Research Article

Received: 18 June 2009 Revised: 2 October 2009 Accepted: 4 October 2009 Published online in Wiley Interscience: 1 December 2009

(www.interscience.wiley.com) DOI 10.1002/jsfa.3824

Chemistry and antioxidant activity of essential oil and oleoresins of black caraway (*Carum bulbocastanum*) fruits: Part 69

Inder Pal Singh Kapoor,[a] Bandana Singh,[a] Gurdip Singh,[a]* Carola S De Heluani,[b] Marina P. De Lampasona[b] and Cesar A N Catalan[b]

Abstract

BACKGROUND: The present study describes the chemical analysis of the essential oil and oleoresins from caraway, which have been studied by using GC–MS. The paper also explains the importance of the extracted oil and oleoresins in the antioxidant activities of target plant species.

RESULTS: GC–MS analysis of caraway essential oil showed 51 compounds representing about 96.6% of the total weight. The major components were dillapiole (44.6%), germacrene-β (14.1%), nothoapiole (8.3%), and β-selinene (6.8%), along with many other components in minor amounts. Major components in ethyl acetate and iso-octane oleoresins are dillapiole, nothoapiole and germacrene-β, whereas in ethanol oleoresin contains dillapiole (25%), sitosterol (21.3%) stigmasterol (9.5%) and nothoapiole (8.1%). The antioxidant activity was evaluated by various antioxidant assays such as peroxide, thiobarbituric acid and *p*-anisidine values. These experiments were further supported by other complementary antioxidant assays such as ferric thiocyanate method in linoleic acid system, reducing power, and scavenging effects on 1,1′-diphenyl-2-picrylhydrazyl (DPPH). Both the caraway volatile oil and its oleoresins showed strong antioxidant activity in comparison with butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT).

CONCLUSION: This study provides additional information about the chemistry and antioxidant activity of caraway. Hence, caraway may be used as natural food preservatives.

Keywords: *Carum bulbocastanum*; essential oil; oleoresins; GC–MS; antioxidant activity

INTRODUCTION

Lipid oxidation is recognised as a free-radical-mediated process which is responsible for both the development of objectionable odour and flavour in food.[1] Tocopherols, butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT) and propyl gallate (PG) are important synthetic antioxidants that protect polyunsaturated fatty acids from oxidative degradation. Their antioxidant effect is a result of their ability to donate their phenolic hydrogen to a lipid peroxide radical.[2,3] However, due to their unstable, highly volatile nature and toxicological side effects[4] there has frequently been some questions about their safety and efficiency since their first introduction to the food industry.[5,6] Various spices, aromatic and medicinal herbs, as well as other plants can accumulate significant amounts of strong antioxidant compounds; therefore, their use in preserving lipid and food systems is a promising alternative to synthetic antioxidants.[7]

Carum bulbocastanum Koch. (Fam. Umbellifarae), commonly known as Shah zeera, is a small genus of annual, biennial or perennial herbs distributed eastward of Garhwal and Kumaon.[8] Caraway fruits are used as a spice and as a carminative in indigenous medicine. Studies have been reported regarding the chemical constituents, antioxidant properties and antimicrobial activity of *Carum* species[9,10] but there seems to be no report on *C. bulbocastanum*. The objectives of this study were (1) to investigate the antioxidant activity of the essential oil and oleoresins of caraway, compared to BHA, BHT and PG by carrying out *in vitro* tests, including determination of peroxide, anisidine and thiobarbituric acid values; scavenging effects on 1,1′-diphenyl-2-picrylhydrazyl (DPPH); reducing power and total antioxidant activity by ferric thiocyanate (FTC) methods; and (2) to determine the chemical composition of its hydrodistilled essential oil and solvent-extracted oleoresins by GC–MS.

MATERIALS AND METHODS

Chemicals

Thiobarbituric acid (TBA), diphenylpicrylhydrazyl radical (DPPH) and linoleic acid were purchased from Across (Mumbai, India) Butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT),

* *Correspondence to: Gurdip Singh, Chemistry Department, D.D.U. Gorakhpur University, Gorakhpur-273009, India. E-mail: gsingh4us@yahoo.com*

a *Chemistry Department, D.D.U. Gorakhpur University, Gorakhpur-273009, India*

b *Instituto de Quimica, Organica Universidad Nacinal de Tucuman, Ayacucho 471, S.M. de Tucuman 4000, Argentina*

propyl gallate (PG) and 2,4- dinitrophenylhydrazine were purchased from S.D. Fine Chemicals Ltd (Mumbai, India). Crude linseed oil was purchased from local oil mill in Gorakhpur, India.

