**Zeitschrift:** Mitteilungen aus Lebensmitteluntersuchungen und Hygiene = Travaux de chimie alimentaire et d'hygiène

**Herausgeber:** Bundesamt für Gesundheit

**Band:** 90 (1999)

**Heft:** 2

**Artikel:** Reaction products of bisphenol-A-diglycidyl ether (BADGE) and bisphenol-F-diglycidyl ether (BFDGE) with hydrochloric acid and water in canned foods with aqueous matrix. Part 2, Results from a survey of the Swiss market

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**DOI:** https://doi.org/10.5169/seals-981781

# Reaction Products of Bisphenol-A-Diglycidyl Ether (BADGE) and Bisphenol-F-Diglycidyl Ether (BFDGE) with Hydrochloric Acid and Water in Canned Foods with Aqueous Matrix

## 2. Results from a Survey of the Swiss Market

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Received 24 December 1998, accepted 16 March 1999

### Introduction

*From oily foods...*

In 1996, it was discovered that many canned foods in oil (like fish) or foods with a substantial proportion of fat or oil (soups, meat, sauces) contained Bisphenol-A-diglycidyl ether (BADGE) at concentrations exceeding the national legal limits of several European countries («not detectable at a detection limit of 20 µg/kg») by factors up to more than 1000 (1). In the mean time, measures have been taken to reduce these concentrations at least below a level of 1 mg/kg as recommended by the EU Scientific Committee of Foods (SCF) (2). Several studies from 1997 have shown that nearly all samples analyzed met this limit (3–5). In Switzerland, almost all products of this type even met the national 20 µg/kg limit. Recent toxicological studies concluded that BADGE is not cancerogenic due to fast enzymatic hydrolysis of the epoxy groups (6). At the same time BADGE.2$H_2O$ was shown to be of low toxicity.

## BADGE

Highest concentrations of BADGE were found in cans coated by organosols (PVC) and polyesters, where it was used as an additive to stabilize the polymer and improve the properties of the coating. In epoxy coatings, BADGE concentrations should be rather low because the epoxy material used is pre-polymerized («advanced») with Bisphenol A; the BADGE concentration in the resulting resin is in the region of a percent and should be further reduced by hardening the lacquer. In cans coated with epoxy polymers (hardened with phenolics, anhydrides or polyamines), foods frequently contained 0.1–1 mg/kg of BADGE, but hardly exceeded 1 mg/kg. From more recent, better optimized coatings, migration is 10–100 times lower.

## Reaction products of BADGE

Further studies revealed, however, that BADGE is by far not the only component released from can coatings that requires attention. When BADGE is applied as a stabilizer for organosol (PVC) coatings, it serves to react with hydrochloric acid (7). Chlorohydroxy compounds are formed (BADGE.HCl and BADGE.2HCl) which are considered as potential cancerogens by analogy to chloropropane diols. In oily foods, their concentrations mostly corresponded to 10–40 % of that of BADGE. In some products, however, almost all BADGE was converted to BADGE.2HCl, with concentrations reaching 3 mg/kg (8).

From epoxy coatings, highly complex mixtures of compounds are released, in HPLC producing «forests» of peaks among which BADGE may almost disappear (9, 10). Many of the migrants were identified as BADGE adducts with one or both epoxy groups reacted with a phenol (mostly tert. butyl phenol used as a chain stopper during advancement) or a hydroxylic solvent (such as butanol, butoxyethanol or methoxypropanol) (11). The sum of the mono-reaction products, which still exhibit an epoxy group, frequently exceeds 1 mg/kg, i.e. the limit set for BADGE. No proof has been provided that the mono-reaction products are detoxified equally rapidly by epoxyhydrolases as BADGE itself.

## BFDGE/NOGE

BADGE seems to be increasingly replaced by Bisphenol-F-type materials (12, 13). The two-ring analogs to BADGE, Bisphenol-F-diglycidyl ether (BFDGE, consisting of three isomers), are accompanied by compounds with 3 and more rings (for each of which there are many isomers). The technical product used is commonly called epoxy Novolak or Novolak Glycidyl Ether (NOGE). NOGE is not accepted as an educt for polymers by European positive lists, except of the o,o-BFDGE, the least important BFDGE isomer, which is encountered in an older German list. It has not been approved as an additive either. In fact, it does not seem meaningful to replace BADGE by less known materials of similar structure.

### ... to the aqueous foods

in the past, oily or fatty foods were considered to be the only risk products because oil swells and well extracts the coatings. Furthermore, oil and fat protect the epoxy groups from hydrolysis. Foods in aqueous phase were expected to be poor extractants and the small amounts of released epoxides to be fully converted to hydrolysis products of low toxicity. In simulating liquids, *Paseiro-Losada* et al. (14) and *Castle* et al. (15) indeed determined that the epoxy groups are hydrolyzed in a few days (depending on the pH). In fact, no BADGE has been found in canned beer or aqueous foods like vegetables, jam or fruits (see below).

Chlorohydroxy compounds, however, are hardly hydrolyzed and must be considered as a potential problem. Since the consumption of foods in aqueous matrix (such as sweet corn) is far higher than that of oily products, proper attention should be paid to them. The SCF has not decided yet (1998), whether the limit of 1 ppm applied to BADGE and its two hydrolysis products should include the two reaction products with hydrochloric acid, BADGE.HCl and BADGE.2HCl. The hydrolyzed BADGE.HCl, BADGE.HCl.$H_2O$, was not even considered so far, presumably because the focus was on oily foods.

In the Canton of Zurich, a market survey was undertaken, determining BADGE, BFDGE and their derivatives with water and hydrochloric acids in 270 canned products without important oil or fat phase, i.e. complementary to the surveys previously carried out. The samples were taken from local stores and covered all relevant products and producers.

The methods used were described in part 1 (16). Reversed phase LC with fluorescence detection (RPLC-FD) was used as the principal analysis. Positive samples were re-analyzed by normal phase LC (NPLC)-FD after acetylation of the extract and, if necessary, by GC-MS of the relevant LC fractions.

## Swiss limits

Samples were evaluated according to the guidelines of the Swiss Federal Office of Public Health (17). There is a legal limit of 20 µg/kg in foods for BADGE (18). A provisional limit was newly defined at 1 mg/kg for the sum of BADGE, BADGE.$H_2O$, BADGE.HCl, BADGE.2HCl and BADGE.HCl.$H_2O$ in analogy to the opinion of the SCF (2). As products in aqueous matrix do not contain the epoxy compounds, the two last HCl-adducts are relevant. Products exceeding this limit were banned from the market, justified by health risks from these toxicologically not investigated compounds. It was also considered that such high concentrations of BADGE.2HCl and BADGE.HCl.$H_2O$ are most likely to result from use of BADGE as an additive to organosols despite that BADGE seems to have never been approved as an additive to polymers. In accordance with the SCF, no legal limit was set for BADGE.2$H_2O$ since there is enough evidence that this cmpound is not of toxicological concern.

The sale of products containing BFDGE and its derivatives was stopped because of the lacking approval of this material as an additive to polymers.

Swiss legislation distinguishes between legal limits (Grenzwert) and tolerance levels (Toleranzwert), the first being related to potential health hazards, the latter to good manufacturing practice. For products exceeding the tolerance level, a warning is issued without taking it from the market. Improvement is expected within due time. For the can coatings, a temporary tolerance limit of 200 µg/kg was defined for the sum of the above compounds plus BADGE.2$H_2O$. BADGE.2$H_2O$ was considered to result from migration of BADGE.

## Results

### *Products exceeding regulated levels*

Figure 1 summarizes the results of the survey. 13 of the 270 products (5 %) were taken from the market. 103 products (38 %) exceeded the temporary tolerance level.

Table 1 lists the 13 products taken from the market. Four of them contained more than 1 mg/kg of BADGE.2HCl plus BADGE.HCl.$H_2O$. The maximum reached 8.6 mg/kg. The consumer of one of these cans ingested about 2.5 mg of these products. Three of the four cans were deep-drawn 2-piece cans from the US containing sweet corn. The fourth was a classical 3-piece can containing asparagus. All four must have been coated with an organosol. The high concentrations of BADGE.2HCl indicate treatment at high temperatures. The two products with BADGE were specialties containing some oil.

