Food contaminants

unintentional entry into food chain

- agriculture production
- pollution of environment
- storage, transportation, sale
- technological and cooking practice

classification

- primary contaminants (exogenous) — outside sources
- secondary contaminants (endogenous) — formation in food

contamination sources

agriculture production

- use of pesticides
- fertilisation
- emission
- water for irrigation
- use of surface water for irrigation
- attack by microorganisms, especially by moulds
- veterinary treatment

storage and processing

- post harvest application of pesticides
- formation from relatively non-toxic pesticides
- attack by microorganisms
- technological and cooking arrangement
- penetration of additives from plastic materials

judgement criteria

- potential risk and effects on human health
- incident frequency, proved as human or animal toxicant
- frequent occurrence in food representing important items of food basket
- persistence and frequency of occurrence in environment, possible conversion to products with higher toxicity, ability to be accumulated in food basket
- amount of entrance environment from industry, agriculture, urban agglomeration and other sources
- importance of food in which the given contaminant is present from the point of international trade

priority contaminants

- **mycotoxins and other microbial toxins**
- **toxic elements**
- **radioactive isotopes**
- **nitroso compounds**
- **polycyclic aromatic hydrocarbons**
- **halogen containing organic compounds**
- **pesticides residua**
- **veterinary drug residua**
- **other contaminants (ethylcarbamate, contaminants from packaging materials)**

standards and recommendation - ***Codex Alimentarius FAO/WHO***

legislation in CZ ***Zákon o potravinách a tabákových výrobcích č. 110/1997 Sb., Vyhláška č. 298/1997 Sb***

perception of health risks associated with food

Order	Scientist	General public
1	biological hazards	pesticides residua
2	natural toxins	industrial contaminants
3	industrial contaminants	additives
4	veterinary drug residua	veterinary drug residua
5	pesticides residua	biological hazards
6	additives	natural toxins

MYCOTOXINS

- toxic secondary metabolites of some moulds
- ~ 20 toxicologically important mycotoxins

producers moulds *Aspergillus, Penicillium, Fusarium*

OCCURRANCE

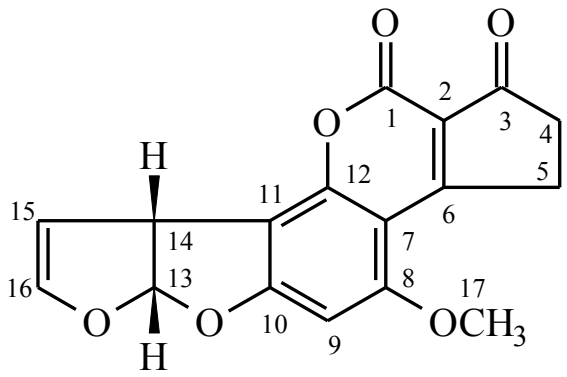
- mouldy food
- residua in animal tissues and products
- foods produced by cultural moulds
- biotechnological products

FACTORS INFLUENCING CONTAMINATION

- biological
- chemical
- other (water activity, temperature)

Aflatoxins

- *Aspergillus* sp. (*A. flavus, A. parasiticus*), temperature, humidity (subtropical and tropical climate conditions)
- aflatoxins B and G
- high level – corn, groundnut, pistachio
- medium level - almond, walnut, raisin, spices
- toxicity (hepatotoxic, mutagenic, carcinogenic)



aflatoxin B_1

Changes in aflatoxin B_1 and M_1 levels during processing of contaminated materials

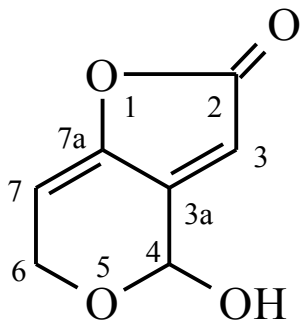
product	processing conditions	losses (%)
Peanuts	roasting, 150 °C, 30 min	20
	roasting in oil	35
peanut products	roasting, 204 °C	50-60
peanut oil	heating, 120°C, 10 min	0
milk	pasteuristion 72°C, 45 s	35
	sterilisation 115°C	19

hygienic limits

e.g.	generally	20 - 40 $\mu g.kg^{-1}$ (sum)
	baby food	2 $\mu g.kg^{-1}$ (M_1)
	infantile food	1 $\mu g.kg^{-1}$ (M_1)

Patulin

- *Penicillium patulinum, P. expansum*
- apple, grapes, orange, ordinary contaminant of fruit concentrates and juices (< 0.1 mg.kg^{-1})



