Uptake kinetics across the leaf cuticle

Properties and Functions of the Green Skin

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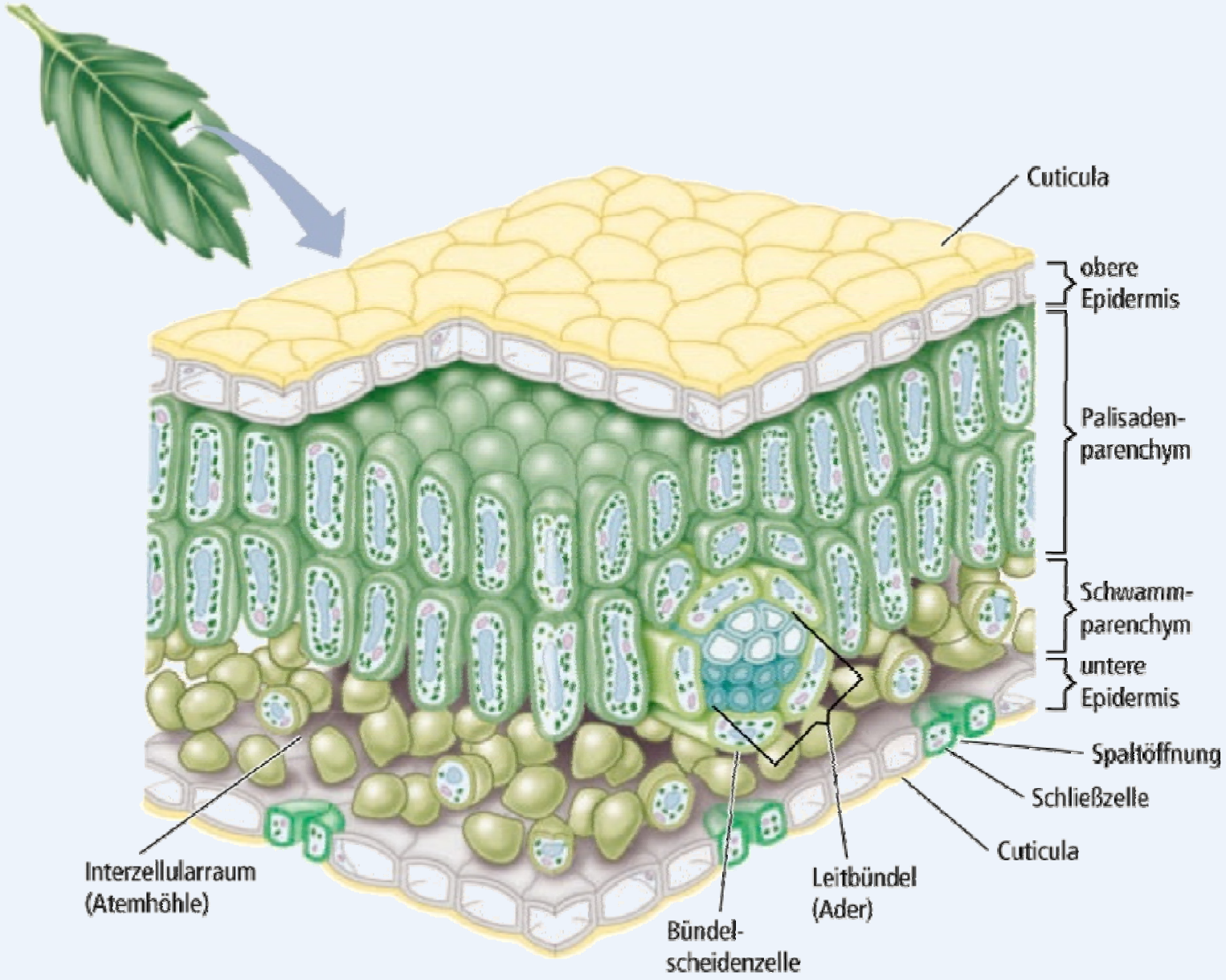
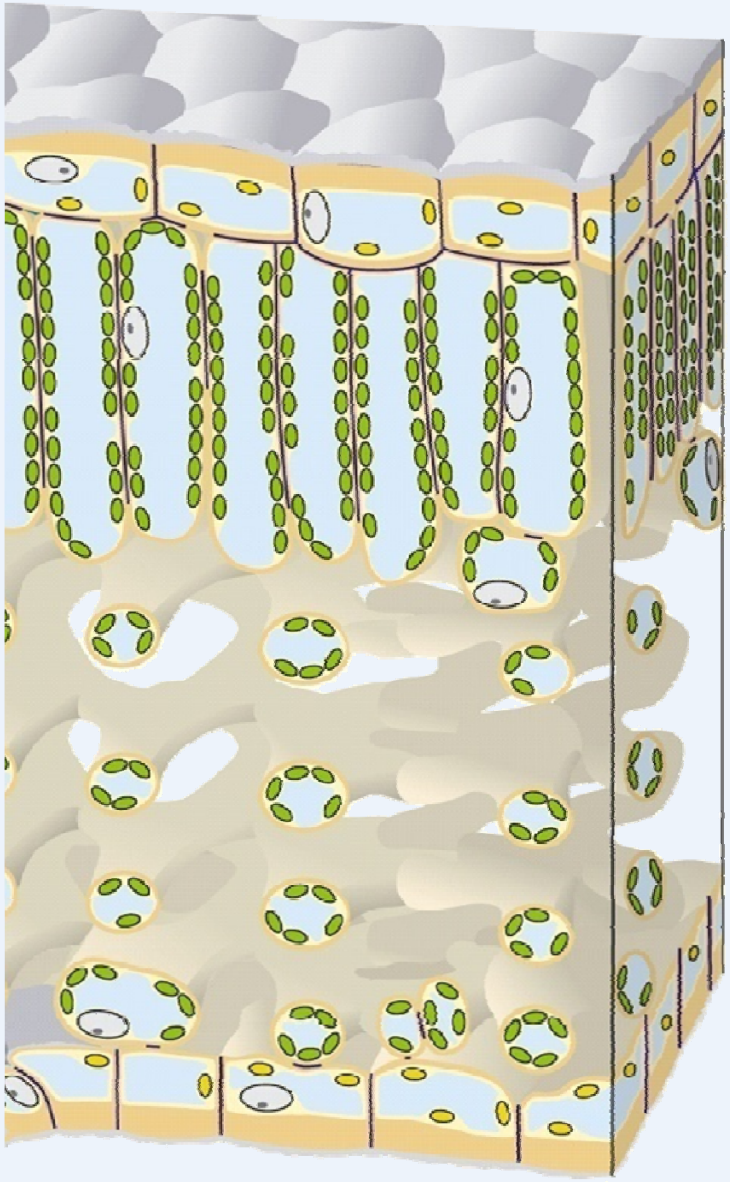

Cuticula
obere Epidermis
Palisaden-parenchym
Schwamm-parenchym
untere Epidermis
Spaltöffnung
Schließzelle
Cuticula
Leitbündel (Ader)
Bündel-scheidenzelle
Interzellularraum (Atemhöhle)

Nabors, 2007

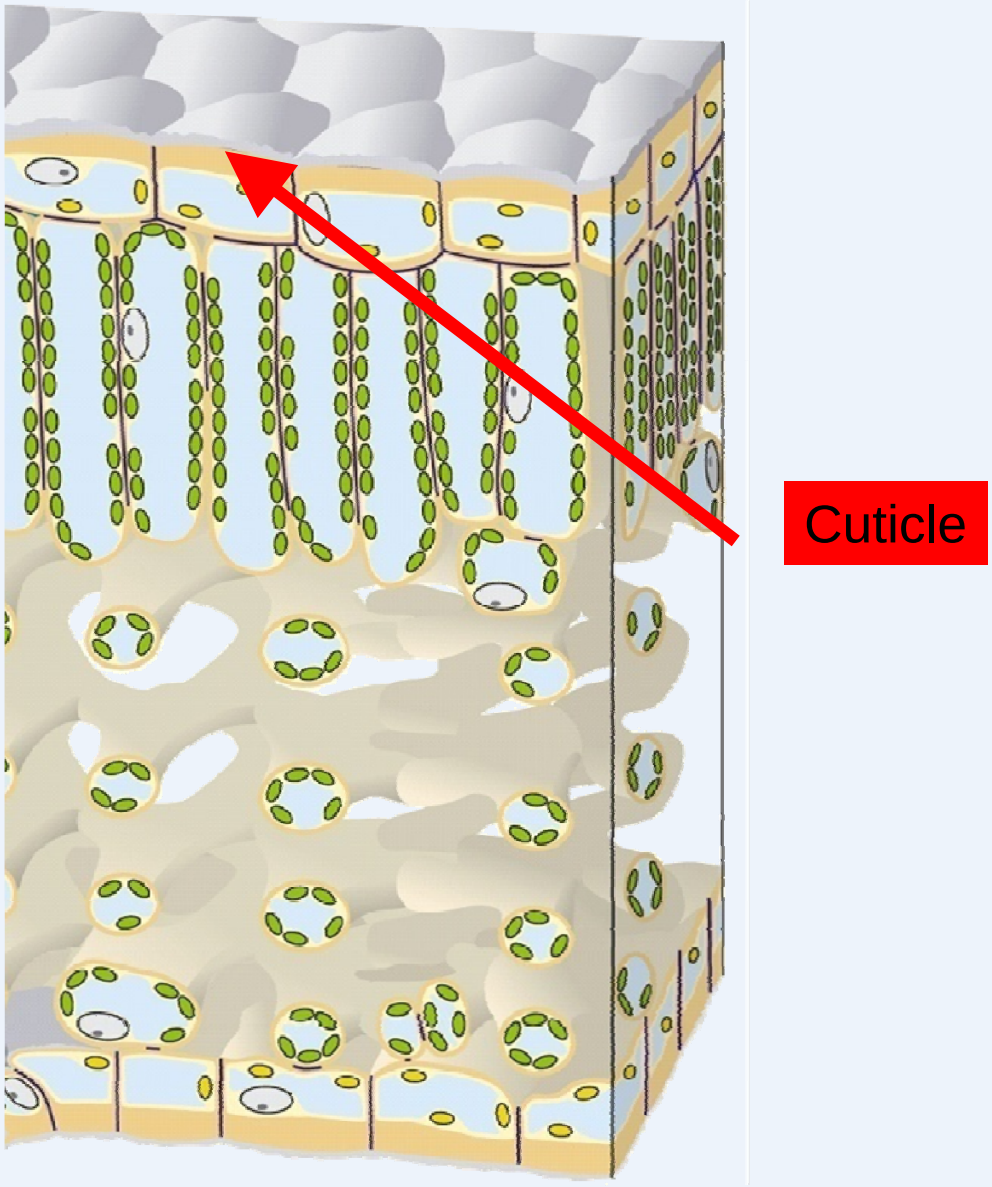
The Skin of Plants



Epidermis

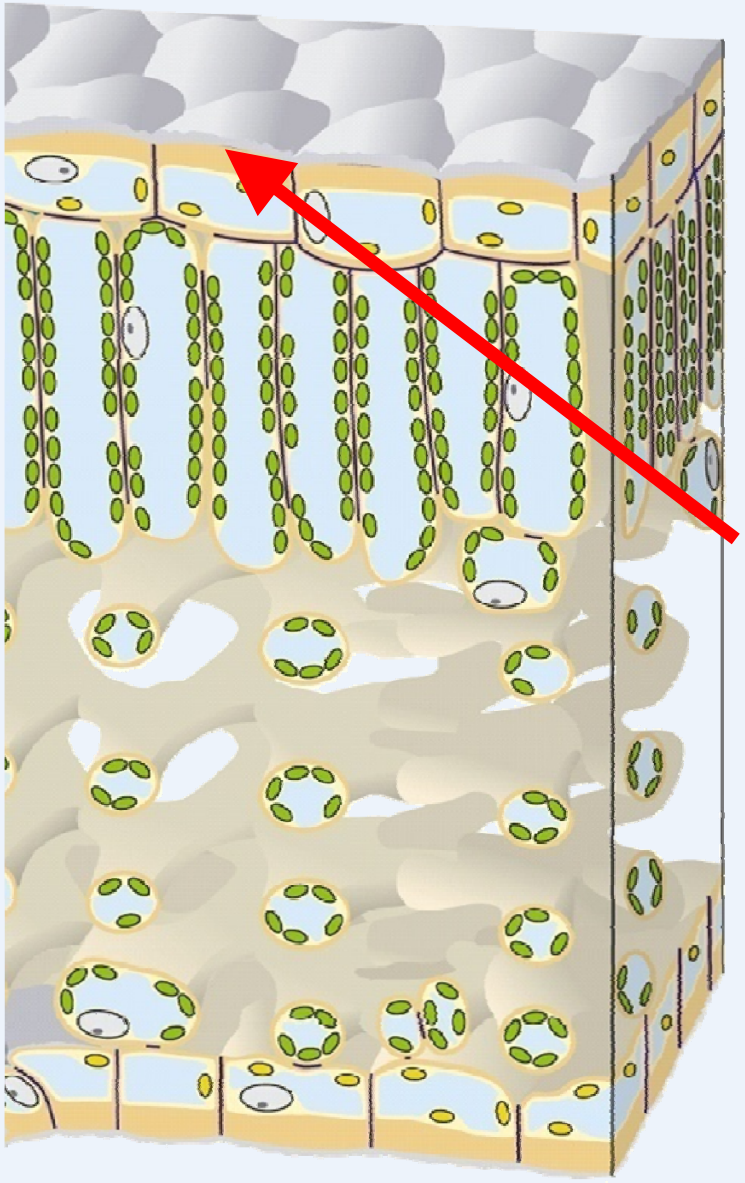
(Wanner, 2004)

Cuticle – the Skin of Plants



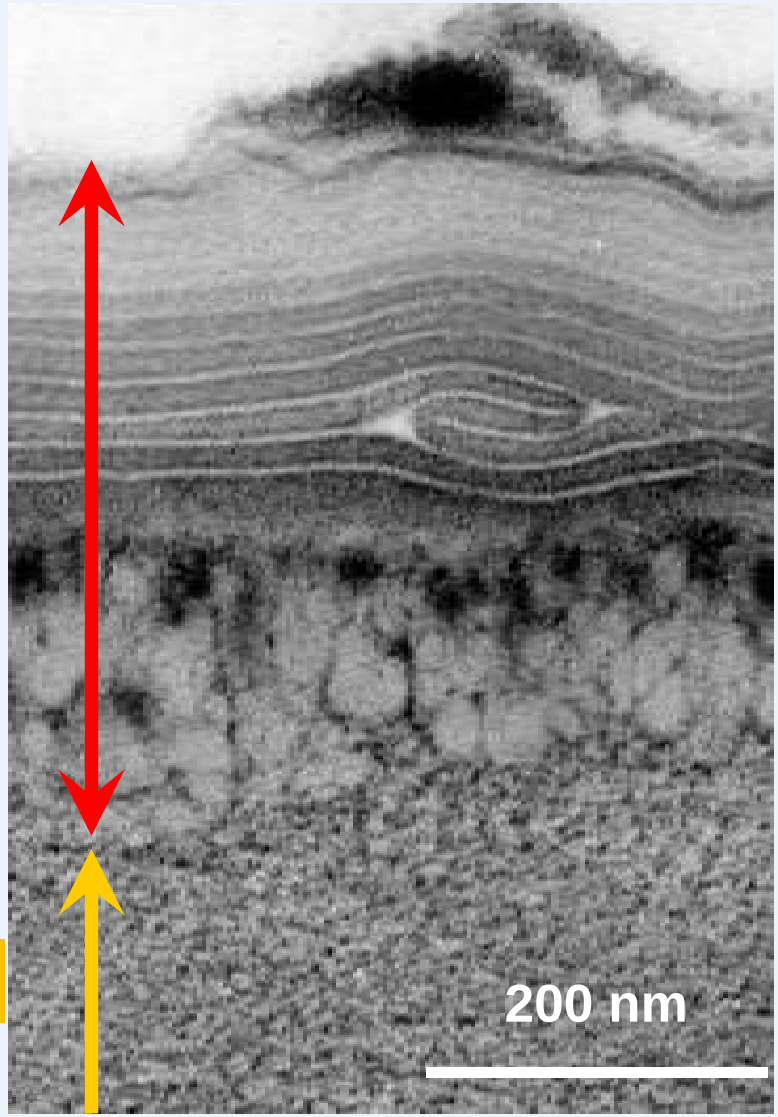
(Wanner, 2004)