Plant material

Fruits of *C. bulbocastanum* were purchased from the local market of Gorakhpur, India, during September 2008 and a voucher specimen has been deposited in the Herbarium of the Science Faculty of DDU Gorakhpur University, Gorakhpur, India.

Extraction of essential oil and oleoresins

The mature and healthy fruits of caraway were thoroughly washed in tap water, dried at a particular temperature (40 °C) using an oven. The dried fruits were then ground to a powder which was used for the extraction of the essential oil and oleoresins. The essential oil was extracted by a hydrodistillation process using a Clevenger's type apparatus in accordance with the method recommended by the European Pharmacopoeia.[11] A light-yellow-coloured oil, with a pleasant odour, was dried over the minimum amount of anhydrous sodium sulfate to remove traces of moisture.

The oleoresins were extracted from caraway by using a Soxhlet apparatus and three different solvents: ethyl acetate, ethanol and iso-octane. The essential oil and oleoresins so obtained were poured into bottles and stored in a refrigerator at 4 ± 1 °C, in the dark, for further use.

Chemical investigation

The chemical analysis of volatile oil and oleoresins of *C. bulbocastanum* was carried out by using gas chromatography–mass spectroscopy (GC–MS). A Hewlett–Packard 6890 gas chromatograph was coupled to a quadruple Hewlett-Packard 5973 mass spectrometer (Hewlett–Packard, Analytical Technologies SA, Buenos Aires, Argentina) equipped with a Perkin–Elmer Elite-5 MS capillary column (5% phenyl methyl siloxane, length 30 m, inner diameter 0.25 mm, film thickness 0.25 µm) (Perkin–Elmer, Argentina). A selective mass detector and an electron ionisation system with an ionisation energy of 70 eV was used for GC–MS. Helium at a flow rate of 1.0 mL min^{-1} was used as the carrier gas. Injector and ion source temperatures were set at 230 °C and 280 °C, respectively, and the split ratio was 80 : 1. The oven temperature for the volatile oil and oleoresins was programmed as follows: 60 °C for 1 min; 60–185 °C at 1.5 °C min^{-1}; 185 °C for 1 min; 185–275 °C at 9 °C min^{-1}; then held at 275 °C for 2 min.

Identification of components

The components were identified by comparing their retention indices and mass spectra with published data,[12,13] and computer matching was done by using the Wiley 275 and National Institute of Standards Technology[14] libraries provided with the computer controlling the GC–MS systems. The retention indices were calculated using a homologous series of *n*-alkanes C8–C18 and the results of volatile oil and oleoresins are reported in Table 1.

Antioxidant activity in linseed oil

The antioxidant potential of caraway oil and oleoresins for linseed oil have been evaluated by different methods such as peroxide, thiobarbituric acid and *p*-anisidine values. Crude linseed oil having an initial peroxide value of 6.3 meq kg^{-1} was taken for the present investigation.

Sample preparation

The caraway oil and oleoresins were added individually to unrefined crude linseed oil at the concentration of 200 ppm (v/v). Synthetic antioxidants such as BHA, BHT and PG were also added to linseed oil at the same concentration, i.e. 200 ppm (v/v). A control sample was prepared under similar condition without any additive. They were subjected to the Schaal oven test[15] in 100 mL open beakers at 60 °C.

The antioxidant activity of oil and oleoresins in the oxidation of linseed oil was examined by comparing the activity of known antioxidants such as BHA, BHT and PG by peroxide,[16] TBA,[17] and *p*-anisidine values.[18]

Complementary antioxidant assays

Further determination of antioxidant activity of caraway oil and oleoresins in the linoleic acid system,[19] the scavenging effect on DPPH[20] and the reducing power[21] were determined by the methods reported earlier.

Statistical analysis

The samples of linseed oil for each treatment/period were taken. Each sample was analysed individually in triplicate. The data were presented as mean ± standard deviation of three determinations (data were not shown). The quantitative data for the essential oil and oleoresin were statistically examined by the Student's *t* test by using the Microsoft Excel statistical analysis program. A probability value of $P \leq 0.05$ was considered to denote the statistically significant differences.

