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NEW ANTIPODAL SESQUITERPENE ALCOHOLS FROM VETIVER OIL

P. S. KALSI, G. S. ARORA and R. S. GHULATI
Department of Chemistry, Punjab Agricultural University, Ludhiana, India

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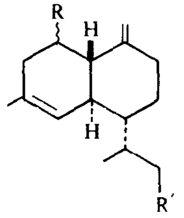
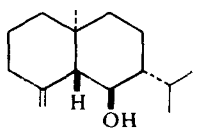
Key Word Index—*Vetiveria zizanioides*; Gramineae; antipodal sesquiterpenes; cadinane; eudesmane.

INTRODUCTION

North Indian vetiver oil from (*Vetiveria zizanioides*) is one of the most complex essential oils and is a rich source of both cadinane and eudesmane sesquiterpenes like khusinol **1**, khusol **2** and laevo-junenol **3** belonging to the rare antipodal types [1–4]. In recent years continued work in our laboratories to determine the composition of this oil has led to the isolation of more antipodal sesquiterpenes [5, 6] related to khusinol which is the major component of this oil. These are epikhusinol **4** and isokhusinol oxide **6**. The present paper reports the isolation and characterization of three more antipodal sesquiterpenes from vetiver oil.



1 R = β-OH; R′ = H
2 R = H; R′ = OH
4 R = α-OH; R′ = H



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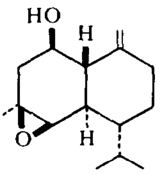

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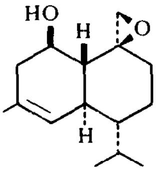

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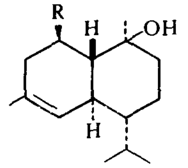
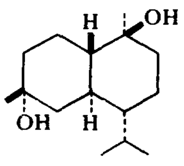
RESULTS

Vetiver oil has been found in our laboratory to increase root length in the hypocotyl cuttings of mung beans. This prompted us to identify hitherto unknown constituents of this oil for biological testing as plant hormones, which could reflect on the biogenesis of some of the components of this essential oil [7]. Of further biogenetic significance is the fact that the samples of North Indian vetiver oil obtained during the past several years differed in their khusinol content as revealed by GLC studies. From the oil with a low content of khusinol, it has been possible to isolate khusinol oxides **5** and **6** and epikhusinol **4** as the minor constituents.

Further processing of the alcoholic fraction of the oil has now led to the isolation of (+)-α-cadinol (**7**), cadina-4α,10β-diol (**8**) and khusinodiol (**9**). In these compounds the β-orientation of the OH group at C-10 seems to have a biogenetic relationship with khusinoloxide (**6**) in which the epoxy group is β-oriented [8]. The presence of epoxy sesquiterpenes and their biogenetic transformation to other related constituents has been well documented [9].



7 R = H
9 R = —OH



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The isolation of enantiomers of **7** and **8** from natural sources has been reported. Although previous workers suspected the presence of more cadinenic antipodal terpenoids in vetiver oil [10], this is the first report of the isolation and characterization of (+)-α-cadinol (**7**) and cadina-4α,10β-diol (**8**) from vetiver oil and of khusinodiol (**9**) from this oil or other sources.

EXPERIMENTAL

Mps are uncorr. NMR spectra were measured in $CDCl_3$ with TMS as internal standard. The yields of compounds reported here are from 4 kg oil.

Khusinodiol (**9**). Mp and mmp identical (129°) with an authentic sample [11]. Isolated (0.25 g) by extensive chromatography of the tail fractions of the oil (20 g) freed from the major sesquiterpenes following the described procedures [5, 12].