Concluded from the high concentrations of the HCl-adducts, the seven products contaminated by BFDGE derivatives were in cans coated with organosols. Since BFDGE is merely a component of NOGE (often present as a small proportion), the concentrations indicated are probably hardly more than the tip of the iceberg.

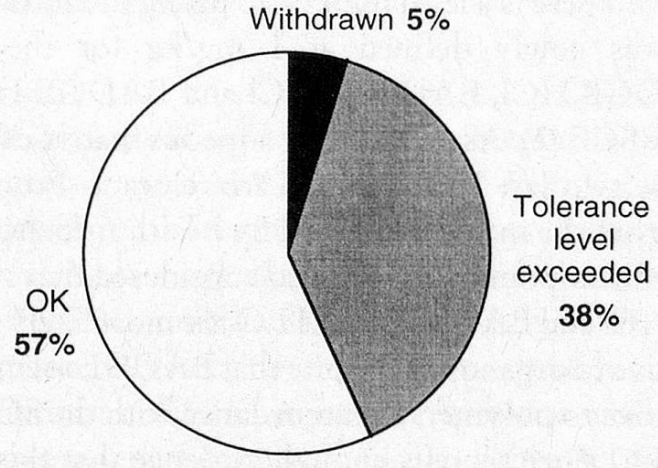


Figure 1 **Classification of the products analyzed according to Swiss regulation**

Table 1
**Products taken from the Swiss market**

| *Can type* | | *Net* | | | *BADGE* | | | | *BFDGE* | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *Body* | *Lid* | *(g)* | *Country* | *Foodstuff* | *.2H$_2$O* | *.HCl.H$_2$O* | *.2HCl* | *BADGE* | *.2H$_2$O* | *.HCl.H$_2$O* | *.2HCi* |
| 2b | b | 340 | USA | Sweet corn | 900 | 3200 | 5400 | | | | |
| 2b | b | 300 | USA | Sweet corn | 700 | 2300 | 4500 | | | | |
| 2b | go | 340 | USA | Sweet corn | 330 | 1160 | 2400 | | | | |
| 3go | go | 430 | Lesotho | Asparagus | 800 | 1500 | | | | | |
| 3g | ea g | 315 | GR | Food preparation | 520 | | | 670 | | | |
| 3g | ea g | 280 | GR | Food preparation | 220 | | | 240 | | | |
| 2w | g | 340 | F | Sweet corn | | | | | 600 | 1400 | 1500 |
| 3me | g | 200 | F | Food preparation | 550 | | | | 60 | 1400 | 470 |
| 2w | g | 340 | F | Sweet corn | | | | | 250 | 600 | 1050 |
| 3go | go | 460 | RSA | Asparagus | 60 | 120 | 35 | | 180 | 400 | 850 |
| 3me | g | 105 | F | Food preparation | 250 | | | | 70 | 300 | 380 |
| 3go | go | 290 | RSA | Asparagus | | 80 | 20 | | | 270 | 180 |
| 2w | ea go | 160 | F | Sweet corn | | | | | 25 | 130 | 210 |

Description of the cans; 2.3: 2 or 3 piece can; ea, easy open lid. Color of the coating: g, gold; go, gold opaque; w, white; b, beige. Labelled country of origin: GR, Greece; F, France; RSA, South Africa. Concentrations in the product as µg/kg. No value: concentrations below detection limits (20 µg/kg).

Table 2
**All samples classified by concentrations (µg/kg) of the components analyzed (numbers of samples)**

| *Compound* | *< 20* | *20–200* | *200–1000* | *> 1000* |
|---|---|---|---|---|
| BADGE.2$H_2O$ | 74 | 84 | 109 | 3 |
| BADGE.HCl.$H_2O$ | 173 | 80 | 13 | 4 |
| BADGE.2HCl | 253 | 11 | 3 | 3 |
| BFDGE derivatives | 263 | 0 | 3 | 4 |

### *Groups according to products*

Table 2 classifies the 270 products analyzed by concentration ranges for the critical components. BADGE.2$H_2O$ was the most abundant migrant found, while only a small minority of the products (7 %) contained measurable concentrations of BADGE.2HCl.

### Vegetables

Table 3 reports the classification of the vegetables (including mushrooms) in concentration ranges as percents. 43 % of the canned vegetables contained more than 200 µg/kg of BADGE.2$H_2O$, 3 even more than 1000 µg/kg. 36 % contained BADGE.HCl.$H_2O$ in a concentration between 20 and 200 µg/kg. BADGE.HCl.$H_2O$ may have been formed by reaction of BADGE with chloride in the food. However, many of these products did not declare addition of salt. The most likely source is BADGE.HCl as an impurity in the BADGE resulting from incomplete formation of the epoxy group. In fact, most epoxy resins analyzed contained BADGE.HCl.

### Sweet corn

From table 3, table 4 picks out those groups of products which were of special interest. Among the 20 samples of sweet corn, 6 had to be withdrawn, 3 because of too high concentrations of HCl-adducts. 55 % contained more than 200 µg/kg of BADGE.2$H_2O$. In fact, sweet corn was the worst product regarding migration of

Table 3
**Canned vegetables classified by concentration ranges (µg/kg) of the components analyzed (percentage of 126 samples)**

| *Compound* | *< 20* | *20–200* | *200–1000* | *> 1000* |
|---|---|---|---|---|
| BADGE.2$H_2O$ | 18 | 39 | 40 | 3 |
| BADGE.HCl.$H_2O$ | 56 | 36 | 5 | 3 |
| BADGE.2HCl | 93 | 4 | 1 | 2 |

Table 4
**Classification of groups of products listed above as vegetables (%)**

| *Sweet corn (n = 20)* | | | | |
|---|---|---|---|---|
| *Compound* | *< 20* | *20–200* | *200–1000* | *> 1000* |
| BADGE.2$H_2O$ | 30 | 15 | 55 | 0 |
| BADGE.HCl.$H_2O$ | 45 | 40 | 0 | 15 |
| BADGE.2HCl | 80 | 5 | 0 | 15 |
| *Asparagus (n = 15)* | | | | |
| *Compound* | *< 20* | *20–200* | *200–1000* | *> 1000* |
| BADGE.2$H_2O$ | 27 | 53 | 20 | 0 |
| BADGE.HCl.$H_2O$ | 27 | 47 | 20 | 7 |
| BADGE.2HCl | 73 | 20 | 7 | 0 |
| *Tomatoes (n = 25)* | | | | |
| *Compound* | *< 20* | *20–200* | *200–1000* | *> 1000* |
| BADGE.2$H_2O$ | 40 | 56 | 4 | 0 |
| BADGE.HCl.$H_2O$ | 88 | 8 | 4 | 0 |
| BADGE.2HCl | 96 | 4 | 0 | 0 |

BADGE and BFDGE derivatives, apparently being packed into the most problematic cans.

## Asparagus

Of 15 samples of canned asparagus, three had to be taken from the market, one because of an excessive concentration of BADGE-HCl-adducts and two because of the presence of NOGE. Concentrations of BADGE.HCl.$H_2O$ and BADGE.2HCl were higher than in any other product, presumably because of relatively frequent use of organosol coatings (which is, of course, more the result of the origin of the product and the cans used there than the product itself).

## Tomatoes

Only one out of 20 products each of canned tomatoes exceeded 200 µg/kg of BADGE.2$H_2O$ and BADGE.HCl.$H_2O$, respectively. Tomatoes were, in fact, the least contaminated vegetable product in this investigation, which might be explained by the facts that of many cans only the lids were coated and at least a majority of the products were not sterilized at 121 °C.

## Fruits

Table 5 reports results for fruits, such as pineapple, peaches or fruit salads. Only in 8 of 66 samples BADGE.2$H_2O$ exceeded 200 µg/kg. The highest concentration of BADGE.HCl.$H_2O$ was 25 µg/kg. This result may be explained by many cans with

Table 5
**Canned fruits classified by concentration ranges (µg/kg). Percentages of 66 samples**

| *Compound* | *< 20* | *20–200* | *200–1000* | *> 1000* |
|---|---|---|---|---|
| BADGE.2$H_2O$ | 64 | 24 | 12 | 0 |
| BADGE.HCl.$H_2O$ | 98 | 2 | 0 | 0 |
| BADGE.2HCl | 100 | 0 | 0 | 0 |

uncoated side walls (totally uncoated cans were eliminated from this survey) as well as by the product not being sterilized.

