Computation. The two-way analyses of variance were conducted using a multiple regression program from Utah State University's Statpac on a Burroughs System 6900 computer. The sedimentation coefficients were calculated from a program run on an IBM 360 computer.

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VOLATILE COMPONENTS OF CALIFORNIA LIVE OAK, *QUERCUS AGRIFOLIA*

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Key Word Index—*Quercus agrifolia*; Fagaceae; California live oak; volatiles.

Abstract—The essential oil isolated from *Quercus agrifolia* leaves (*ca* 0.02% wt) was investigated using GC, GC/MS and IR. The most abundant components were *E*-hex-2-enal, *Z*-hex-3-en-1-ol, *Z*-hex-3-en-1-yl acetate and nonanal, respectively, which together comprise 51% of the oil. Of the 15 compounds identified 10 contained a C_6 straight-chain carbon skeleton as part of their structures. Only traces of terpenes were present with linalool and α-terpineol the only terpenes identified with certainty.

INTRODUCTION

The California live oak, *Quercus agrifolia* is a perennial evergreen tree of the black oak group typical of coastal and central California. This investigation of the volatile components present in the leaves of live oak was part of a long-range study in the food-chain relationships of browsing ruminants with respect to the damage they do to industrially important browse species. Although the many different oak species growing in California exhibit a wide range of palatability for browsing deer, the members of the black oak group are generally highly palatable species [1]. Critical observation of deer, both in the field and under penned conditions at the Hopland Field Station of the University of California, has shown that they use olfaction to make their initial selection of forage. In this report we present the results of the first investigation of the volatile components present in the foliage of an oak species.

RESULTS AND DISCUSSION

The aroma of live oak leaves is quite mild. *Ca* 0.2 g of essential oil per kg of fresh leaves can be isolated from the leaves by conventional steam distillation and extraction techniques. Analysis of the essential oil by high resolution glass capillary GC indicated the presence of *ca* 105 volatile components, the majority of which were present in amounts too small to permit identification.

Table 1 lists the volatile components identified in live oak essential oil, the percent composition of the components in the oil and the basis for identification of each component. Identifications of components were based primarily on spectral data with further confirmation by GC retention indices. The mass and IR spectra for the compounds identified in the oil compared favorably with lit. spectra [2, 3] or with the spectra of known compounds measured under the same experimental conditions. The Kovats' indices, listed in Table 1, were measured in

Table 1. Volatile components of California live oak foliage oil

Component	% composition in oil	Identification: Spectra	Identification: Kovats' indices† CBW-20 M	Identification: Kovats' indices† SF96(50)
E-Hex-2-enal	24.0	MS, IR	1234	842
Hexyl acetate	0.2	MS	1305	992
Z-Hex-3-en-1-yl acetate	5.6	MS, IR	1327	990
Hexan-1-ol	2.3	MS, IR	1356	867
Undec-3-en-2-one*	0.7	MS	1359	—
E-Hex-3-en-1-ol	0.3	MS	1374	—
Z-Hex-3-en-1-ol	15.7	MS, IR	1387	852
Nonanal	5.6	MS	1400	1078
E-Hex-2-en-1-ol	0.3	MS, IR	1409	888
E-Hex-3-en-1-yl butyrate	1.0	MS	1467	1163
Linalool	1.2	MS, IR	1545	1087
α-Terpineol	1.1	MS	1692	1184
Hexanoic acid	0.9	MS, IR	1740	—
Methyl salicylate	1.3	MS, IR	1784	1180
Unknown alcohol	1.0	MS	1942	—
Unknown ketone	1.6	MS, IR	2026	—
Z-Hex-3-en-1-yl benzoate	0.2	MS	2119	1550
Hexadecan-2-one*	0.2	MS, IR	2130	—
Eugenol	0.7	MS, IR	2141	1359
Sesquiterpene alcohol	3.6	MS	2158	—
Torreyol*	0.2	MS	2164	—
Sesquiterpene alcohol	0.2	MS, IR	2200	—

*Components tentatively identified in essential oil.
†Temperature programmed runs, 70° to 190° at 1°/min.

programmed runs and compared well with indices for known compounds determined in the same manner.

The compounds present in largest amount in the essential oil were *E*-hex-2-enal, *Z*-hex-3-en-1-ol, *Z*-hex-3-en-1-yl acetate and nonanal, respectively, which together comprise 51% of the oil. Of the compounds identified with certainty there are five esters, six alcohols, two aldehydes, two phenols (one containing an ester group) and one acid. It is interesting to note that 10 of these compounds possess a C_6 straight-chain carbon skeleton as part of their structures. The two phenols identified were methyl salicylate and eugenol, each present in *ca* 1% in the oil. Only small amounts of terpenes were found in the essential oil. Linalool and α-terpineol were identified, each present in *ca* 1% concentration, and spectral evidence was obtained for the presence of three sesquiterpene alcohols. These sesquiterpene alcohols appear to be cadinols, one of which was tentatively identified as torreyol by comparison of the mass spectrum with that in the lit. [4]. Spectral evidence was also obtained for the presence of three ketones. Two of them were tentatively identified as undec-3-en-2-one and hexadecan-2-one but, due to the lack of known reference compounds, positive identification was not possible for any of these ketones.

