Asian Journal of Chemistry; Vol. 28, No. 8 (2016), 1790-1792

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2016.19830

Chemical Transformations of Carotol Isolated from Carrot Seed Oil

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Received: 8 January 2016; *Accepted*: 16 March 2016; *Published online*: 30 April 2016; AJC-17892

Previous phytochemical studies on the essential oil of carrot seed revealed the presence of carotol as the major compound. In the present study the essential oil of carrot seed extracted by Dean and Stark apparatus was analyzed by gas chromatography-mass spectrometry. A total of 51 compounds were identified. Carotol, a sesquiterpenoid was found to be the major compound whereas daucol, daucene, β-cubenene and β-farnesene were the minor compounds present. Carotol (52 %) was isolated by column chromatography. Chemical reactions of carotol with N-bromosuccinimide, selenium dioxide/*t*-butyl hydrogen peroxide, phenol/sulfuric acid and *p*-toluene sulfonic acid were carried out and structures of these compounds were elucidated on the basis of FTIR, ^{1}H NMR and ^{13}C NMR spectroscopy.

Keywords: Carrot seed oil, Carotol, GC-MS, Daucol, Daucene.

INTRODUCTION

Essential oils of family Apiaceae have been widely used for their pharmacological activities such as antibacterial, anti-fungal, antiviral, antiparasitic, insecticidal and antiplasmodic [1,2]. Apiaceae is one of the best known families of flowering plants, which comprise 300-450 genus and 3000-3700 species producing biologically active essential oils [3]. Essential oils from Daucus genus comprises about 60 species of weedy plants, widely distributed and commonly cultivated for their fleshy edible roots which possessed antioxidant activity [4,5]. Carrot is herbaceous, biannual flowering plant and one of the popular root vegetables grown throughout the world with crisp texture when fresh. It is one of the ten most economically important vegetable crops in the world [6]. The essential oil of carrot seed extracted from the dried seeds of *Daucus carota* by hydrodistillation is yellowish brown liquid, possess woody, earthy sweet smell [7]. The essential oil of carrot seed is the source of sesquiterpenes *i.e.* carotol (38.8 %), β-caryophyllene (10.7 %), caryophyllene oxide (4.3 %) and daucol (2.0 %) [8]. The compounds of carrot seed essential oil and transformation reactions of carotol are reported.

EXPERIMENTAL

Analysis of carrot seed oil for the separation of compounds present in the essential oil was carried out using the GC-MS (QP2010 Plus, Shimadzu), equipped with an Rtx-5 MS capillary column (30.0 m × 0.20 mm i.d., 0.25 μm film thickness). MS parameters used were; ionization voltage (EI) 70 eV, peak width 2 s, mass range 40-600 amu and detector voltage 1.5 V. Peak identification was carried out by comparison of the mass spectra available on database of NIST08, WILEY8, Perfumery and Flavor and Fragrance libraries. FT-IR spectra were measured in $CHCl_3$ solution or nujol on a Perkin Elmer, Model RX-1 FT-IR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer. All spectra were recorded at room temperature, the solvent for each spectrum is given in parentheses. Chemical shifts are reported in ppm and are relative to TMS internally referenced to the residual solvent peak.

Extraction of essential oil: *D. carota* var. *sativus* seeds (PC-34) were obtained from Directorate of Seeds, Punjab Agricultural University, Ludhiana, India. Carrot seeds were crushed and essential oil was extracted by hydrodistillation method using Dean-Stark Apparatus. The seeds (500 g) were taken in 10 L round bottomed flask and 7.5 L of distilled water was added to it. The contents were thoroughly mixed and flask kept at room temperature overnight. The contents were refluxed for 15 h. The essential oil layer was collected in conical flask. The essential oil was partitioned thrice using diethyl ether (3 × 50 mL). The diethyl ether layer (upper layer) containing essential oil was stored over anhydrous sodium sulfate to remove traces of moisture present, if any. Evaporation of diethyl ether gave carrot seed essential oil (8 g). Essential oil of carrot seeds was collected from several batches after hydro distillation. The essential oil of carrot seed was yellowish brown liquid with strong and pleasant odour having refractive index and density of 1.45 and 0.987 g cm^{-3}, respectively. Thin layer chromatography of the carrot seed essential oil showed three

coloured spots having R_f values of 0.34 (purplish-black), 0.69 (dark purple) and 0.93 (pinkish-brown). The essential oil was soluble in organic solvents like acetone, benzene, methanol, dichloromethane and insoluble in water. The chemical composition of the essential oil was determined (Table-2) using gas chromatography-mass spectrometry (GC-MS).