Cuticle – the Skin of Plants



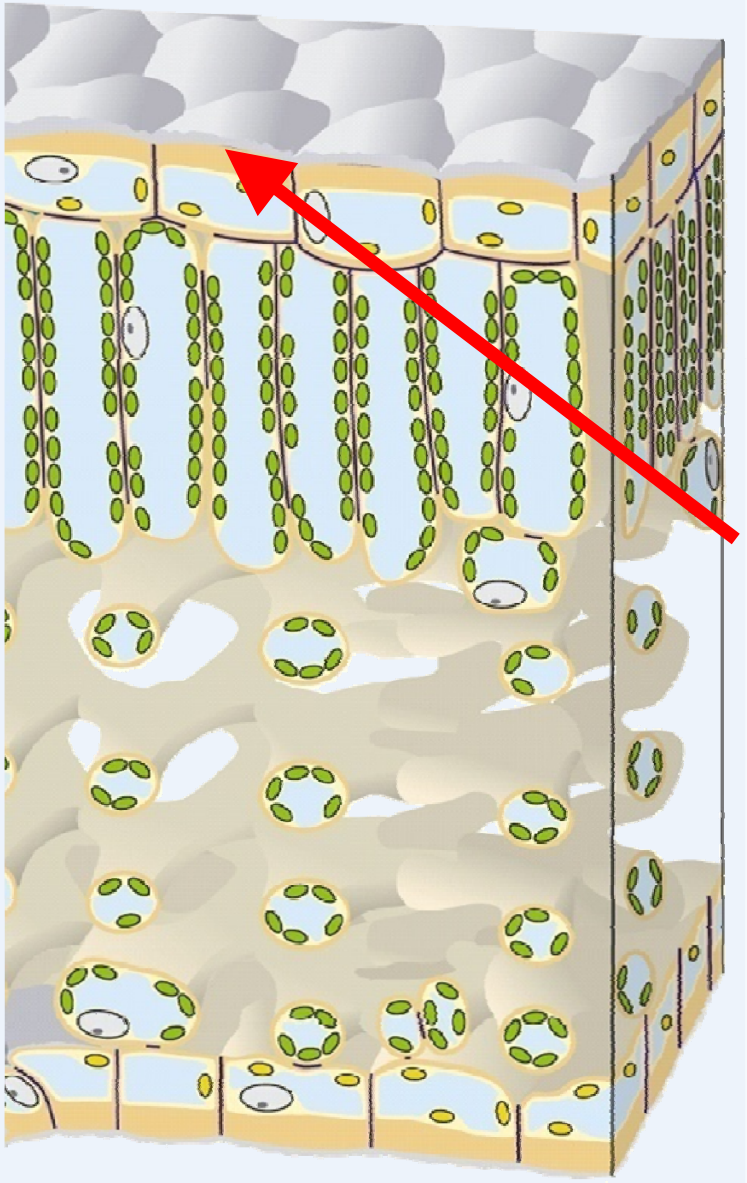
Cuticle

Cell wall



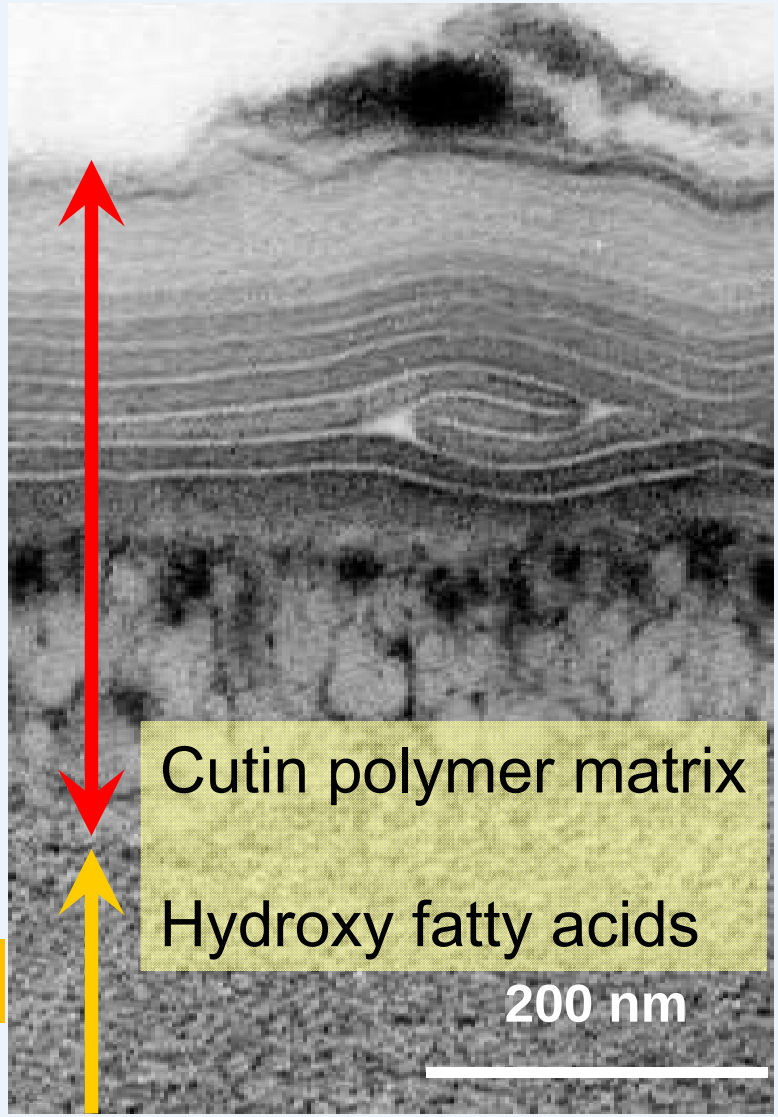
(Wanner, 2004)

Cuticle – the Skin of Plants

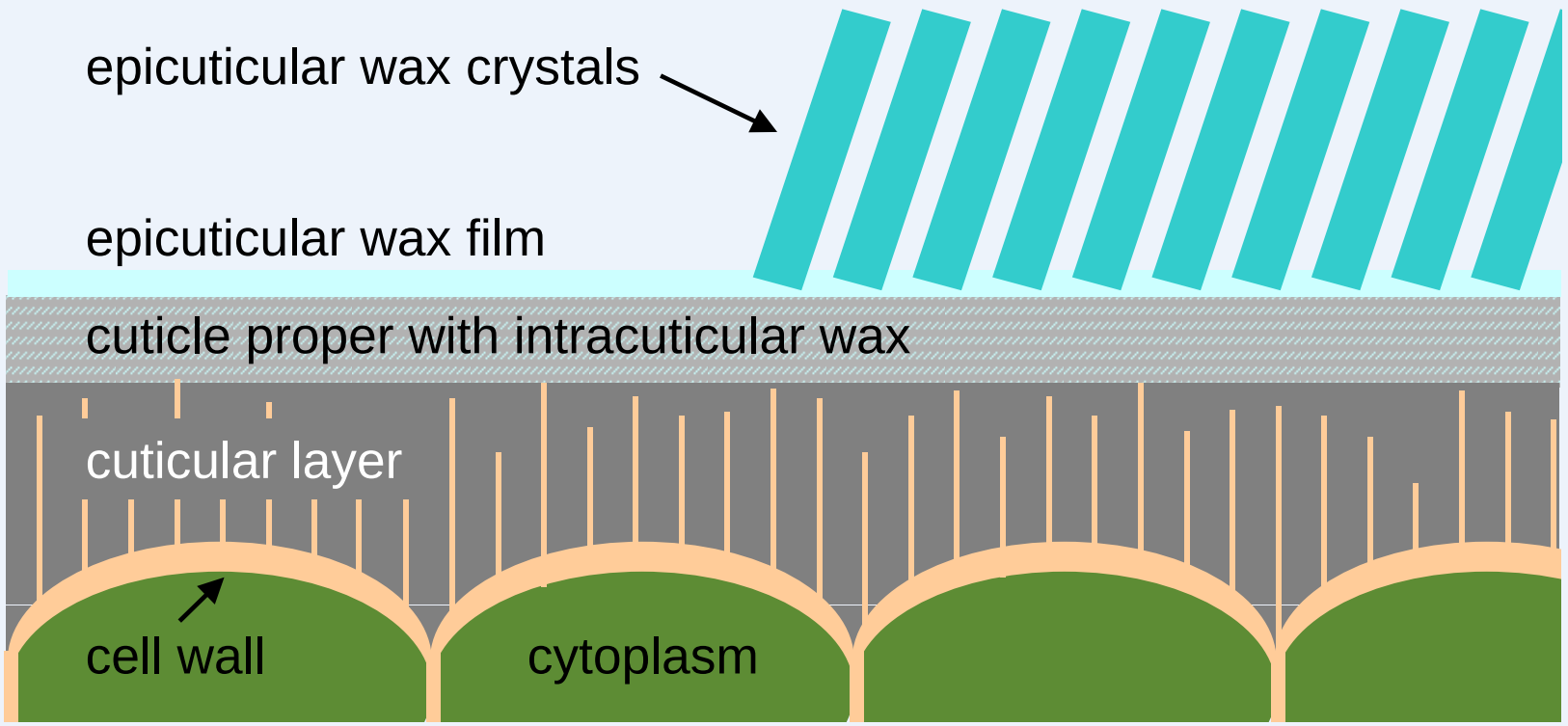


Cuticle

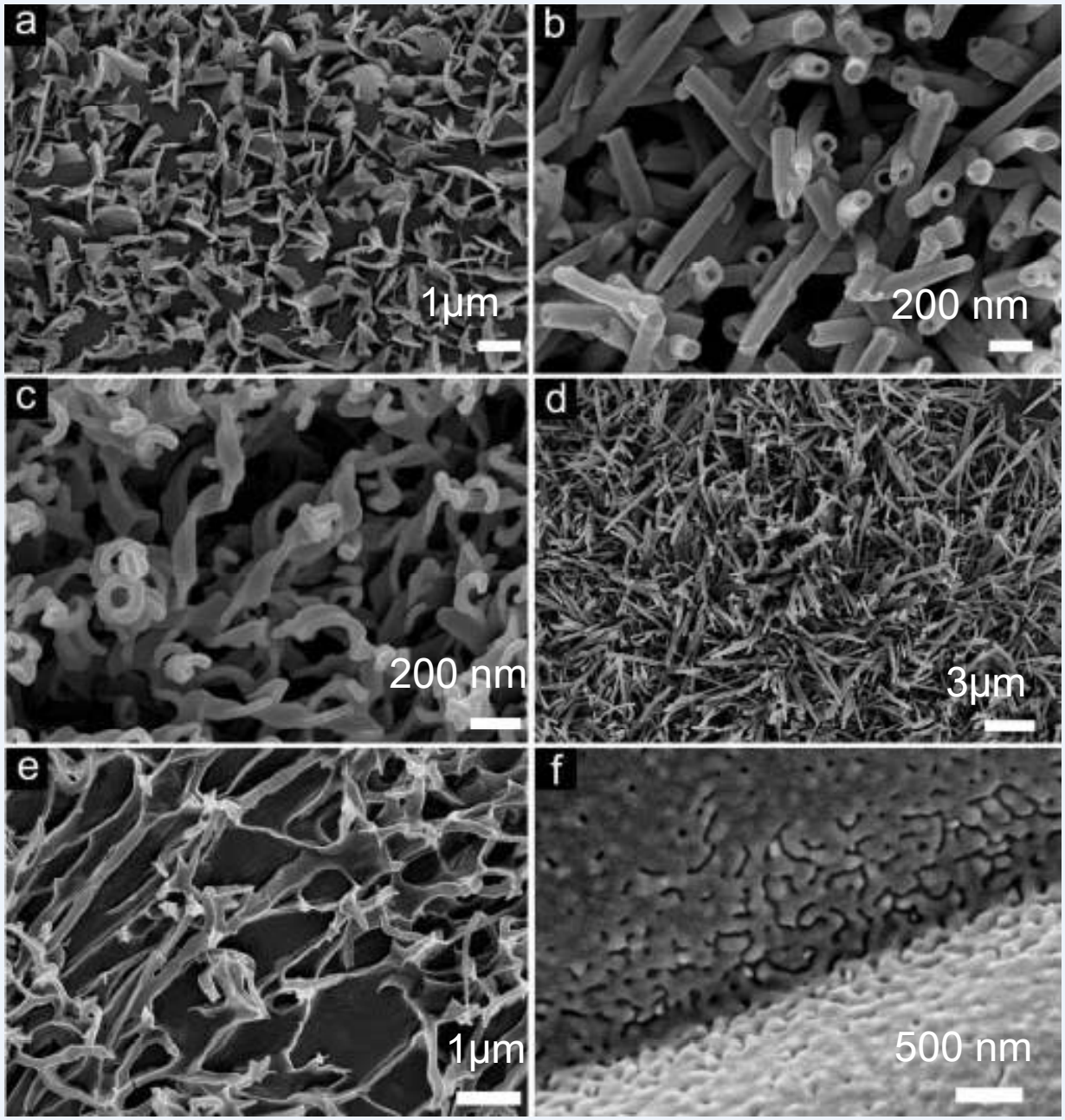
Cell wall



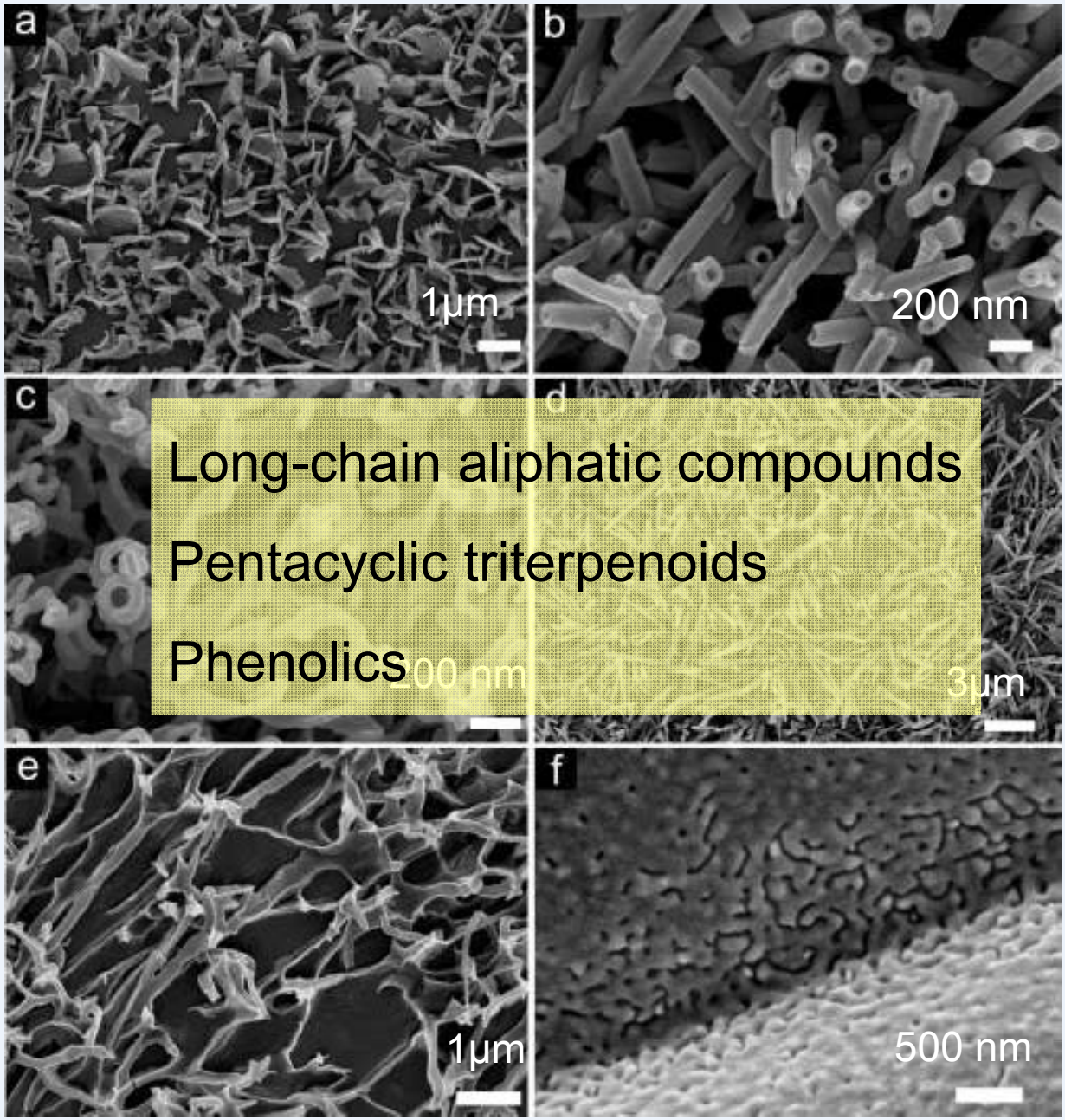
(Wanner, 2004)



(Müller & Riederer, J. Chem. Ecol., 2005)



(Jeffree in: Biology of the Plant Cuticle, 2006)

