resulting from α-substituted tetrahydrofuran derivatives are commonly observed for these compounds [22] Ions at *m/z* 111, 43, 139 and 127, corresponding to the respective fragments $[M-(MeC{\equiv}O)]^+$, $[MeC{\equiv}O]^+$, $[M-Me]^+$ and $[M-(CH{=}CH_2)]^+$ are evident in the spectrum of arbusculone

Examples of naturally occurring furanoid terpenes are known [23–26], and it has been suggested [23] that the biosynthetic precursor of at least some of these compounds is linalool **22** or its biogenetic equivalent Furthermore, it has recently been demonstrated that linalyl pyrophosphate is an intermediate in the biogenesis of certain regular monoterpenes [27, 28]

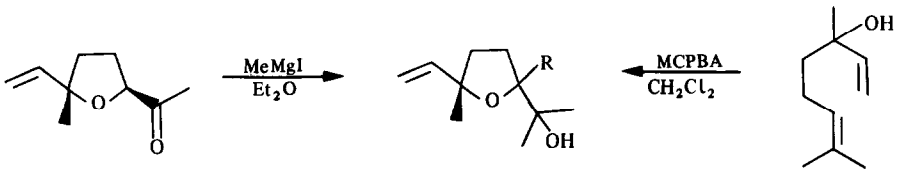
Confirmation of structure, including absolute stereochemistry, was achieved by chemical transformation to a known compound (Scheme 2) Treatment of arbusculone with methylmagnesium iodide afforded a product with GC and spectral characteristics identical to *trans*-linalyl oxide **23a**, while being distinctively different from the *cis*-isomer **23b** Authentic samples of the alcohols were obtained from the reaction of linalool with *m*-chloroperbenzoic acid In addition, the alcohol synthesized from arbusculone possessed a rotation of +5 7°, which corresponds to the (2*S*,5*S*)-isomer of linalyl oxide [29–33]

The optical purity of arbusculone was determined by comparison of its Grignard product to an authentic sample of (+)-*trans*-(2*S*,5*S*)-linalyl oxide The latter material gave an optical rotation of +4 5°, however this material was subsequently shown to be only 82% optically pure The ^{1}H NMR spectrum of the authentic oxide complexed with the optically active shift reagent tris[3-trifluoromethylhydroxymethylene]-d-camphorato europium(III) [34] showed non-equivalence at two separate signals The vinyl hydrogen absorption initially at δ5 83 was resolved into two multiplets in a ratio of *ca* 4 5 1 (downfield signal upfield signal) A similar ratio was found for the partially resolved terminal methylene proton signal These data establish that the oxide synthesized from arbusculone is optically pure, as is the ketone precursor which must therefore possess the (2*S*,5*S*) absolute configuration as shown

Although **21** has not been reported as a naturally occurring molecule, it has been synthesized as an intermediate in the total synthesis of the diastereomeric norsesquiterpene davanafurans [35] Thomas and Dubini converted (−)-*trans*-linalyl oxide* to the (2*R*,5*R*) *en*-antomer of arbusculone while the *cis*-ketone was prepared from (2*S*,5*R*)-**23** The spectral data obtained from the methyl ketone isolated from *A arbuscula arbuscula* is in complete agreement with that reported by Thomas for the *trans*-isomer and the sign of the optical rotation is also consistent with the assigned structure Furthermore, base-catalysed epimerization of natural **21** followed by GC analysis verified the *trans*-disposition of the starting material since this isomer is known to have a shorter retention time on Carbowax 20M [30]

