Asian Journal of Chemistry; Vol. 28, No. 5 (2016), 1004-1006

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2016.19567

Carotol: A Sesquiterpenoid Isolated from Carrot Seed Oil

K.K. CHAHAL*, P. KAUR, D. KATARIA and R. KAUR

Department of Chemistry, Punjab Agricultural University, Ludhiana-141 004, India

*Corresponding author: E-mail: drkkchahal@pau.edu

Received: 12 August 2015; *Accepted*: 9 October 2015; *Published online*: 30 January 2016; AJC-17734

Essential oil obtained from carrot (*Daucus carota*) seeds by hydrodistillation was analyzed by gas chromatography-mass spectrometry (GC-MS). A total of 51 compounds, accounting for 97.8 % of the total oil were identified. Carotol, a sesquiterpenoid was found to be the major compound present in the carrot seed essential oil while the other compounds were daucol, daucene, β-cubenene, β-farnesene, *etc*. Carotol was isolated from carrot seed essential oil by column chromatography which was chemically transformed into daucol, carotol ether, 4-chloro carotol and carotol amide. The structures of these compounds were elucidated on the basis of FTIR, ^{1}H NMR and ^{13}C NMR.

Keywords: *Daucus carota*, Seed oil, Sesquiterpenoid, Carotol, Daucol.

INTRODUCTION

Daucus, a major genus in the Umbelliferae family comprises of about 60 species, widely distributed and commonly cultivated for their fleshy edible roots [1]. Carrot (*Daucus carota*), a flowering plant of this family is usually orange in colour, although purple, red, black, white and yellow varieties also exist [2]. The genus name *Daucus* is derived from daukos, given by the Greeks to some members of the Umbelliferae family and the species name, *carota* originates from the word carotos meaning carrot [3]. Chemical composition [4-8] of carrot fruit essential oil obtained by hydrodistillation has been the subject of frequent research. The composition of carrot seed essential oil, isolation of sesquiterpenoid carotol (**1**) and its transformation products are reported.

EXPERIMENTAL

GC-MS: QP2010 plus, Shimadzu, Japan equipped with an RTX-5 MS capillary column (30.0 m × 0.20 mm, 0.25 μm film thickness). Oven was initially maintained at 50 °C for 2 min, raised to 180 °C at 3 °C/min, then to 280 °C at 10 °C/min. The interface temperature was 260 °C and the ionization mode was electron impact (70 eV). The mass selective detector was operated in the scan mode between 40 and 600 *m/z*. Data acquisition was started 3 min after injection. Peak identification was carried out by comparison of the mass spectra available on database of NIST08, WILEY8, Perfumery and Flavour and Fragrance libraries.

^{1}H NMR (400 MHz) and ^{13}C NMR (400 MHz): Bruker AC (in $CDCl_3$) using TMS as an internal reference. IR: Perkin Elmer, Model RX-1 FT-IR spectrophotometer.

Daucus carota var. *sativus* seeds (PC-34) were obtained from Directorate Seeds, Punjab Agricultural University, Ludhiana, India.

Extraction of essential oil: Carrot seeds were crushed and the powdered material was extracted by hydrodistillation 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 was kept at room temperature overnight. The contents were refluxed for 15 h using Dean-Stark apparatus. The essential oil layer containing little water was collected separately in conical flask. The essential oil was partitioned thrice using diethyl ether (3 × 50 mL). The diethyl ether layer (upper layer) containing oil was stored over anhydrous sodium sulfate to remove traces of moisture present. Evaporation of diethyl ether gave carrot seed essential oil (8 g). 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 oil was soluble in organic solvents like acetone, benzene, methanol, dichloromethane and insoluble in water. The analysis of the chemical composition of the essential oil was done by gas chromatography-mass spectrometry (GC-MS). The retention time and percent area of compound present in carrot seed essential oil are given in Table-1.

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 122.5 °C was collected as a fraction using petroleum ether:dichloromethane (20 %) as eluting solvents which was monitored by thin layer chromatography (TLC).