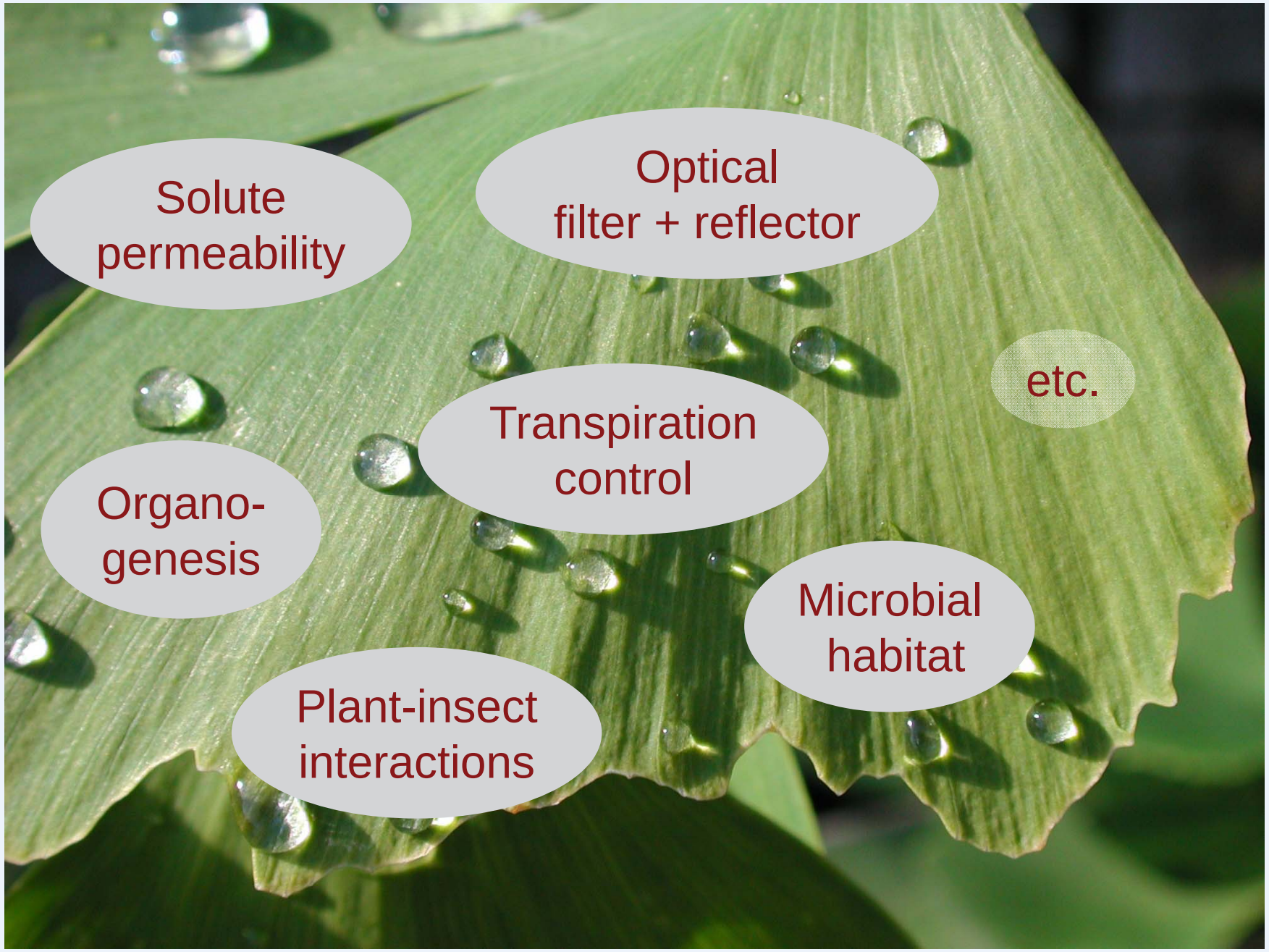


Long-chain aliphatic compounds

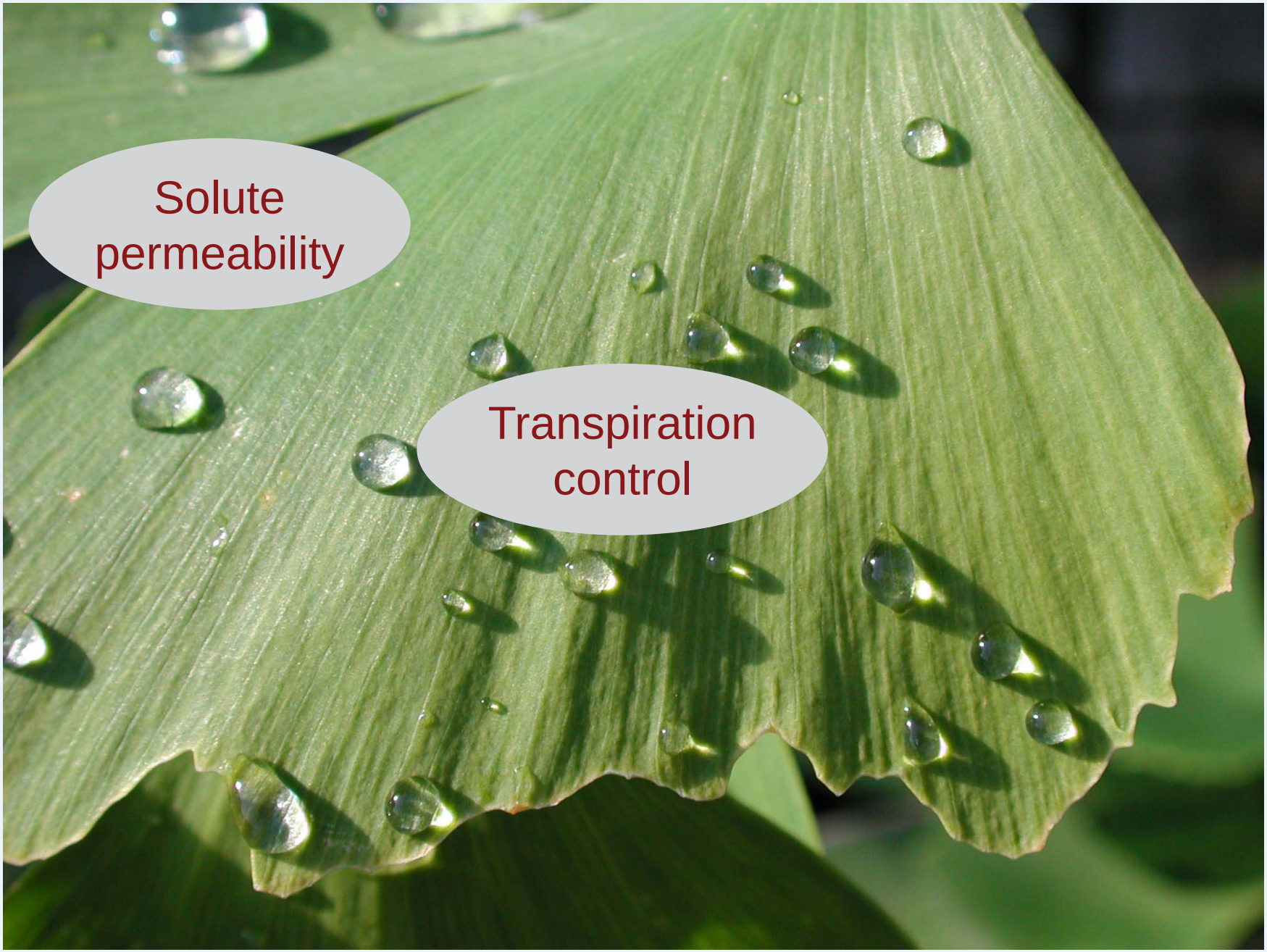
Pentacyclic triterpenoids

Phenolics

(Jeffree in: Biology of the Plant Cuticle, 2006)



(Cliff Hart, Syngenta)



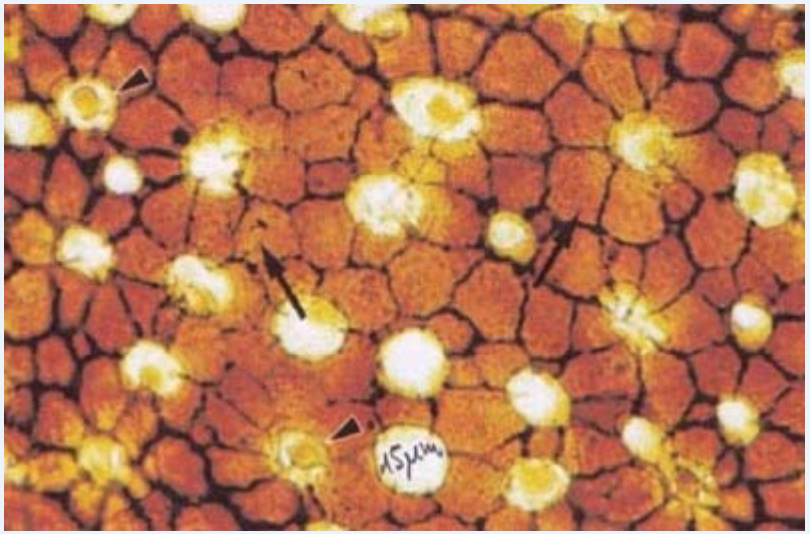
(Cliff Hart, Syngenta)

Colonisation of continents

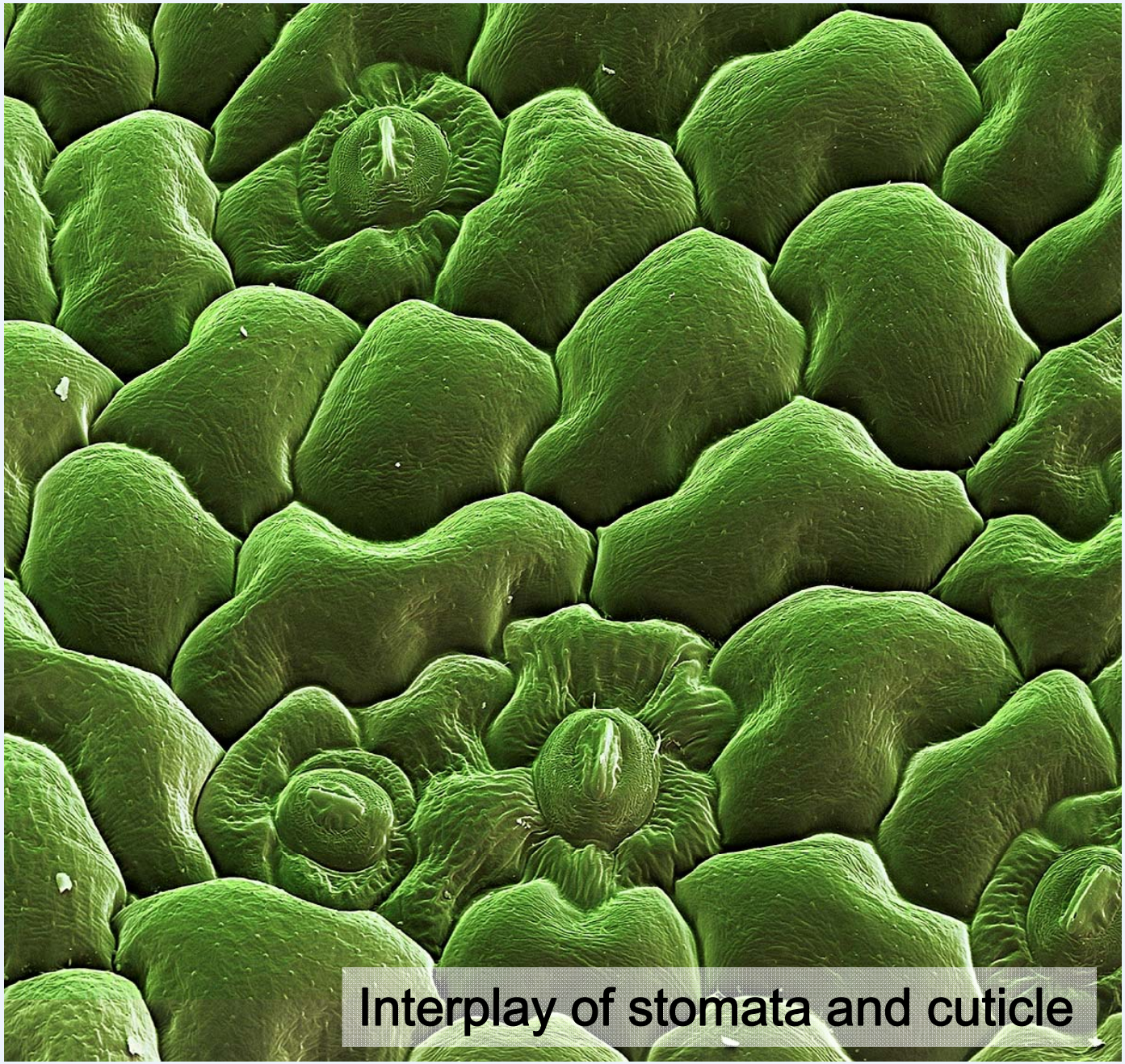
450 million years bp

http://www.darwin.museum.ru/dino/be_dino/paleoz.asp?4

Fossile cuticles
starting from Silurian
< 440 Ma



A stoma of *Aglaophaton major* with the two kidney-shaped guard cells from Early Devonian



(Diller, 2008)

Resistance model of plant transpiration

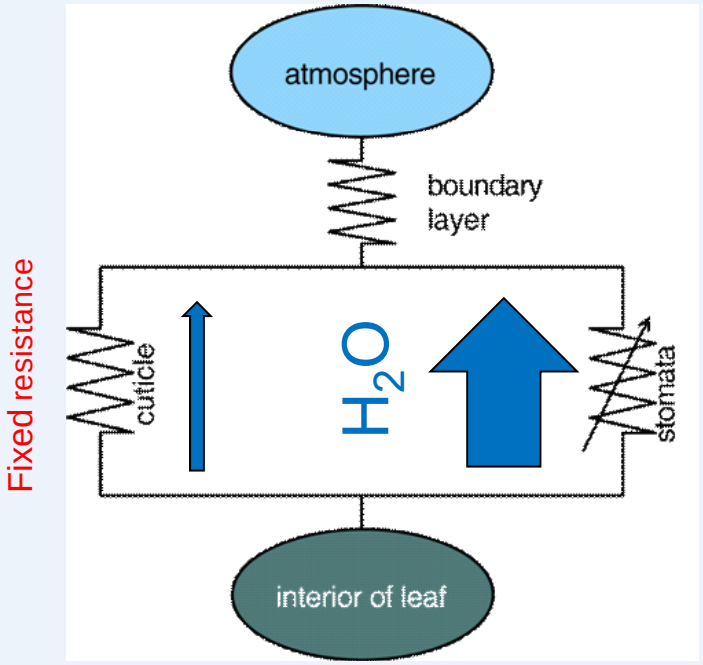


Fig. 1. No drought stress in light

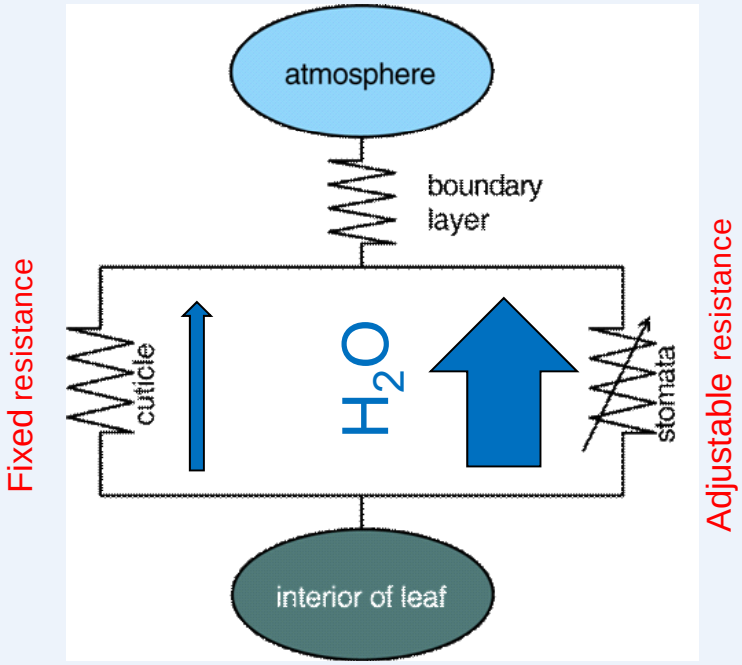


Fig. 1. No drought stress in light

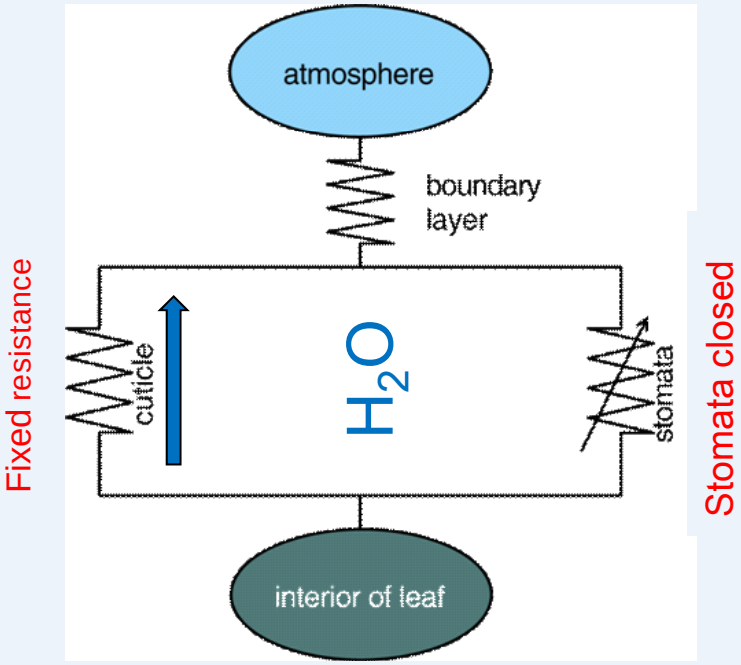
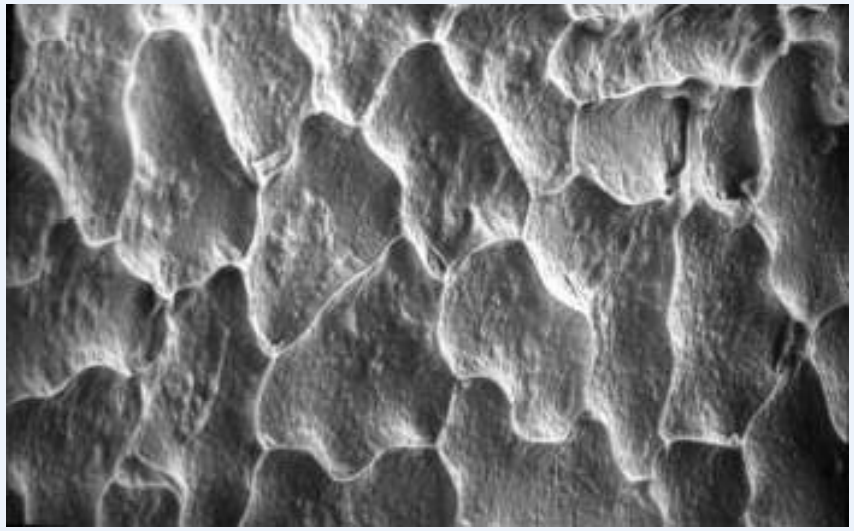