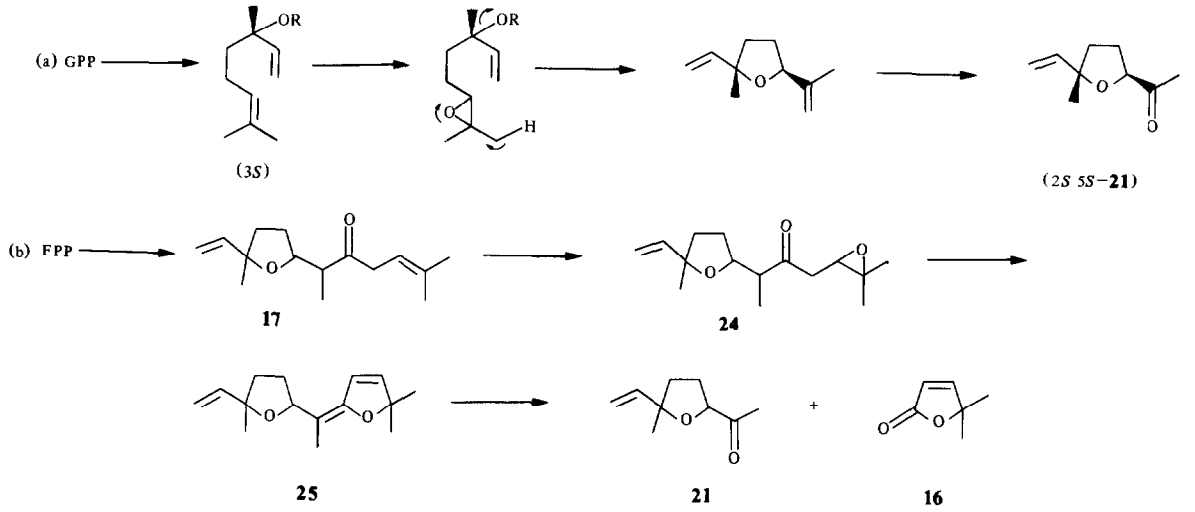
As previously stated, the biosynthesis of the furanoid monoterpenes may involve a linalyl-type structure as the immediate C-10 precursor Naturally occurring arbusculone would require the (+)-(3*S*)-isomer, and this antipode of linalool and linalyl acetate has been isolated from various plant systems [36] A biogenetic sequence leading to (2*S*,5*S*)-**21** from geranyl pyrophosphate can be envisioned to occur as shown in Scheme 3a According to

*Thomas erroneously refers to the (2*R*,5*R*) enantiomer of linalyl oxide as the (+)-*trans* form [27–31]



(2*S*,5*S*)-**21** **23a** R = —H **23b** R = ◄H **22**

Scheme 2 Chemical transformations of arbusculone



Scheme 3 Possible biosynthetic sequences leading to arbusculone

this sequence, the nine carbon molecule isolated from sagebrush is a degraded head-to-tail monoterpene which thereby obeys the biogenetic isoprene rule An alternative source of arbusculone can be proposed to be farnesyl pyrophosphate (Scheme 3b) Several sesquiterpenes containing a furanyl sub-unit like that found in **21** have been isolated from *A pallens* [35, 37–39]

Davana ether **25** has been characterized as a constituent of *A pallens*, and has been synthesized from davanone **17** as shown in Scheme 3b Oxidative cleavage of the tetrasubstituted double bond would result in the formation of arbusculone and terelactone This scheme, which requires the (7*R*,10*S*)-isomer of davanone, would therefore explain the occurrence of both the C-9 and C-6 terpenes in the essential oils of *A arbuscula arbuscula* Terelactone can also be explained as a degradation product of GPP, but in either case it would be derived from a regular terpene precursor

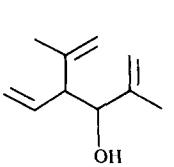
At the present time there is no sound biochemical evidence favoring either the GPP or FPP route for the biogenesis of arbusculone The isolation and identification of presumed intermediates would furnish valuable information concerning this problem and studies along these lines are now in progress However, we have been unsuccessful in our attempts to find linalool or linalyl oxide in the essential oils of *A arbuscula arbuscula*

While screening for linalool, a new irregular monoterpene with GC properties similar to those of linalool was isolated from the volatile mixture as a colorless oil, $[\alpha]_D$ +9 4° (98% pure by analytical GC) Absorptions in the IR spectrum at 3420, 3060 and 1640 cm^{-1} indicate an unsaturated alcohol In accord with this, the intense band at 900 cm^{-1} is a feature commonly associated with *gem*-disubstituted double bond systems (–$\dot{C}$=CH_2) The ^{1}H NMR spectrum of this substance contains an H-6 singlet at δ1 75 which can be attributed to a pair of equivalent methyl groups on unsaturated carbons The singlet at δ1 94 is consistent with a hydroxyl absorption, while the overlapping doublet of doublets at δ2 89 has a chemical shift greater than that of a normal allylic methine signal, but typical of that of a doubly allylic system (–$\dot{C}$=CH–$\dot{C}$H–$\dot{C}$=$\dot{C}$–) The remaining non-olefinic doublet at δ4 12 can be assigned to a hydrogen α to an alcohol (–$\dot{C}$H–$\dot{C}$H–OH), and double irradiation experiments have shown that this signal is coupled to that occurring at δ2 89

