CS_2 Blinds in *Brassica* Crops: False Positive Results in the Dithiocarbamate Residue Analysis by the Acid Digestion Method

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Various members of the Brassicaceae family (cauliflower, savoy cabbage, red cabbage, turnip-rooted cabbage) grown without any application of pesticides were analyzed according to the acid digestion method commonly used for the determination of dithiocarbamate fungicide residues. Depending on postharvest treatments, high non-anthropogenic CS_2 values up to 4 mg/kg were found in some cases, especially in frozen raw cabbage samples, exceeding maximum residue limits. To explore phytogenic CS_2 occurrences, two model substances (phenylisothiocyanate and methyl tryptaminedithiocarbamate) representing natural mustard oils and brassinines, respectively, were analyzed for their acid hydrolysis decomposition products. In both cases, COS was found generally, but CS_2 was readily formed during acid digestion, too, when sulfides were present. The results obtained clearly demonstrate that CS_2 values determined by using the acid digestion method of crops rich in secondary metabolism sulfur compounds have to be interpreted carefully.

Keywords: *Dithiocarbamates; residue analysis; carbon disulfide; blinds; Brassicaceae*

INTRODUCTION

Dithiocarbamate formulations belong to the most extensively used fungicides in agriculture. Because of poor solubilities in common organic and aqueous solvents and, additionally, lack of stability during homogenization of plant samples, the use of extraction methods and subsequent chromatographic residue analysis encounters great problems. Therefore, acid treatment of the whole sample, evolving carbon disulfide (CS_2) as analyte to be determined either by headspace gas chromatography or by spectrophotometry, still seems to be the residue analysis method accepted best (Deutsche Forschungsgemeinschaft, 1991; Comittee for Analytical Methods, 1981; Friedrichs et al., 1995). Maximum residue limits (MRLs) of dithiocarbamate residues are correspondingly given in units of milligrams of CS_2 per kilogram. One disadvantage, however, is the inability to distinguish among the various classes of dithiocarbamates having different toxicological properties, for example, *N*,*N*-dimethyldithiocarbamates, ethylenebis-[dithiocarbamates], or thiram. An even more serious problem is encountered when plants with phytogenic carbon disulfide are analyzed. Findings of probably non-anthropogenic CS_2 in different plants belonging to the family of Brassicaceae or Alliaceae have been reported marginally (Gilsbach, 1996, 1997; Bergmüller et al., 1996; Nyanzi, 1995), some of which even reached the MRLs. Thus, identification and quantitation attempts for surveillance purposes may be foiled. The aim of this study was to define typical ranges of phytogenic CS_2 evolved on acid digestion with regard to postharvest treatments or food processing of various *Brassica* produces as well as to find possible reasons for CS_2 blinds.

Because Brassicaceae are known for their content of various sulfur-containing compounds, such as mustard oil glycosides releasing isothiocyanates after enzymatic reaction or brassinines being antifungal indole derivates [reviewed by Gross (1993)] (Figure 1), these substance classes are presumed to be possible CS_2 precursors. To study the behavior of naturally occurring brassinines during acid digestion, methyl tryptaminedithiocarbamate (here called "pseudobrassinine") as a model substance was synthesized and subjected to the acid digestion method. Phenylisothiocyanate representing *Brassica*-borne mustard oils was investigated in the same way. On the basis of the results, causes for CS_2 blinds in Brassica are discussed with respect to the concerned substance classes.

MATERIALS AND METHODS

Chemicals and Reagents. All reagents used were of analytical grade unless specified otherwise. Tryptamine (98%), dimethyl sulfate, *N*,*N*-dimethylformamide, phenylisothiocyanate >98% (GC), carbon disulfide, and sodium sulfide hydrate (32−38% sulfide) were purchased from Fluka (Deisenhofen, Germany); anhydrous sodium carbonate, anhydrous sodium sulfate, methanol, and diethyl ether were from Merck (Darmstadt, Germany). Methanol and diethyl ether were distilled before use. Deionized water was further purified by employing a Milli-Q-Plus-185 (Millipore, Eschborn, Germany) water purification system.

Apparatus. An acid digestion apparatus for decomposition/distillation of dithiocarbamate fungicides in accordance with DFG Method S15 with modified absorption tubes was used (Schwack and Nyanzi, 1993). Photospectrometric measurements of absorption solutions were carried out with a Varian Cary 1E UV−vis double-beam spectrophotometer (Darmstadt, Germany) equipped with 1 cm quartz cuvettes coupled to a personal computer with Cary 45 software version 3. Photometric parameters were as follows: slit width, 0.2 nm; scanned region, 360−240 nm for CS_2 or 330−220 nm for COS, respectively, with background correction and measurement versus blank value of reagents.