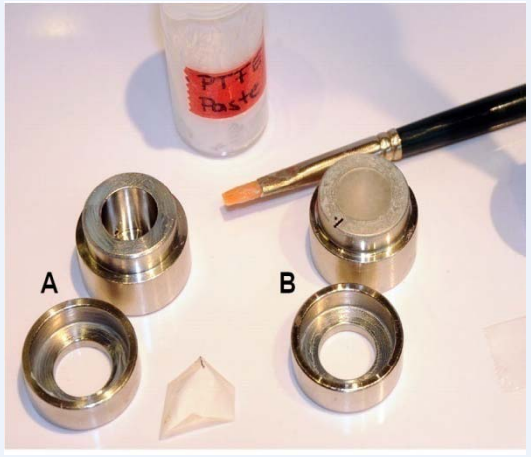
Fig. 2. Drought stress or in darkness

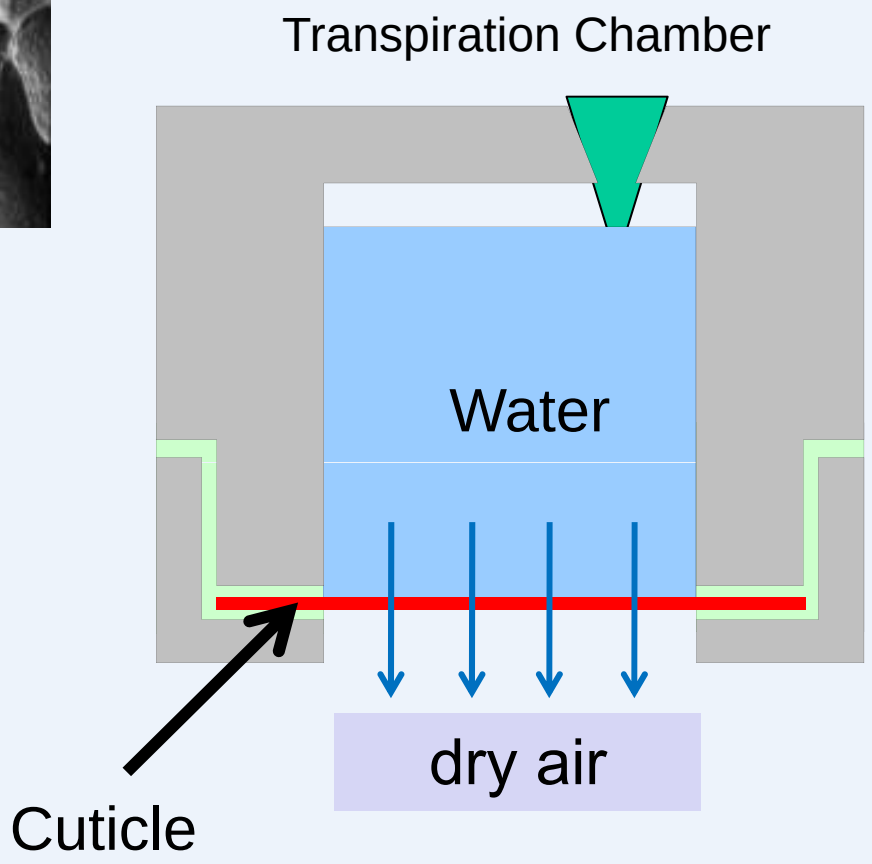
Transpiration control by stomata is possible only if residual (= cuticular) water loss is by orders of magnitude lower than stomatal conductance

