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CAROTA-1,4-β-OXIDE, A SESQUITERPENE FROM *DAUCUS CAROTA*

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Key Word Index—*Daucus carota*; plant growth regulators; sesquiterpene; caryophylla-2,6-β-oxide; carota-1,4β-oxide

Abstract—A new sesquiterpene ether, carota-1,4-β-oxide, has been isolated from the essential oil of the seeds of carrot (*Daucus carota*). The structure and stereochemistry of this compound have been established by spectroscopic and chemical methods by its synthesis from carotol.

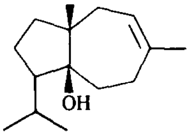
INTRODUCTION

A previous study of the essential oil from the carrot seeds, *Daucus carota* L. revealed the presence of several terpenoids like α-pinene, β-pinene, limonene, bergamotene, caryophyllene, γ-bisaboline, geranyl acetate, geraniol, carotol (**1**) and daucol (**2**) [1–8]. In our continued attempt to isolate the various terpenoids from different essential oils [4–8] and to test them as plant growth regulators we have isolated a new hitherto unknown sesquiterpene ether (**3**) from the hydrocarbon fraction of the essential oil of carrot seeds. The work was undertaken since the carrot plant is not attacked by the insects in the field [9] due to the presence of antifeedants. The present paper reports the isolation and identification of this new sesquiterpene carota-1, 4-β-oxide and its synthesis from carotol (**1**).

RESULTS AND DISCUSSION

The hexane fraction of the essential oil from carrot seeds of the northern part (Punjab State) of India afforded, after extensive column chromatography, a pure yellow liquid (**3**), $C_{15}H_{26}O$, which on mass spectral analysis at 70 eV showed *m/z* 222.3658 $[M]^+$(calculated for $C_{15}H_{26}O$; 222.3654). The IR bands at 1480, 1460, 1450, 1080 and 1090 cm^{-1} showed the absence of any other oxygenated functional group except an ether linkage. This finding was supported by NMR spectral signals at δ0.81 (3H, *d*, $J = 6.15$ Hz), 1.05 (3H, *d*, $J = 6.15$ Hz), 1.0 (3H, *s*) and 1.32 (3H, *s*). The comparison of this ^{1}H NMR spectrum with those of the major components of the oil, viz. carotol (**1**) and daucol (**2**), hints that this new compound might be related to them. Consequently, the C-skeleton of **3** was confirmed by its dehydrogenation studies over Pd/C, where it yielded mainly daucalene (**4**), a component also obtained from carotol and daucol under similar reaction conditions [**10**] and was identified as the TNB complex by comparison of IR, mp and mmp. This established the carbon skeleton of compound **3** as in carotol or daucol.

Biogenetically, it appears that either carotol or daucol is the immediate precursor of the new compound **3**. It looks probable that **3** is either produced by the removal of hydroxyl from daucol, or by electrophilic attack of an enzyme on the double bond with concomitant neutralization by the hydroxyl group, of the carbonium ion formed at C-3. A survey of the literature revealed that caryophylla-2,6-β-oxide, a natural product from *Lippia citriodora* [11] has been synthesized from 2-hydroxy-



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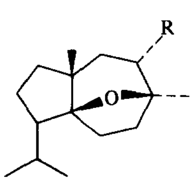
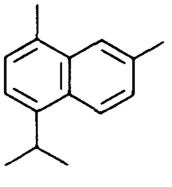


2 R = OH
3 R = H



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caryophyllene by an oxymercuration-demercuration (OM-DM) reaction [11]. With this view in mind carotol was subjected to the OM-DM reaction when compound **3** (IR, NMR)was obtained in quantitative yields. This reaction not only confirmed its structure but also established the stereochemistry as depicted in structure **3**.

EXPERIMENTAL

The essential oil was extracted from the powdered carrot seeds by steam distillation. The NMR shifts are in δ values and TMS was used as the internal standard. THF was distilled over Na–benzophenone just prior to use.

Isolation of compound **3**. The essential oil (66 g) obtained by steam distillation of powdered carrot seeds was subjected to CC over silica gel (1 kg). The hexane fraction (5 l) was evapd to yield a hydrocarbon fraction (4 g). The hydrocarbon fraction (1 g) was rechromatographed over silica gel–$AgNO_3$ 10% (100 g). The elution of the column with hexane–Et_2O (4:1) (10 × 50 ml) yielded a thick yellow liquid (60 mg, TLC pure). [Analysed for $C_{15}H_{26}O$ C, 81.06; H, 11.60; requires C, 81.02; H, 11.79%]. IR ν_{max}^{film} cm^{-1}: 1480, 1460, 1450, 1080, 1090.

NMR ($CDCl_3$): δ0.81 (3H, *d*, $J = 6.15$ Hz), 1.05 (3H, *d*, $J = 6.15$ Hz), 1.0 (3H, *s*) and 1.32 (3H, *s*).

Dehydrogenation of compound **3** *with* Pd/C. Sesquiterpene **3** (30 mg) was mixed with an equal quantity of Pd/C (30%). The mixture was heated at 300° for 10 hr in an atmosphere of CO_2. The product was filtered through a bed of alumina. Elution of the column with petrol gave a naphthalenic hydrocarbon identified a daucalene from the mp (88°) of its picrate. Both carotol and daucol on dehydrogenation under similar conditions gave the same naphthalenic hydrocarbon (mp, mmp of picrate 88°).

Oxymercuration-demercuration of carotol (**1**). To a 100 ml flask equipped with magnetic stirring bar, and reflux condenser was added 50 ml of dry THF under N_2. The flask was charged with 10 mmol of mercuric acetate (3.2 g) followed by carotol (10 mmol, 1.5 ml) dissolved in 5 ml of dry THF. The reaction mixture was stirred vigorously for 10 min at room temp. followed by the addition of 10 ml of 3 N NaOH and 10 ml of 3 N NaOH containing 0.5 N $NaBH_4$. The contents were stirred for 2 hr at room temp. The THF layer was sepd and the aq. layer extracted with Et_2O (3 × 25 ml). The combined THF–Et_2O layer was washed with brine and dried (Na_2SO_4). The evapn of the solvent at red. pres. afforded a thick mobile liquid which was chromatographed over silica gel to afford 1.2 ml of the pure liquid ether with C_6H_6 as the eluent. The compound had superimposable IR and NMR spectra over the naturally occurring ether (**3**).

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