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ORIGINAL ARTICLE

A new sprout inhibitor of potato tuber based on carvone/β-cyclodextrin inclusion compound

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Abstract A monoterpene, D-carvone or (4*S*)-(+)-carvone, present in the essential oil of caraway seeds (*Carum carvi* L.), acts as a sprouting inhibitor agent for potato tubers in storage. The aim of the present study was to investigate the possibility of using carvone/β-cyclodextrin inclusion compound as a sprout inhibitor agent for potato tubers. A Raman study of the interactions between β-cyclodextrin (β-CD) and included carvone molecule in solid state is also reported; the results confirm the synthesis of inclusion compound at pilot scale level.

Keywords Carvone · β-cyclodextrin · Inclusion compound · Sprout inhibitor · Potato tuber

Introduction

Potato is the fourth most important food crop in the world mainly due to its starch content and high quality protein, substantial amounts of essential vitamins, minerals, and very low fat content. Sprouting is a common problem during winter storage of potato tubers. Chlorpropham (CIPC), a carbamate, is a traditional chemical often applied to prevent this problem and increase the storage period. Despite its relatively low toxicity, there is a demand for alternative non-chemical sprout suppressants, either legislative or marketing reasons.

The use of volatile plant compounds in post-harvest potato storage is an ancient concept [1, 2].(4*S*)-(+)-Carvone, present in the essential oil of caraway seeds (*Carum carvi* L.), is being used as a sprouting inhibitor agent for potatoes and seed potatoes in storage [2]. However, this compound is extremely volatile and therefore unstable. Inclusion of carvone into β-cyclodextrin reduces volatility and improves stability [2]. In this work, the effect of carvone/β-cyclodextrin inclusion compound was studied. A Raman spectroscopic study of the interactions between β-CD and carvone in solid state is also reported.

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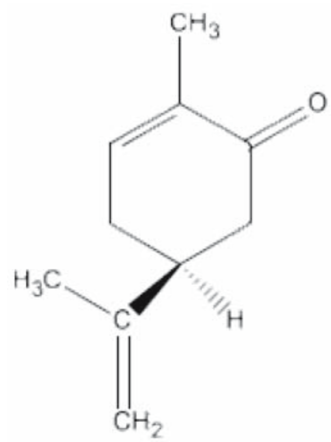
Methodology

β-CD (KLEPTOSE) was kindly offered by Roquette, France, and the *S*-carvone (2-methyl-5-(1-methylethenyl)-2-cyclohexen-1-one or (4*S*)-(+)-Carvone)-Scheme I-was purchased from Aldrich or extracted from *Carum carvi* L. (caraway) seeds by supercritical method and/or hydrodistillation (2.2–2.9 g/100 g of dried seeds) [3, 4].

Inclusion compound preparation (pilot scale)

β-CD (273 g) was dissolved in 15 L of distilled water to form a clear solution, at 353 K in a *B. Braun Biotech*



(4S)- (+) -Carvone

Scheme 1

Biostat ED DCU2 Fermentor. The *S*-carvone (37.7 mL) was added drop-wise to *β*-CD solution. The mixture was vigorously stirred over night with a magnetic stirrer at room temperature. White precipitate was filtered and dried for 1–2 days over ambient atmosphere (ca. 90% (m/m) yield).

The *β*-CD carvone inclusion compound was characterized by ^{1}H-NMR and Raman spectroscopic studies [5, 6].

Potato tuber storage experiments

2004–2005 Preliminary experiment

This experiment was conducted for 6 weeks using the potato cultivar ''Monalisa''. Five wood containers of 70×50 cm^2 each were placed in a cool storage room at 283 K, and 80–90% relative humidity (RH), with 15 cm of distance between them. Seventy potato tubers (ca. 140 g/potato) making 10 kg of total weight were layered in each container.

