Food Chemistry **41** (1991) 129–134

Comparative Studies on the Major Volatiles of Kalazira (*Bunium persicum* Seed) of Wild and Cultivated Sources

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(Received 16 May 1990; revised version received and accepted 13 September 1990)

ABSTRACT

Kalazira (Bunium persicum *seed) is an expensive spice in India, extensively used for culinary purposes and for flavouring food and beverages. A comparison of the major volatiles of the oils of* Bunium persicum *of commerce (Kalazira) collected from the wild with that of the cultivated material indicated that the oil distilled from the latter is superior in quality, containing higher percentages of aldehydes responsible for the flavour of the seeds and lower percentages of terpene hydrocarbons, i.e. γ-terpinene and* p-*cymene. Thus matured seeds of cultivated origin yielded an oil rich in cuminaldehyde (27·3–34·1%),* p-*mentha-1,3-dien-7-al and* p-*mentha-1,4-dien-7-al (29·6–36·8%), while oil from the wild source contained more γ-terpinene (25·6–42·9%) and* p-*cymene (24·0–27·8%) and less aldehydes, being similar to the oil obtained from the immature seeds of cultivated source. The study also confirmed that the crop responds well to cultural treatments, yielding more than four times more seeds per plant as compared to wild ones. Apart from seeds, the straw available in large quantity also yielded an oil (1·20%) resembling the matured seeds in chemical composition.*

Food Chemistry 0308-8146/91/$03·50

INTRODUCTION

Bunium persicum (Boiss) Fedtsch 'Kalazira' is an economically important umbellifer growing wild in dry temperate regions of Jammu-Kashmir, Himachal Pradesh, Afghanistan and Baluchistan (Sarin, 1967; Dutt *et al.*, 1972; Raina & Jamwal, 1989). The seeds, rich in essential oil, are consumed widely as an indispensable condiment. In the indigenous system of medicines, seeds are regarded as stimulants and carminatives and found to be useful in diarrhoea and dyspepsia. Recent relentless extraction of seeds obtained from the wild, has forced the plant into the endangered category. Work has been undertaken to ascertain the factors responsible for the depletion of *B. persicum* in nature. The prime cause of depletion has been found to be the thoughtless and unscientific commercial exploitation of its seeds for rapid financial gains. The competition for its seeds is so severe that, instead of collecting the ripe seeds, the entire plant is removed even when the seeds are immature.

Consequently, the Ministry of Environment and Forests, Government of India, has initiated an action plan for the conservation of the plant by establishing a high altitude farm (height 2100 m, above sea level) in the Paddar valley, in Jammu & Kashmir (India). Locally collected germplasm is now under cultivation at the farm.

In the present communication, a comparison of the major volatiles of the wild growing plants with the cultivated crop was undertaken to select better quality seed material for commercial ventures.

MATERIALS AND METHODS

The seeds from wild and cultivated plants were collected in the months of June–July 1989, powdered and hydrodistilled in a Clevenger apparatus to obtain their essential oils. The oil samples were dried over anhydrous sodium sulphate and stored at low temperature. The oils were analysed qualitatively by thin-layer chromatography on silica gel G plates using benzene and benzene-ethyl acetate (95:5) as the solvent systems: 2% vanillin sulphuric acid and 2,4-dinitrophenylhydrazine were used as the spray reagents for the identification of spots. The quantitative analyses of the oil samples was done on a NUCON 5700 gas chromatograph using a stainless steel column (6ft × 0·25 in.) packed with 10% Reoplex-400 on Chromosorb W with a nitrogen flow rate of 45 ml/min. The operation was performed at a programmed rate of 6°/min from 90–180°C. The GC was also done on 10% SE-30 on Chromosorb W packed in a 6 ft × 0·25 in glass column at a programmed rate of 6°/min from 90–210°C. The major components on the gas chromatograph were identified by relative retention time and enrichment technique.