4-hydroxy-4H-furo(3,2-c)pyran-2(6H)-on (patulin)

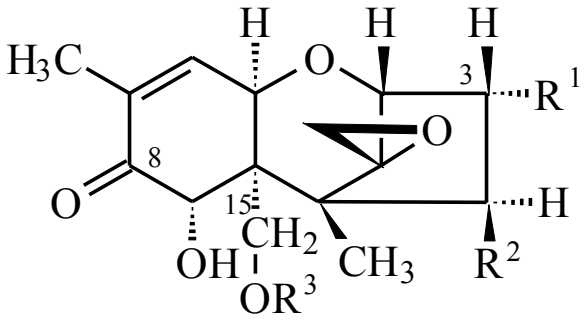
- relatively stable at pH 3.0-6.5
- antibiotic, antifungant, antivirus effects vs. cancerogenity, mutagenity

changes during processing and storage

- storage –slow decrease
- juice thickening by vacuum distillation under vacuum – decrease for about 25%
- pasterisation (90°C/10 s) - decrease for about 20%
- ethanol fermentation – rapid degradation
- micro-wave heating - decrease for about 40 - 95%

trichothecenes

- *Fusarium sp.*
- cereals, oil plants, beer
- deoxynivalenol, nivalenol, T-2 toxin



deoxynivalenol, R^1 = OH, R^2 = H, R^3 = H

BACTERIAL TOXINS

- exotoxins a endotoxins
- exotoxins – enterotoxins, cytotoxins neurotoxins

hygienic limits not determined

botulotoxins

- *Clostridium botulinum*
- neurotoxins, polypeptides, 19 amino acids
- non acidic preserved food products (smoked meats)
- anaerobic conditions, pH 4.8-8.5, 30 °C
- inactivation 80 ° C/10 min., 100 ° C/seconds
- factors water activity, temperature, NaCl, nitrites

other bacterial toxins

- *Staphylococcus aureus, C. perfringens, Bacillus cereus*

infection, propagation and formation of toxins in digestive tract

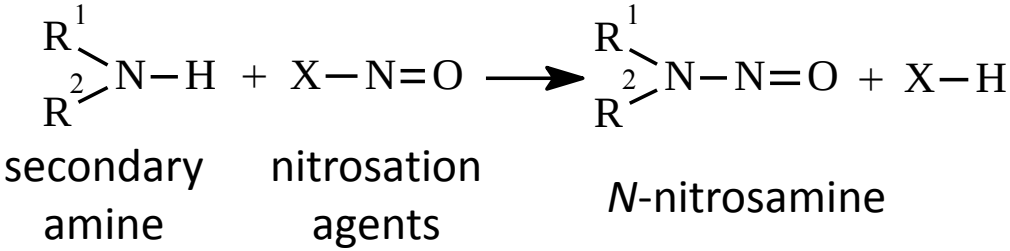
- *Escherichia coli, Salmonella enteritidis, S. typhimurium*

primary source meat, milk and eggs

NITROSO COMPOUNDS

reaction products of secondary amines with nitrosation agents:

nitration of secondary amines



secondary amine — nitrosation agents — *N*-nitrosamine

- **secondary amines: amino acids, biogenic amines etc.**
- **nitrosation agents: nitrosyl cation NO^+ , nitrogen oxides**
- **factors: pH, temperature, time, catalyst, reaction inhibitor**

classification

- **volatile nitrosamines: N-nitrosodimethylamine**
- **non-volatile nitrosamines N-nitrososarcosine**

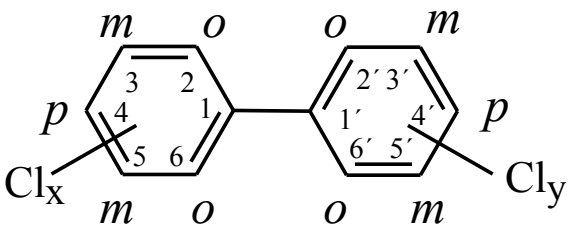
TOXICOLOGY

- **mutagenic, teratogenic, carcinogenic effects**

PERSISTENT ORGANOCHLORINE COMPOUNDS

polychlorinated biphenyls

- **209 congeners**



ring 1 ring 2

$C_{12}H_{10-(x+y)}Cl_{x+y}$

(x+y = 1-10, x = number Cl in circle 1, y = number Cl in circle 2)