For UV irradiation experiments, a Suntest CPS+ sunlight simulator (Heraeus, Kleinostheim, Germany) was employed.

Preparative HPLC was carried out on a Kronlab Sunslow 100 liquid chromatograph (Sinsheim, Germany), combined

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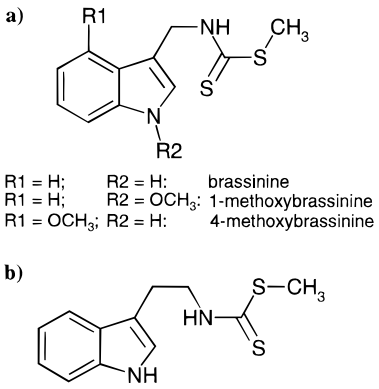

Figure 1. (a) Examples of known brassinines isolated from Brassicaceae (Gross, 1993); (b) synthesized model substance pseudobrassinine.

with a Kronlab variable wavelength monitor (detection wavelength = 220 nm) and a Kronlab HPLC column [guard column, 20 mm i.d. × 250 mm; column, 20 mm i.d. × 250 mm; Nucleosil RP18, 7 μm; flow rate, 20 mL/min; eluent, water/methanol = 40/60 (v/v)].

Photometric Methods. For the determination of CS_2 as methyl xanthate in all plant samples, the methanolic KOH reagent was used as described by Nyanzi and Schwack (1995). Simultaneous determination of CS_2 and COS for digestion experiments of model substances (pseudobrassinine and phenylisothiocyanate) was carried out with the ethylenediamine reagent as published by Nyanzi and Schwack (1993).

For CS_2 calibration, carbon disulfide was pipetted directly to reagent solutions as usual, whereas COS calibrations were made by digesting (the same way as plant samples) 0.5−3 mL of a piperidinium piperidinethiocarbamate solution in acetone (120 mg/L), when the ethylenediamine reagent was used as absorption solution.

The spectra of both methyl xanthate and the ethylenediamine adducts of COS and CS_2, respectively, were recorded as their second derivatives (Schwack and Nyanzi, 1994).

Syntheses. *Piperidine thiocarbamate, piperidinium salt* (reference substance for COS calibration) was synthesized as described by Schwack and Nyanzi (1993).

Methyl Tryptaminedithiocarbamate (Pseudobrassinine, $C_{12}H_{14}N_2S_2$). To a stirred solution of 600 mg of tryptamine in 10 mL of dimethylformamide was rapidly pipetted 3 mL of CS_2. After 1 h, 500 mg of anhydrous Na_2CO_3 and 2 mL of dimethyl sulfate (Caution: carcinogenic! The experiments must be done inside a well-vented fume cupboard and skin contact must be strictly avoided.) were added, and stirring was continued for 2 h. After the addition of 50 mL of water, the crude product was extracted three times with 20 mL of diethyl ether, and the extract was dried over Na_2SO_4 and evaporated. The residue was taken up in 10 mL of methanol and fractionated by preparative HPLC. The main fraction (200−300 mL) was collected, the methanol evaporated, and the product extracted three times with 20 mL of diethyl ether. The solution was dried over Na_2SO_4 and evaporated to dryness, yielding a slightly yellow precipitate of pseudobrassinine: mp 69−70 °C (uncorrected); UV (CH_3OH) λ_{max} 221 and 271 nm; ^{1}H NMR, ^{13}C NMR, and EI-MS data were fully consistent with spectral data recently published by Pedras and Okanga (1998).

Samples and Sample Preparation. *Cauliflower (Brassica oleracea var. botrytis).* Fifty-five flowers with up to 10 floral leaves not trimmed in the field, grown during the summer/autumn of 1995 without any use of fungicides, were received 2 days after harvest from Coöperatie Nautilus b.a. (Lelystad, The Netherlands) and were stored in refrigerators at 5 °C for up to 50 days before analyses or postharvest treatments were performed. During daily controls, samples with bruises, rot, or other damages were separated from the healthy ones. Postharvest treatments were (a) none, direct analysis; (b) irradiation for 120 min with a sunlight simulator; (c) storage at −5 °C for 6 h and then at 5 °C for 18 h, when the whole treatment was repeated; and (d) cutting into quarters and freezing at −18 °C for 60 days, then keeping at room temperature for 6 h. General sample preparation was as follows: leaves were separated from flowers and both were divided into three batches for double determination of CS_2 and one determination of dry solids content (for calculations on fresh weights).