Isolation of carotol from essential oil: The carrot seed essential oil (8 g) was chromatographed over silica gel (480 g). The column was eluted with solvents in order of increasing polarity (petroleum ether: dichloromethane) and carotol (**1**, 4.2 g) with boiling point 122 °C was collected as a fraction using petroleum ether:dichloromethane (20 %) as eluting solvents.

General procedure for reaction of carotol with N-bromosuccinimide: A solution of carotol (1 g) in acetone (10 mL) and N-bromosuccinimide (0.2 g), water (2 mL) were mixed and silica gel (60-120 mesh) (0.04 g) was added to it. The mixture was stirred at room temperature for 2 h. After the completion of reaction (TLC), the mixture was diluted with 50 mL of water and extracted with dichloromethane. The dichloromethane layer was concentrated and pure brown coloured product (**2**, 0.8 g) was obtained by column chromatography.

General procedure for reaction of carotol with selenium dioxide: Selenium dioxide (5.0 mg) was added to *t*-butyl hydrogen-peroxide (1.5 mL) and the mixture was stirred for 0.5 h. To this mixture a solution of carotol (2.0 g) in dichloromethane (25 mL) was added. The reaction mixture was stirred for 5 h at room temperature. The progress of reaction was monitored by TLC, after the completion of reaction, the mixture was diluted with cold water and extracted with dichloromethane. The pure greenish yellow coloured compound (**3**, 1.28 g) was isolated by column chromatography.

General procedure for reaction of carotol with phenol: To a solution of phenol (0.5 g) in diethyl ether (20 mL), carotol (1 g) and sulfuric acid (2 mL) were added. The mixture was stirred and heated on oil-bath for 8 h. The mixture was cooled and diluted with ether (100 mL) and successively washed with

TABLE-1
SPECTROSCOPIC DATA OF CAROTOL (**1**) AND ITS DERIVATIVES (**2-5**)