physical-chemical properties of technical PCB

- thermostability and photostability
- incombustible
- chemically inert
- high permitivity and excellent heat properties
- excellent miscibility with organic solvents
- high boiling points

bioacumulation

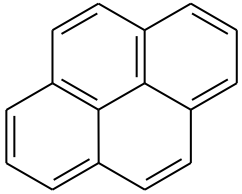
- bioconcentration (passive diffusion)
- biomagnification (due to transfer in food chain)

typical environmental distribution of PCBs in the eighties of the 20th century

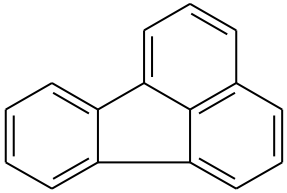
components of environment	concentration ($mg.kg^{-1}$)
vegetation	0.001 – 0.01
zooplankton	0.005 – 2.0
marine invertebrates	0.005 – 10
fish	0.01 – 25
marine mammal	0.1 - 1000 (in fat)
birds	0.1- 1000 (in fat)
eggs	0.05 - 500 (in fat)
humans	0.1 - 50 (in fat)

POLYCYCLIC AROMATIC HYDROCARBONS (PAH)

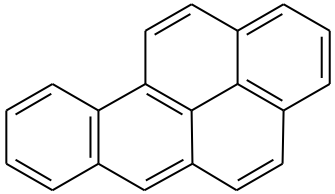
compounds with 2-6 condensed benzene rings



pyrene



fluarenthene



benzo[*a*]pzrene (B[*a*]P)

- **formation by pyrosynthesis of organic matter (500-900 °C, for example by combustion of fossil fuels)**
- **some have mutagenic, carcinogenic activity**

PESTICIDES

- higher harvest
- negative influence of agricultural chemisation

classification

- according to activity
  - insecticides (Insects)
  - acaricides (Mites)
  - fungicides (Fungi)
  - herbicides (Plant)
  - molluscicides (Snails)
  - rodenticides (Rodents)
  - regulators of plant growth, dessicators

insecticides

- **interaction with cell membranes, neurotoxicity (persistent chlorinated hydrocarbons)**
- **inhibition of acetylcholinesterase, neurotoxicity (organophosphates, carbamates, pyrethroids)**
- **inhibition of chitin biosyntesis (esters of benzoylcarbamide)**

herbicides

- **interference with biosynthesis of nucleic acids (phenoxyalkanoic and benzoic acids)**
- **interference with photosynthesis (triazines, uracils)**
- **reaction with cell membranes (bipyridyls)**
- **retardation of germination (nitroanilines)**

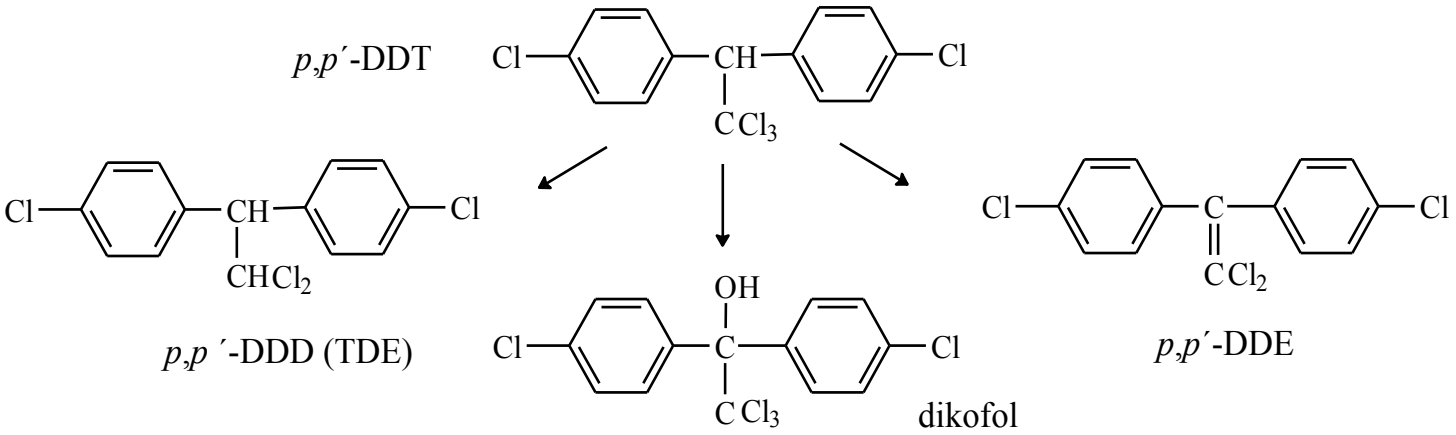
fungicides

- **inhibition of enzymatic systems (ethylenebisdithiocarbamates, phtalimides)**
- **interference with DNA biosynthesis (benzimidazoles)**