Savoy cabbage (*Brassica oleracea var. sabauda, 22 samples*), *red cabbage* (*Br. oleracea var. capitata convar. rubata, 23 samples*), *turnip-rooted cabbage* (*Br. oleracea var. gongylodes, 24 samples*), *cauliflower* (*20 samples*), *and leek* (*Allium porrum, 16 samples*) were grown during the summer/autumn of 1996, own cultivation, without any use of pesticides. Upon harvesting, nonedible parts were cut off (kitchen-like processing) and samples were batched or treated, respectively, as follows: (a) healthy crops; (b) plants slightly damaged by stodge/partial rot; (c) waste of (b); (d) healthy samples frozen raw at −18 °C for 14−20 days, then kept at room temperature for 6 h; (e) healthy samples blanched for 3 min at 80 °C in water, then frozen the same way as (d); (f) healthy samples cooked for 20 min, then following procedure d. For the analysis of sample groups d−f, three plants were combined to yield a cross section of the specimen that was analyzed two or three times each.

Acid Digestion of Model Substances. Five milligrams of pseudobrassinine or phenylisothiocyanate, respectively, was dissolved in 25 mL of acetone; 1 mL of the solutions was added to 100 mL of pure water so as to substitute the plant matrix volume, and the hydrolysis was executed the same way as for plant samples. For the detection both the ethylenediamine and the xanthate reagent were used. In a second experiment, 1 mL of an aqueous sodium sulfide (Na_2S) solution (5%, w/v) was also added to the hydrolysis attempts when only the xanthate reagent was used (CS_2 determination).

RESULTS AND DISCUSSION

CS_2 from Cauliflower Depending on Postharvest Treatments. Values of carbon disulfide (CS_2) found in cauliflower depending on postharvest treatment manner are presented in Table 1. Unless flowers and leaves looked fresh and were of solid texture without visible damages, even longer storage times up to 30 days did not give rise to increased formation of CS_2. Maximum levels found were 82 μg/kg of fresh weight. Plant parts infested with soft rot or mold generally showed higher values with great variabilities. This may be caused not only by different storage times but also by the influence of different microorganisms, which were not identified or classified in this study. One moldy cauliflower, for example, gave 1000 μg/kg CS_2 after 28 days, whereas another one with soft rot only showed 51 μg/kg after 48 days. Similar ranges were found in leaves, but it has to be pointed out that any healthy leaf evolved small CS_2 amounts, at least.

Stress inflicted upon plants by ultraviolet irradiation led to slightly increased CS_2 contents, which were almost negligible for healthy plants. However, UV stress had a great effect on CS_2 formation of infested plants, reaching values up to 4 mg/kg. Again, more CS_2 was found in healthy leaves than in the corresponding blossoms.

Samples frosted twice (−5 °C) simulating periods of night frost showed higher values than the irradiated ones, but in comparable ranges. Infested blossoms reached top values of >4 mg/kg. Interestingly, very high concentrations with little variability occurred with totally healthy plants cut into quarters, frozen (−18 °C), and allowed to defrost before analysis, a treatment common in residue analysis laboratories. All values

Table 1. CS_2 Evolution from Acid Digestion of Cauliflower (Micrograms per Kilogram of Fresh Weight, Range, Mean) Depending on Postharvest Treatments

treatment	none	UV irradiation	2 × frosted (−5 °C)	frozen (−18 °C)
healthy inflorescences	nd[a]−82 mean = 28 (n = 8)	nd−272 mean = 108 (n = 8)	83−549 mean = 307 (n = 6)	2890−3286 mean = 3040 (n = 4)
partially rotten inflorescences	51−1450 mean = 527 (n = 9)	126−4040 mean = 1220 (n = 9)	572−4218 mean = 1540 (n = 11)	
healthy leaves	22−498 mean = 315 (n = 8)	257−1570 mean = 742 (n = 10)	89−638 mean = 332 (n = 3)	987−1440 mean = 1200 (n = 4)
rotten or wilted leaves	104−1300 mean = 600 (n = 9)	766−5160 mean = 2100 (n = 8)	871−1840 mean = 1350 (n = 11)	

[a] Not detected (<5 μg/kg).