(+)-*α-Cadinol* (**7**) *and cadina*-4α,10β-*diol*(**8**). Fractions rich in (+)-α-cadinol and cadina-4α,10β-diol and other components could be easily freed from khusinodiol and other compounds by the Jones' chromic acid oxidation of the mixture under mild conditions followed by chromatography. This afforded, among other products, a known keto alcohol (mp 99°, UV absorption λ_{max} 238 nm, ε 9000) obtained earlier [11] from the oxidation of khusinodiol. After the elimination of khusinodiol and other oxidizable components, the mixture of alcohols was subjected to chromatography over Si gel. Eluting sequentially with *n*-hexane, C_6H_6 and Et_2O. C_6H_6 eluted 120 mg of an essentially pure alcohol (+)-α-cadinol which was purified by crystallization, mp 75°, $[\alpha]_D^{30}$ + 49° (lit. [10] $[\alpha]_D$ + 45°, mp 74–75°) IR ν_{max}^{Nujol} cm^{-1}: 3335 (OH), 815 (—CH=C). NMR: δ 0.77 and 0.89 (3H, each *d*, *J* = 7 Hz, Me_2CH—), 1.12 (3H, *s*, Me), 1.80 (3H, *s*, $W_{\frac{1}{2}}$ = 5 Hz, Me), 5.49 (1H, *s*, $W_{\frac{1}{2}}$ = 6 Hz, —C<u>H</u>=C), 1.70 (1H, OH). The ether fraction contained cadina-4α,10β-diol and other more polar components. This on further chromatographic separation afforded the former (110 mg) in a pure form, mp 117°, $[\alpha]_D^{32}$ + 60° (lit. [1] $[\alpha]_D$ 65°, mp 118–119°). IR ν_{max}^{Nujol} cm^{-1}: 3400, (OH) NMR: δ 0.75 and 0.87 (3H, each *d*, $J = 7$ Hz, Me_2CH—), 1.02 and 1.21 (6H, *s*, 2 × Me).

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GUADALUPOL AND EPIGUADALUPOL, REARRANGED SESQUITERPENE ALCOHOLS FROM *LAURENCIA SNYDERIAE* VAR. *GUADALUPENSIS*

Bruce M. Howard* and William Fenical
Institute of Marine Resources, Scripps Institution of Oceanography, La Jolla, CA 92093, U.S.A.

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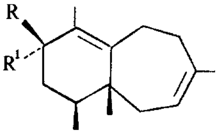
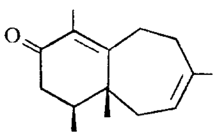
Key Word Index—*Laurencia synderiae* var. *guadalupensis*; Rhodomelaceae; marine natural products; chemistry; perforenone; sesquiterpene alcohols.

Examinations of the natural products chemistry of the marine alga *Laurencia snyderiae* Dawson (Rhodomelaceae, Rhodophyta) from various habitats have resulted in the isolation of the brominated sesquiterpenoid β-snyderol [1] from the La Jolla, California population, and the unique diterpenoid neocincinndiol hydroperoxide [2] from the Santa Catalina Island, California population. Investigation of the lipid components of *Laurencia snyderiae* var. *guadalupensis*, collected from Isla Guadalupe, Mexico, has now resulted in the isolation of two new epimeric sesquiterpene alcohols, guadalupol (**1**) and epiguadalupol (**2**), the structures of which are reported here.



1 R′ = OH; R = H
2 R′ = H; R = OH
3 R′ = OAc; R = H
4 R′ = H; R = OAc



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Open column silica gel chromatography of the chloroform–methanol (1:1) extract of the fresh alga gave, upon benzene elution, fractions which contained a mixture of **1** and **2** as oils in equal amounts. Both alcohols exhibited prominent $M^+ - H_2O$ fragments at *m/e* 202 for $C_{15}H_{22}$ in their mass spectra, and hydroxyl absorptions (3500 cm^{-1}) in their IR spectra. Treatment of **1** and **2** with acetic anhydride–pyridine gave the acetates **3** and **4** which suggested these alcohols to be secondary. The ^{1}H NMR spectrum of **1** illustrated a vinyl proton (δ 5.15, *bm*), an α-hydroxy methine proton (δ 3.61, *s*), a methyl doublet (δ 0.86, *d*, $J = 7$ Hz) and six protons between 1.70 and 2.50. The epimeric alcohol **2** provided a ^{1}H NMR spectrum which also exhibited a vinyl proton (δ 5.20, *bm*), a high field methyl (δ 0.75, *s*), a methyl doublet (δ 0.86, *d*, $J = 7$ Hz) and six protons between 1.70 and 2.50. Jones' oxidation of **1** and **2** at +5° yielded the same α,β-unsaturated ketone, **5**, (IR, $\gamma_{C=O}$ 1670 cm^{-1}) which

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* Present address: Department of Chemistry, San Francisco State University, 1600 Holloway Ave, San Francisco, CA 94132, U.S.A.