PERSISTENT CHLORINATED HYDROCARBONS

contact insecticides

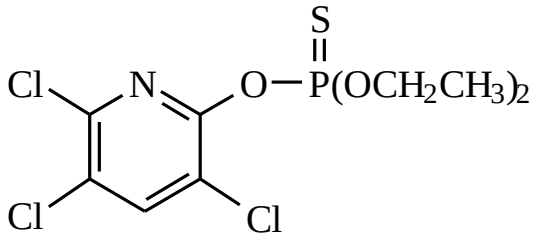
DDT, aldrin, dieldrin, toxafen, heptachlor, hexachlorbenzen (HCB), ⍰-HCH, lindan, hexachloran, pentachlorfenol



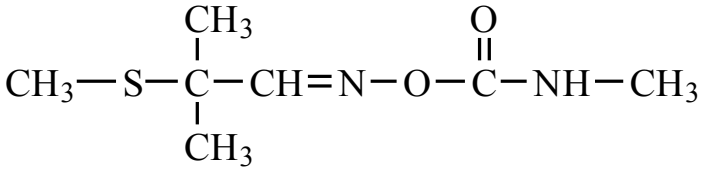
products of p,p´-DDT transformation

MODERN PESTICIDES

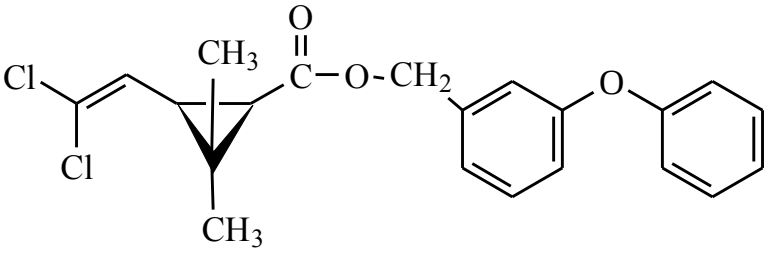
Insecticides



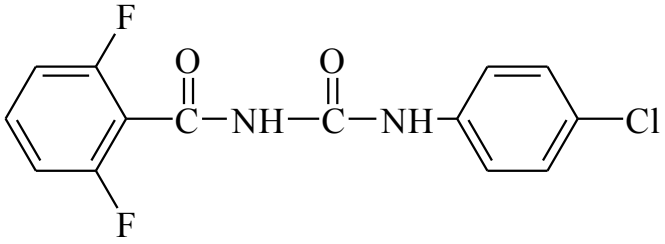
chlorpyrifos (organophosphate)



aldicarb (carbamate)



permethrin (pyrethroid)