The potato tubers of each of the four containers were submitted to different treatments: 1—homogenous distribution of 6 mL de *S*-(+)-carvone by regular sprinkling, once a week; 2—homogenous distribution of 25 g of the inclusion compound carvone/*β*-cyclodextrin, once a week; 3—homogenous distribution of 10 g of the common sprout inhibitor, chlorpropham (CIPC); 4—homogenous distribution of 337 g of caraway seeds. The fifth container was left without any treatment, as a control. Measurements of the number and the length of sprouts in each treatment and in control were made weekly. The results were expressed as sprouting percentage in relation to the total number of potato tubers in each treatment (70).

2005–2006 Experiment

This experiment was conducted for 14 weeks using the potato cultivar ''Agria''. Five bigbags, each with 77 kg of potato tubers, were placed in a cool storage room at 283 K, and 80–90% RH. The potato tubers of four of the ''bigbags'' were submitted to different treatments: 1—homogenous distribution of 200.2 g of the inclusion compound carvone/*β*-cyclodextrin, every 15 days; 2—homogenous distribution of 77 g of the common sprout inhibitor, CIPC, twice during the experiment; 3—homogenous distribution of 2595 g of caraway seeds, once during the experiment; 4—homogenous distribution of 46.2 mL of *S*-(+)-carvone by regular sprinkling; every 15 days. Measurements of the number and the length of sprouts in each treatment and in control were made every 15 days on 10 randomly chosen potato tubers, and the results expressed as explained above.

Raman spectroscopic studies

The sample was inserted in a Kimax capillary tube and room temperature ($T = 298$ K) raman spectra were recorded on a T64000 Jobin Yvon spectrometer, working in the subtractive configuration (i.e., double premonochromator stage in subtractive configuration, plus third stage spectrograph), with relevant slit widths set to 320 μm and the intermediate slit between premonochromator and spectrograph wide open (14 mm). The detecting device was a CCD detector. An Ar^+ laser (Innova 300–05 model with power track, from Coherent) at 514 nm provided ca. 100 mW at the sample position.

Results and discussion

Studies of sprouting inhibition of potato tuber

According to the results obtained in the preliminary experiment (Fig. 1), the carvone treatment had the most efficient sprout inhibitory effect as it was already found in other studies [1, 2]. However, the inclusion compound treatment also demonstrated a potential inhibitory effect compared with the control.

In the second experiment, the potato tubers treated with carvone (Treatment 4) rotted due to the sprinkling and the accumulation of humidity. The results obtained in the other treatments showed that the inclusion compound treatment had the most efficient sprout inhibitory effect followed by CIPC, and caraway seeds (Fig. 2). These studies deserve further investigation.

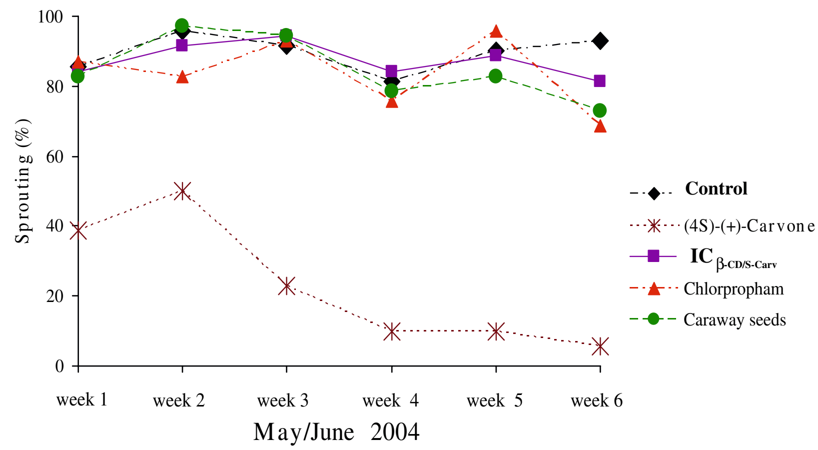


Fig. 1 Sprouting (%) reported in each treatment and in the control over the preliminary experiment period (May–June of 2004)