### Food preparations

67 % of the canned food preparations, like ravioli, soups and sauces, contained more than 200 µg/kg of BADGE.2$H_2O$, 17 % more than 200 µg/kg of BADGE.HCl.$H_2O$ (table 6). Nearly all cans were fully coated. It is assumed that these products had been sterilized.

Table 6
**Canned food preparations classified by concentration ranges (µg/kg). Percentages of 80 samples**

| *Compound* | *< 20* | *20–200* | *200–1000* | *> 1000* |
|---|---|---|---|---|
| BADGE.2$H_2O$ | 10 | 23 | 67 | 0 |
| BADGE.HCl.$H_2O$ | 52 | 40 | 17 | 0 |
| BADGE.2HCl | 90 | 7 | 3 | 0 |

### *Distribution between liquid and solids*

For a number of products, the liquid and the solid phase were analyzed separately in order to determine the distribution of the components within the can content. Table 7 shows the concentrations of BADGE.2$H_2O$, BADGE.HCl.$H_2O$ and BADGE.2HCl in the two phases as well as the percentage of the material in the solids calculated through the net weight and the weight of the solids.

Most of the migrated material seems to be concentrated in the solids. For BADGE.2$H_2O$ the results range between 76 % (asparagus) and over 95 % (beans). For BADGE.HCl.$H_2O$ partitioning into the solids was even higher and of BADGE.2HCl no significant amount was found in the liquid surrounding the asparagus, indicating an almost total localization in the solids. This suggests that the aqueous phase primarily behaves as a transport medium between the coating and the solids. Extraction from the liquid into the solids is probably an important reason for the high efficiency by which aqueous foodstuffs extract the coatings (see below).

Table 7

**Distribution of BADGE.2$H_2O$, BADGE.HCl.$H_2O$ and BADGE.2HCl between the solid and the liquid phase in the canned product as well as the percentage of the material in the solids**

| *Coating* | *Net* | *Solids* | *Product* | *in solids (µg/kg)* | | | *in liquid (µg/kg)* | | | *% in solids* | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *Body/lid* | *g* | *g* | | *.2$H_2O$* | *.HCl.$H_2O$* | *.2HCl* | *.2$H_2O$* | *.HCl.$H_2O$* | *.2HCl* | *2$H_2O$* | *.HCl.$H_2O$* |
| 3go/go | 290 | 175 | Asparagus | 453 | 980 | 325 | 168 | 56 | < 20 | 80 | 96 |
| 3go/go | 460 | 270 | Asparagus | 167 | 228 | 43 | 73 | 18 | < 20 | 76 | 95 |
| 3w/w | 425 | 260 | Peas | 490 | 38 | < 20 | 65 | < 20 | < 20 | 92 | > 75 |
| 3go/go | 340 | 285 | Sweat corn | 168 | 53 | 15 | 64 | 13 | < 20 | 93 | 95 |
| 3w/ea g | 150 | 140 | Sweat corn | 222 | 49 | 19 | 70 | 5 | < 20 | 98 | 99 |
| 3g/g | 425 | 250 | Mango | 236 | < 20 | < 20 | 102 | < 20 | < 20 | 77 | |
| 3g/g | 800 | 440 | Beans | 339 | < 20 | < 20 | 21 | < 20 | < 20 | 95 | |

For the characterization of the can coating, see table 1

*Extraction from the can coating*

The extent by which aqueous foods extract the coating was determined by comparison of the concentrations found in the foodstuffs and those in the acetonitrile extract performed after emptying the can. Since the epoxy compounds extracted into the aqueous food are hydrolyzed, the BADGE.2$H_2O$ concentration in the food was compared with the sum of BADGE, BADGE.$H_2O$ and BADGE.2$H_2O$ in the coating. BADGE.HCl.H2O in the food was related to BADGE.HCl and BADGE.HCl.H2O in the acetonitrile extract, neglecting a possible formation of BADGE.HCl by reaction of an epoxy group with chloride from salt.

The results of table 8 show a strong variation of the extraction efficiencies. For instance, asparagus extracted between 16 and more than 96 % of BADGE and its hydrolysis products from the can coating. Differences are probably related to the type of coating (characterized by its color at the left of the table). Results for sweet corn, mushrooms and peas were in the same range. BADGE.HCl/ BADGE.HCl.H2O and BADGE.2HCl were extracted more efficiently than BADGE and its hydrolysis products.

Table 5 has shown that fruits contained clearly less migrants from the coating than the other products. In some cases (e.g. the sample of canned peach halves of table 8) this is partly explained by the non-coated side wall of the can. However, the other results clearly show that the main reason is a far lower extraction efficiency (2–8 % only for BADGE and its hydrolysis products). In contrast to the vegetable products listed in the upper part of the table, fruits are not sterilized.

Table 8 also shows the frequently high contents of BADGE in the coatings of these rather randomly selected samples. Adding the BADGE extracted by the food, many of the cans had the potential of contaminating the products at a level exceeding 1 mg/kg. It must, furthermore, be assumed that BADGE reacts with food components forming compounds not detected by the analytical methods used, i.e. the real presence of BADGE could still be underestimated.

The coatings of three of the four fruit cans contained substantially more BADGE.2$H_2O$ than BADGE. It may have resulted from hydrolysis of BADGE inside the coating (acidity of the product), but could also have been present as such in the lacquer. The latter seems more probable when considering the low concentration of BADGE.$H_2O$: hypothetical hydrolysis of BADGE in the coating should have been expected to result in BADGE.$H_2O$ concentrations clearly exceeding those of BADGE.

In the coating of the cans containing vegetable products, hardly any BADGE.2$H_2O$ was found. Since the coatings of cans for fruits and vegetables are likely to be similar, this might indicate an almost complete extraction of BADGE.2$H_2O$ during sterilization. The two products with no residual BADGE in the coating but important concentrations of BADGE.2$H_2O$ in the foods (one of the asparagus and the peas) further suggest the possibility that almost all of the BADGE.2$H_2O$ has been extracted as such.

Table 8

**Proportion of BADGE and its reaction products extracted from the can coating into foods in aqueous matrix. Concentrations in the foods and in the acetonitrile extracts of the coatings as well as the percentage of extracted material**