The very low amounts of volatile components, present in the highly palatable live oak foliage, and the almost complete lack of the strongly inhibitory [5] monoterpene alcohols is consistent with the concept that the level of inhibitory compounds present is related to the palatability of the range forest species to browsing ruminants [1]. An investigation of the volatile components present in oak species from each of the other two main oak groups, the white oak group and the intermediate oak group, is in progress with the hope that the data can be applied to a chemotaxonomic study of oak hybrid species growing in the arboretum at Davis.

EXPERIMENTAL

Isolation of essential oil. Mature foliage (*ca* 2.5 kg) was collected from a 100+ year old live oak tree growing on the campus of the University of California, Davis. The essential oil (*ca* 0.02% yield) was isolated from the leaves by steam distillation and extraction methods previously described [6].

GC. Analytical separations were made on a 59 m × 0.25 mm i.d. glass capillary column coated with Carbowax 20 M or a 127 m × 0.75 mm i.d. open tubular stainless steel column coated with SF-96(50) plus Igepal 880 (5% w/w) using FID. The oven temp. program was 5 min isothermal at 20° then programming at 1°/min to 160° for the glass capillary column and programmed from 70° to 190° at 1°/min for the SF-96 (50) stainless steel column. Injector and detector temps., 250°; carrier gas, He; split ratio, 30:1 for the glass capillary column. Kovats' indices were determined, both isothermally, at 70°, 130° and 190° and by the programmed runs described above on the CB 20 M and SF-96(50) columns.

Individual components were isolated from the essential oil by prep. GC using a 305 cm × 4 mm i.d. glass column packed with 5% Carbowax 20 M or 5% SE-30 using FID and a 15:1 effluent splitter. Column temp. programs were as described above. Fractions were collected from the GC exit port in 25 cm thin-walled glass capillaries cooled with solid CO_2.

GC/MS. A quadrupole instrument interfaced to a data system was used. EIMS, 70 eV ionization potential. The glass capillary

Carbowax 20 M column was used with the same GC conditions as described above.

IR. Obtained on thin films on ultra-micro demountable NaCl plates in a spectrometer fitted with a beam condenser.

Quantitative analysis. The percentage composition of components in the essential oil (Table 1) was based on the area percentage of each component on the GC trace measured by electronic integration.

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A STRUCTURE OF FAURINONE, A SESQUITERPENE KETONE ISOLATED FROM *VALERIANA OFFICINALIS**

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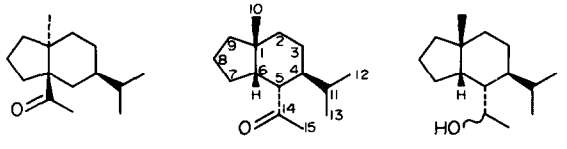
Key Word Index—*Valeriana officinalis*; Valerianaceae; sesquiterpenoid; faurinone; IR; ^{1}H NMR; ^{13}C NMR; mass spectrometry.

Abstract—A sesquiterpenoid, $C_{15}H_{26}O$, was isolated from *Valeriana officinalis* of which the spectral data (IR, NMR and mass spectra) were in agreement with those of faurinone. Based on ^{13}C NMR, and ^{13}C and ^{1}H NMR shift and decoupling experiments a new structure for faurinone is proposed.

From the sesquiterpene part of the essential oil of *Valeriana officinalis* L. s. l., we isolated, by prep. GC and TLC a ketone, $C_{15}H_{26}O$, of which the spectral characteristics, IR, NMR and mass spectra, were identical with those of faurinone (**1**), first reported by Hikino *et al.* [1]. A ^{13}C NMR spectrum of this compound revealed the presence of only one quaternary carbon atom, which was not in accordance with the proposed structure **1** [2].

Based on extensive ^{1}H and ^{13}C NMR shift and decoupling experiments, we propose structure **2** for faurinone. Addition of the shift reagent Eu(fod)$_3$ to a solution of faurinone results in the separation of the NMR signals of the methyl group of the acetyl group, H-5 and H-4, all originally positioned around δ 2.2. The relative shifts of these protons are: H-5, 119 and H-4, 90, based on 100 for the methyl of the acetyl group. The H-5 is a double doublet, (J = 10.4 and 4.8 Hz) and is coupled to H-4 (J = 10.4 Hz), which is a double triplet (J = 10.4 and 3.8 Hz). The second proton to which H-5 is coupled is H-6 (J = 4.8 Hz). Correlation with the ^{13}C NMR spectrum by selective decoupling experiments showed that H-4–H-6 are all doublets and, thus, all CH-groups. Another proton showing a large relative shift (97) is the CH of the isopropyl group. The relative shift of one of the methyl groups of the isopropyl group is 66, compared to a relative shift of 24 for the second methyl group of the isopropyl group.

This information together with the results of the selective ^{13}C NMR decoupling experiments and other ^{1}H NMR decoupling experiments with different Eu(fod)$_3$ concentrations leads us to structure **2** for faurinone, the configuration with an equatorial acetyl and an equatorial isopropyl group. Hikino *et al.* [2] based the position of the



2 **3**

*Part of this study was presented at the 12th International Workshop on Essential Oils, Marburg, West Germany, 1981, as a poster.