The olefinic region of the ^{1}H NMR spectrum contains two multiplets at δ5 02 and 5 95 which integrate for six protons and one proton, respectively The latter absorption has a chemical shift and splitting pattern typical of a vinyl group hydrogen (–CH=CH_2) The remaining four protons at δ5 02 must therefore exist as the terminal methylene hydrogens of two double bonds due to the intense IR absorption at 900 cm^{-1}, and the lack of bands at 690 and 960–970 cm^{-1}

Based upon the above information, only structure **26** can be assigned to which we have given the trivial name, isolyratol This santolinyl skeletal system has biogenetic precedence and is the fourth example of the skeleton oxygenated at the position occupied by the hydroxyl group [3, 14, 40]

We have identified the major components of the volatile oils from *A arbuscula arbuscula*, and have characterized a minor constituent as a new irregular monoterpene by spectral means The presence of the C_6 and C_9 terpenes, terelactone and arbusculone, is interesting since their co-occurrence may indicate a direct biosynthetic link Furthermore, the existence of non-head-to-tail monoterpenes in this sagebrush supports the idea that these compounds may be taxonomically significant with respect to the tribe Anthemideae of the Asteraceae



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EXPERIMENTAL

^{1}H NMR chemical shifts are given as δ-values (ppm) with TMS as internal standard ^{13}C NMR spectra were recorded at 25 1 MHz Optical rotations were measured at ambient temp in a 1-dm cell and are expressed in g solute per 100 ml of soln GC/MS data were obtained on a 2 m × 2 mm glass Carbowax 20 M (1 %) column, and 2 m × 4 mm glass OV-17 (1 %) column TLC analyses were performed on pre-coated sheets (0 2 cm) of silica gel G (E Merck) with detection by an anisaldehyde–HOAc–H_2SO_4 spray reagent, and CC was done on Baker 60–200 mesh silica gel All solvents were distilled prior to use, and spectral grade solvents were used for all spectroscopic measurements An FID instrument was used for GC analyses The analytical columns employed were a 13 m × 2 mm and 3 m × 2 mm Carbowax 20 M (10%) on silanized 100–120 mesh Anakrom AB, and a 13 m × 2 mm Tween-80 (6%) on silanized 80–100 mesh Anakrom AB, all in silanized Al tubing Prep GC was performed on a thermal conductivity instrument using a 8 m × 6 mm Carbowax 20 M (10%) on silanized 60–80 mesh chromosorb P and 5 m × 4 mm Tween-80 (6%) on silanized 80–100 mesh Anakrom AB Al columns GC integration data were obtained by calculating relative peak areas using the 'cut and weigh' method

A arbuscula arbuscula was collected near Paradise Valley, Nevada, in March, 1972, and on July 13, 1978 The University of Utah Herbarium contains pressed samples of the materials used in this study

Preliminary analysis A small amount of freshly picked plant material was ground to a fine mulch in an Osterizer and extracted with pentane in a glass Soxhlet for 2–4 days The soln was carefully concd on a vacuum rotary evaporator at room temp and the extract subjected to closed system vacuum bulb-to-bulb distillation at 100° The volatile oil was then analysed by GC

Large scale extraction Leaves and flower heads were ground and continuously extracted with pentane for 5 days in a large glass Soxhlet The extract was carefully concd *in vacuo*, and vacuum bulb-to-bulb distilled once (60°, 0 002 mm Hg) The remaining green wax was short-path distilled under red pres (0 40 mm Hg, 27–36°) The resulting oils (0 77% dry wt) were eluted through a 4 cm × 85 cm silica gel column with EtOAc–petrol hexanes (1 4) Each of the 15 ml fractions was analysed for the desired component by GC, however, it was found that decomposition was taking place on the column

A small sample of the oil was eluted through a silica gel plug in a Pasteur pipette with EtOAc–petrol (1 4) Rapid elution resulted in no noticeable change in the composition of the oils, as evidenced by GC analysis However, slowly eluted (0 5 hr) oils showed a distinct decrease in the relative peak area associated with the desired component (50%)

Terelactone (**16**) was isolated as a colorless oil by prep GC on the 8 m Carbowax 20 M column IR (neat) ν_{max} cm^{-1} 3060, 2970, 1745, 1600, 1465, 1385, 1370, 1280, 1200, 1135, 1070, 970, 950, 900, 890, 830 and 705, ^{1}H NMR ($CDCl_3$, 90 MHz) δ1 47(6H, *s*), 5 93(1H, *d*, *J* = 6 Hz), and 7 35 (1H, *d*, *J* = 6 Hz), ^{13}C NMR ($CDCl_3$) δ25 1, 25 1, 86 5, 119 4, 161 5, 172 3, MS (EI) *m/z* (rel int) 97 (100), 69 (60), 43 (35), 112 (14), 41 (12), 59 (8), 71 (8), 67 (7), 98 (7), 54 (7), MS (CI, isobutane) *m/z* (rel int) 113 (100%) $[M+1]^+$, 225 (65), 114 (30), 226 (9), 115 (4)