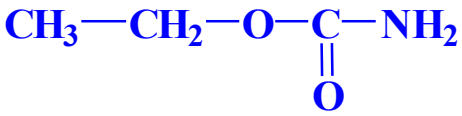


diflubenzuron

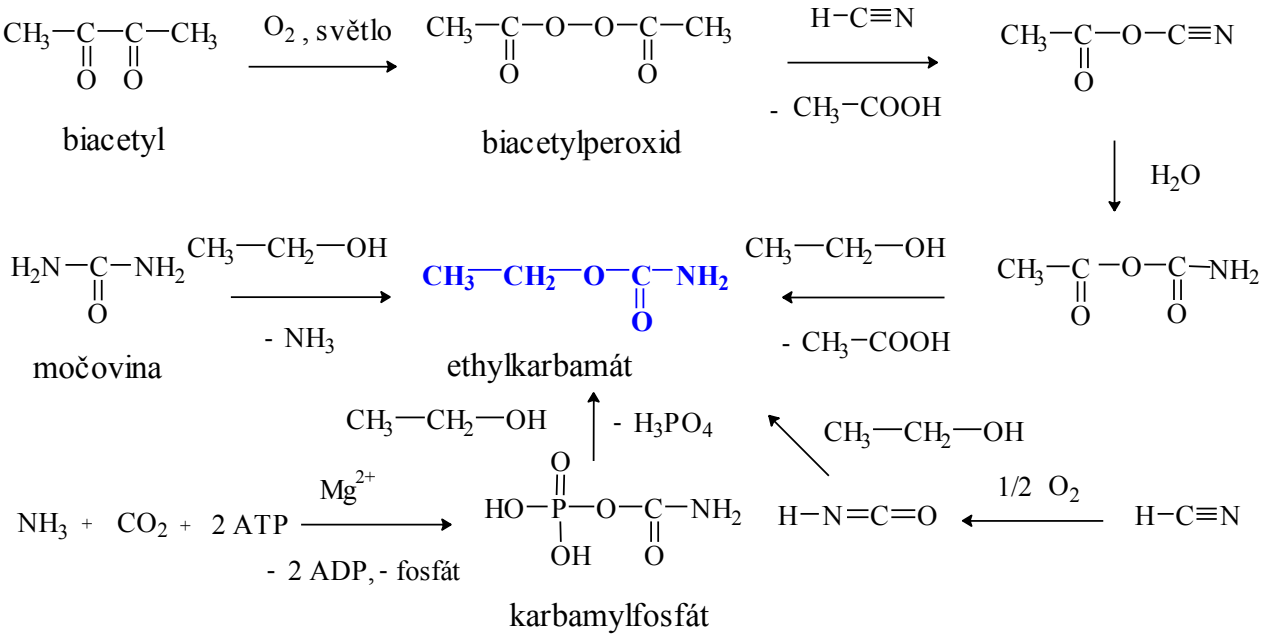
(esters benzoylcarbamide)

other contaminants

ethyl carbamate



- natural compound of product of fermentation
- potential human carcinogen
- hygienic limits for wine, fruit distillates



	Concentration ($\mu g.kg^{-1}$)
Food	
Bakery products	nd-20
Fermented dairy products	nd
Fermented sauces	nd-18
Vinegars	nd-33
Yeast extracts	41
Alcoholic beverages	
Beers	nd-1
Wines	nd-24
Rice wines (sake)	81-164
Liquers	nd-170
Vodka	nd-2140
Whisky	nd-1000
Rum	nd-1020
Brandy	nd-2100
Fruit brandy	nd-7920
Stone fruit brandy	nd-22 000

nd = not detected

chloropropanols

secondary / endogenous contaminants

process / technological contaminants

1978 Velíšek J., Davídek J., Hajšlová J., Kubelka V., Janíček G., Mánková B.: Chlorohydrins in protein hydrolysates. *Z. Lebensm. Unters. Forsch.*, **167**, 241-244

Z. Lebensm. Unters. Forsch. 167, 241–244 (1978)

Zeitschrift für
Lebensmittel-
Untersuchung
und -Forschung

Chlorohydrins in Protein Hydrolysates

Jan Velíšek, Jiří Davídek, Jana Hajšlová, Vladislav Kubelka*, Gustav Janíček, and Blanka Mánková
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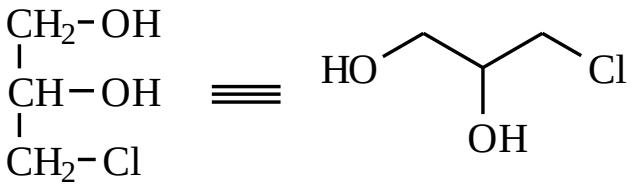
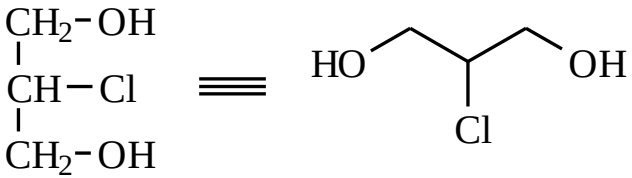
Chlorhydrine in Eiweißhydrolysaten

Zusammenfassung. Es wurden vier Proben der Neutralfraktionen von Eiweißhydrolysaten mittels der

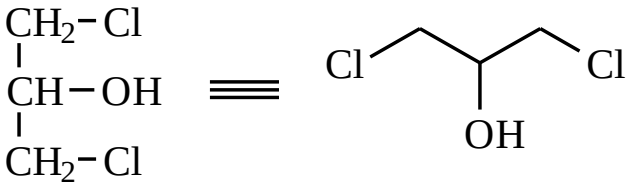
Seasonings containing amino-acids, namely the chemical hydrolysates of proteins, used for the improvement of flavour of foods and to enhance their meaty flavour, have become important commodities in fabricated