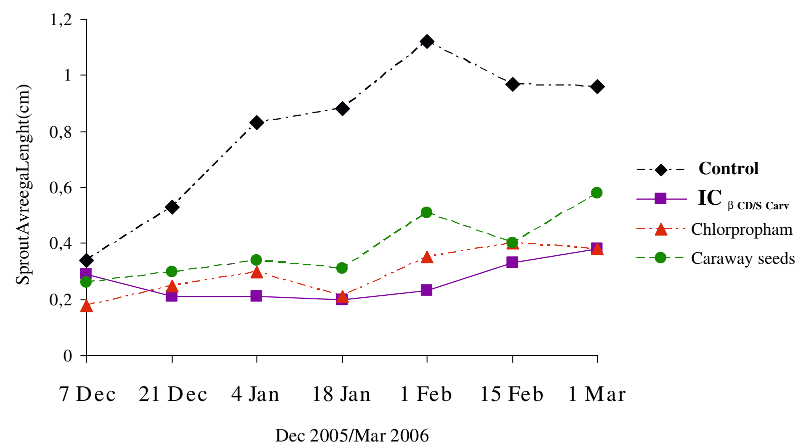


Fig. 2 Sprout average length (cm) of sprouted tubers reported in each treatment and in the control over the second experiment period (December 2005–1 March 2006)

Inclusion compound raman spectroscopic characterization

The stoichiometry and the apparent inclusion constants were determined in previous work by "Job plots" and linear regression methods, respectively. The apparent association constant at room temperature for the 1:1 inclusion of *S*-(+)-carvone in β-cyclodextrin is 1330 mol. dm^{-3} (cv = 10%), at T = 286 K [5, 6] .

Figure 3 presents the Raman spectra of Inclusion Compound, IC $_{\beta\text{-CD/S-Carv}}$ (a) β-cyclodextrin, β-CD (b) *S*-Carvone (c) in the region 1500–1750 cm^{-1}. The more relevant spectral features presented in these spectra are νC=C (1624–1647 cm^{-1}) and νC=O (1668–1706 cm^{-1}) [7].

Table 1 summarizes the most important spectral results which occur in a frequency region relatively free from other νC-H bands. It can be seen that positive significant frequency shifts of νC=O (1670.3–1677.3 cm^{-1}).

The spectral comparisons emerging both from Raman spectra show in Figure 4 and Table 1 leads to confirmation that inclusion occurs, using C=O bond as vibrational probe. The observed shift in spectral bands is consistent with presence of inclusion compounds, but does not prove that solid material consist only inclusion compounds. As a hydrogen bond acceptor, the C=O bond of carvone can act as the anchoring group for the guest in the inclusion process. The observed no significant change in the νC=C band implies that this vibration is not affect by inclusion. In fact, the results of molecular mechanics calculations on model systems help in the interpretation of these experimental results. The *S*-Carv inside β-CD have the C=O group of carvone involved in a hydrogen bonding interaction with one hydroxyl group of β-CD. In the most stable inclusion compound model, the (*S*-carvone) C=O···H–O(β-CD) interaction is directed to one primary hydroxyl group of β-CD, C=O···HOC(6) [6].

Conclusion

The results herein reported for carvone and inclusion compound carvone/β-cyclodextrin indicates that these