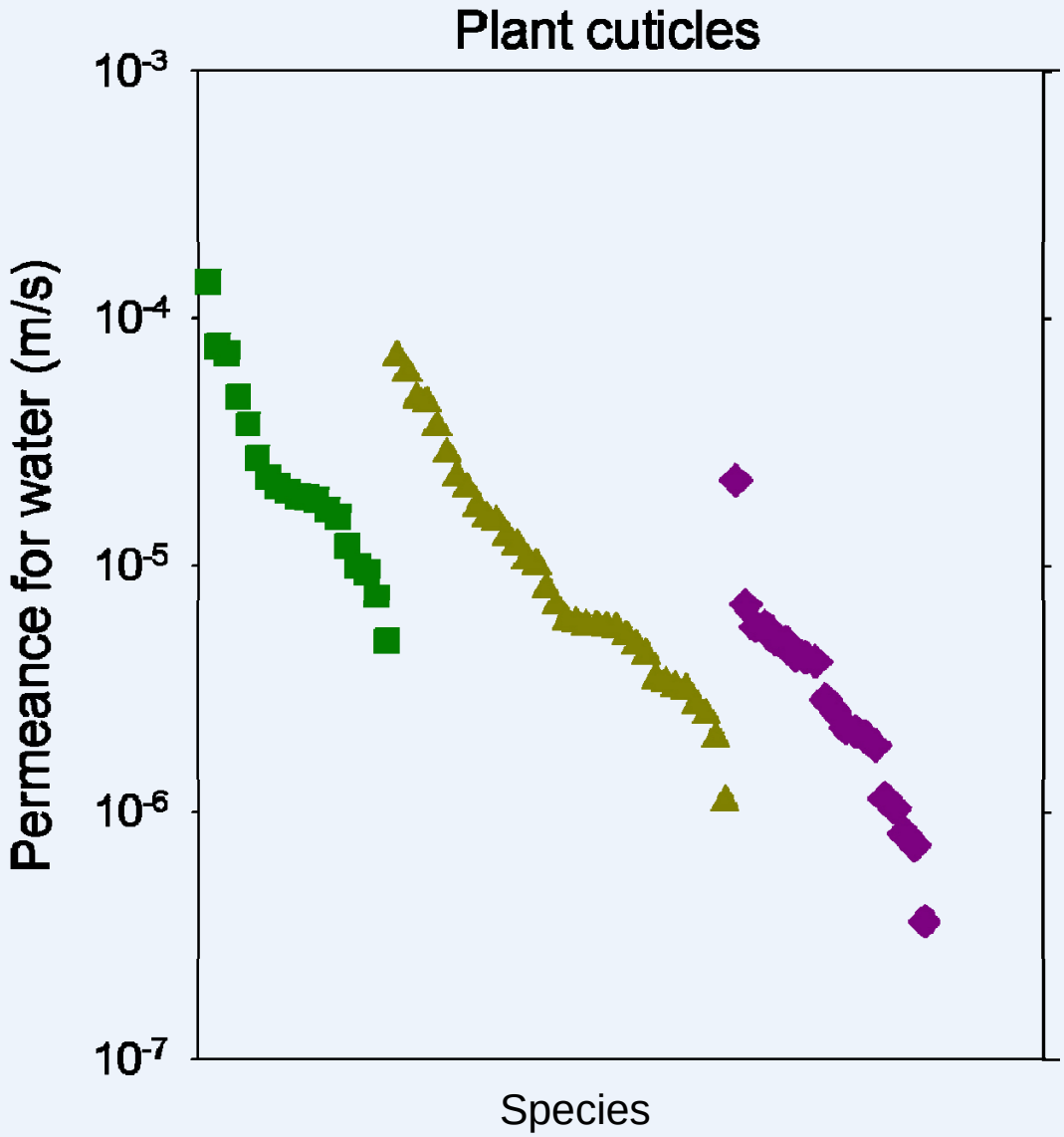
Cuticular water permeability

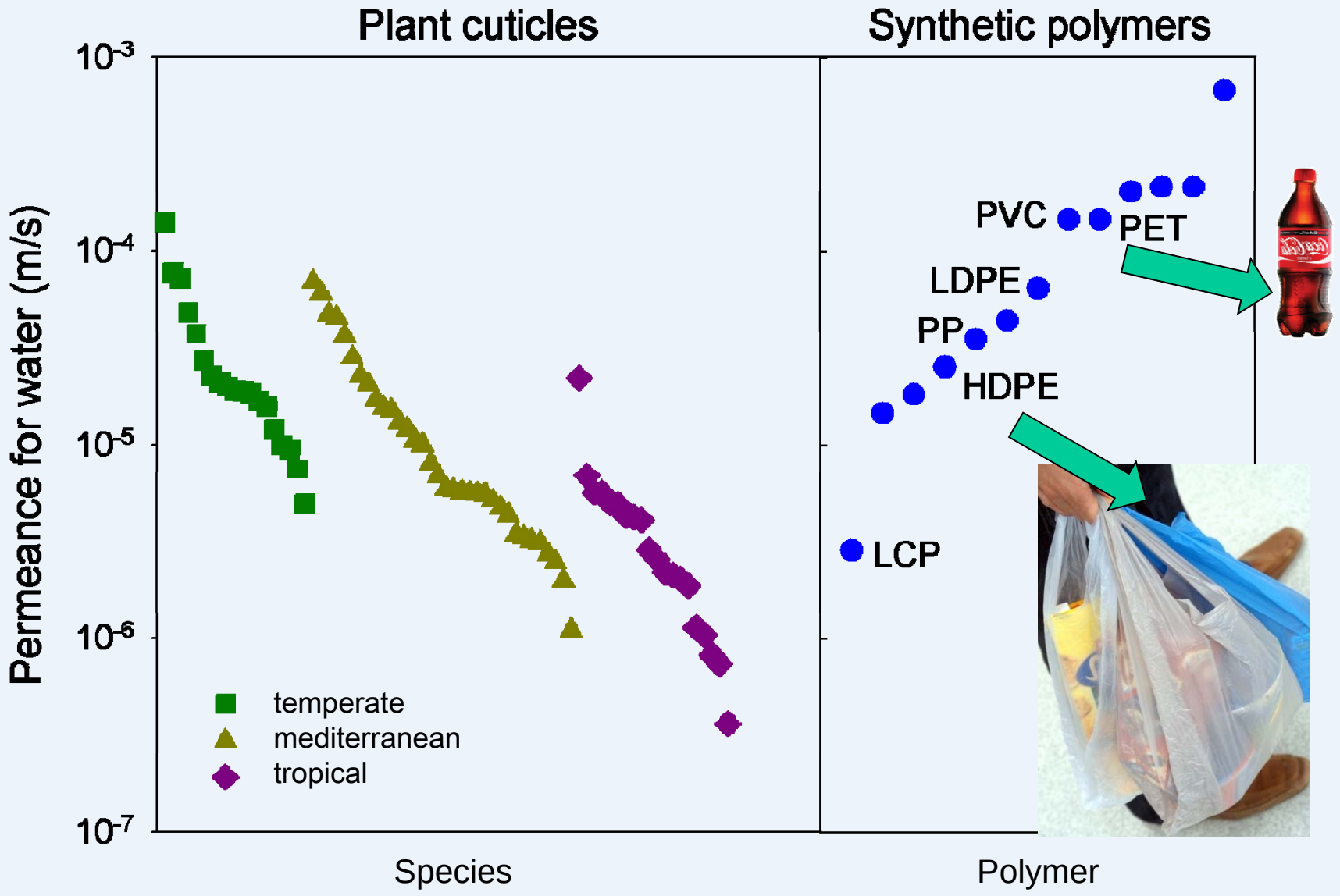


Citrus aurantium
Isolated Leaf Cuticle
100 nm – 20 µm

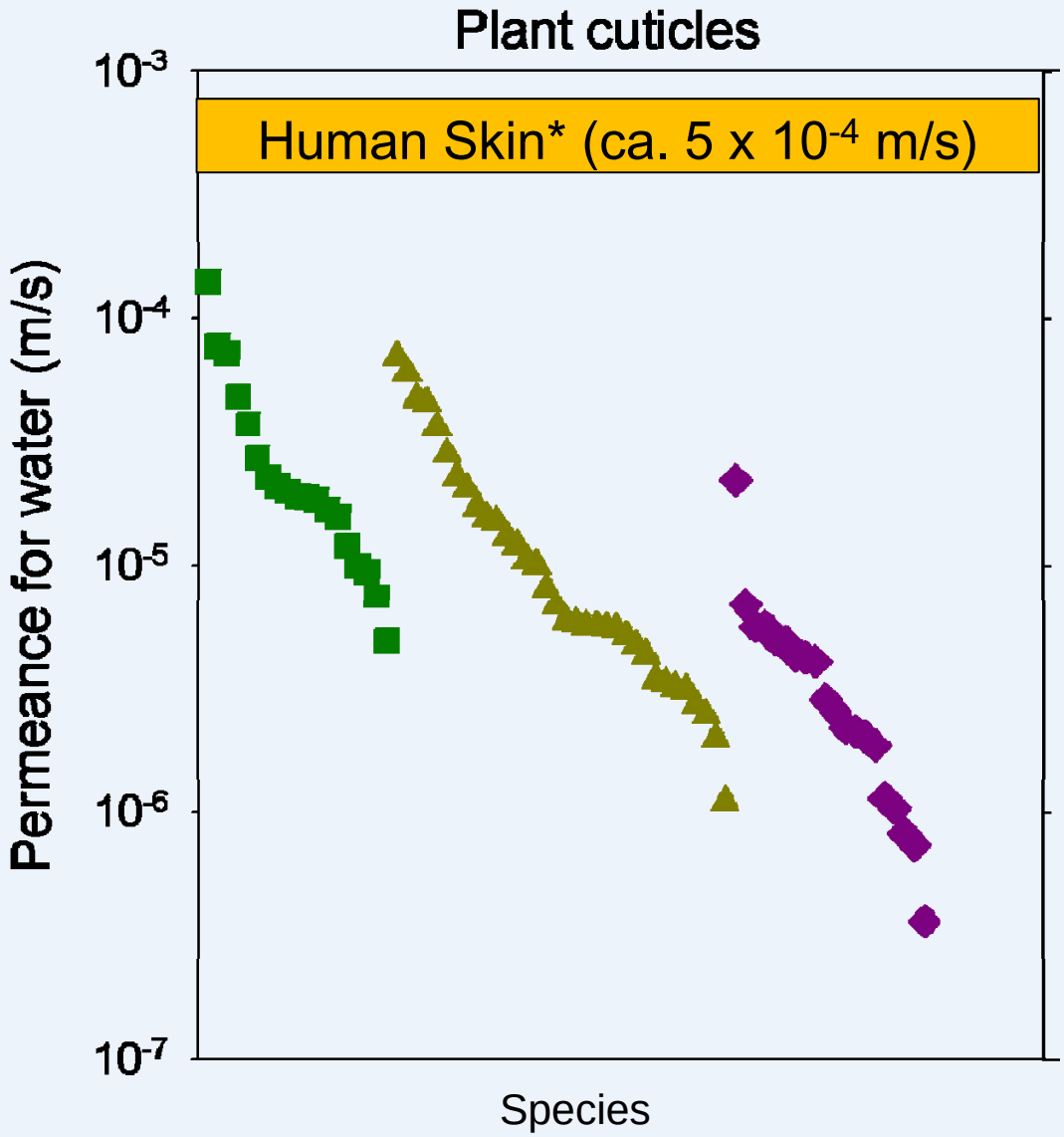





Plant cuticles
Permeance for water (m/s)
10-3
10-4
10-5
10-6
10-7
Species



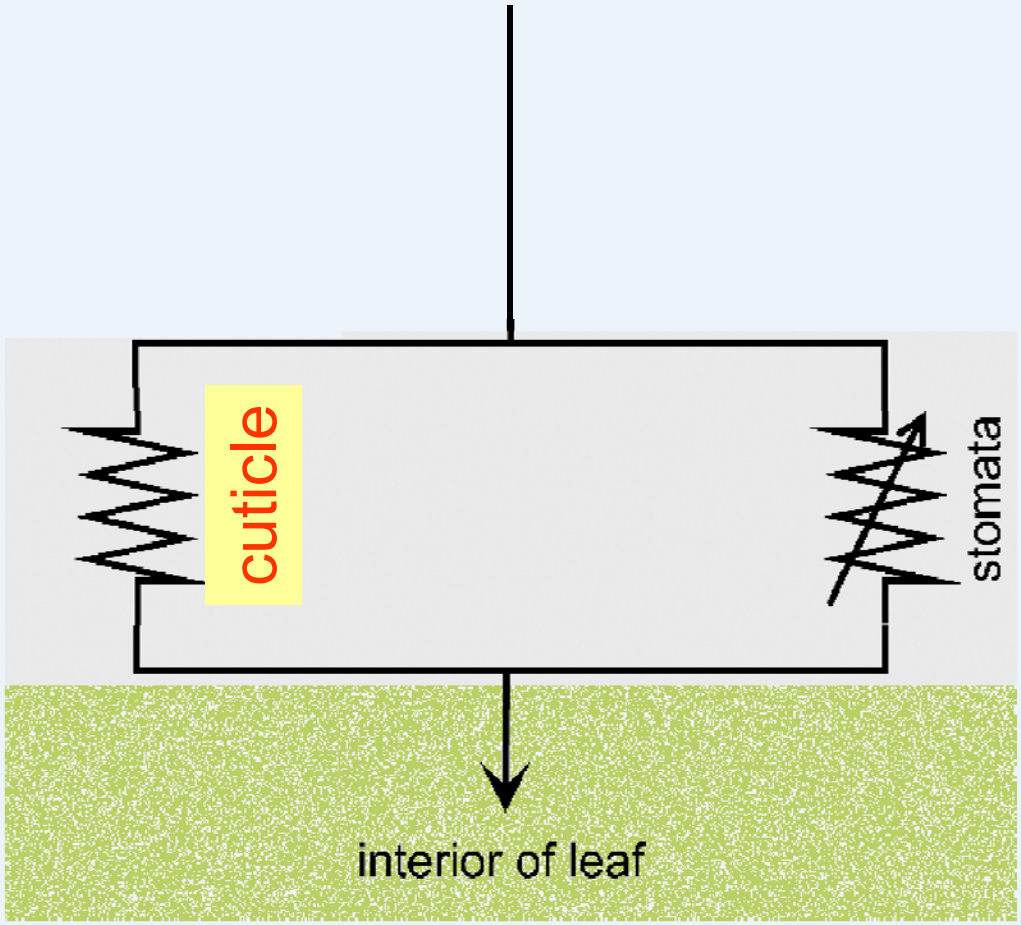
Highly efficient transpiration barrier



(*M. Machado et al. / International Journal of Pharmaceutics *384 (2010) 73–77)*

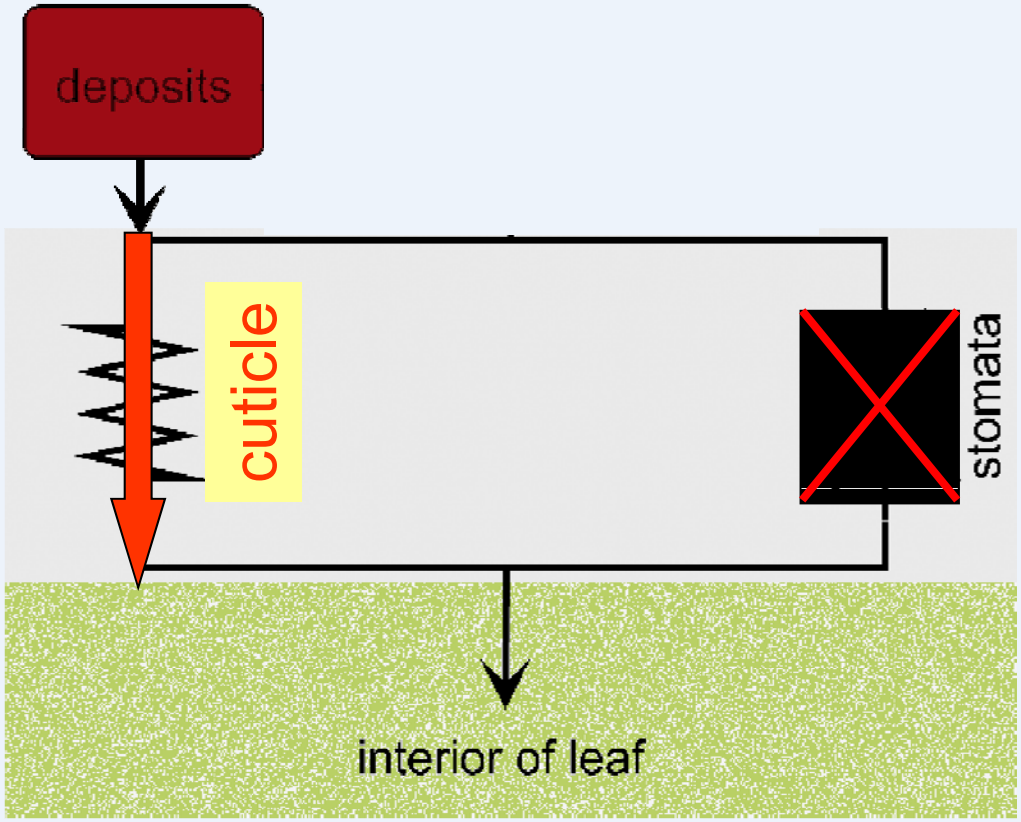
Cuticular permeation of neutral lipophilic compounds (e.g. pesticides, pollutants, plant metabolites)

General resistance model of leaf uptake



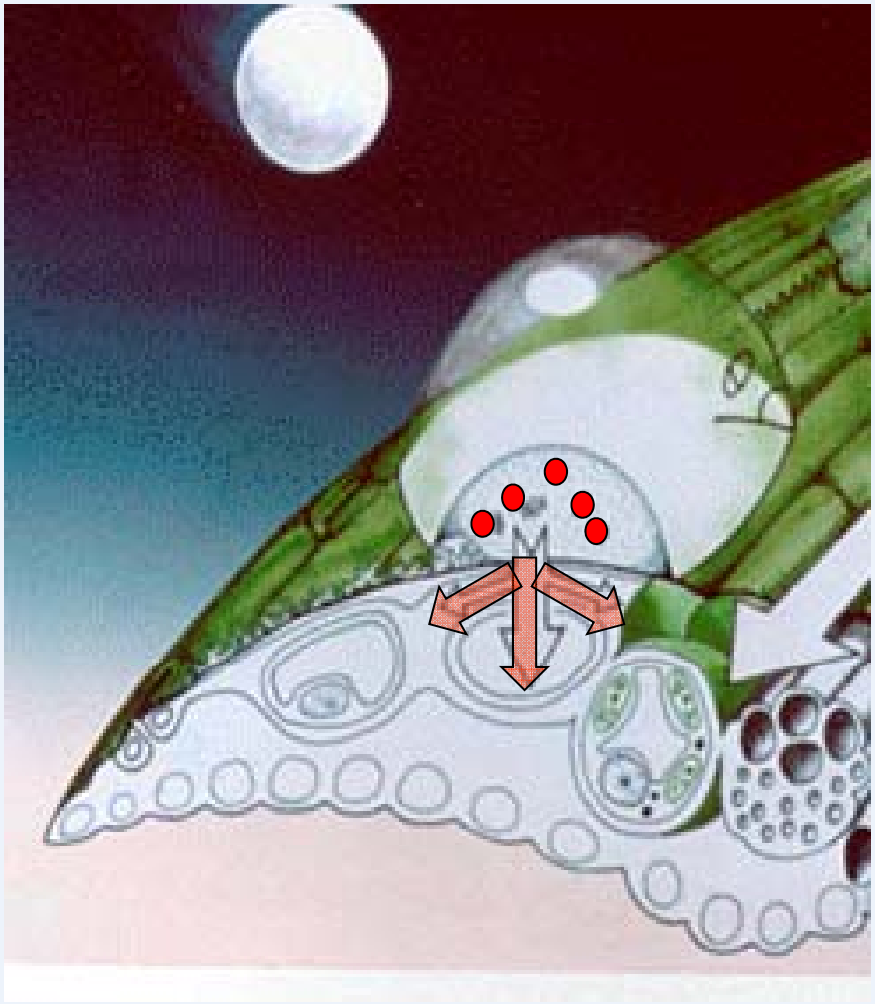
(Riederer in Plant Toxicology, 2004)

Pathways for foliar uptake of non-volatile active ingredients of agrochemicals

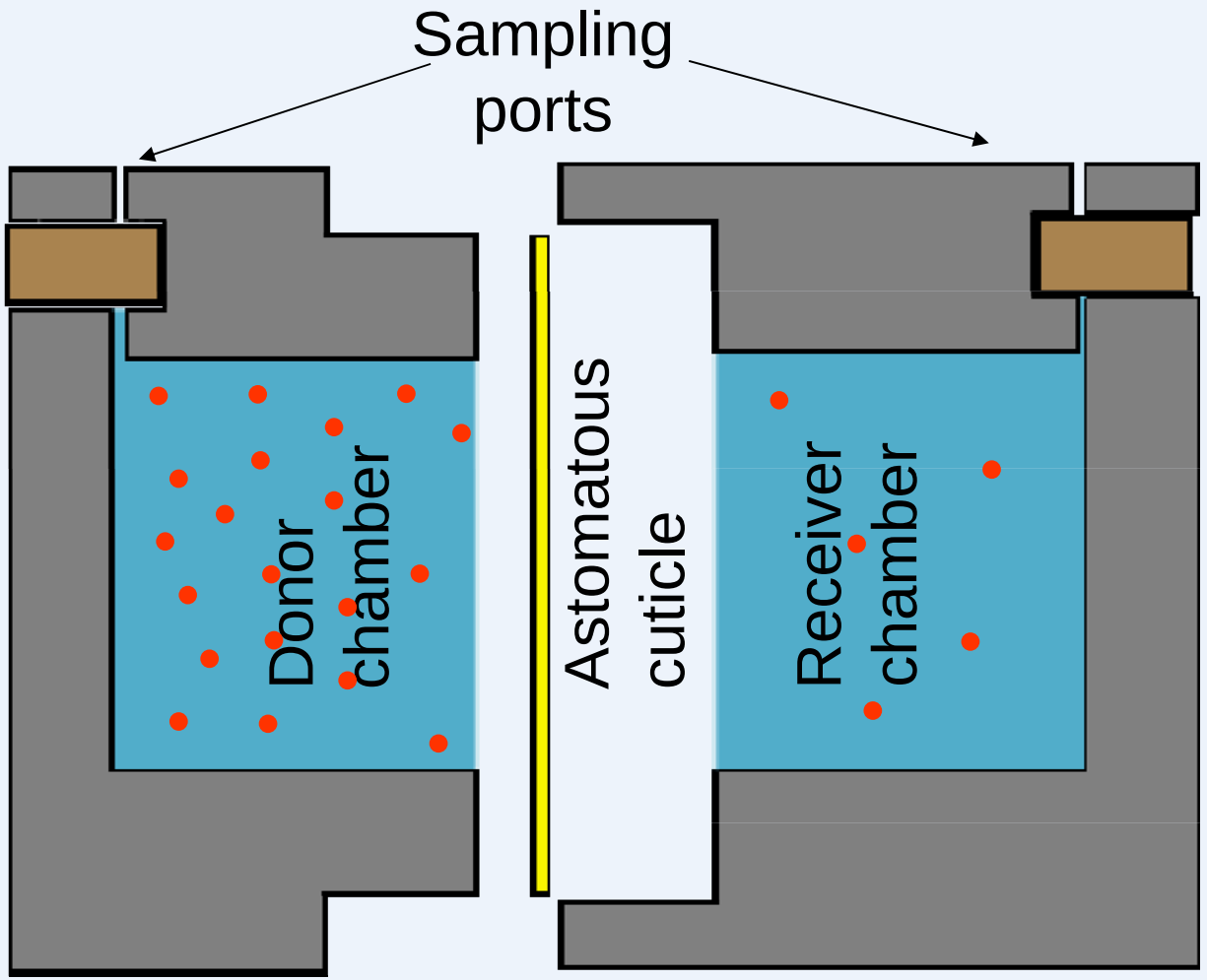


(Riederer in Plant Toxicology, 2004)

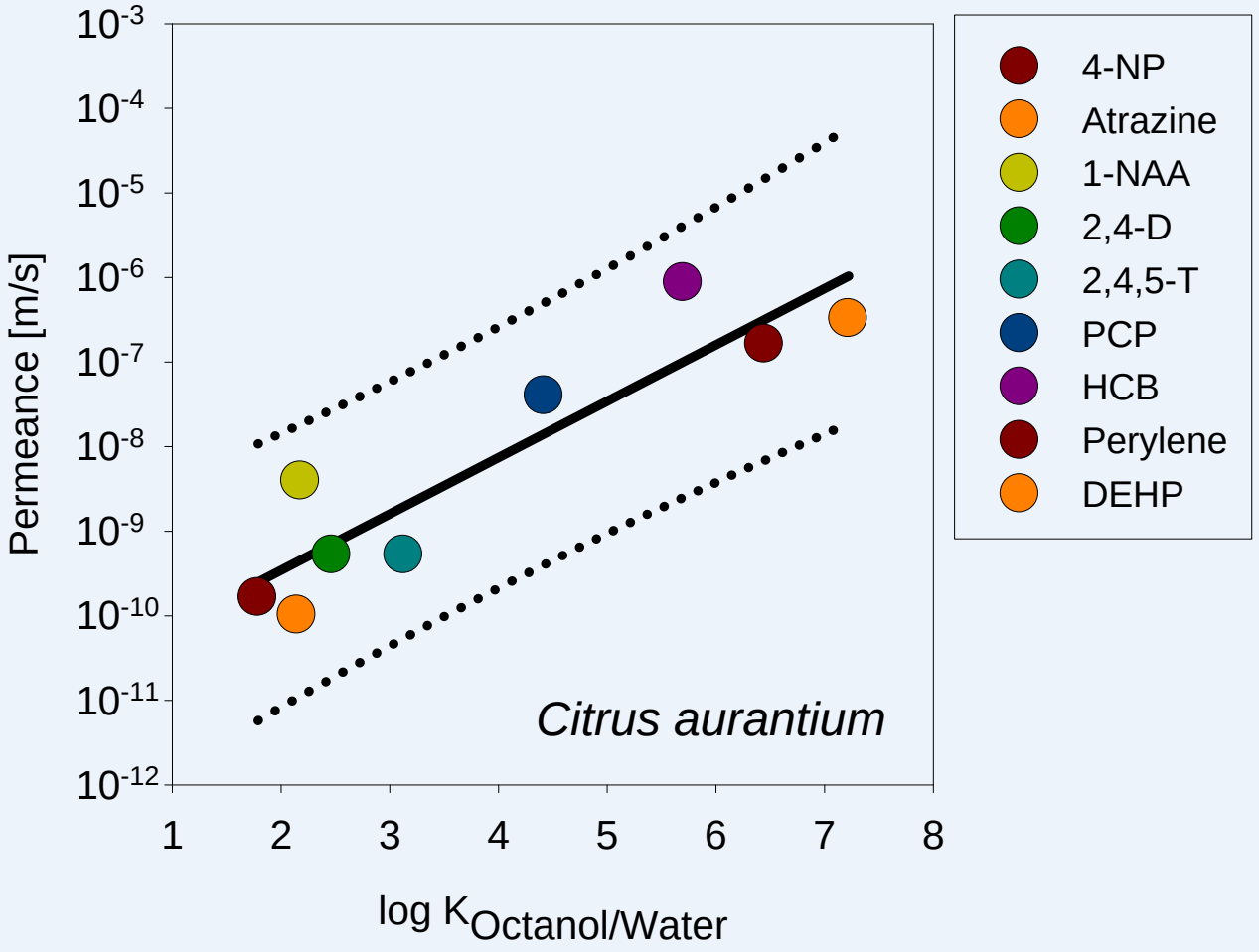
Pesticide uptake



Pesticide uptake

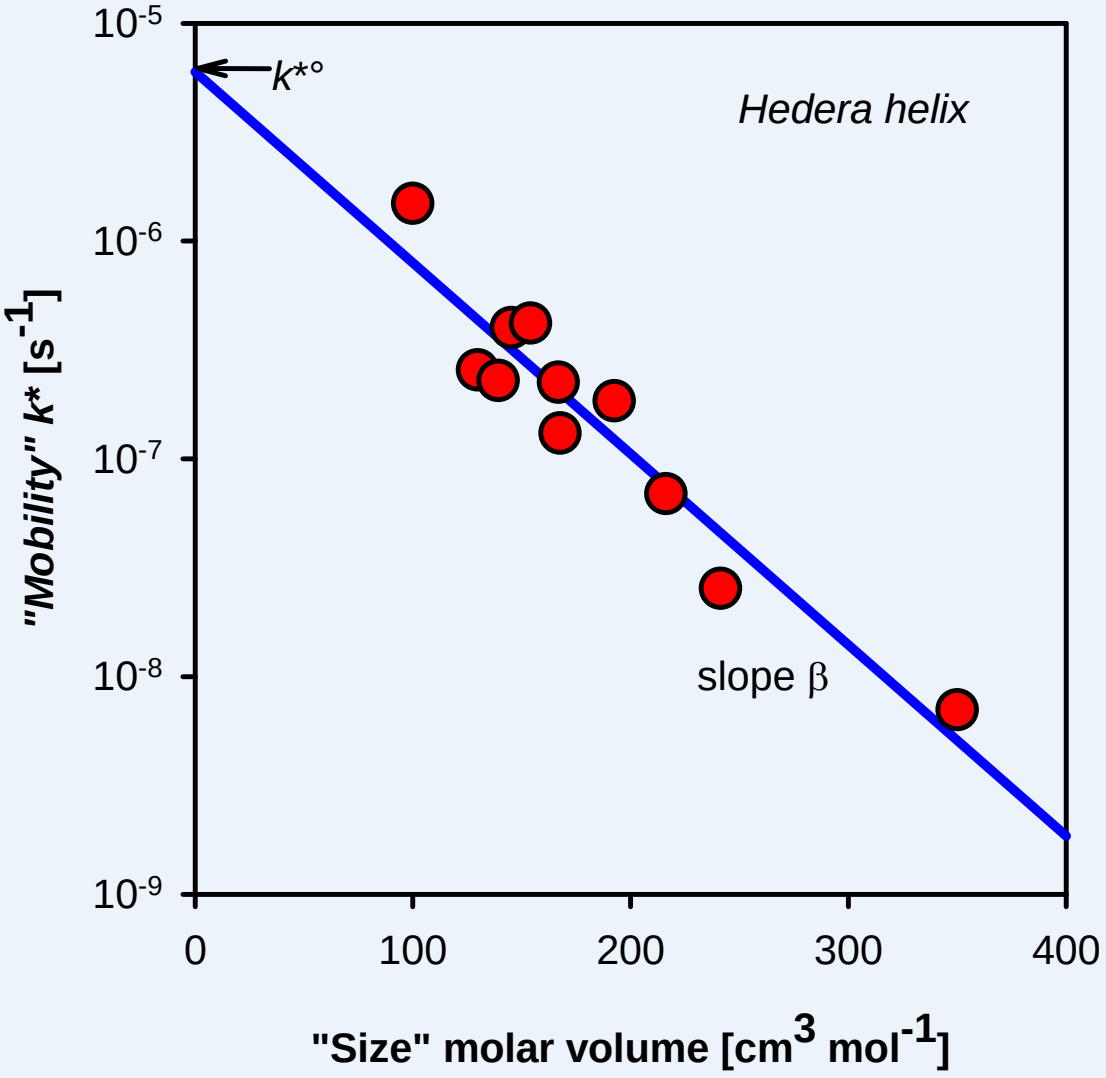

Sampling
ports
Donor
chamber
Astomatous
cuticle
Receiver
chamber

Effect of lipophilicity on permeability



(Data from Kerler, Riederer and Schönherr)