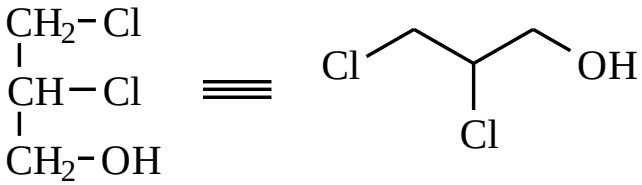
3-chloropropan-1,2-diol (**3-MCPD**)



2-chloropropan-1,3-diol (2-MCPD)



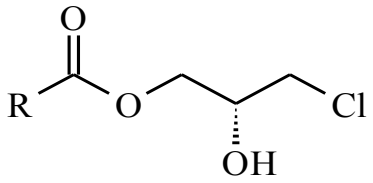
1,3-dichloropropan-2-ol (1,3-DCP)



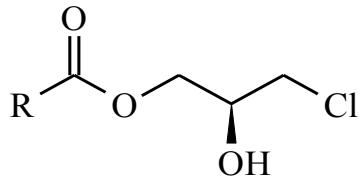
2,3-dichloropropan-1-ol (2,3-DCP)

esters of chloropropanols

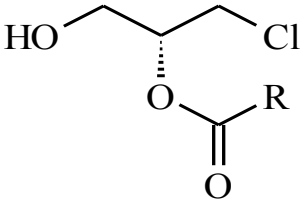
monoesters of 3-MCPD with fatty acids



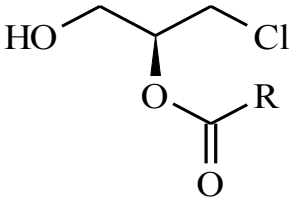
(2*R*)-1-acyl-3-chloropropan-1,2-diol



(2*S*)-1-acyl-3-chloropropan-1,2-diol

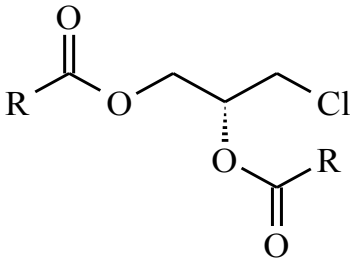


(2*R*)-2-acyl-3-chloropropan-1,2-diol

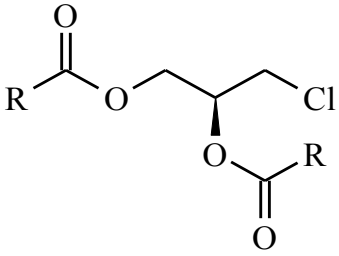


(2*S*)-2-acyl-3-chloropropan-1,2-diol

diesters of 3-MCPD with fatty acids



(2*R*)-1,2-diacyl-3-chloropropan-1,2-diol



(2*S*)-1,2-diacyl-3-chloropropan-1,2-diol

7 groups of esters → more than hundred of individual compounds

Fat components:
TAG, DAG, MAG

+

Chloride source:
NaCl, HCl

↓ Thermal processing (NaCl)
Acid-catalysed hydrolysis (HCl)

ESTERS OF
CHLORPROPANOL

factors of formation

- ❑ content of fat and its composition (ratio of TAG, DAG, MAG)
- ❑ content of chlorides
- ❑ content of water
- ❑ temperature and time of heating
- ❑ pH

CONTAMINANTS FROM PACKAGING MATERIALS

corrosion , migration

- **metals**
- **glass and ceramics**
- **paper**
- **wood**
- **polymeric materiales**

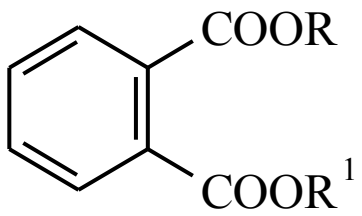
  residua of raw materials

  residua of auxiliary substances (additives)

  residua of degradation products or additives

PHTALATES

- plasticizer of plastics
- possible teratogenic, carcinogenic effects
- estrogenic activity
- hygienic limits (book 3, tab.12.59) permitted level, alc. drinks=1.0 $mg.kg^{-1}$ (DBP+ DEHP)



Dibutylphthalate $R = R^1 = (CH_2)_3CH_3$

bis(2-ethylhexyl)phthalate $R = R^1 = CH_2CH(CH_2CH_3)(CH_2)_3CH_3$

occurrence in food

- contamination of raw materials
- contamination of finished products from packaging material

factor influencing migration

- kind of polymers
- kind of food
- temperature
- time of contact
- quantity in food and others.