TABLE-1
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

General procedure for reaction of carotol with perbenzoic acid: A solution of carotol (1.5 g) in chloroform (10 mL) was treated with an excess of perbenzoic acid solution in chloroform. After keeping at room temperature for 24 h, the completion of reaction was checked by TLC. The reaction mixture was diluted with water washed with sodium thiosulfate and sodium bicarbonate solution, finally with water and then dried over sodium sulfate. Evaporation of solvent afforded a white crystalline compound (**2**, 1.3 g) which gave a single spot on TLC plate was identified as daucol (**2**) (m.p. 113 °C).

General procedure for reaction of carotol with mercuric acetate: Mercuric acetate (3.2 g) was added to a flask containing carotol (2.2 g) in 5 mL of dry tetrahydrofuran. The reaction mixture was stirred vigorously for 10 min at room temperature and 10 mL of 3 N sodium hydroxide and 10 mL of 3 N sodium borohydride was added. The contents were stirred for 2 h. The tetrahydrofuran and the aqueous layer were separated using diethyl ether (3 × 25 mL). The combined tetrahydrofuran and ether layer was washed with brine and dried over sodium sulfate. The evaporation of solvent afforded a white crystalline compound (**3**, 1.96 g) identified as carotol ether (**3**) (m.p. 127.5 °C).

General procedure for reaction of carotol with dry HCl gas: A slow stream of dry hydrochloric acid gas was bubbled through a solution of carotol (1.0 g) in diethyl ether (20 mL) at 0 °C till the solution was saturated. The reaction mixture was diluted with water and thoroughly extracted with ether (3 × 50 mL). The mixture was finally dried over sodium sulfate. Evaporation of the solvent yielded a brownish liquid (**4**, 0.86 g) identified as 4-chloro carotol (**4**) (b.p. 145 °C).

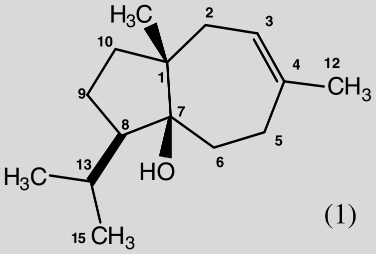
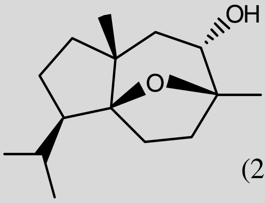
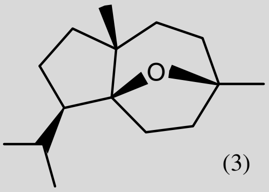
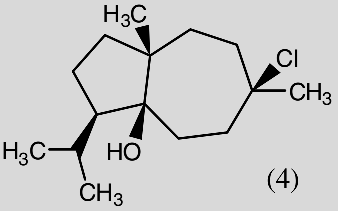
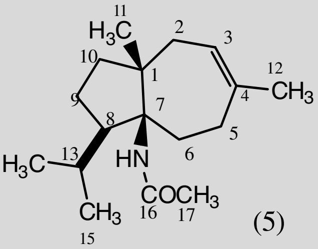
General procedure for reaction of carotol with acetonitrile: In a round bottom flask 6 mL each of glacial acetic acid and concentrated sulfuric acid was added, stirred for 5 min using magnetic stirrer. 1 g of carotol was added slowly followed by 20 mL of acetonitrile in the flask. The contents were stirred for 48 h and followed by work up of the reaction mixture. The mixture was poured onto ice and neutralized with 50 % sodium hydroxide solution. The aqueous layer was partitioned with ether and the combined ether extracts were washed with brine and dried over sodium sulfate. A yellowish brown sticky mass (**5**, 0.95 g) was obtained. It was identified as carotol amide (**5**) (m.p. 134.5 °C).

Structure of carotol (**1**) and its derivatives (**2-5**) were identified on the basis of IR, ^{1}H NMR and ^{13}C NMR spectral data (Table-2).