| *Can* | *Product* | *Food (µg/kg)* | | | *Coating-extract (µg/kg can content)* | | | | | | *Extraction by food (%)* | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Body/ lid* | | *.2$H_2O$* | *.2HCl* | *.HCl.$H_2O$* | *BADGE* | *.2$H_2O$* | *.$H_2O$* | *.2HCl* | *.HCl.$H_2O$* | *.HCl* | *BADGE* | *.2HCl* | *.HCl* |
| 3g/g | Asparagus | 90 | < 20 | 70 | < 20 | < 50 | < 20 | < 20 | < 50 | < 20 | > 80 | | |
| 3go/go | Asparagus | 800 | < 20 | 1500 | 70 | < 20 | < 20 | < 20 | < 20 | 20 | 92 | | 99 |
| 3go/g | Asparagus | 140 | 370 | 550 | 722 | < 20 | < 20 | 392 | 87 | 635 | 16 | 49 | 46 |
| 3go/go | Asparagus | 60 | 35 | 120 | < 5 | < 20 | < 20 | 40 | < 20 | 20 | > 90 | 47 | 86 |
| 3go/go | Asparagus | 453 | 325 | 980 | < 20 | < 20 | < 20 | < 20 | < 20 | < 20 | > 96 | > 96 | > 98 |
| 3go/go | Asparagus | 167 | 43 | 228 | 110 | 9 | 33 | < 20 | < 20 | 39 | 54 | | 85 |
| 2b/b | Sweet corn | 900 | 5400 | 3200 | 1920 | < 20 | < 20 | 890 | < 20 | 2000 | 32 | 86 | 62 |
| 3go/go | Sweet corn | 390 | 40 | 170 | 1175 | < 20 | < 20 | < 20 | < 20 | 63 | 25 | | 73 |
| 3go/go | Sweet corn | 240 | < 20 | 60 | 403 | < 20 | 26 | < 20 | < 20 | 36 | 36 | | 63 |
| 3go/go | Sweet corn | 168 | 15 | 53 | 238 | < 20 | 24 | < 20 | < 20 | 23 | 39 | | 70 |
| 3w/ea g | Sweet corn | 222 | 19 | 49 | 238 | 21 | 24 | < 20 | < 20 | 23 | 46 | | 68 |
| 3g/g | Mushrooms | 40 | < 20 | 30 | < 20 | < 20 | < 20 | < 20 | < 20 | < 20 | > 60 | | |
| 3w/w | Peas | 490 | < 20 | 38 | < 20 | 13 | < 20 | < 20 | < 20 | < 20 | > 96 | | |
| 3me/go | Peaches | < 20 | < 20 | < 20 | 84 | 30 | 56 | < 20 | < 20 | < 20 | < 20 | | |
| 3w/w | Cherries | 40 | < 20 | < 20 | 328 | 1361 | 204 | < 20 | 218 | < 20 | 2 | | |
| 3w/w | Plums | 90 | < 20 | < 20 | 727 | 1362 | 215 | < 20 | 149 | 71 | 4 | | |
| 3w/w | Plums | 100 | < 20 | < 20 | 283 | 605 | 238 | 33 | 158 | 52 | 8 | | |

For the characterization of can coating, see table 1

*Effect of sterilization*

The effect of heating during sterilization was simulated with three canned products containing fruits, all cans with white internal coating. The content of one can was analyzed. Another full can of the same lot was heated in a pressure cooker at about 120 °C for 1.5 h. As shown in table 9, the simulated sterilization increased the concentrations of BADGE.$H_2O$ in the fruits by a factor of 2.5 to 5. Two of these cans also released significant amounts of BADGE reacted with butoxyethanol on one side and with water on the other (BADGE.BuEtOH.$H_2O$), the concentrations of which increased to a similar extent.

Table 9

**Concentrations of BADGE.2$H_2O$ and BADGE.BuEtOH.$H_2O$ in canned fruits as bought («before») and after heating at about 120 °C for 1.5 h («after»)**

| *Product* | *BADGE.2$H_2O$* | | *BADGE.BuEtOH.$H_2O$* | |
|---|---|---|---|---|
| | *before* | *after* | *before* | *after* |
| Cherries | 40 | 207 | < 20 | 85 |
| Plums | 108 | 279 | 89 | 263 |
| Plums | 91 | 447 | | |

The strong influence of sterilization on the concentration of BADGE.2$H_2O$ in the food was confirmed by a comparison of the products known to be mostly not sterilized (filled in hot), i.e. tomatoes and fruit, and products sterilized in the can, such as vegetables and food preparations. From the 91 cans with tomatoes and fruits, 57 % contained less than 20 µg/kg BADGE.2$H_2O$ and merely 10 % exceeded the tolerance level of 200 µg/kg (table 10). Of the 179 presumably sterilized products, however, only 12 % contained less than 20 µg/kg BADGE.2$H_2O$ while 58 % of the results exceeded 200 µg/kg. The same effect is observed for the HCl-adducts. Only 4 % of the non-sterilized products contained more than 20 µg/kg BADGE.HCl.$H_2O$, while it were 52 % of those sterilized. The non-sterilized products were mostly unsalted, which leaves open whether the HCl-adducts primarily originate from BADGE.HCl in the coating or more from BADGE reacting with chloride ions in the food.

Table 10

**Canned food classified by concentration ranges (µg/kg), distinguishing between 179 presumably sterilized (+) and 91 non-sterilized samples (–)**

| | *< 20* | | *20–200* | | *200–1000* | | *> 1000* | |
|---|---|---|---|---|---|---|---|---|
| *Sterilization* | + | – | + | – | + | – | + | – |
| BADGE.2$H_2O$ | 12 | 57 | 30 | 33 | 56 | 10 | 2 | 0 |
| BADGE.HCl.$H_2O$ | 48 | 96 | 43 | 3 | 7 | 1 | 2 | 0 |
| BADGE.2HCl | 91 | 99 | 6 | 1 | 2 | 0 | 2 | 0 |

*Type of can and coating*

Table 11 shows data from an attempt to evaluate coatings through simple characteristics. Only sterilized products were considered, i.e. no fruits or tomatoes. Of the 9 products in 2-piece cans (most containing sweet corn), 6 had to be taken from the market. These cans are deep-drawn, i.e. the side wall and the bottom are made from the same piece. Most commonly the coating is applied before shaping and must be highly flexible, a requirement best fulfilled by organosols. The high temperature often involved causes the formation of large amounts of HCl-adducts. On the other hand, the migration of BADGE and NOGE derivatives from two of the nine cans was below the tolerance level, indicating that it is possible to produce «clean» 2-piece cans.

Table 11
**Evaluation of can types for sterilized products**

| *Can* | *Coating color* | *Number of samples* | *Evaluation (%)* | | |
|---|---|---|---|---|---|
| | | | *OK* | *above tolerance* | *above limit* |
| 2 piece | all | 9 | 22 | 11 | 67 |
| 3 piece | | | | | |
| easy open | all | 19 | 26 | 68 | 5 |
| normal | g | 51 | 57 | 43 | 0 |
| | go | 24 | 33 | 54 | 13 |
| | gr | 6 | 33 | 67 | 0 |
| | w | 62 | 16 | 84 | 0 |

Among the 3-piece cans, there were 19 samples with an easy open lid. Since these lids were often shaped after coating (mostly with organosols), previous results indicated a higher migration than for the classical cans (1). The data in table 11 does not enable to draw an unambiguous conclusion on this.

Among the classical 3-piece cans without an easy open lid, the coatings of a golden color ranked best. The coatings of an opaque gold included the organosols with high levels of HCl-adducts, but since a third of the related products remained below the tolerance level, no simple classification is possible on this aspect either. The white coatings were characterized by low migration of HCl-adducts, but the highest release of BADGE.$2H_2O$.

## Conclusions

Swiss regulations distinguish between legal limits based on toxicological concern and tolerance level essentially aiming at the enforcement of good manufacturing practices, such as a minimization of migration. The results obtained for the canned foods in aqueous matrix should be reviewed from this optic.

5 % of the samples were taken from the market because the HCl-adducts of BADGE and NOGE (of which merely BFDGE has been analyzed) are of toxicological concern. If up to several milligrams of these compounds are ingested with a single can, there must be good evidence that they are non-toxic. It is difficult to understand why such products could be on the market for more than a decade without really being questioned. Firstly, there has been no testing of the toxicity of the HCl-adducts although their presence must have been anticipated since they are resulting from the intended use of BADGE. Secondly, the use of BADGE and NOGE has never been authorized as an additive, probably because it was predictable that it is not integrated into the polymer. It appears that enforcement of regulations has failed.

38 % of the samples exceeded the temporary tolerance value of 200 µg/kg for the sum of all the BADGE derivatives. Of the 103 samples involved, 7 primarily contained HCl-adducts whereas in 93 only the concentration of BADGE.2$H_2O$ significantly exceeded 200 µg/kg. These high concentrations of BADGE.2$H_2O$ came as a surprise because this compound was assumed to be the hydrolysis product of BADGE being released into the food. On the one hand, the acetonitrile extracts from emptied cans have confirmed that many coatings still contain large amounts of BADGE, supporting the hypothesis. On the other hand, many of the cans manufactured and filled in Switzerland have been tested for BADGE (acetonitrile extracts, 24 h at 25 °C), with results mostly being below 2 µg/$dm^2$. Hence, concentrations in the food exceeding 20 µg/kg could not be explained this way.