Table 2. CS_2 Evolution from Acid Digestion of Various Brassicaceae and Leek (Micrograms per Kilogram of Fresh Weight, Range, Mean) Depending on Food Processing Manner

treatment	unprocessed, healthy	unprocessed, with stodge/rot cut off	unprocessed, waste of col 3	raw and frozen (−18 °C)	blanched and frozen	cooked and frozen
savoy cabbage	22−77 mean = 48 (n = 6)	59−117 mean = 88 (n = 7)	112−625 mean = 387 (n = 4)	1396−1892 mean = 1690 (n = 3)	30−43 mean = 35 (n = 3)	nd[a] (n = 3)
red cabbage	68−147 mean = 98 (n = 6)	65−122 mean = 92 (n = 5)	87−722 mean = 418 (n = 5)	837−2280 mean = 1410 (n = 3)	200−400 mean = 300 (n = 3)	71−107 mean = 83 (n = 3)
turnip-rooted cabbage	nd−9 mean = 3 (n = 8)	20−42 mean = 31 (n = 4)	534−607 mean = 573 (n = 4)	561−1060 mean = 790 (n = 4)	50−78 mean = 66 (n = 4)	nd−25 mean = 18 (n = 4)
cauliflower	nd−33 mean = 11 (n = 4)	63−240 mean = 131 (n = 4)		918−2400 mean = 1620 (n = 4)	392−475 mean = 435 (n = 4)	51−193 mean = 131 (n = 4)
leek	nd (n = 4)			84−202 mean = 146 (n = 3)	22−31 mean = 28 (n = 3)	nd−18 mean = 6 (n = 3)
table mustard (medium)	58000−88000 mean = 80000 (n = 4)					

[a] Not detected (<5 μg/kg).

(2.8−3.3 mg/kg) clearly exceeded European MRLs for blossom cabbage vegetables (1.0 mg/kg; Council of the European Community, 1998). Especially the low legal limit for any pesticide residue in baby food (0.01 mg/kg) can easily be exceeded by naturally derived CS_2 in visually intact cauliflowers afflicted with slight stress factors.

CS_2 from Various Brassicaceae and Leek Depending on Food Processing Manner. As summarized in Table 2, unprocessed and visually intact plants showed no CS_2 or only small levels. Samples with single lesions, stodge, or partial infections evolved more CS_2 despite trimming by removing all bad parts. As expected, the removed waste itself amounted to higher findings, but no strict separation of tissue parts with and without the capability of forming CS_2 was achieved, indicating that surrounding tissues, still looking healthy and even in greater distances from affected spots, tend to form CS_2 or CS_2 precursors, respectively. One exception was red cabbage, which stayed in about the same range in both cases. These findings may be problematic in some instances with regard to MRLs, but those for baby foods can easily be exceeded.

Highest values were again reached after freezing of trimmed raw samples. Particularly, red cabbage and cauliflower showed CS_2 values exceeding MRLs in many cases and simulating dithiocarbamate residues. Under freezing conditions, CS_2 was found in leek, too (Table 2).

Tissue compartments destroyed during freezing and defrosting give rise to enzymatic reactions that liberate isothiocyanates from glucosinolates of cabbage vegetables. The resulting mustard oils are quite reactive and can follow many pathways, including the formation of CS_2 as already published by Pechácek et al. (1997). Therefore, foods rich in mustard oils pose serious problems for the food analyst. Especially table mustard, which can be used to season dishes, showed CS_2 contents violating MRLs if it is added at usual levels of 0.1% (w/w) or more (see Table 2).

As mentioned before, brassinines (Figure 1) as another sulfur-containing substance class are formed as a part of defense mechanisms chiefly against fungal diseases and may also be responsible for CS_2 formation, particularly in moldy samples. A lot of different sulfur-containing substances in Alliaceae, such as alkyl thiosulfonates, alkyl sulfides, or dialkyl disulfides, which are liberated by enzymatic reactions, can also be supposed to form CS_2 or its precursors via side reactions. Because nearly all enzymes lose their functional capability during heat processes, the drop of CS_2 evolved in all samples after blanching or cooking (Table 2) could be explained both as a failure of enzymatic CS_2 (pre-) formation and as devolatization of already incurred CS_2 and CS_2-forming reactants.

Behavior of Isothiocyanates and Brassinines during Acid Digestion. It is known that irritation of cruciferous plants by certain abiotic stress factors or by infection with phytopathogens leads to enforced formation of bassinines as shown by Rouxel et al. (1989, 1991). Therefore, a correlation between content of brassinines and the capability to produce CS_2 may be assumed.