RESULTS AND DISCUSSION

Hydrodistillation of the crushed seeds of *Daucus carota* afforded the essential oil which was chromatographed over silica gel to isolate carotol. The essential oil analysis showed the presence of sesquiterpene alcohols and hydrocarbons which were identified by GC-MS using the NIST, WILEY MS library search [9]. GC-MS data of isolated carrot seed oil showed the presence of carotol (**1**) as the major compound. Other minor compounds were daucol (**2**), daucene, (E)-β-farnesene, β-cubebene, longifolenaldehyde, β-elemene, (E)-caryophyllene, β-bisabolene, *etc*. The data was in consonance with earlier reports [7,10-12].

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

Compounds	IR (cm^{-1})	^1H NMR (δ)	^{13}C NMR (δ)
 (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)	3305, 2950, 2931, 2872, 1470, 1151, 1053	0.81 (3H, d, *J* = 8.1, C_{14}), 1.05 (3H, d, *J* =8.12, C_{15}), 1.33 (3H, s, C_{12}), 2.15 (1H, m, C_{13}), 3.73 (1H, dd, C_3)	45.13 (C_1), 41.07 (C_2), 71.47 (C_3), 85.33 (C_4), 32.96 (C_5), 31.46 (C_6), 91.20 (C_7), 52.42 (C_8), 29.47 (C_9), 26.76 (C_{10}), 23.46 (C_{11}), 22.95 (C_{12}), 40.98 (C_{13}), 22.37 (C_{14}), 21.78 (C_{15})
 (3)	2951, 2870, 1480, 1460, 1450, 1080 and 1090	0.81 (3H, d, *J* = 6.12, C_{14}), 1.05 (1H, d, *J* = 6.12, C_{15}), 1.05 (3H, s, C_{12}), 1.26 (3H, s, C_{11}).	44.86 (C_1), 40.86 (C_2), 38.3 (C_3), 85.6 (C_4), 39.2 (C_5), 33.3 (C_6), 92.4 (C_7), 62.4 (C_8), 31.08 (C_9), 29.2 (C_{10}), 25.7 (*C_{11}), 23.5 (*C_{12}), 53.6 (C_{13}), 21.6 (*C_{14}) and 21.6 (*C_{15}).
 (4)	3306, 2951, 2870 and 823	0.85 (3H, d, *J* = 6.4 C_{14}), 0.99 (3H, s, C_{11}), 1.05 (3H, d, *J* =6.64, C_{15}) and 1.32 (3H, s, C_{12})	52.51 (C_1), 25.85 (C_2), 40.85 (C_3), 82.66 (C_4), 38.53 (C_5), 33.64 (C_6), 91.73 (C_7), 33.59 (C_8), 32.26 (C_9), 31.54 (C_{10}), 26.28 (*C_{11}), 25.85 (*C_{12}), 23.63 (C_{13}), 21.64 (*C_{14}) and 21.82 (*C_{15}).
 (5)	3298, 2965, 1652, 1281	1.01 (3H, d, *J* = 6.12, C_{15}), 1.04 (3H, d, *J* = 6.12, C_{14}), 1.83 (1H, m, C_{13}), 1.70 (3H, s, C_{12}), 5.2 (1H, s, C_3).	45.8 (C_1), 36.2 (C_2), 122.3 (C_3), 138.9 (C_4), 29.18 (C_5), 32.56 (C_6), 69.60 (C_7), 63.72 (C_8), 21.10 (C_9), 25.00 (C_{10}), 17.42 (*C_{11}), 22.78 (*C_{12}), 34.6 (C_{13}), 21.3 (*C_{14}) and 21.3 (*C_{15}).

*Values may interchange

The derivatives of carotol (**1**) were synthesized by reaction with perbenzoic acid, mercuric acetate, dry HCl gas and acetonitrile that afforded daucol (**2**), carotol ether (**3**), 4-chlorocarotol (**4**) and carotol amide (**5**), respectively as products.

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