RESULTS AND DISCUSSION

Chemical composition

The data (MS fragmentation and retention indices) obtained from GC–MS analysis were carefully interpreted to identify the various compounds present in caraway essential oil and oleoresins (Table.1). A total of 51 compounds were identified in caraway oil representing about 96.6% of the total weight. The major compounds were dillapiole (44.6%), germacrene-β (14.1%), nothoapiole (8.3%), β-selinene (6.8%), and β-caryophylline (3.5%). There were many other components in minor amounts. Singh and colleagues has also reported the presence of dillapiole (29.9%) and germacrene-β (21.4%) as the major compounds of *Carum* oil.[22] These differences in the chemical composition and yield of the oil from the same plant part could be due to the environmental, developmental, genetic or some other factors.[23,24]

Ethanol oleoresin showed the presence of 17 components constituting about 82.6% of the total amount, with the major compounds being dillapiole (25%), sitosterol (21.3%), stigmasterol (9.5%) and nothoapiole (8.1%). Ethyl acetate oleoresin comprised 38 components (90.2%); the major ones being dillapiole (34%), nothoapiole(15%), germacrene-β (12.0%), and β-selinene (6.8%). The iso-octane oleoresin contained 43 compounds (90.3%), of which dillapiole (30%), nothoapiole (16.8%), germacrene-β (14.8%) and β-selinene (5.8%) were the most prevalent.

Antioxidant activity in linseed oil

The oxidation of lipid has long been classified as the major deterioration affecting both the sensory and the nutritional quality of food.[22] Hydroperoxides are the primary oxidation products that are measured by the peroxide value method (Fig. 1).

Table 1. Chemical composition of essential oil and various oleoresins of *Carum bulbocastanum* fruits

Compound	%MS C_1	%MS C_2	%MS C_3	%MS C_4	RI*	Identification†
α-Pinene	0.2	Trace	–	–	929	MS, RI, co-GC
Camphene	0.1	–	–	–	944	MS, RI, co-GC
Sabinene	Trace	–	–	–	967	MS, RI, co-GC
β-Pinene	0.4	–	–	Trace	973	MS, RI, co-GC
Myrcene	Trace	–	–	–	986	MS, RI, co-GC
p-Cymene	0.1	Trace	–	Trace	1020	MS, RI, co-GC
Limonene	0.1	Trace	–	Trace	1024	MS, RI, co-GC
1,8-Cineole	Trace	–	–	–	1027	MS, RI, co-GC
cis-β-Ocimene	Trace	–	–	–	1031	MS, RI, co-GC
trans-β-Ocimene	Trace	–	–	–	1042	MS, RI, co-GC
γ-Terpinene	0.1	Trace	–	Trace	1053	MS, RI, co-GC
p-Cresol	Trace	0.9	Trace	0.5	1076	MS, RI, co-GC
Terpinolene	Trace	–	–	–	1082	MS, RI, co-GC
Linalool	Trace	–	–	Trace	1099	MS, RI, co-GC
Camphor	0.1	Trace	–	–	1140	MS, RI, co-GC
Borneol	0.1	Trace	–	–	1164	MS, RI, co-GC
Terpinen-4-ol	Trace	–	–	–	1173	MS, RI, co-GC
p-Cymen-8-ol	Trace	–	–	–	1182	MS, RI, co-GC
α-Terpineol	Trace	Trace	–	–	1189	MS, RI, co-GC
Cuminal	0.1	Trace	–	Trace	1234	MS, RI
Carvone	–	–	–	Trace	1237	MS, RI
Bornyl acetate	1.7	1.1	Trace	0.9	1276	MS, RI, co-GC
Cuminol	Trace	0.1	Trace	0.2	1285	MS, RI
p-Vinyl guaiacol	–	–	Trace	0.1	1304	MS, RI
p-Mentha-1,4-dien-7-ol	–	–	–	0.2	1322	MS, RI
α-Terpinyl acetate	0.1	Trace	–	–	1339	MS, RI
β-Elemene	1.3	1.2	–	0.9	1380	MS, RI
β-Caryophyllene	3.5	3.5	–	2.8	1406	MS, RI, co-GC
Cuminyl acetate	Trace	0.2	–	0.1	1416	MS, RI
γ-Elemene	1.8	2.8	–	1.5	1420	MS, RI
trans-α-Bergamotene	0.3	0.2	–	0.1	1424	MS, RI
α-Humulene	0.4	0.3	–	0.3	1441	MS, RI, co-GC
trans-β-Farnesene	0.2	0.2	–	–	1448	MS, RI
Germacrene-D	0.4	0.2	–	0.6	1468	MS, RI
β-Selinene	6.8	7.4	–	5.8	1477	MS, RI
α-selinene	2.0	2.2	–	1.8	1484	MS, RI
Germacrene-A	0.2	–	–	0.3	1493	MS, RI
β-Bisabolene	0.3	–	–	0.1	1501	MS, RI
(*E*, *E*)-α-Farnesene	–	0.9	–	–	1502	MS, RI
cis-γ-Bisabolene	0.4	Trace	–	0.6	1507	MS, RI
Myristicin	3.0	1.8	0.9	1.3	1515	MS, RI, co-GC
trans-γ-Bisabolene	0.2	0.2	–	0.2	1518	MS, RI
Zonarene	0.2	1.3	–	0.2	1523	MS, RI
Selina-3,7(11)-diene	0.3	1.7	–	0.3	1530	MS, RI
Germacrene-B	14.1	12.0	Trace	14.8	1547	MS, RI
trans-Nerolidol	0.1	Trace	–	Trace	1555	MS, RI
Spathulenol	0.3	0.2	–	Trace	1563	MS, RI, co-GC
Caryophyllene oxide	0.6	0.3	–	0.2	1566	MS, RI, co-GC
Curzerenone	1.9	–	–	–	1589	MS, RI
Dillapiole	**44.6**	**34.0**	**25.0**	**30.0**	**1622**	**MS, RI, co-GC**
Apiole	1.0	–	Trace	0.3	1667	MS, RI, co-GC
α-Bisabolol	–	0.1	–	1.1	1676	MS, RI
Germacrone	0.4	–	–	–	1677	MS, RI
pi-α-Bisabolol	–	1.3	–	–	1678	MS, RI
Eudesm-7(11)-en-4-ol	Trace	–	–	–	1683	MS, RI
Isospathulenol	0.9	–	–	0.4	1702	MS, RI
Nothoapiole	8.3	15.3	8.1	16.8	1758	MS, RI