Effect of molecular size on mobility



Steep size selectivity

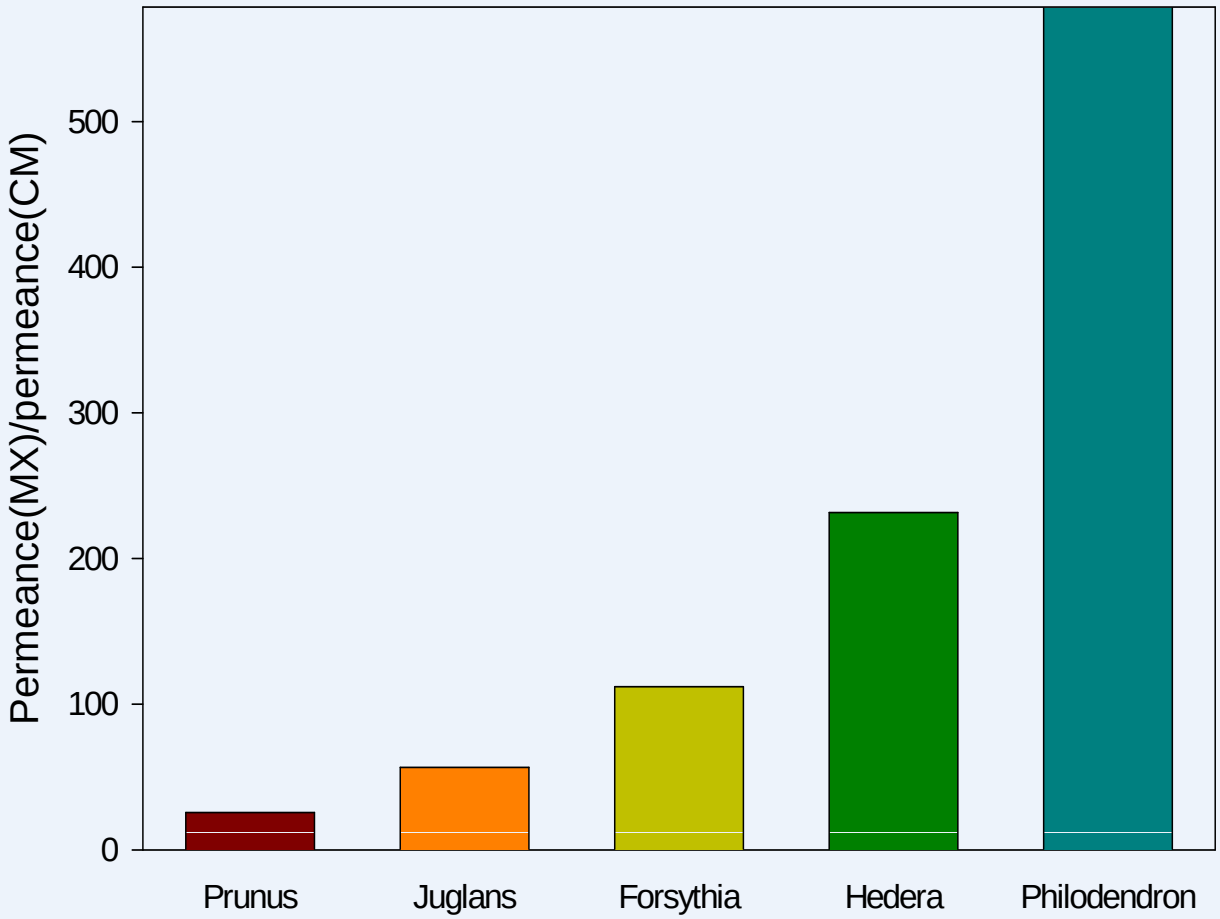
(Data from Buchholz et al. 1998)

For lipophilics:

solution-diffusion membrane

What makes up the cuticular resistance?

Effect of wax extraction on water permeability

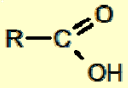


Waxes make up the barrier

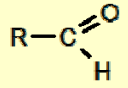
But: amount of waxes has no influence

=>Composition of cuticular waxes?

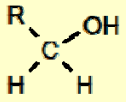
Cuticular waxes are complex mixtures (up to 150 compounds per species)



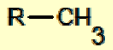
Alkanoic acids



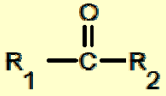
Alkanals



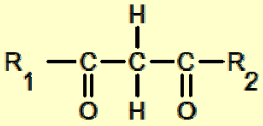
1-Alkanols



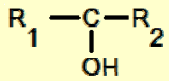
Alkanes; Alkenes



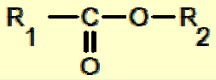
Ketones



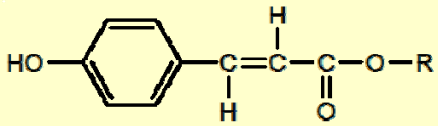
β-Diketones



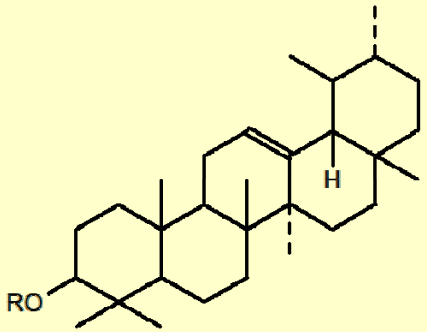
Secondary alkanols



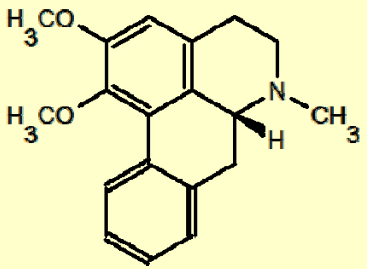
Alkyl esters



Aromatic esters



Triterpenoids and Derivatives (e. g. α-Amyrin)



Alkaloids (e. g. Nuciferin)

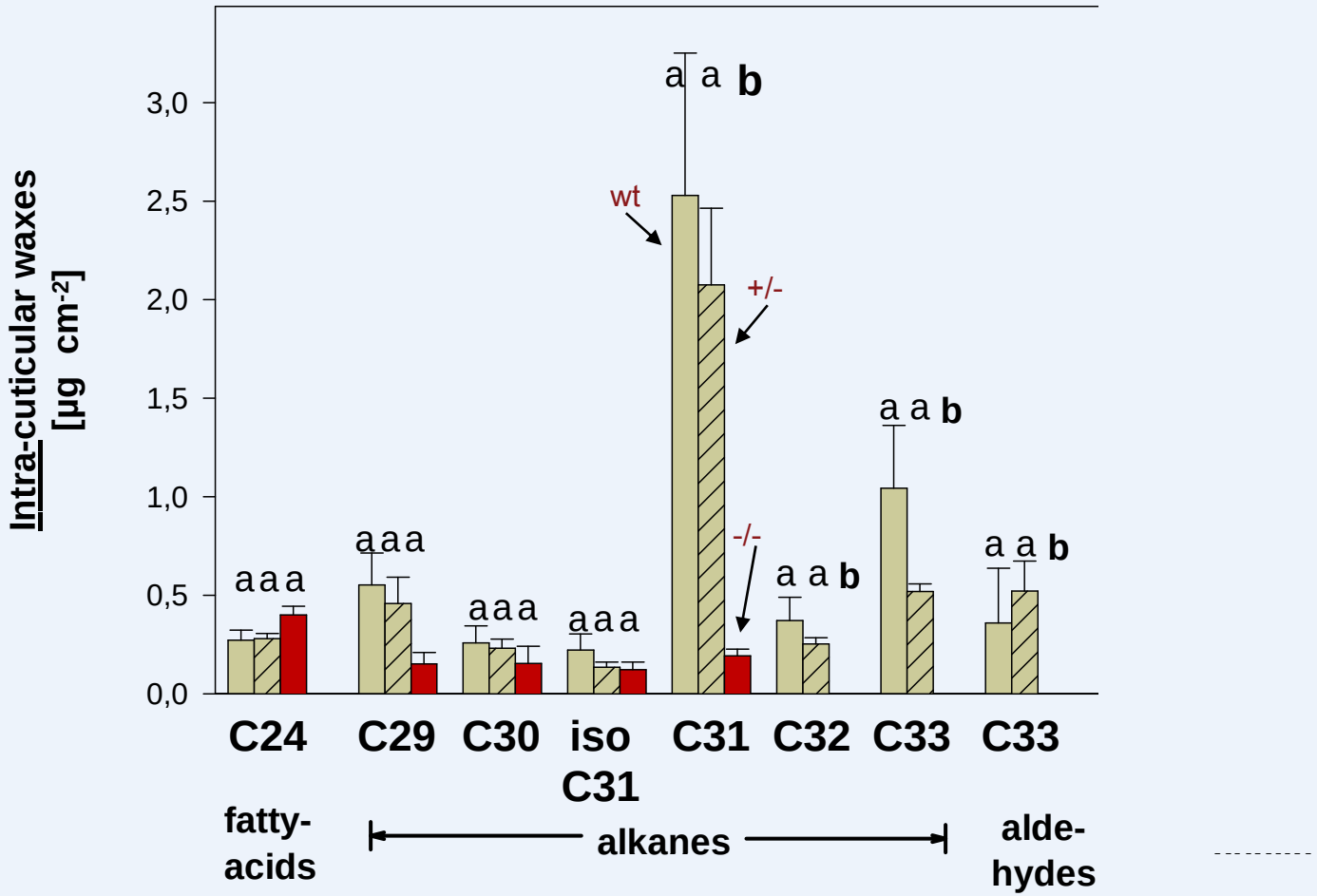
Model organism for molecular studies: tomato

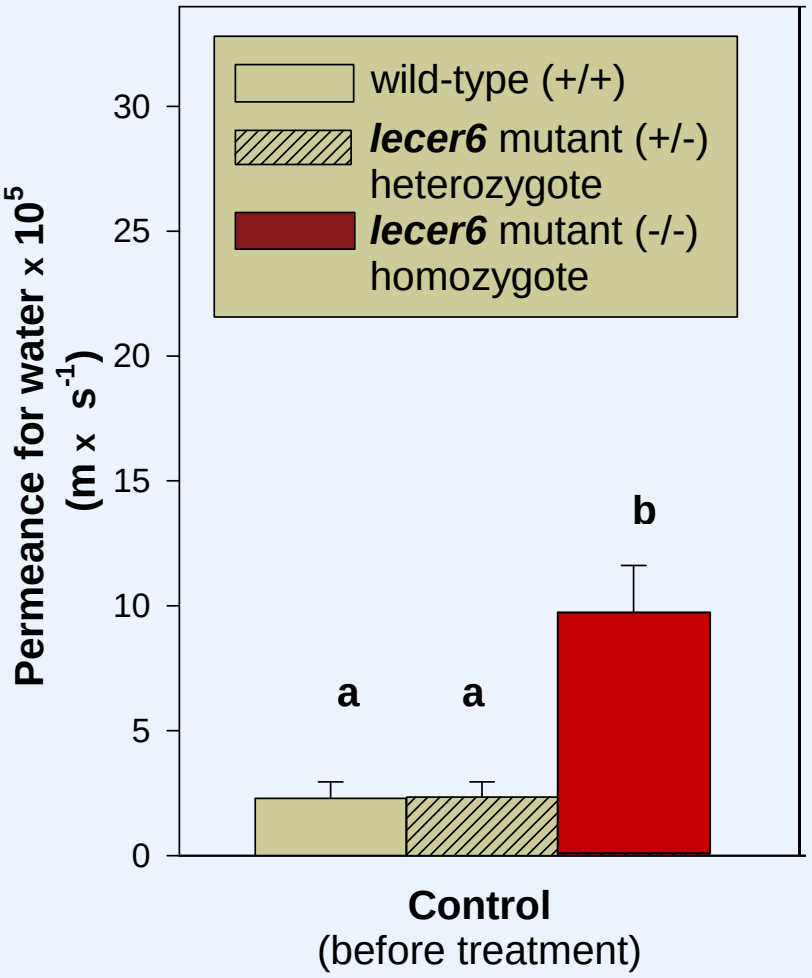
Wax biosynthesis => function

wild type

VLCFA-elongase deficient mutant

(Vogg et al., J. Exp. Bot., 2004)


Intra-cuticular waxes
[µg cm-2]
3,0
2,5
2,0
1,5
1,0
0,5
0,0
wt
+/-
-/-
a a b
a a b
a a b
a a a
a a a
a a a
a a a
C24
C29
C30
iso C31
C31
C32
C33
C33
fatty-acids
alkanes
alde-hydes