## Summary

From the local market, 270 products of canned food in aqueous matrix were analyzed for BADGE, BFDGE and their reaction products with water and hydrochloric acid. With the exception of two products containing some oil, none of them contained expoxy compounds. 11 products had to be taken from the market because the sum of BADGE.2HCl plus BADGE.HCl.$H_2O$ exceeded the provisional Swiss legal limit of 1 mg/kg or because of substantial contents of non-authorized BFDGE derivatives. The most important products of concern were sweet corn in deep-drawn 2-piece cans and asparagus in classical 3-piece cans. 103 products exceeded the temporary tolerance value of 200 µg/kg defined for the sum of all derivatives, in most cases because of BADGE.2$H_2O$. More than 75 % of the contaminant material was in the solids of the foods. Extraction of coatings by foods reached efficiencies of around 50 % for sterilized products, but remained below 10 % for the non-sterilized. Chlorohydroxy compounds were extracted more efficiently.



## Zusammenfassung

270 Dosenkonserven mit Lebensmitteln in wässeriger Phase vom lokalen Markt wurden auf BADGE, BFDGE und deren Reaktionsprodukte mit Wasser und Chlorwasserstoff untersucht. Mit Ausnahme zweier ölhaltiger Produkte wurden in

keiner Probe Epoxyverbindungen gefunden. 11 Konserven mussten vom Markt zurückgezogen werden, weil die Summe der Konzentrationen von BADGE.2HCl und BADGE.HCl.$H_2O$ den schweizerischen provisorischen Grenzwert von 1 mg/kg überschritt oder namhafte Mengen von nicht zugelassenen BFDGE-Derivaten gefunden wurden. Die wichtigsten betroffenen Produkte waren Süssmais in tiefgezogenen 2-Teil- und Spargeln in klassischen 3-Teil-Dosen. 103 Produkte überschritten den vorläufigen Toleranzwert von 200 µg/kg für die Summe aller BADGE-Derivate, meistens wegen BADGE.2$H_2O$. Mindestens 75 % der Kontaminantien befanden sich in den Festteilen des Lebensmittels. Die sterilisierten Lebensmittel lösten rund die Hälfte von BADGE und dessen Hydrolysenprodukten aus dem Lack, die nicht sterilisierten weniger als 10 %. Die Chlorhydroxyverbindungen wurden noch besser extrahiert.


## Résumé

Les teneurs en BADGE, BFDGE et leurs produits de réaction avec l'eau et l'acide chlorhydrique ont été analysés dans 270 échantillons de conserves en boîte provenant du marché local. A l'exception de deux échantillons huileux, aucune contenait de composés epoxy. Onze produits ont été retirés du marché parce que la somme des concentrations en BADGE.2HCl et BADGE.HCl.$H_2O$ dépassait la limite provisoire suisse de 1 mg/kg ou parce qu'ils contenaient des quantités importantes de dérivés du BFDGE, dont l'utilisation n'est pas autorisée. Parmi les produits les plus concernés se trouvait du maïs dans des boîtes sous-vide en 2 parties ou des asperges dans des boîtes classique en 3 parties. 103 produits dépassaient la valeur de tolérance provisoire de 200 µg/kg pour la somme de tous les dérivés du BADGE, principalement en raison du BADGE.2$H_2O$. Plus de 75 % des contaminants se trouvaient dans la partie solide des l'aliments. Les aliments stérilisés en boîte dissolvent près de la moitié du BADGE et de ses produits hydrolysés présents dans le verni. Les aliments non-stérilisés en boîte dissolvent moins de 10 %. Les composés chlorohydroxy ont été encore mieux extraites.



## Key words

Canned foods, Migration from can coatings, Bisphenol-A-diglycidyl ether, Bisphenol-F-diglycidyl ether, Hydrolysis products, Hydrochlorination products


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# Studio degli Aspetti Microbiologici (Trasformazione e Conservazione) di un Prodotto Vegetale Fermentato (Brovada Friulana)

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Presentato il 22 gennaio 1998, accettato il 15 marzo 1999

## Introduzione

La brovada è un prodotto tipico regionale friulano (Friuli-Venezia Giulia) costituito da rape bianche *(Brassica rapa* ssp. *rapa)* fatte fermentare a contatto con vinacce (1).

La conservazione dei vegetali per fermentazione è un processo conosciuto fin dall'antichità ed ancora oggi largamente utilizzato. I prodotti più importanti sono crauti, cetrioli, olive; mentre altri vegetali quali carote, cipolle, peperoni, pomodori, e rape presentano una diffusione locale e più limitata (2).

La produzione di brovada è tipicamente artigianale e segue cicli stagionali: da settembre, periodo di maturazione delle rape, fino ad aprile. Per tradizione locale infatti, la brovada è un piatto che si consuma nei mesi più freddi dell'anno, cotta insieme ad un particolare tipo di insaccato fresco simile al cotechino chiamato «musèt».

### *Tecnologia di produzione*

Le rape intere, dopo la raccolta, vengono lavate meccanicamente per eliminare terra, radichette ed altre parti grossolane. Trascorsi 1–2 giorni per effettuarne l'asciugatura, le rape vengono poste a macerare in tini con strati alterni di vinacce; lo strato superficiale è formato da vinacce. Il riempimento dei tini viene completato con liquido di governo costituito da liquido di torchiatura delle vinacce e aceto in ragione del 5–6 %; i tini vengono quindi chiusi con coperchi di legno. Le vinacce utilizzate per la fermentazione delle rape possono provenire da diversi tipi di uva, pre-

feribilmente nera come Cabernet, Merlot, oppure miste. Il tempo di permanenza delle rape nei tini è di 30–40 giorni ad una temperatura di circa 15°–17 °C. Trascorso tale periodo le rape vengono tolte dai tini, sbucciate in maniera rudimentale, tagliate a fini listelli, confezionate in sacchetti termosaldati di materiale plastico da circa un chilogrammo ed avviate al mercato locale, con una conservabilità massima consigliata di 30 giorni in ambiente «fresco» (fig. 1).

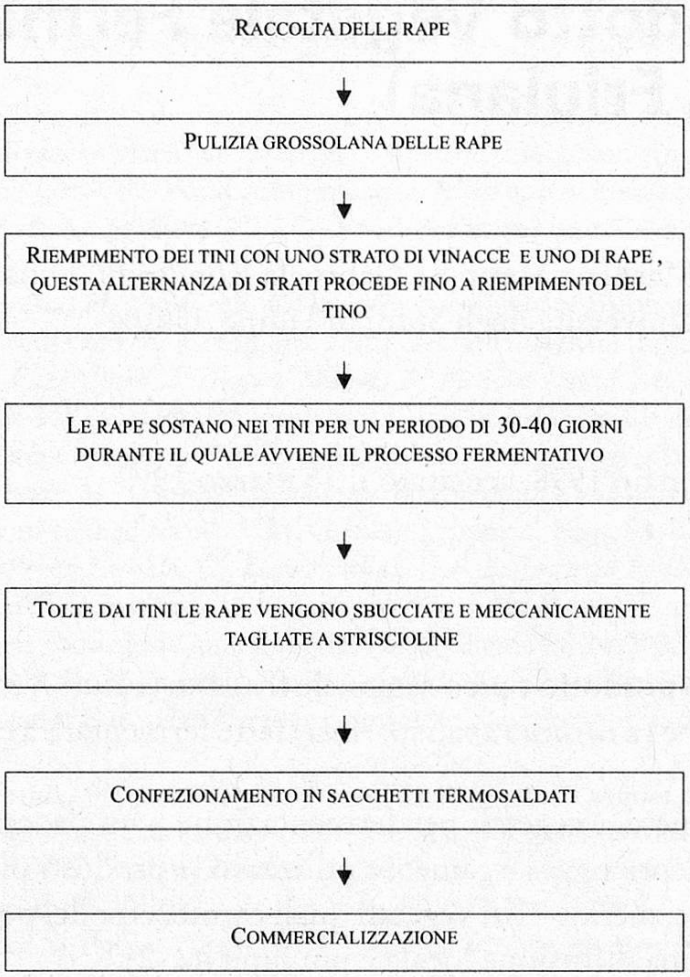


Figura 1 **Diagramma di flusso della produzione della «brovada»**

Il prodotto si presenta con una consistenza elastica, colore crema-rosato.