Table 1. (*Continued*)

Compound	%MS C_1	%MS C_2	%MS C_3	%MS C_4	RI*	Identification†
Neophytadiene	–	0.4	–	0.3	–	MS
Palmitic acid	–	–	–	0.4	–	MS, co-GC
Phytol	–	–	–	0.2	–	MS, co-GC
Linoleic acid	–	–	0.6	1.6	–	MS, co-GC
Oleic acid	–	–	5.1	0.1	–	MS, co-GC
3-β-Acetoxy derivative of a triterpene [M+] 466	–	–	–	5.3	–	MS, co-GC
Stigmasterol	0.9	1.3	9.5	–	–	MS, co-GC
Sitosterol	1.2	0.6	21.3	–	–	MS, co-GC
α-Amyrin	–	–	3.4	–	–	MS, co-GC
3-β-Acetoxy derivative of a triterpene [M+] 466	–	–	8.1	–	–	MS
Stigmast-7-en-3-β-ol	–	–	0.6	–	–	MS, co-GC
Total	**96.6**	**90.2**	**82.6**	**90.3**		

Percentages are the mean of three runs and were obtained from electronic integration measurements using selective mass detector.
Values for dillapiole are in bold type. Dillapiole is the major component of all the essential oils and oleoresins.
C_1, = essential oil; C_2, = ethyl acetate oleoresin; C_3, = ethanol oleoresin; C_4, = isopropanol oleoresin.
Trace: <0.05; * the retention index (RI) was calculated using a homologous series of *n*-alkanes C8–C18; † Co-GC: co-injection with an authentic sample.

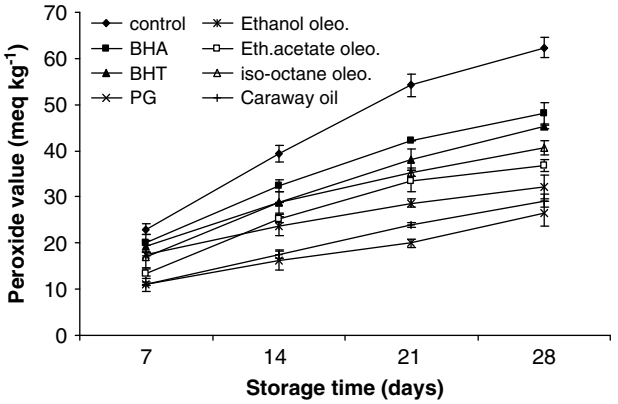

Figure 1. Inhibitory effect of caraway oil and oleoresins on primary oxidation.