Crude plant oils from previous extractions were eluted through a silica gel column with EtOAc–petrol (1 4) Fractions containing the spot of R_f 0 33 were combined and concd *in vacuo* to yield a yellowish oil This material was further purified by MPLC on silica gel with the above solvent to yield a colorless oil

Arbusculone (**21**) was isolated as a clear oil via prep GC on the 8 m Carbowax 20 M column $[\alpha]_D$ −48 1° (*c* 0 64, $CHCl_3$), IR (neat) ν_{max} cm^{-1} 3065, 2980, 2910, 2850, 1710, 1635, 1410, 1370, 1355, 1238, 1185, 1130, 1100, 1065, 1020, 1000, 925, 890, 870 and 740, ^{1}H NMR ($CDCl_3$, 90 MHz) δ1 39 (3H, *s*), 1 47–2 31 (4H, *m*) 2 22 (3H, *s*), 4 34 (1H, *dd*, *J* = 6 0 and 8 0 Hz), 5 03 (1H, *dd*, *J* = 10 5 and 1 5 Hz), 5 17 (1H, *dd*, *J* = 17 7 and 1 5 Hz), and 5 83 (1H, *dd*, *J* = 17 7 and 10 5 Hz), ^{13}C NMR ($CDCl_3$) δ26 1 (*q*), 26 6 (*q*), 28 8 (*t*), 36 7 (*t*), 83 7 (*d*), 85 0 (*s*), 112 2 (*t*), 142 9 (*d*) and 210 7 (*s*), MS (EI) *m/z* (rel int) 111 (100%), 93 (73), 43 (59), 55 (56), 81 (32), 41 (27), 67 (24), 69 (21), 77 (20), 91 (19), 139 (4), 127 (3) and 154 (1), MS (CI, isobutane) *m/z* (rel int) 155 (100%) $[M+1]^+$, 137 (43), 156 (26), 111 (13), 139 (5)

Isolyratol (**26**) was isolated 98% pure as a colorless oil by prep GC on the 5 m Tween-80 column $[\alpha]_D$ +9 4° (*c* 4 24, $CHCl_3$), IR (neat) ν_{max} cm^{-1} 3420, 3060, 2960, 2910, 1640, 1445, 1435, 1375, 1290, 1210, 1010 and 900 cm^{-1}, ^{1}H NMR ($CDCl_3$, 90 MHz) δ1 75 (6H, *s*), 1 94 (1H, *s*), 2 89 (1H, *dd*, *J* = 8 1 and 8 7 Hz), 4 12 (1H, *d*, *J* = 8 1 Hz), 5 02 (6H, *m*), and 5 95 (1H, *m*), ^{13}C NMR ($CDCl_3$) δ17 7 (*q*), 20 9 (*q*), 56 3 (*d*), 76 1 (*d*), 113 2 (*t*), 113 2 (*t*), 117 7 (*t*), 137 0 (*d*) and 144 9 (*s*), MS (EI) *m/z* (rel int) 82 (100%), 67 (91), 71 (79), 41 (77), 43 (49), 39 (47), 79 (33), 53 (22), 81 (19), 84 (13), and 152 (2)

Reaction of **21** *with methylmagnesium iodide* To 37 mg (0 24 mmol) of ketone **21** and 8 ml of dry Et_2O was added in a dropwise manner to the soln via syringe freshly prepared methylmagnesium iodide [41] in Et_2O (0 4 ml, 1 04 mmol) The mixture was stirred at room temp for 20 hr and decomposed with 8 ml of 20% aq NH_4Cl soln The Et_2O layer was decanted from the aq layer and the latter extracted with Et_2O (3 × 5 ml) The combined organic phases were washed with H_2O (10 ml), dried ($MgSO_4$) and concd *in vacuo* to yield 32 6 mg (0 19 mmol) of a clear oil (80%) GC analysis showed the presence of two peaks with R_t 10 3 (4 8%) and 14 1 (95 2%) min on the 13 m Tween-80 column at 130° The second peak was isolated by prep GC on the 5 m Tween-80 column as a colorless oil $[\alpha]_D$ +5 7° (*c* 1 37, CCl_4), IR (neat) ν_{max} cm^{-1} 3390, 3060, 2950, 2850, 1635, 1406, 1370, 1240, 1175, 1130, 1100, 1055, 1030, 995, 925, 900 and 890, ^{1}H NMR ($CDCl_3$, 60 MHz) δ1 13 (3H, *s*), 1 23 (3H, *s*), 2 02 (5H, *m*), 3 81 (1H, *m*), 5 10 (2H, *m*), 5 93 (1H, *dd*, *J* = 17 8 and 8 4 Hz)