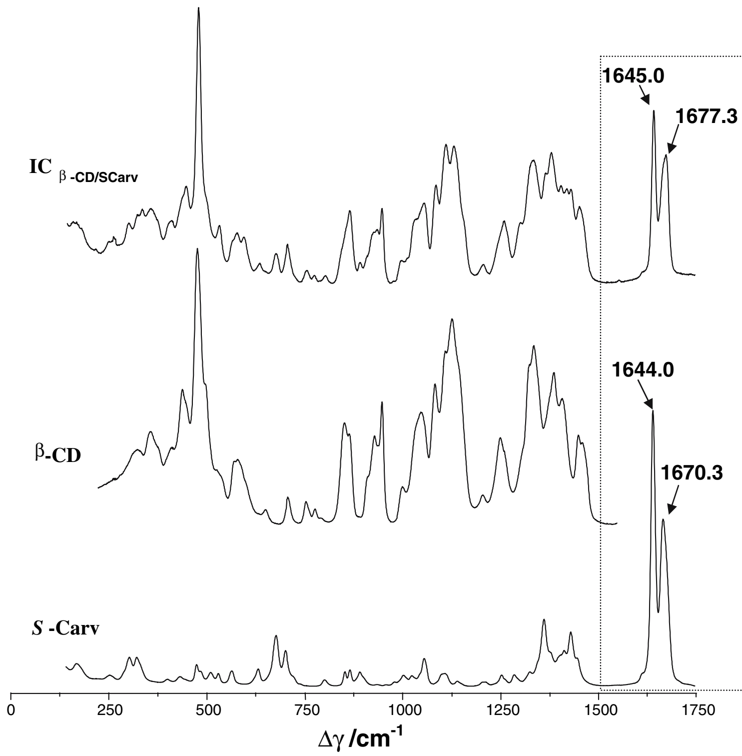


Fig. 3 Raman spectra of Inclusion Compound $IC_{S\text{-}Carv/\text{-}\beta CD}$ (a) β-cyclodextrin, β-CD; (b) *S*-Carvone, *S*-Carv; (c). The intensity change and shift of 1600–1700 cm^{-1} bands shows that inclusion occurs

Table 1 Raman frequencies (cm^{-1})

System	νC=O	$\Delta\nu$C=O	νC=C	$\Delta\nu$C=C
β-CD	–(*)		–(*)	
Carv	1670.3	–	1644	
$IC_{Carv/\beta\text{-}CD}$	1677.3	+7	1645	+1

(*)β-CD window spectral region are νC=O (1668–1706 cm^{-1}); νC=C (1624–1647 cm^{-1})

systems satisfy the basic requirements for use in sprout suppression in *Solanum tuberosum* L**.** tubers.

In addition, the inclusion compound carvone/β-cyclodextrin treatment can be considered as a potential new sprout inhibitor. Further studies should be done in order to clarify the economic advantages of the use of inclusion compound carvone/β-cyclodextrin as potato tuber sprout suppressant.

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References

1. Vaughn, S., Spencer, G.F.: Volatile monoterpenes inhibit potato tuber sprout. Amer. Potato J. **68**, 821–831 (1991)
2. Oosterhaven, J.: Different aspects of S-Carvone, a natural potato sprout inhibitor. WAU dissertation n° 1988, Ph.D. Thesis, Wageningen University, 1995
3. Baysal, T., Starmans, D.A.J.: Supercritical carbon dioxide extraction of carvone and limonene from caraway seed. J. Supercrit. Fluids **14**, 225 (1999)
4. Bouwmeester, H., Davies, J., Toxopeus, H.: Enantiomeric composition of carvone, limonene, and carveols in seeds of dill and biennial caraway varieties. J. Agric. Food Chem. **43**(12), 3057–3064 (1995)
5. Moreira da Silva, A., Empis, J., Teixeira-Dias, J.: Preferencial inclusion in β-cyclodextrin of one of the enantiomers of carvone: a ^{1}H-NMR study in aqueous solution. J. Inclusion Phenom. **33**, 81–97 (1999)
6. Moreira da Silva, A., Empis, J., Teixeira-Dias, J.: Inclusion of carvone enantiomers in β-cyclodextrin: thermal behaviour and H/D, D/H exchanges. J. Carb. Res. **337**, 2501–2505 (2002)
7. Moreira da Silva, A., Amado, A.M., Ribeiro Claro, P.J., Empis, J., Teixeira Dias, J.J.C.: β-Cyclodextrin complexes of benzaldehyde, vanillin and cinnamaldehyde: a Raman spectroscopic study. J. Carb. Chem. **14**(4&5), 677–684 (1995)