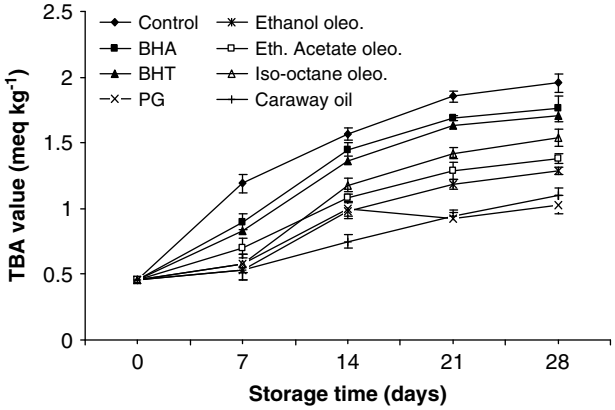

Figure 2. Inhibitory effect of caraway oil and oleoresins in terms of TBA value.

The primary oxidation product is an unstable compound that produces a number of secondary products such as alkenes, alcohol, malonaldehyde, aldehyde and acids, some of which smell badly at low threshold values. Any of these products are highly reactive themselves. Hence, simultaneously with the measurement of peroxide value, the change in secondary oxidation products such as malonaldehyde and 2-alkenals, which are measured by using thiobarbituric acid (Fig. 2) and *p*-anisidine (Fig. 3), were also determined every 7 days during 28 days of storage. Malondialdehyde, used as an index of lipid peroxidation, was determined by a selective third-order derivative. Figure 1 demonstrates the change in peroxide value (PV) in linseed oil with different additives. During this time the PV of the control sample increased from 6.3 meq kg^{-1} to 62.4 meq kg^{-1}, which is significantly ($P < 0.02$) higher than the samples containing volatile oil and oleoresins. The PVs of samples containing caraway oil and its oleoresins were always less than BHA and BHT, but both are not significantly ($P < 0.05$) better antioxidants when the oil is compared to PG.

The malonaldehyde formation of all the additives increases with storage time. From Fig. 2 it is clear that caraway oil and oleoresins

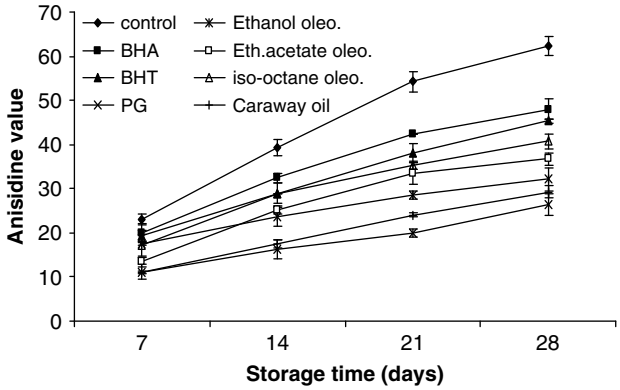

Figure 3. Inhibitory effect of caraway oil and oleoresins on the formation of 2-alkenals.

showed a moderate inhibition at a concentration of 200 ppm, and was comparable with BHA and BHT but lower than PG. These results were well correlated with the *p*-anisidine value. The effectiveness of the added materials in stabilising linseed oil was found to be in

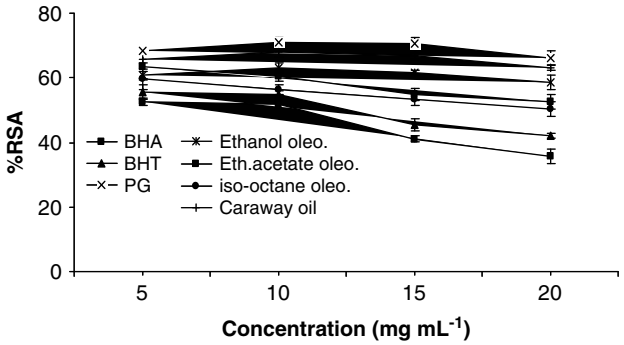

Figure 4. Radical scavenging effect of caraway oil and oleoresins on DPPH.