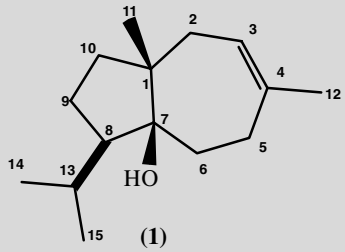
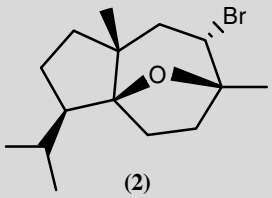
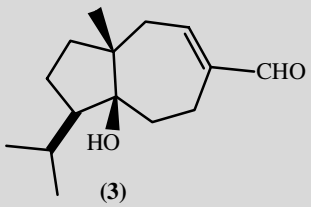
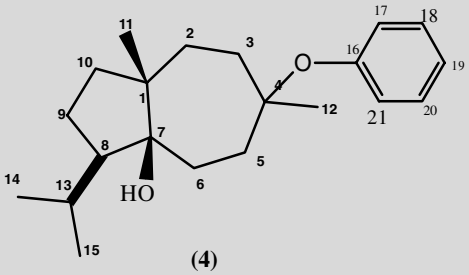
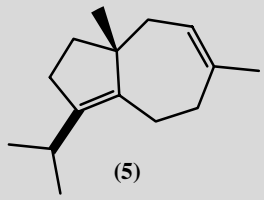
Compounds	IR (cm^{-1})	^{1}H NMR	^{13}C NMR
 **(1)**	3520, 2953, 2927, 1448, 1461 and 1374	0.93 (3H, d, J = 8.1, C_{14}), 0.99 (3H, d, J = 8.12, C_{15}), 1.03 (3H, s, C_{12}), 1.95 (1H, m, C_{13}), 5.3 (1H, m, C_3)	49.82 (C_1), 25.23 (C_2), 122.11 (C_3), 138.46 (C_4), 27.84 (C_5), 29.40 (C_6), 84.43 (C_7), 39.40 (C_8), 38.59 (C_9), 34.38 (C_{10}), 24.36 (C_{11}), 24.05 (C_{12}), 52.48 (C_{13}), 21.44 (C_{14}), 21.38 (C_{15})
 **(2)**	3298, 1652 and 1547	1.00 (3H, d, J = 8.12, C_{14}), 1.10 (3H, d, J = 8.12, C_{15}), 1.30 (3H, s, C_{12}), 1.90 (1H, m, C_{13}), 4.21 (1H, m, C_3)	44.35 (C_1), 44.68 (C_2), 56.94 (C_3), 85.90 (C_4), 32. 76 (C_5), 31.46 (C_6), 91.90 (C_7), 52.85 (C_8), 30.56 (C_9), 26.15 (C_{10}), 25.16 (C_{11}), 23.41 (C_{12}), 40.92 (C_{13}), 21.83 (C_{14}), 21.63 (C_{15})
 **(3)**	3508, 2943, 1682, 1647 and 1461	0.93 (3H, d, J = 8.12, C_{14}), 0.99 (3H, d, J = 8.12, C_{15}), 1.29 (3H, s, C_{12}), 1.88 (3H, m, C_{13}), 6.60 (1H, m, C_3).	49.08 (C_1), 26.98 (C_2), 145.73 (C_3), 153.48 (C_4), 27.58 (C_5), 27.61 (C_6), 84.55 (C_7), 39.64 (C_8), 38.91 (C_9), 33.81 (C_{10}), 24.02 (C_{11}), 194.06 (C_{12}), 51.28 (C_{13}), 21.33 (C_{14}), 21.26 (C_{15}),
 **(4)**	3608, 1219 and 1159	1.0 (3H, d, J = 8.12, C_{14}), 1.10 (3H, d, J = 8.12, C_{15}), 1.26 (3H, s, C_{12}), 4.21 (1H, m, CH), 7.5 (4H, s, $C_{16\text{-}21}$).	47.38 (C_1), 26.14 (C_2), 30.38 (C_3), 85.93 (C_4), 30.57 (C_5), 31.46 (C_6), 57.13 (C_7), 44.65 (C_8), 40.92 (C_9), 32.76 (C_{10}), 23.38 (C_{11}), 25.15 (C_{12}), 52.84 (C_{13}), 21.61 (C_{14}), 21.79 (C_{15}), 110.45 (C_{16}), 134.24 (C_{17} and C_{21}), 148.97 (C_{18} and C_{20}), 112.71 (C_{19})
 **(5)**	1673, 1453 and 1372	0.70 (3H, d, J = 8.12, C_{14}), 0.80 (3H, d, J = 8.12, C_{15}), 1.46 (3H, s, C_{12})	48.31 (C_1), 26.66 (C_2), 116.75 (C_3), 142.51 (C_4), 32.88 (C_5), 35.19 (C_6), 117.94 (C_7), 143.02 (C_8), 39.86 (C_9), 32.71 (C_{10}), 19.42 (C_{11}), 20.26 (C_{12}), 52.84 (C_{13}), 21.38 (C_{14}), 21.41 (C_{15})