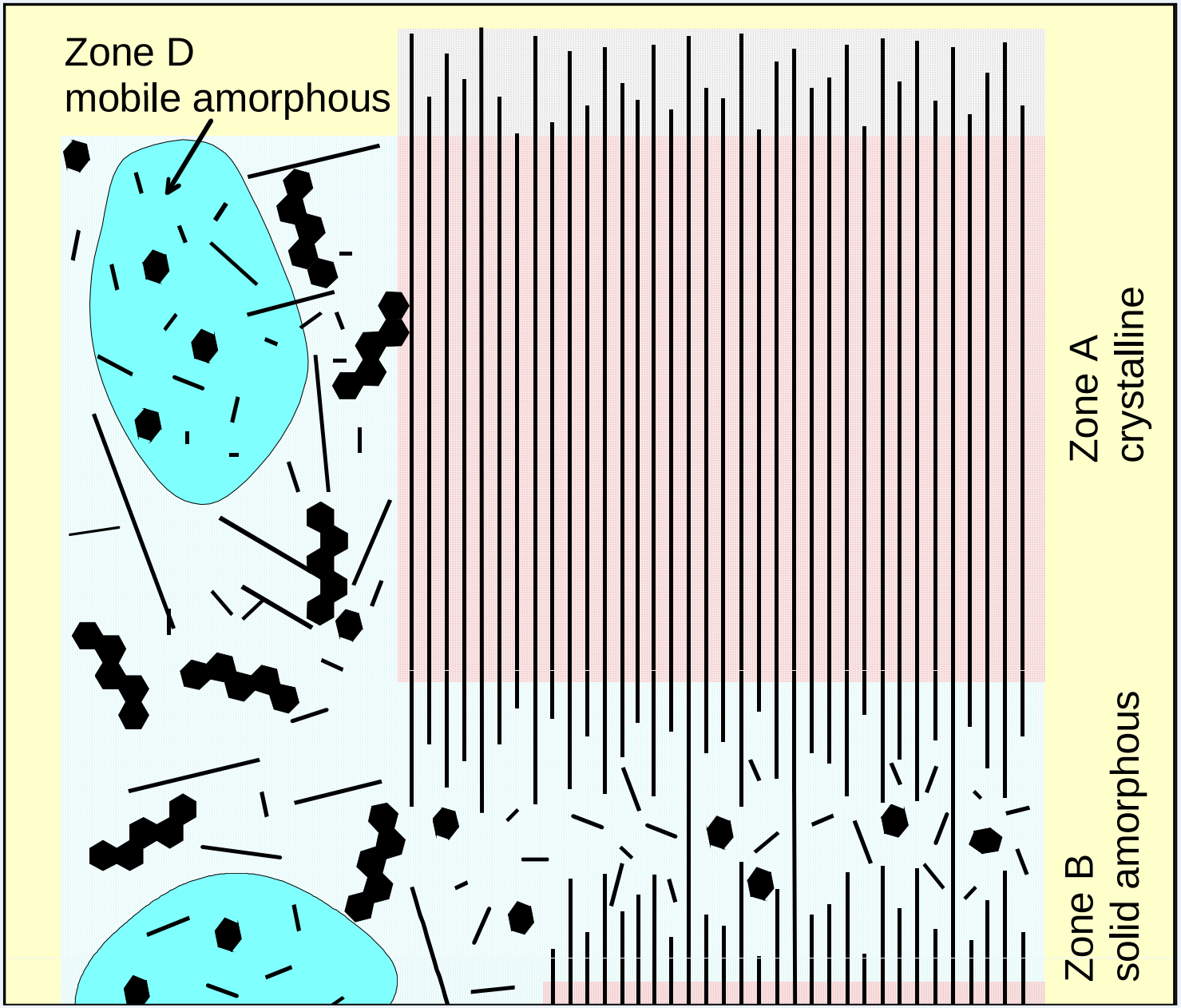
wax chemistry

has effect on

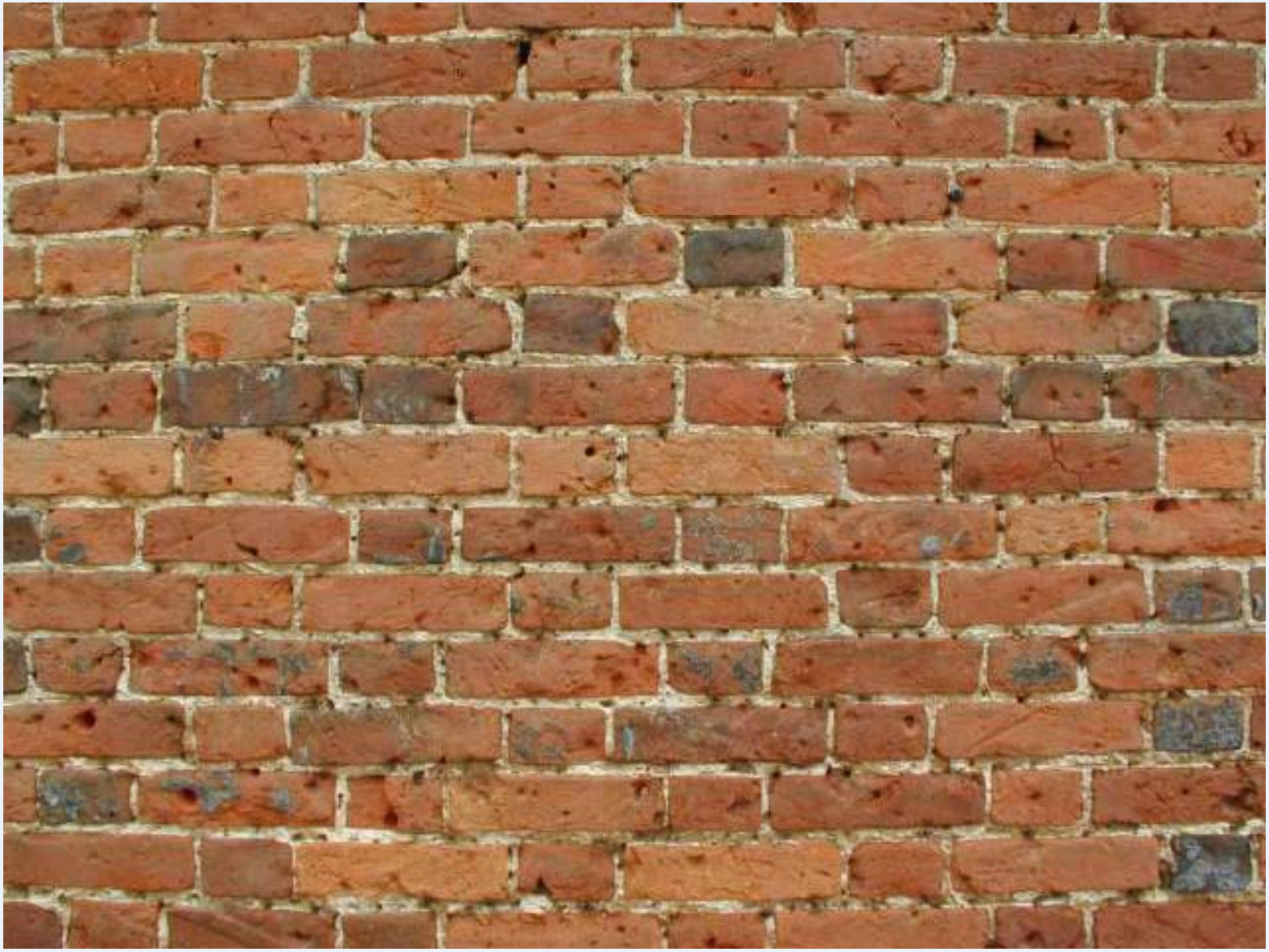
water permeability

Structure of waxes on molecular scale?

- solid state NMR,
- ATR-Fourrier Transform Infrared spectroscopy

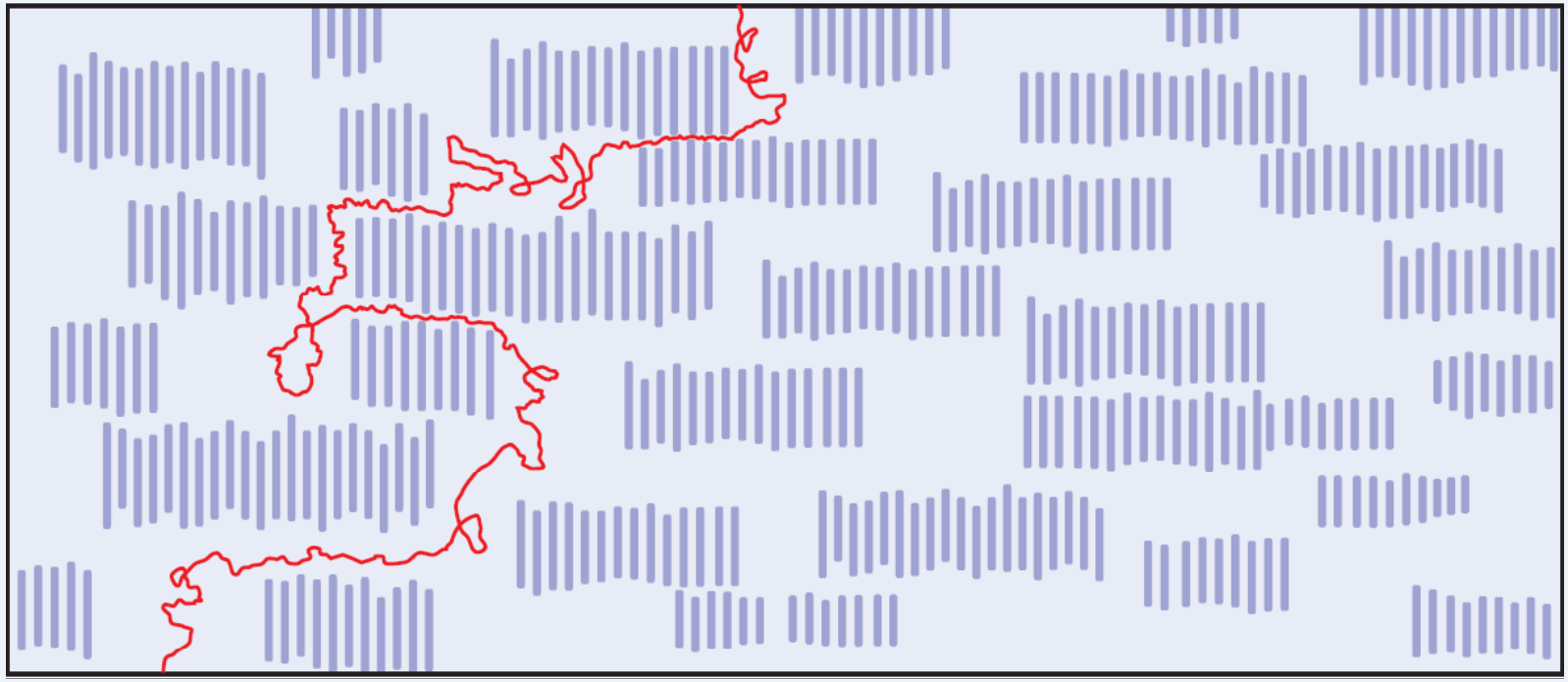


(Riederer & Schreiber, 1995)

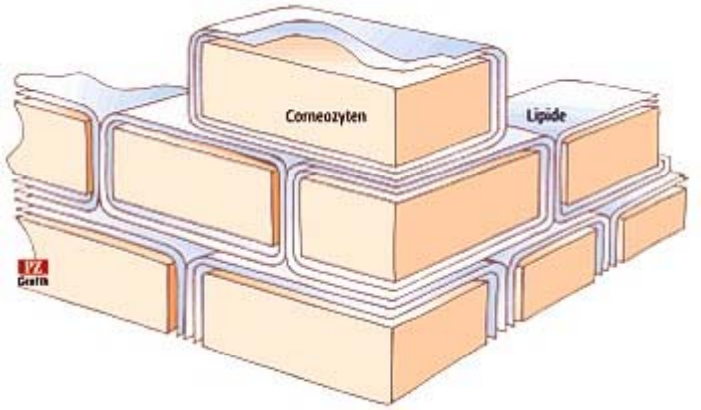


http://www.deskpicture.com/DPs/Miscellaneous/PittedBrickWall_g.jpg

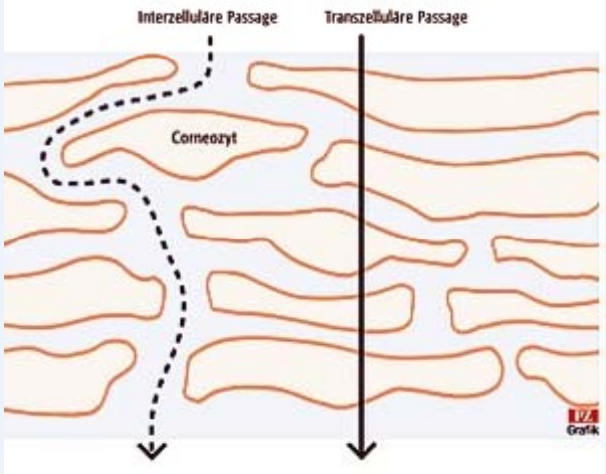
„Bricks“ are excluded from diffusion
„Mortar“ only is accessible



Diffusion path is tortuous and long
=> very low diffusion coefficients in the wax (10^{-20} m^2 s^{-1})

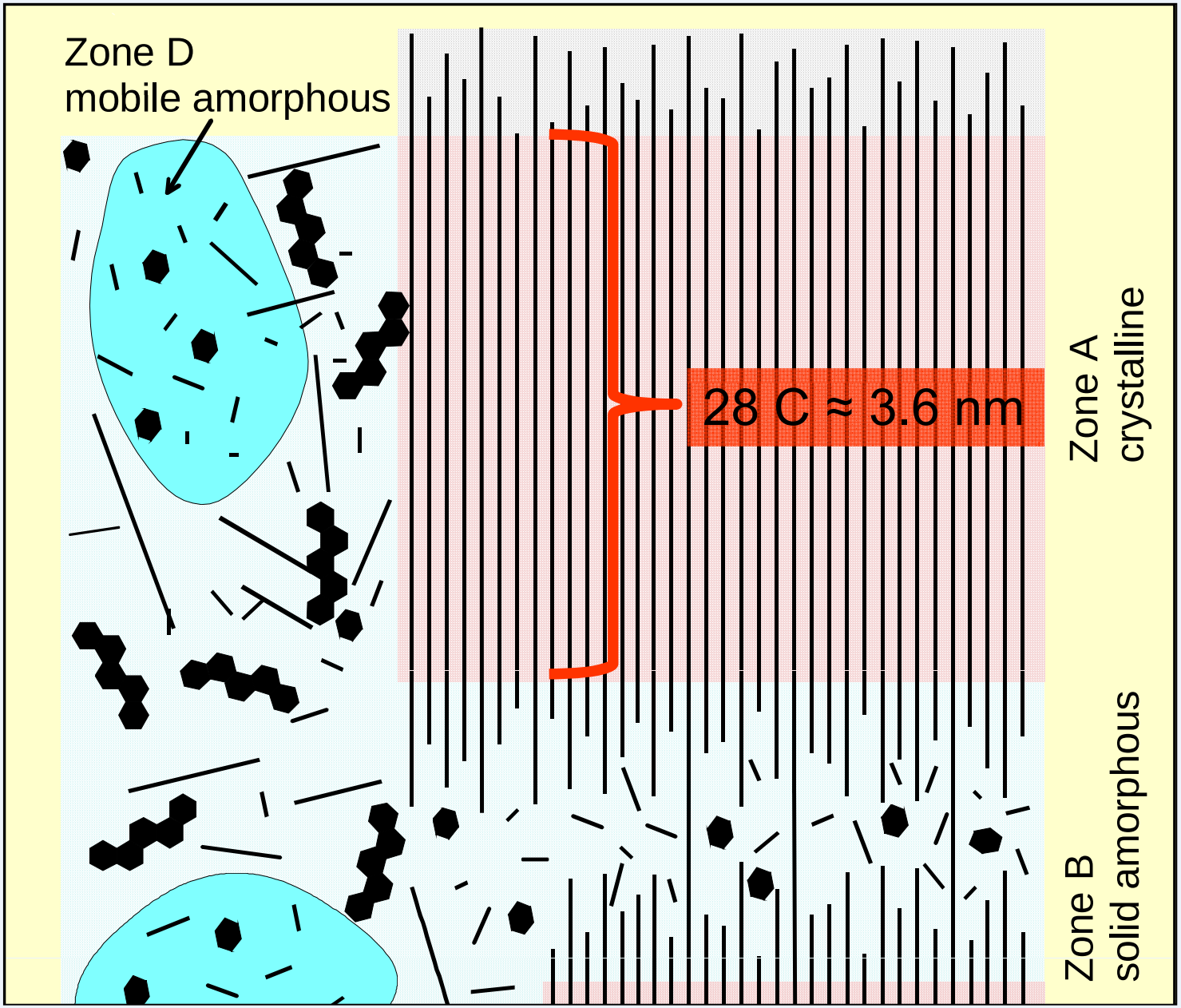


SC thickness ca. 20 µm



corneocyte thickness ca 0.1 - 2 µm

http://www.pharmazeutische-zeitung.de/index.php?id=2957



(Riederer & Schreiber, 1995)