The constituents of the oils were isolated by silica gel column chromatography, eluting with hexane, benzene, and chloroform. The fractions were analysed by means of ^{1}H-NMR (60 MHz and 90 MHz) and ^{13}C-NMR (22·49 MHz) on Varian T-60 A and Jeol FX-90 QFT models using $CDCl_3$ as solvent and TMS as internal standard. The carbonyl components were also separated by the formation of dimedone derivatives and by 2,4-dinitrophenylhydrazones and studied by MS fragmentation and mps.

The components on the ^{1}H-NMR and ^{13}C-spectra were identified by comparison of chemical shift values with those reported in the literature (Formacek & Kubeczka, 1982).

RESULTS AND DISCUSSION

A comparative study of the wild type plants (Agarwal *et al.*, 1979; Shankaracharya & Shankarnaryana, 1988) vis-à-vis regularly cultivated types was undertaken to investigate the commercial utilization of the cultivated material. Study of the phenotypic variability revealed that the two types vary greatly in plant characters, in the number of tillers, number of umbels (primary, secondary and tertiary)/plant and flowers/umbel. Clearly, the cultivated types yielded more umbels and seeds of better quality than did the wild ones. A number of samples of the two varieties, i.e. cultivated (seven samples) and wild (four samples), were collected and compared for their oil content and composition.

Significant qualitative and quantitative differences were observed among the major volatiles in the oils from the two sources (Table 1). Among the cultivated samples, maximum oil percentage was found in the unripe light-weight seeds which compared only with the commercial wild sample. Chemically, both these oils are similar, with terpene hydrocarbons constituting about 40·3 to 68%, the major being *p*-cymene and γ-terpinene, while α-pinene, β-pinene and α-terpinene are present in minor quantities. The carbonyl contents in both of them showed minor differences (Table 1). These aldehydes were identified as cuminaldehyde, *p*-mentha-1,3-dien-7-al, *p*-mentha-1,4-dien-7-al, and *p*-menth-3-en-7-al. Some minor compounds (about nine), present in traces (0·5 to 2%) were also detected but it was not possible to identify them.

However, in the fully matured seeds the total carbonyl content seems linked with maturity stage of the seeds, rising to the highest level (60·1–72·0%) when they are fully mature, with a corresponding decrease in

TABLE 1
Oil Percentages and Composition of Different Samples of *B. persicum*

Details	*Mature seeds* (*Cultivated*)				*Immature seeds (cultivated)*		*Wild seeds (commercial)*	*Straw*
	SM	*SMP*	*SMS*	*SMT*	*SI*	*SIT*		
1. Oil percentage	5·5	6·5	5·1	4·9	14·30	8·25	7·0–10·2	1·0–1·25
2. Major chemical components percentages								
α-Pinene	0·25	trace	0·70	trace	0·10	0·35	0·20–0·85	0·52
β-Pinene	0·50	0·25	0·35	0·25	0·50	0·55	0·50–1·3	0·67
Limonene	0·41	0·12	0·30	0·20	0·41	0·40	0·40–1·0	0·32
α-Terpinene	trace	trace	trace	trace	trace	trace	trace	trace
p-Cymene	16·5	17·5	17·7	11·2	25·7	19·0	24·0–27·8	30·1
γ-Terpinene	14·4	15·4	19·0	10·9	23·9	20·0	25·6–42·9	13·7
p-Menth-3-en-7-al	1·23	0·92	0·61	1·06	0·50	0·80	0·98–1·56	4·72
Cuminaldehyde	33·6	31·8	27·3	34·1	22·6	26·3	12·0–24·1	25·1
p-Mentha-1,3-dien-7-al + *p*-Mentha-1,4-dien-7-al	29·6	30·7	32·3	36·8	21·9	28·9	11·6–19·0	19·7

SM = Matured seeds whole crop: SMP—Primary umbels; SMS-Secondary umbels; SMT-Tertiary umbels.
SI = Immature seeds, whole crop: SIT—Tertiary umbels (Immature).