Epimerization of **21** To a soln of 0 05 g of Na in 2 5 ml of MeOH was added 4 mg of ketone and the mixture stirred at room temp for 21 hr The contents were then diluted with 2 ml H_2O, extracted with pentane (4 × 1 ml) and the combined pentane layers dried ($MgSO_4$) Concn *in vacuo* followed by GC analysis (167 m Carbowax 20 M capillary column, 128°) indicated the presence of two major components in a 1 3 1 0 ratio with R_ts of 14 5 (starting material) and 15 4 min, respectively

Oxidation of **22** *with* m-*chloroperbenzoic acid* To a soln of 1 g (6 5 mmol) of linalool (Aldrich) and 7 ml of CH_2Cl_2 was added 1 3 g (7 6 mmol) of *m*-chloroperbenzoic acid (Aldrich) dissolved in 2 ml of CH_2Cl_2, and the soln stirred at 0° for 1 hr before warming to room temp for an additional 24 hr The reaction mixture was filtered, washed with satd $NaHSO_3$ (2 × 10 ml) and satd $NaHCO_3$ solns (2 × 10 ml) and dried ($MgSO_4$) Concn *in vacuo* yielded 1 g (6 0 mmol, 92%) of a slightly yellowish oil shown to be a four component mixture by GC with R_ts of 14 4 (45%), 15 7 (45%), 35 7 (4 6%) and 37 3 (5 4%) min on the 13 m Tween-80 column at 133°

Trans-linalyl oxide (**23a**) was isolated as a colorless oil by prep GC (R_t 14 4 min above) on the 5 m Tween-80 column IR (neat) ν_{max} cm^{-1} 3420, 3060, 2960, 2850, 1635, 1460, 1370, 1240, 1170, 1135, 1100, 1055, 1030, 995, 925, 900 and 890, ^{1}H NMR ($CDCl_3$, 60 MHz): δ1 13 (3H, *s*), 1 23 (3H, *s*), 1 32 (3H, *s*), 2.02 (5H, *m*), 3 81 (1H, *m*), 5 10 (2H, *m*), and 5 93 (1H, *dd*, *J* = 17 8 and 8 4 Hz)

Cis-linalyl oxide (**23b**) was isolated by prep GC (R_t 15 7 min above) on the 5 m Tween-80 column as a colorless oil IR (neat) ν_{max} cm^{-1} 3420, 3060, 2960, 2855, 1635, 1460, 1370, 1170, 1100,

Table 1

Spectrum	Eu-opt (M)	Non-equivalence	Separation (Hz)
1 (90 MHz)	0 028	$-C\underline{H}=CH_2$	15
2 (90 MHz)	0 053	$-C\underline{H}=CH_2$	28
3 (90 MHz)	0 078	$-C\underline{H}=CH_2$	44
		$-CH=C\underline{H}H$	6
4 (90 MHz)	0 105	$-C\underline{H}=CH_2$	63
		$-CH=C\underline{H}H$	4 5
5 (100 MHz)	0 105	$-C\underline{H}=CH_2$	48 4
		$-CH=C\underline{H}H$	8 6

1060, 1035, 995, 920, 890, and 845, ^{1}H NMR ($CDCl_3$, 60 MHz) δ1 12 (3H, *s*), 1 20 (3H, *s*), 1 28 (3H, *s*), 2 07 (5H, *m*), 3 84 (1H, *m*), 5 10 (2H, *m*), 6 30 (1H, *dd*, J = 17 8 and 8 4 Hz)

Optical purity determination of authentic (+)-(2S,5S)-trans-*linalyl oxide* (**23a**) The optically active shift reagent $(C_{12}H_{14}F_3O_2)_3Eu$ (Ventron), was added to a 5 mm NMR tube containing a soln of 14 mg of alcohol **23a**, $[\alpha]_D^{22}$ +4 5° (*c* 2 9, CCl_4), and 0 4 ml of CCl_4 ^{1}H NMR spectra were recorded with each incremental addition of the shift reagent, the results are shown in Table 1

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