Pseudobrassinine (Figure 1) as a model for brassinines was synthesized, because of the easier availability of tryptamine instead of 3-indolylmethylamine. For the determination of CS_2 either the xanthate reagent or the ethylenediamine reagent was used. The former gives no signal with COS and specifically detects CS_2; the latter allows simultaneous determination of CS_2 and COS, whereas the usually recommended copper diethanola-

Table 3. CS_2 and COS Findings after Acid Digestion of Model Substances (n = 2)

substance	CS_2 (% turnover)	COS (% turnover)
pseudobrassinine	nd[a]	43/48
phenylisothiocyanate	nd	61/63
pseudobrassinine + Na_2S	0.9/0.9	*b*
phenylisothiocyanate + Na_2S	10.6/10.8	*b*

[a] Not detected (<1 μg/digestion). [b] COS not detectable with the xanthate reagent used.

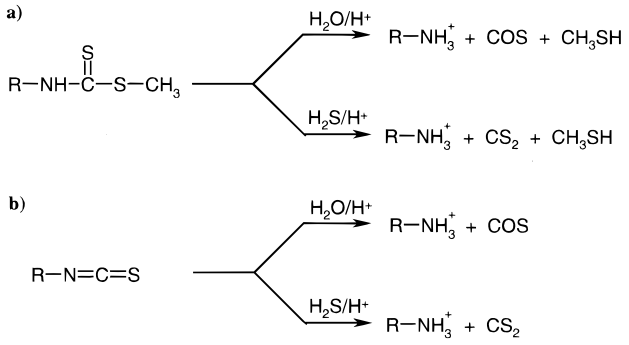

Figure 2. Proposed hydrolysis pathways of dithiocarbamic acid esters (a) and isothiocyanates (b) during acid digestion, forming COS and CS_2.

mine reagent charts both CS_2 and COS without any possibility of distinction (Schmitt and Niebergall, 1988). The determinations are not disturbed by an excess of H_2S, even if washing solutions (especially NaOH) are exhausted, because different UV spectra are obtained.

The results obtained on acid digestion of pseudobrassinine and phenylisothiocyanate as a representative of mustard oils, respectively, are shown in Table 3. As is to be expected, the digestion of pseudobrassinine follows a hydrolysis pathway (Figure 2a), which leads to liberation of COS; CS_2 was not detected. Fission of the S−CH_3 bond as a precondition to directly liberate CS_2 seems to be improbable, because mercaptomethane acts as a good nucleofuge. Similar results were found after hydrolysis of phenylisothiocyanate, with higher amounts of COS.

However, codigestion of phenylisothiocyanate with an excess of Na_2S resulted in the formation of >10 mol % CS_2, indeed. Therefore, H_2S is supposed to be capable of reacting with isothiocyanate, yielding dithiocarbamic acid as a transient on digestion terms. Its following decay will produce CS_2 (Figure 2b). The low CS_2 findings of the pseudobrassinine/Na_2S codigestion experiments showed that dithiocarbamic esters predominantly follow the proposed hydrolytic pathways, which, to some degree, can be in competition with thiolysis (Figure 2a), inside the digestion solution. Contrarily, CS_2 formation from isothiocyanates can occur in the whole digestion/distillation apparatus, especially when volatile mustard oils meet H_2S inside the condenser, explaining the remarkably higher CS_2 turnover found (Table 3).

CONCLUSIONS

The occurrence of phytogenic CS_2 sources in cabbage vegetables makes the evaluation of negotiability of analyzed food samples difficult or even impossible. Especially frozen samples showed values up to 4 mg/kg, easily exceeding MRLs. Lower CS_2 levels, found with heat-processed samples, may still be a problem to surveilling baby food samples. In this regard, representatives of the Alliaceae family can cause problems, too.

Summarizing the acid digestion results of the model substances, it can be assumed that neither brassinines nor isothiocyanates as natural components are responsible for the phytogenic formation of CS_2 on their own, but the capability of generating CS_2 in the presence of sulfide has been shown for both. It is conceivable that in-situ formation during digestion is probably surpassed by autolytic reactions or microbial decay of the plant providing H_2S and biogenic amines as a possible base for the generation of "natural" dithiocarbamates.

Our results clearly show that the evolution of CS_2 during acid digestion of crops is not unambiguous proof for the presence of dithiocarbamates. If CS_2 is found, a subsequent identification of unobstructed dithiocarbamates as real residues is necessary.

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