the terpenes (32·0–38·1%). This trend is very clearly reflected in all the umbel types—primary, secondary and tertiary. Since *p*-cymene and γ-terpinene are the precursors of aldehydes-cuminaldehyde and menthadienals, in the biogenetic pathways, a gradual reduction of the terpenes (from 50·7 to 32·0%) with simultaneous increase in the accumulations of aldehydes was discernible. These major aldehydes of the seed volatiles are responsible for the cumin-like aroma (Varo & Heinz, 1970*a*,*b*). It has been observed that the cuminaldehyde, *p*-mentha-1,3-dien-7-al and *p*-mentha-1,4-dien-7-al, have nearly the same aroma and it is desirable to have their concentration in the seed volatiles for the spicy flavour (Tassan & Russell, 1975). Moreover, *p*-mentha-1,4-dien-7-al is heat-labile and undergoes disproportionation into *p*-mentha-1,3-dien-7-al and *p*-menth-3-en-7-al (Tassan & Russell, 1975). This also explains the lower concentration of *p*-mentha-1,4-dien-7-al than that of *p*-mentha-1,3-dien-7-al with extended storage period.

Surprisingly, the oil percentage decreases with the maturation of the seeds and falls to 5·5% (from 14%), but the weight of seeds per plant increases as they mature, being bigger in size than the immature ones. Generally, 10·0–12·0 g mature seeds are harvested from cultivated plants, whereas the wild ones yield only 1·0–3·0 g. Therefore, more than four times the weight of

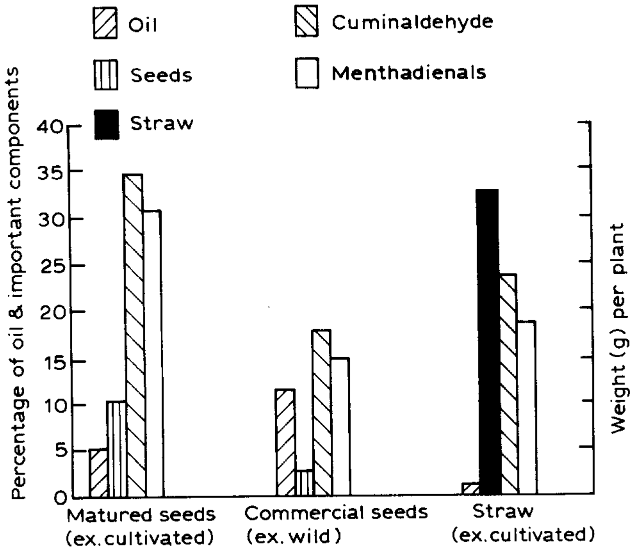

Fig. 1. Comparative profile of *B. persicum* samples.

mature seeds in comparison to immature seeds of the wild collection compensates for the decrease in oil percentage yielding overall (qualitatively and quantitatively) superior oil with high aldehyde contents (Fig. 1).

Apart from seeds, the straw, left after the harvesting of seeds, too, is a rich source of volatile oil and oleoresin. This waste material available in large quantities (approx. 33·0 g/plant) yields about 1·2% oil, resembling the mature seeds (Table 1) in chemical composition.

Interestingly, the ratio of cuminaldehyde to *p*-menthadienals remains the same in the oils derived from wild seeds, cultivated seeds and the straw.

CONCLUSION

The cultivation of *B. persicum* which has been undertaken for the first time, will not only save it from extinction, but also augment the supply of superior quality seed and cuminaldehyde-rich oil, so far not possible to produce from the wild collection. Additionally, the *B. persicum* residue, straw, which contains large quantities of essential oils may be exploited as an alternate source of cumin oil.

ACKNOWLEDGEMENT

The authors are thankful to the Director, Regional Research Laboratory, Jammu, for providing the facilities and to the Instrumentation Division of the Institute for providing GC and spectral data. Two of the authors (AKR & PSJ) are also thankful to the Ministry of Environment and Forests for financial assistance.

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