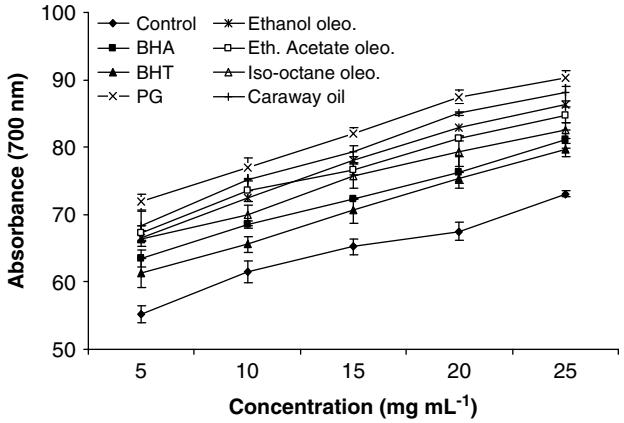

Figure 6. Reducing power of caraway oil and oleoresins.

the order: PG > caraway oil > ethanol oleoresins > ethyl acetate oleoresins > iso-octane oleresins > BHT > BHA > control.

Complementary antioxidant assay

Antioxidants react with DPPH (a stable free radical) to convert it to 1,1′-diphenyl-2-picrylhydrazine. The degree of discoloration indicates the radical scavenging potential of the antioxidants (Fig. 4). Caraway oil and oleoresins exhibited marked DPPH free-radical scavenging activity in a concentration dependent manner. From Fig. 4, it is clear that caraway oil showed better scavenging power than BHA and BHT but lower than that of PG at all the concentrations. Of the three oleoresins, the best activity was shown by ethanol oleoresins followed by ethyl acetate oleoresins.

The ferric thiocyanate method was used to compare the inhibitory action of essential oil and oleoresins with those of selected standard antioxidants. In this method, the peroxide level was evaluated during the initial stage of lipid peroxidation.[25] High absorbance is an indication of a high concentration of formed peroxides. The absorbance of linoleic acid emulsion without the addition of essential oil, oleoresins or antioxidants increased rapidly and there was a significant ($P < 0.05$) difference between the blank and the tested essential oil or oleoresins. As can be seen in Fig. 5, the essential oil and oleoresins were able to reduce the formation of peroxides. Caraway oil and ethanol oleoresin were found to be the most effective among all the additives.

Reducing power is an indicator of the antioxidant activity of a given reagent or product. This method evaluates the aptitude of essential oil and oleoresins to reduce a potassium ferricyanide solution which leads to increase of absorbance at 700 nm. Figure 6 shows the reducing ability of caraway essential oil and oleoresins compared to BHA, BHT and PG. The reducing power of all the samples was found to be significantly higher ($P < 0.05$) than the control and depended on their concentrations. Caraway oil and its ethanol oleoresin showed better reducing power than the other oleoresins. Their activities were higher than BHA and BHT but lower than that of PG. The DPPH scavenging and reducing power of caraway oil and oleoresins might be due to their hydrogen-donating ability[26] and is generally associated with the presence of reductones.[27] The components present in caraway oil and oleoresins could act as good reductants that could stabilise free radicals and terminate the chain reaction.

It is difficult to give a definite explanation for all results obtained within the scope of the present study. The better antioxidative potential of caraway essential oil and oleoresins may be due to the presence of various types of compounds. Dillapiole and nothoapiole are the first two major components. It is reported that an aromatic ring having electron repelling substituents could increase the antioxidant activity.[28] There are many studies emphasising that the phenolic group plays an important role in antioxidant activity[29–31] and reporting significant scavenging effects of phenolic compounds against the DPPH free radical. Hence, the presence of phenolic compounds such as sitosterol, stigmasterol, spathulenol and nothoapiole (Table 1) may be responsible for their antioxidant properties. Moreover, the antioxidant activities observed in caraway oil and oleoresins could be due to the synergistic effects of two or more compounds present in them. Lu and Foo[32] reported that most natural antioxidative