Le vinacce delle varie lavorazioni non sempre vengono eliminate, possono essere conservate per le lavorazioni dell'anno successivo in vasche coperte da uno spesso strato di sabbia in un luogo al riparo dalla luce.

Pur rientrando nella categoria dei vegetali a fermentazione lattica, la brovada a differenza di altri prodotti, presenta caratteristiche non costanti in quanto i microrganismi responsabili della fermentazione sono quelli che naturalmente si trovano sulle rape e sulle vinacce e non vengono utilizzate colture di microrganismi selezionati come può avvenire nella tecnologia di preparazione dei crauti (3–5), prodotto che si avvicina maggiormente come caratteristiche organolettiche e tecnologiche alla

brovada. Inoltre la temperatura di conservazione, la composizione del liquido di governo e la qualità delle vinacce sono sensibilmente variabili.

Risulta quindi complesso fare una precisa caratterizzazione microbiologica del prodotto.

La brovada risulta anche di difficile conservazione; infatti nel prodotto confezionato parte della microflora di fermentazione rimane ancora vitale ed a questa si aggiunge una flora contaminante ambientale dovuta alla sbucciatura e taglio delle rape. Nonostante il valore di pH sia di circa 3,6, la brovada confezionata non è un prodotto stabile ed i microrganismi presenti provocano periodicamente fenomeni di gonfiore del sacchetto.

Data quindi la peculiare tipologia del prodotto, ci è parso interessante effettuare alcune indagini chimiche e microbiologiche con un duplice obiettivo: fornire una possibile caratterizzazione e studiare i problemi connessi con la sua conservazione nell'ottica anche di una più ampia distribuzione commerciale.

## Materiali e metodi

Sono stati seguiti 4 cicli di lavorazione per determinare l'evoluzione della flora microbica durante l'intero processo produttivo: le analisi microbiologiche sono state effettuate sulla materia prima (rapa), ogni 7 giorni durante la fase di trasformazione nei tini e ogni 15 giorni durante il periodo di conservazione a 12 °C ± 1 °C nelle confezioni di materiale plastico termosaldato (sull'etichetta compare la scritta «conservare in luogo fresco»). Sono stati inoltre esaminati campioni di vinacce e liquido di governo.

Sono state eseguite le seguenti determinazioni:

- conta batterica totale su piastre di terreno Plate Count Agar (Oxoid), pH 7,0 ± 0,2 incubate a 30 °C per 48 ore
- batteri lattici totali su piastre di terreno MRS Agar (Oxoid), pH 6,2 ± 0,2 incubate a 30° in condizioni di microaerofilia (10 % $CO_2$, 6 % $O_2$) per 72 ore
- lieviti e muffe su piastre di Malt Extract Agar (Oxoid), pH 5,4 ± 0,2 incubate a 30 °C per 48 ore
- determinazioni di pH
- determinazione dell'acido D-L lattico e acido acetico per via enzimatica (Boehringer Mannheim)

L'identificazione dei batteri isolati è stata effettuata secondo lo schema proposto dal Bergey's Manual of Sistematic Bacteriology (6, 7), mentre i lieviti isolati sono stati identificati secondo le metodiche proposte da Kreger van Rij (8).

### *Prove di conservazione*

Per migliorare la stabilità del prodotto è stato preso in considerazione il IV ciclo di lavorazione sul quale sono state condotte le seguenti prove di pastorizzazione (9):

a) trattamento termico superficiale del prodotto confezionato in buste di materiale plastico a 80 °C per 10 min

b) trattamento termico superficiale del prodotto confezionato in buste di materiale plastico a 80 °C per 15 min

I processi di pastorizzazione sono stati effettuati presso l'azienda produttrice dei campioni. I campioni erano stati confezionati in sacchetti di materiale plastico termoresistente chiusi con termosaldatura in unità da 500 g. Il trattamento termico dei punti a) e b) è stato effettuato in vasca termostatata, a bagnomaria con termocoppia inserita all'interno del sacchetto di brovada tra il film plastico e lo strato di brovada a contatto con lo stesso film plastico per seguire il profilo di penetrazione del calore. Il ciclo di pastorizzazione è stato valutato dal momento in cui veniva rilevato il raggiungimento degli 80 °C sulla parte esterna del prodotto.

I prodotti confezionati sono stati conservati a temperatura di 12 °C ± 1 °C.

Subito dopo il confezionamento, a 15 e a 30 giorni di conservazione sono state effettuate le analisi microbiologiche relative a conta batterica totale, batteri lattici totali e lieviti e muffe.

Le determinazioni sono state condotte in triplo.

Sono stati utilizzati come controllo campioni dello stesso ciclo di lavorazione confezionati secondo il metodo usuale e non pastorizzati.

Per tutti i campioni sono state effettuate determinazioni di pH.

E' stata valutata inoltre la modificazione del colore dovuta al trattamento termico attraverso l'utilizzo di un colorimetro tristimolo (Chroma Meter CR200 Minolta, Japan), con scala di riferimento di Hunter nel sistema di misura C.I.E. in cui lo spazio viene definito in termini di lucentezza (L) e di coordinate cromatiche (a) e (b); in questo lavoro è stato valutato il parametro L (luminosità) che rappresenta la componente grigia: da 0 (nero) a 100 (bianco).

Tale colorimetro dà un'indicazione diretta delle differenze di colore approssimate a quelle dell'occhio umano. Ciò risulta utile non tanto a specificare un colore in termini assoluti, quanto a misurare differenze di colore.

Le misurazioni sono state effettuate direttamente su campioni di brovada. Ogni valutazione è stata effettuata su tre campioni con 10 misurazioni per campione. Non esistono in letteratura riferimenti bibliografici di valutazione del colore per questo prodotto, ma è stata valutata la misurazione del colore per altri vegetali o prodotti di origine vegetale (10, 11).

## Risultati e discussione

All'inizio della fermentazione nei tini, la microflora lattica totale non presenta cariche elevate, queste sono dell'ordine di $10^3$–$10^4$ UFC/g, e provengono dalle rape ed in minor misura dalle vinacce. Nei giorni successivi i batteri lattici si moltiplicano attivamente raggiungendo valori $10^7$ UFC/g, in un caso $10^8$ UFC/g. Le cariche di lattici si mantengono pressoché costanti o diminuiscono di poco fino a 30–35 giorni, quando le rape vengono tolte dai tini. Durante la fermentazione della rapa *(Brassica rapa)* sono presenti anche lieviti appartenenti al genere *Saccharomyces* le cui cariche sono però molto variabili da lavorazione a lavorazione. Essi derivano principalmen-

te dalle vinacce, ma a causa della disomogeneità di queste ultime, i lieviti possono presentare valori da $10^2$ a più di $10^7$ UFC/g. Le cariche iniziali si modificano poco durante il processo fermentativo, rimanendo quasi invariate fino al termine di tale periodo (fig. 2). Dopo la fase di estrazione delle rape dai tini, la trinciatura ed il confezionamento con liquido di governo, che nella prassi comune avviene senza subire trattamenti termici di pastorizzazione, le cariche di batteri lattici della brovada pronta per la vendita si mantengono elevate intorno a $10^5$–$10^7$ UFC/g e tali rimangono fino al termine della vita commerciale del prodotto. Le temperature consigliate dai produttori («al fresco» cioè intorno a 12° ± 1 °C) consentono infatti un prolungamento dell'attività fermentativa dei lattici all'interno della confezione. Analogamente anche i lieviti non presentano variazioni significative durante la conservazione, anche se in alcuni casi tendono ad aumentare (fig. 3).

L'identificazione delle specie lattiche isolate alle varie fasi di fermentazione è riportata nella tabella 1.

I lattici presenti appartengono al genere *Lactobacillus;* la specie *L. hilgardii* è stata isolata dalle vinacce e successivamente anche in tutte le fasi del processo fermentativo e di conservazione. Dalle rape inoltre sono stati isolati cocchi omofermentanti identificati come *Pediococcus parvulus*. A differenza di quanto riportato da alcuni autori (2, 12) dove il processo fermentativo nei crauti è condotto all'inizio principalmente dalla specie eterofermentante *Leuconostoc mesenteroides,* specie ritenuta interessante per l'utilizzo come starter nella preparazione degli stessi (3–5), nel caso della brovada questa specie non è mai risultata essere presente.