TABLE-2
GC-MS DATA OF CARROT SEED ESSENTIAL OIL

S. No.	Name	Retention time (min)	Area (%)
1	α-Pinene	7.732	0.22
2	β-Pinene	9.354	0.76
3	Myrcene	9.971	0.36
4	Limonene	11.524	0.90
5	Phenylacetaldehyde	12.190	0.07
6	*trans*-Linalool oxide	14.170	0.09
7	Linalool	14.715	0.87
8	*trans*-Pinocarveol	16.420	0.18
9	*trans*-Verbenol	16.724	0.18
10	Non-(2E)-enal	17.426	0.11
11	3-Cyclohexen-1-ol	18.204	0.06
12	3-Cyclohexene-1-methanol	18.832	0.11
13	Myrtenol	19.105	0.19
14	Verbenone	19.672	0.10
15	*trans*-Carveol	20.132	0.14
16	Carvone	21.249	0.11
17	Bornyl acetate	23.149	0.08
18	α-Terpinyl acetate	25.926	0.22
19	Daucene	27.283	5.68
20	γ-Cadinene	27.466	1.46
21	α-*cis*-Bergamotene	28.714	0.18
22	(E)-Caryophyllene	28.878	1.22
23	α-*trans*-Bergamotene	29.579	1.82
24	β-Santalene	29.909	0.35
25	(E)-β-Farnesene	30.507	5.40
26	β-Cubebene	31.021	3.19
27	α-Curcumene	31.495	0.16
28	β-Elemene	32.154	3.23
29	β-Bisabolene	32.565	2.95
30	Sesquisabinene	33.138	0.67
31	α-Chamigren	33.312	0.27
32	Salvial-4(14)-en-1-one	33.522	0.17
33	Longifolenaldehyde	34.588	3.23
34	(*E*)-Farnesene epoxide	35.209	0.33
35	Caryophyllene oxide	35.442	0.09
36	Carotol	36.660	52.73
37	β-Caryophyllene-4,5α-oxide	36.996	0.38
38	Caryophylla-3(15),7(14)-dien-6-ol	37.233	0.86
39	Alloaromadendrenoxide-(1)	37.433	0.84
40	Daucol	37.763	5.10
41	Eudesm-4(14)-en-11-ol	38.632	0.96
42	2,6,10-trimethylundecan-(5E)-2,5,9-trien-4-one	38.802	0.24
43	α-Cedrane	38.981	0.59
44	α-Bisabolol	39.202	0.09
45	1-Heptatriacotanol	39.498	0.19
46	Juniper camphor	39.672	0.08
47	14-β-Pregna	40.075	0.08
48	Farnesol	40.567	0.08
49	Dihydrojasmone	42.156	0.29
50	Phytone	44.763	0.14
51	9-(*Z*)-9-octadecenoic acid	48.371	0.08

10 % aqueous sodium hydroxide (4 × 50 mL) and then with water until free of alkali. The mixture was dried over anhydrous sodium sulfate. The reaction product (**4**, 0.32 g) as a solid was purified by column chromatography on silica gel with petroleum ether as eluent having melting point 46 ºC.

General procedure for reaction of carotol with *p*-toluene sulfonic acid: Carotol (1 g) dissolved in benzene and *p*-toluene sulfonic acid (5 %) was added to it. The mixture was stirred for 2 h and the completion of the reaction was checked by thin layer chromatography. After the completion of the reaction benzene was evaporated and dichloromethane (50 mL) was added to it. The dichloromethane solution was washed three times with water. After the evaporation of solvent pure compound (**5**, 0.81 g) having melting point 108 °C was obtained. The spectroscopic data of carotol and its derivatives are given in Table-1.

RESULTS AND DISCUSSION

Carrot seed essential oil was yellowish brown liquid with strong, and pleasant odour having refractive index and density of 1.45 and 0.987 g cm^{-3}, respectively. The essential oil was soluble in organic solvents like acetone, benzene, methanol, dichloromethane and insoluble in water. The analysis of chemical composition of the essential oil was done byGC-MS. The retention time and percent area of compound present in essential oil of carrot seed are given in Table-2. The essential oil analysis by GC-MS showed the presence of sesquiterpene alcohols and hydrocarbons. A total of 51 compounds, amounting to 97.8 % of the total oil, were identified, the data showed the presence of carotol (**1**) as the major compound. Other minor compounds identified were daucol, daucene, (E)-β-farnesene, β-cubebene, longifolen-aldehyde, β-elimene, (E)-caryophyllene, β-bisabolene, *etc*. The data was in consonance with earlier reports of chemical composition of carrot seed essential oil [9,10].

Carotol was isolated by column chromatography. In continuation of our earlier work on derivatives of carotol [11] more transformation reactions are reported. Various chemical transformations were carried out on the double bond and alcoholic group of carotol. The derivatives of carotol (**1**) synthesized by reaction with N-bromisuccinimide, selenium dioxide, phenol and *p*-toluenesulphonic acid afforded 3-bromocarotol ether (**2**), carotol aldehyde (**3**), 4-phenoxy carotol (**4**) and daucene (**5**), respectively as products.

ACKNOWLEDGEMENTS

One of the authors (DK) is grateful to University Grant Commission (UGC) New Delhi, India for providing Rajiv Gandhi National Fellowship.

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