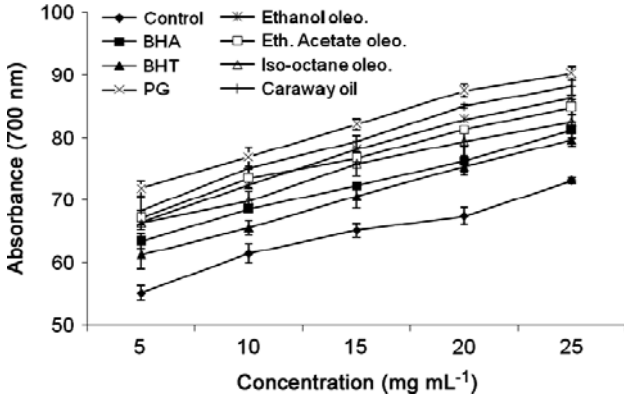

Figure 5. Antioxidant activity of caraway oil and oleoresins on linoleic acid.

compounds often work synergistically with each other to produce a broad spectrum of antioxidative properties that create an effective defence system against free radicals. Caraway oil and oleoresins consist of a very complex mixture of various classes of organic compounds (Table 1), which may produce synergistic effect on the process of lipid oxidation.

CONCLUSIONS

GC–MS analysis of caraway essential oil showed the major compounds to be dillapiole, germacrene-β, nothoapiole and β-salinine. There were many other compounds in minor amounts. The major compounds in the ethyl acetate and iso-octane oleoresins are dillapiole, nothoapiole and germacrene-β; whereas the ethanol oleoresin contains dillapiole, sitosterol, stigmasterol and nothoapiole.

Caraway oil and its oleoresins, which are rich in dillapiole and nothoapiole, possess good antioxidant activity, and hence could be used as a natural antioxidant for linseed oil. They are valuable for increasing the shelf life of foodstuffs and as a protector for highly unsaturated linseed oil, replacing synthetic antioxidants such as BHT and BHA.

ACKNOWLEDGEMENT

We are grateful to The Head, Chemistry Department, DDU Gorakhpur University, Gorakhpur, for providing laboratory facilities. Thanks are also due to Council of Scientific and Industrial Research (CSIR) for the award of Emeritus Scientist to Dr Gurdip Singh and to CST, U.P., for financial assistance.