I batteri lattici eterofermentanti prevalgono per circa tre settimane, poi la loro attività diminuisce e il processo fermentativo risulta principalmente a carico delle specie omofermentanti.

Durante il periodo di consevazione sono risultati essere principalmente presenti le specie *L. plantarum* e *P. parvulus*.

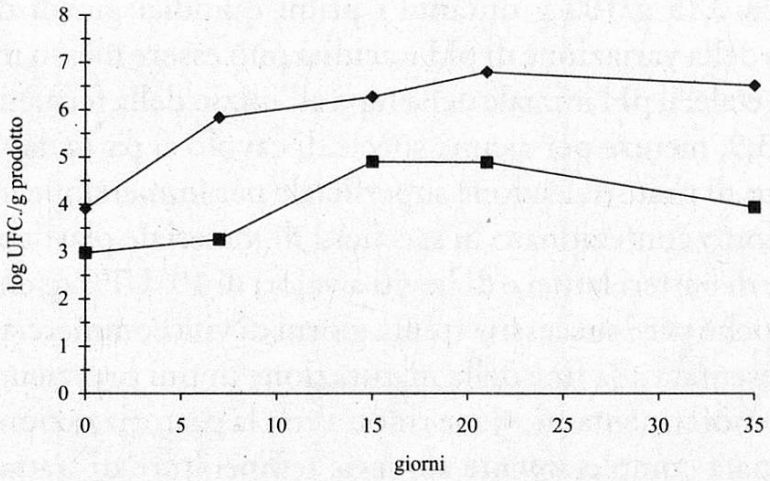


Figura 2 **Evoluzione della flora lattica e dei lieviti durante il processo fermentativo della rapa (◆: batteri lattici, ■: lieviti)**

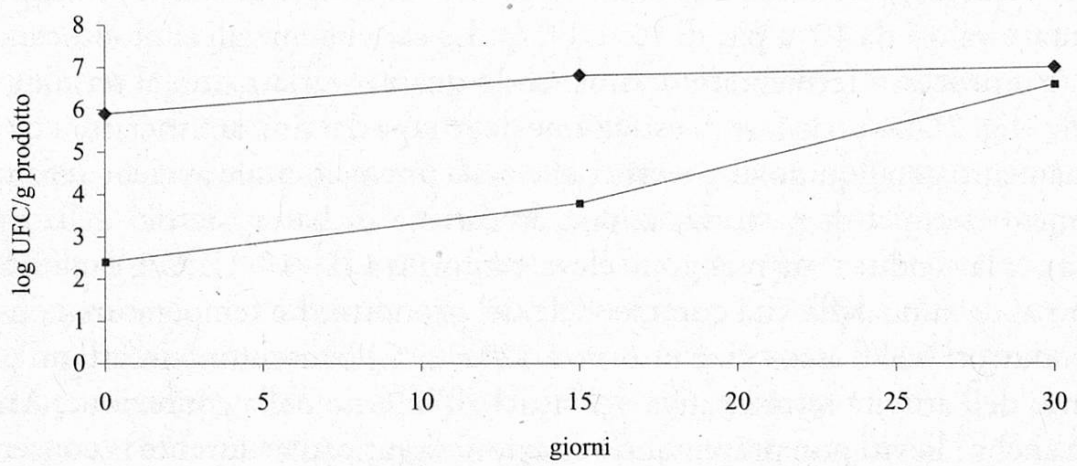


Figura 3 **Evoluzione della flora lattica e dei lieviti durante la fase di conservazione della brovada non pastorizzata in sacchetti di materiale plastico termosaldato (◆: batteri lattici, ■: lieviti)**

Tale dinamica è analoga a quanto riportato a proposito del processo fermentativo dei crauti ed altri vegetali fermentati, in cui all'inizio della trasformazione del vegetale si assiste ad un maggior sviluppo di specie eterofermentanti con produzione di acido acetico, acido lattico ed altre componenti volatili che conferiscono particolari caratteristiche organolettiche, mentre nelle fasi finali della tecnologia di produzione prevalgono le specie omofermentanti (13).

Durante il corso della fermentazione avviene una diminuzione di pH fino a circa 3,6 in relazione ad un aumento del contenuto di acido lattico che raggiunge dopo tre settimane valori di 0,9 g/100 g, rimanendo pressoché costante per il restante periodo di permanenza delle rape nei tini. L'aumento di acido lattico durante le ultime fasi della fermentazione presuppone che la trasformazione del vegetale sia operata prevalentemente dalla flora lattica omofermentante. L'acido acetico raggiunge il valore massimo di circa 0,15 g/100 g durante i primi quindici giorni di fermentazione (fig. 4). L'effetto della variazione di pH e acidità può essere messo in relazione anche alla specie di vegetale; il pH iniziale della rapa all'inizio della fermentazione si attesta a valori tra 3,8–3,9, mentre per alcune specie di cavolo si parte da valori di 5,7 (14).

Il trattamento di pastorizzazione superficiale per immersione in acqua a 80 °C x 10 min del prodotto confezionato in sacchetti di materiale plastico termoresistente riduce le cariche di batteri lattici e di lieviti a valori di $10^2$ UFC/g che si mantengono quasi invariati anche per i successivi trenta giorni di vita commerciale (fig. 5). La flora lattica, rappresentata alla fine della maturazione in tini prevalentemente da lattobacilli e cocchi omofermentanti, viene ridotta con la pastorizzazione, ma comunque non viene eliminata completamente a queste temperature di trattamento, considerando inoltre che la temperatura al cuore del prodotto al termine del ciclo di pastorizzazione è di 54 °C (15). Il prolungamento del trattamento termico superficiale a 15 min, pur diminuendo ulteriormente la carica microbica, determina una variazio-

Tabella 1
**Specie di batteri lattici durante il processo fermentativo della rapa e durante la conservazione del prodotto finito**

| | *Vinacce* | *Rapa in tino inizio lavorazione* | *Rapa in tino a 7gg* | *Rapa in tino a 14gg* | *Rapa in tino a 21gg* | *Rapa in tino a 28gg* | *Conservazione a 1gg* | *Conservazione a 15gg* | *Termine conservazione* |
|---|---|---|---|---|---|---|---|---|---|
| *Lact. hilgardii* | x | | x | x | x | x | x | x | |
| *Lact. fructosus* | | | x | | | | | x | x |
| *Lact. confusus* | | | x | | | | | | |
| *Lact. sanfrancisco* | | x | x | | x | | | x | |
| *Lact. fructivorans* | | | | x | | x | | | |
| *Lact. viridescens* | | x | | | x | | | | x |
| *Lact. alimentarius* | | | | | | x | | | |
| *Lact. buchneri* | | | | | | x | | | |
| *Lact. amylophylus* | | | | | | x | | x | |
| *Lact. curvatus* | | | | | | x | | | |
| *Lact. casei* | | | | | | | x | x | |
| *Lact. plantarum* | | | x | x | | | x | x | |
| *Pedioc. parvulus* | | x | x | | | | x | x | x |

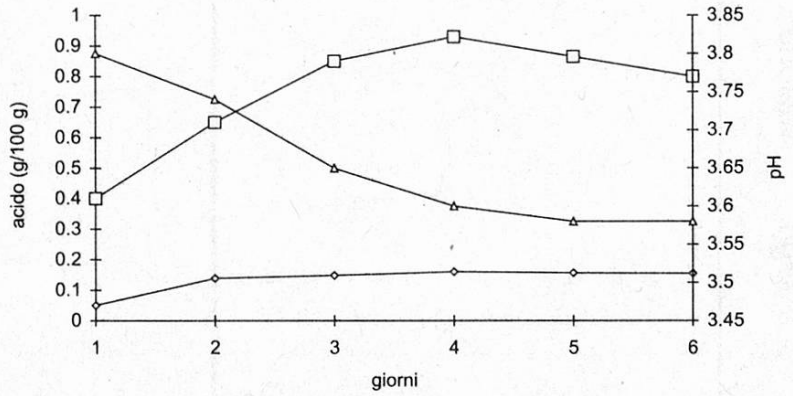


Figura 4 **Formazione di acido lattico e acido acetico e variazioni di pH durante il processo fermentativo della rapa (Brassica rapa ssp. rapa) (□: acido lattico, ◆: acido acetico, ▲: pH)**

ne riscontrabile visivamente della consistenza della brovada che risulta più simile ad un prodotto cotto, più molle e con rilascio di liquido di governo.