REFERENCES

1 Yanishlieva NV, Eldin AK, Marinova EM and Toneva AG, Kinetics of antioxidant action of α- and γ-tocopherols in soybean and sunflower triacylglycerols. *Eur J Lipid Sci Technol* **104**:262–270 (2002).
2 Burton GW and Ingold KU, Vit-E as in-vitro and in-vivo antioxidant. *Ann N Y Acad Sci* **570**:7–22 (1989).
3 Burton GW and Ingold KU, Autooxidation of biological molecules the antioxidant activity of Vit-E and related chain breaking phenolic antioxidants in-vitro. *J Am Chem Soc* **103**:6472–6477 (1981).
4 Dapkevicius A, Venskutonis R, Van Beek TA and Linssen PH, Antioxidant activity of extracts obtained by different isolation procedures from some aromatic herbs grown in Lithuania. *J Sci Food Agric* **77**:140–146 (1998).
5 Mahdavi DL and Salukhe DK, Toxicological aspects of food antioxidants, in *Food Antioxidants,* ed. by Mahdavi DL, Deshpande SS and Salukhe DK. Dekker, New York, p. 267 (1995).
6 Barlaw SM, Toxicological aspects of antioxidants used as food additives. in *Food Antioxidants*, ed. by Hudson BJF. Elsevier, London, pp. 253–307 (1990).
7 Madsen HL, Christiansen AL, Brockhoff P and Bertelsen G, Antioxidative activity of summer savory (*Satureja hortensis* L.) and rosemary (*Rosmarinus officinalis* L.) in minced, cooked, pork meat. *Z Lebensm Unters Forsch* **203**:333–338 (1996).
8 Anonymous, *Wealth of India, Raw Materials*, vol. II. CSIR, New Delhi, p. 88 (1950).
9 Singh G, Maurya S, Lampasoma MP and Catalan C, Studies on essential oils. Part 44: Chemical, antifungal, antioxidant activity of *Foeniculum vulgare* volatile oil and its oleoresins. *Food Control* **17**:745–752 (2006).
10 Iacobellis NS, Cantore PL, Capasso F and Senatore F, Antibacerial activity of *Cuminum cyminum* L. and *Carum carVi*. essential oils. *J Agric Food Chem* **53**:57–61 (2005).
11 Maisonneuve SA, *Sainte Ruffine European Pharmacopoeia*, vol 1. Canada (1983).
12 Adams RP, *Identification of Essential Oil Components by Gas Chromatography/Quadruple Mass Spectrometry*; Allured Publishing, Carol Stream, IL (2001).
13 Massda Y, *Analysis of Essential Oils by Gas Chromatography and Mass Spectrometry*, Halsted/Wiley, New York (1976).
14 NIST Mass Spectral Search Program for the NIST/EPA/NIH Mass Spectral Library, Version 2.0. (2005).
15 Bandoniene D, Gruzdiene D and Venskutonis PR, Antioxidant activity of sage extracts in rape seed oil irradiated with UV rays. *Nahrung/Food* **45**:105–108 (2001).
16 Association of Official Analytical Chemists, AOAC official method 965.33:Peroxide value of oils and fats, in *Official Methods of Analysis of AOAC International*, 17th edition. Hortwitz W, ed. AOAC, Gaithersberg, MD (2002).
17 Pokorny J and Dieffenbancher A, Results of a collaborative study and the standardized methods. *Pure Appl Chem* **16**:1165–1170 (1998).
18 Singh G, Marimuthu P, Heluani CS and Catalan C, Antimicrobial and antioxidant potentials of essential oil and acetone extract of *Myristica fragrans* Houtt. *J Food Sci* **70**:2 (2005).
19 Mitsuda H, Yuasumoto K and Iwami K, Antioxidation action of indole compounds during the autooxidation of linoleic acid. *Eiyo to Shokuryo* **19**:210–214 (1996).
20 Cuendet M, Hostettmann K, Potterat O and Dyatmiko W, Iridoid glucosides with free radical scavenging properties from *Fagraea blumei*. *Helv Chim Acta* **80**:1144–1152 (1997).
21 Senevirathne M, Kin SH, Siriwardhana N, Ha JH, Lel KW and Jeon YJ, Antioxidant potential of *Ecklonia cava* on reactive oxygen species, scavenging, metal chelating, reducing power and lipid peroxidation inhibition. *Food Sci Technol Int* **12**:27–38 (2006).
22 Singh G, Marimuthu P, Heluani CS and Catalan C, Antioxidant and biocidal activities of *Carum nigrum* (seed) essential oil, oleoresin, and their selected components. *J Agric Food Chem* **54**:174–181 (2006).
23 Bailer J, Aichinger T, Hackl G, de Hueber K and Dachler M, Essential oil content and composition in commercially available dill cultivars in comparison to caraway. *Ind Crops Prod* **14**:229–239 (2001).
24 Galambosi B and Peura P, Agrobotanical features and oil content of wild and cultivated forms of caraway (*Carum carvi* L). *J Essent Oil Res* **8**:389–397 (1996).
25 Glucin I, Elias R, Gepdiremen A, Boyer L and Koksal E, A comparative study on the antioxidant activity of fringe tree (*Chionanthus virginicus* L.) extracts. *Afr J Biotechnol* **6**:410–418 (2007).
26 Bauhmann J, Wurn G and Bruchlausen FV, Prostaglandin synthetase inhibiting radical scavenging properties of some flavanoids and related compound. *Naunyn–Schmiedebergs Arch Pharmacol* **308**:R27 (1979).
27 Duh P-D, Antioxidant activity of Budrock (*Arctium laooa* Linn): its scavenging effect on free radical and active oxygen. *J Am Oil Chem Soc* **75**:455–461 (1998).
28 Zhang HY, Theoretical methods used in elucidating activity differences of phenolic antioxidants. *J Am Oil Chem Soc* **76**:745–748 (1999).
29 Huang SW and Frankel EN, Antioxidant activity of tea catechins in different lipid systems. *J Agric Food Chem* **45**:3033–3038 (1997).
30 Baratta MT, Dorman HJD, Deans SG, Figueiredo AC, Baroso JG and Ruberto G, Antimicrobial and antioxidant properties of some commercial essential oils. *Flav Frag J* **104**:286–292 (1998).
31 Singh G, Marimuthu P, Murali HS and Bawa AS, Antioxidative and antimicrobial potentials of essential oils and extracts isolated from various spice materials. *J Food Safe* **25**:130–145 (2005).
32 Lu F and Foo LY, Antioxidant activities of polyphenol from sage (*Salvia officinalis*). *Food Chem* **75**:197–202 (2001).