Le analisi al colorimetro per valutare variazioni di colore della brovada dovute al trattamento termico superficiale di stabilizzazione a 80 °C x 10 min, non hanno rilevato differenze significative del parametro L rispetto al prodotto non pastorizzato, per tutta la durata della conservazione.

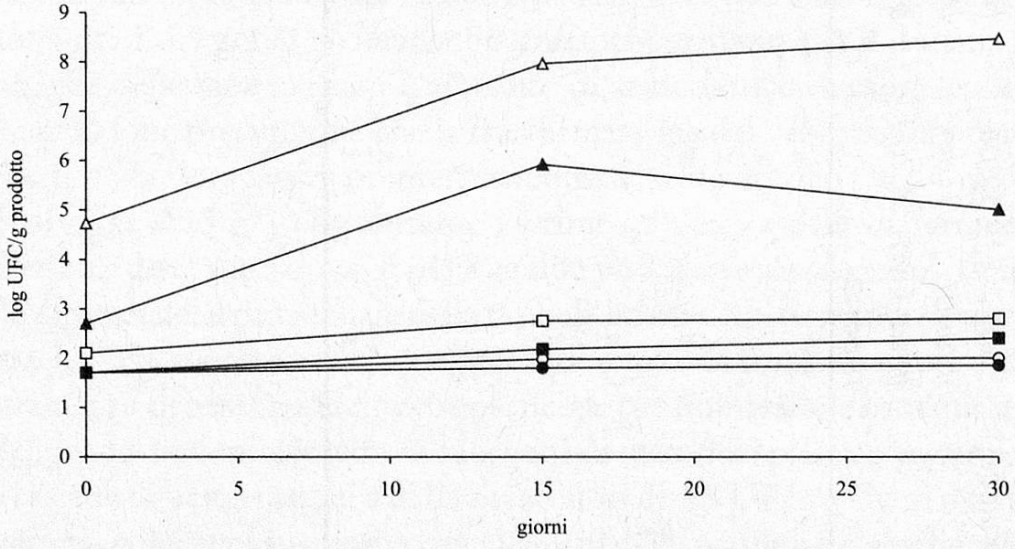


Figura 5 **Evoluzione dei batteri lattici e dei lieviti a diversi trattamenti di pastorizzazione superficiale a 80 °C: sviluppo di batteri lattici (Δ) e di lieviti (▲) del sacchetto confezionato non pastorizzato; sviluppo di batteri lattici (□) e di lieviti (■) dopo pastorizzazione superficiale per 10 min del sacchetto confezionato; sviluppo di batteri lattici (○) e di lieviti (●) dopo pastorizzazione superficiale per 15 min del sacchetto confezionato.**

## Conclusioni

La fermentazione spontanea che avviene per la produzione della brovada friulana (*Brassica rapa* ssp. *rapa* fermentata) presenta caratteristiche simili ai crauti (12).

Dalle indagini condotte in questo lavoro la brovada si presenta come un prodotto abbastanza stabile dal punto di vista commerciale per il basso valore di pH 3,6, ma la scarsa attenzione alle temperature di conservazione durante le fasi di distribuzione sul mercato determinano la necessità di attuare degli interventi per rendere più stabile il prodotto. Il trattamento di pastorizzazione superficiale in sacchetti di materiale plastico termoresistente a 80 °C x 10 min è risultato essere efficace a questo scopo senza modificazioni particolari del prodotto stesso. Inoltre tale trattamento troverebbe facile applicazione anche in un tipo di produzione artigianale come appunto avviene per la brovada e consentirebbe una maggiore diffusione del prodotto su una zona più ampia di territorio, incontrando la tendenza moderna del consumatore che si orienta sempre più spesso verso la scelta di prodotti tipici regionali.


## *Riassunto*

La brovada, prodotto tipico del Friuli-Venezia Giulia (Italia), è simile ai crauti e deriva dalla trasformazione di rape bianche *(Brassica rapa* ssp. *rapa)* a contatto con vinacce attraverso un processo fermentativo ad opera principalmente di batteri lattici. In questo lavoro è stato valutato l'andamento della flora microbica dei batteri lattici e dei lieviti durante l'intero processo di trasformazione e successiva conservazione del prodotto dopo confezionamento. Tra i batteri lattici le specie presenti sono risultate appartenere ai generi *Lactobacillus* e *Pediococcus,* mentre predominante tra i lieviti risultava il genere *Saccharomyces.*

Sono state eseguite delle prove di conservazione utilizzando trattamenti di pastorizzazione sul prodotto confezionato (trattamento superficiale). Il trattamento di pastorizzazione superficiale (80 °C x 10 min) è risultato essere vantaggioso per aumentare il tempo di conservazione del prodotto.



## Zusammenfassung

Die sogenannte «Brovada» ist ein typisches Gericht aus Friaul-Julisch-Venetien (Italien). Sie ähnelt Sauerkraut und wird aus weissen Rüben (*Brassica rapa* ssp. *rapa*) hergestellt, die geraspelt und anschliessend mit Trester einem Gärungsprozess überwiegend mit Hilfe von Milchsäurebakterien unterzogen werden. In der vorliegenden Arbeit wurde die Entwicklung der mikrobiellen Flora der Milchsäurebakterien und der Hefen während des gesamten Gärungsprozesses sowie die anschliessende Konservierung des Produktes nach der Abfüllung bewertet. Die beteiligten Milchsäurebakterien gehören zur Gattung *Lactobacillus* und *Pediococcus,* während es sich bei der Hefe überwiegend um die Gattung *Saccharomyces* handelt.

Die Haltbarkeitstests wurden unter Verwendung von Pasteurisierungsmethoden am abgefüllten Produkt (Oberflächenbehandlung) vorgenommen. Die Ober-

flächenpasteurisierung (80 °C x 10 min) zeigte steigernde Wirkung auf die Haltbarkeitsdauer des Produkts.


## Résumé

La «brovada» est un produit typique de la région Friuli-Venezia Giulia (Nord-est de l'Italie) qui ressemble à la choucroute. Elle est obtenue en transformant des raves blanches (*Brassica rapa* ssp. *rapa*) en contact avec des marcs de raisin et grâce à un procédé de fermentation créé principalement par des bactéries lactiques. Cette recherche a permis d'évaluer le développement de la flore microbienne des bactéries lactiques et des levures tout au long du procédé de transformation et pendant la conservation du produit après conditionnement. Les espèces de bactéries lactiques présentes appartenaient aux genres *Lactobacillus* et *Pediococcus,* tandis que le genre prédominant parmi les levures était le *Saccharomyces.*

On a effectué des essais de conservation en utilisant des traitements de pasteurisation sur produit conditionné (traitement superficiel). Une pasteurisation superficielle (80 °C x 10 min) s'est révélée adéquate pour augmenter le temps du conservation du produit.

## Summary «Microbiological Aspects (Processing and Storage) of a Fermented Vegetable («Brovada»)»

«Brovada» is a typical product of the Friuli region (Italy) similar to sauerkraut. Brovada is the product resulting from the natural lactic acid bacteria fermentation of white turnips (*Brassica rapa* ssp. *rapa*) in the presence of vinasse. In this study, the distribution of bacteria and yeast species was evaluated during fermentation and storage of a commercially packed product.

*Lactobacillus spp., Pediococcus spp.* and *Saccharomyces spp.* were the most frequently identified bacteria and yeasts, respectively.

Surface pasteurisation treatments of commercially packed «brovada» were investigated to improve product shelf-life. Surface treatment (80 °C for 10 min) of commercially packed «brovada» increased the product's shelf-life.



## Key words

Fermented turnip, Vegetables, Lactic acid bacteria, Yeasts, Pasteurization


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