Manipulating crystallinity

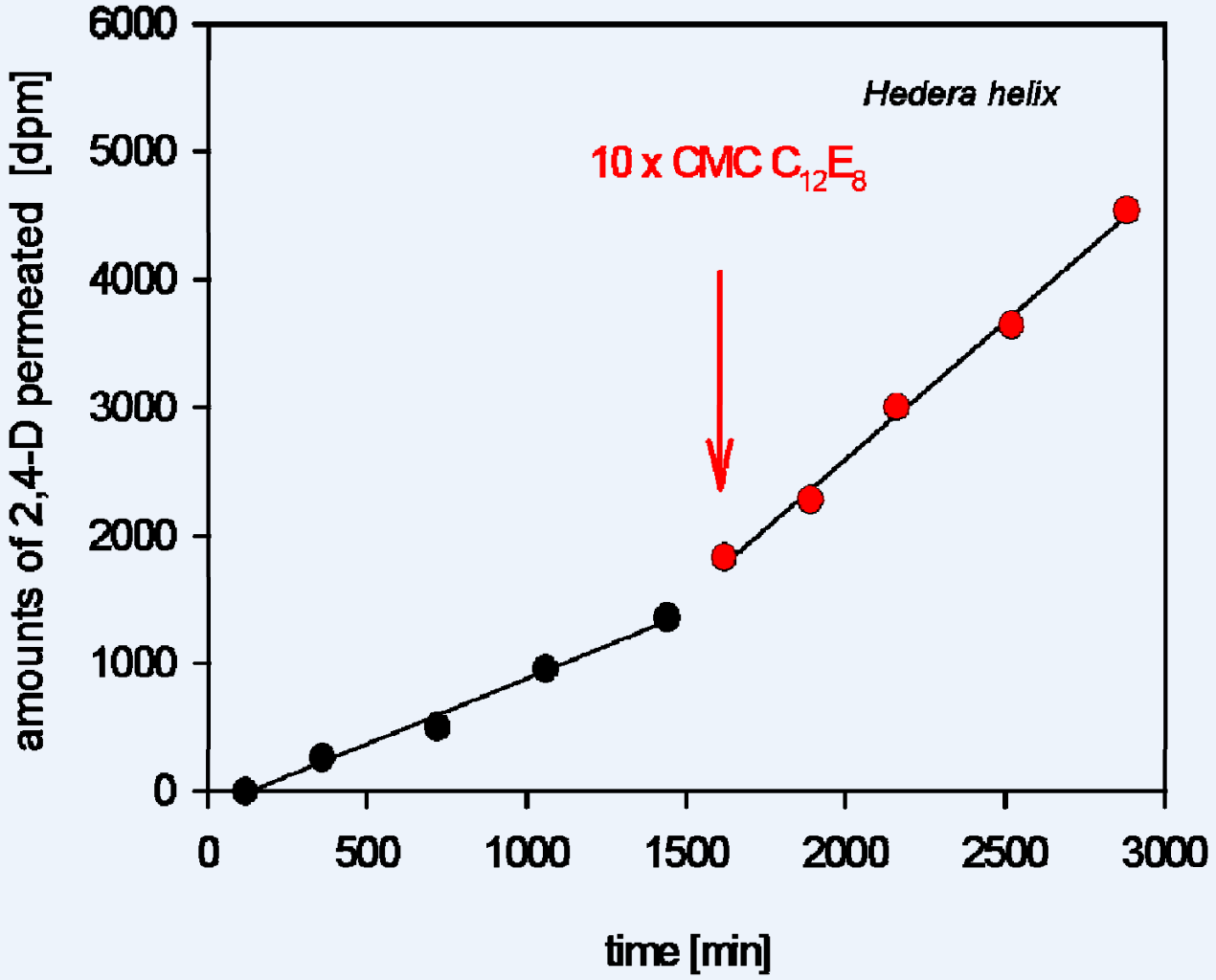
„Penetration enhancers“

Me-oleate

Alcohol ethoxylates

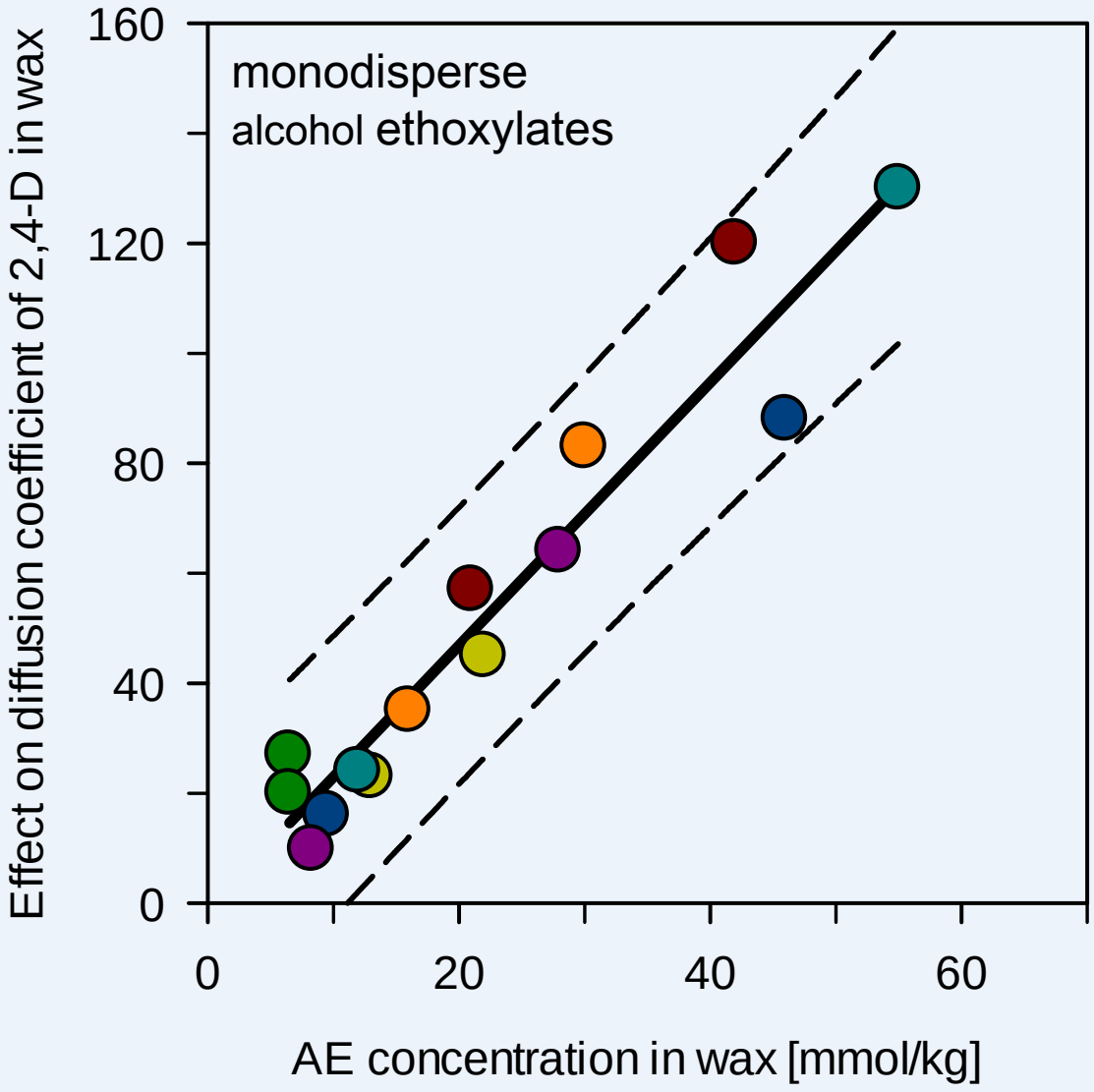
Pentaethylene glycol monododecyl ether
C12E5

Effect of an alcohol ethoxylate on 2,4-D permeability



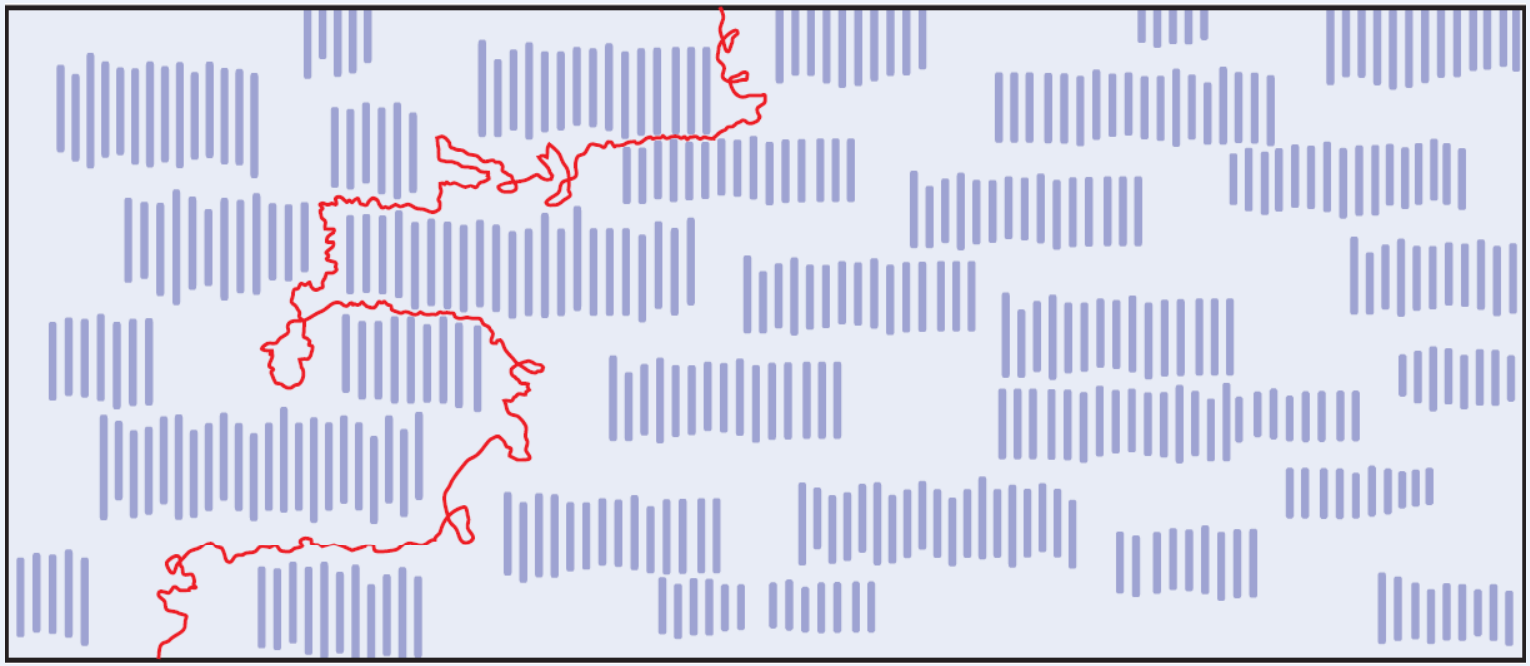
(Burghardt et al., 1998)

Effect of alcohol ethoxylates on 2,4-D diffusion coefficient

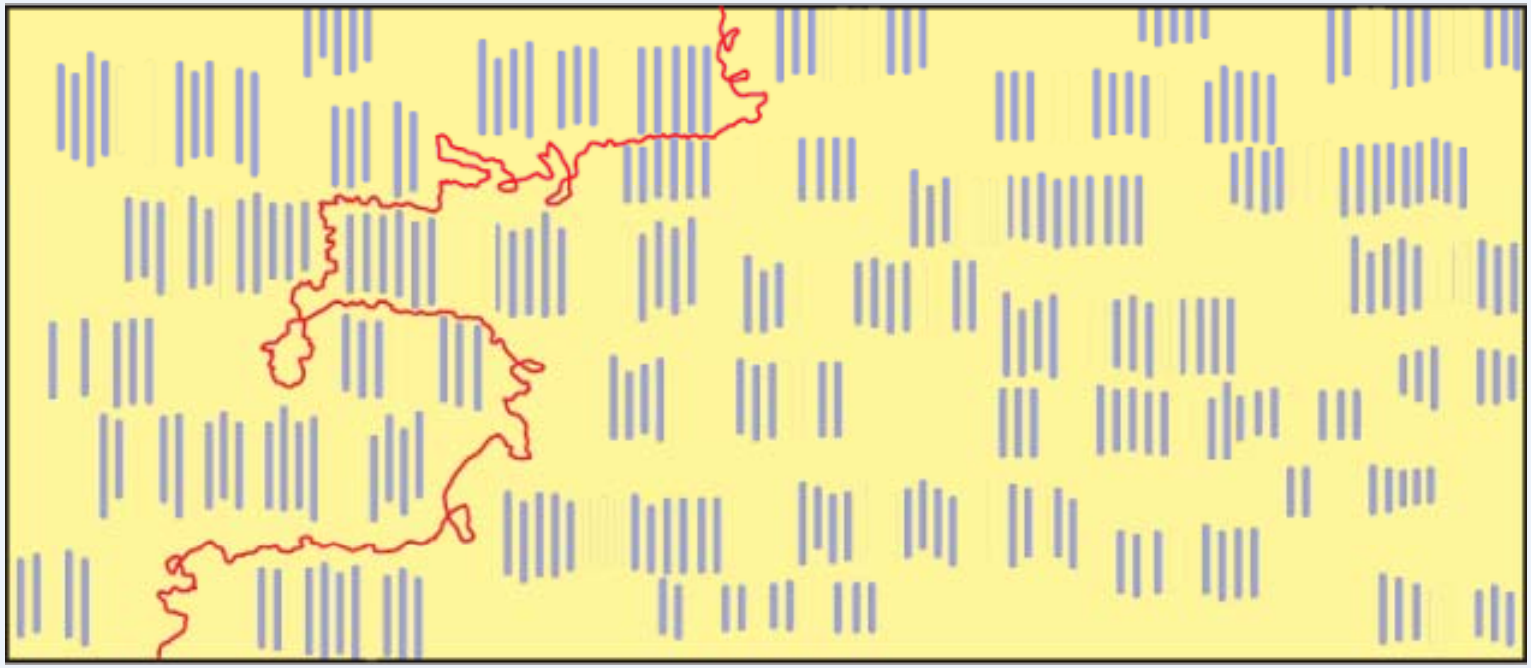


Riederer M et al. (1995) J Agric Food Chem 43: 1067-1075

Native structure of wax barrier



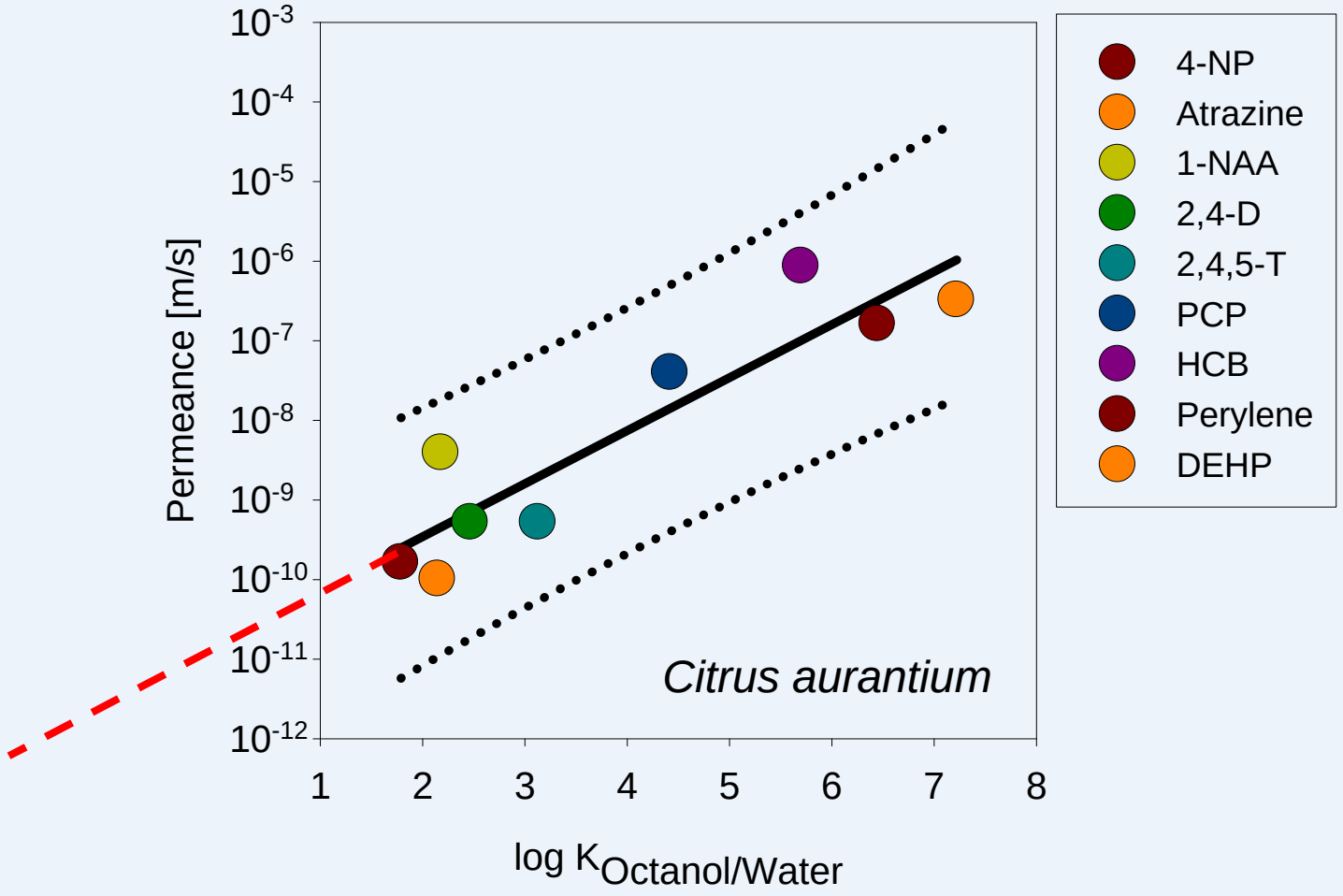
With plasticizer



Penetration of polar compounds

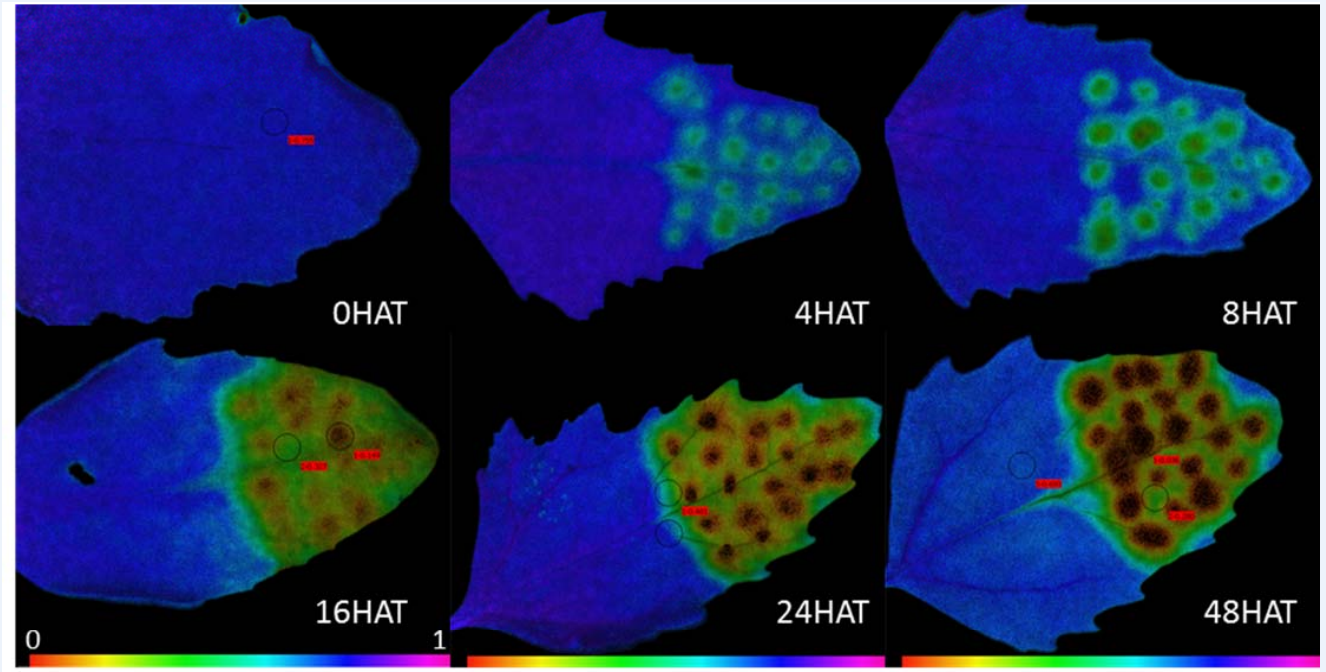
(solution-diffusion?)

Effect of lipophilicity on permeability



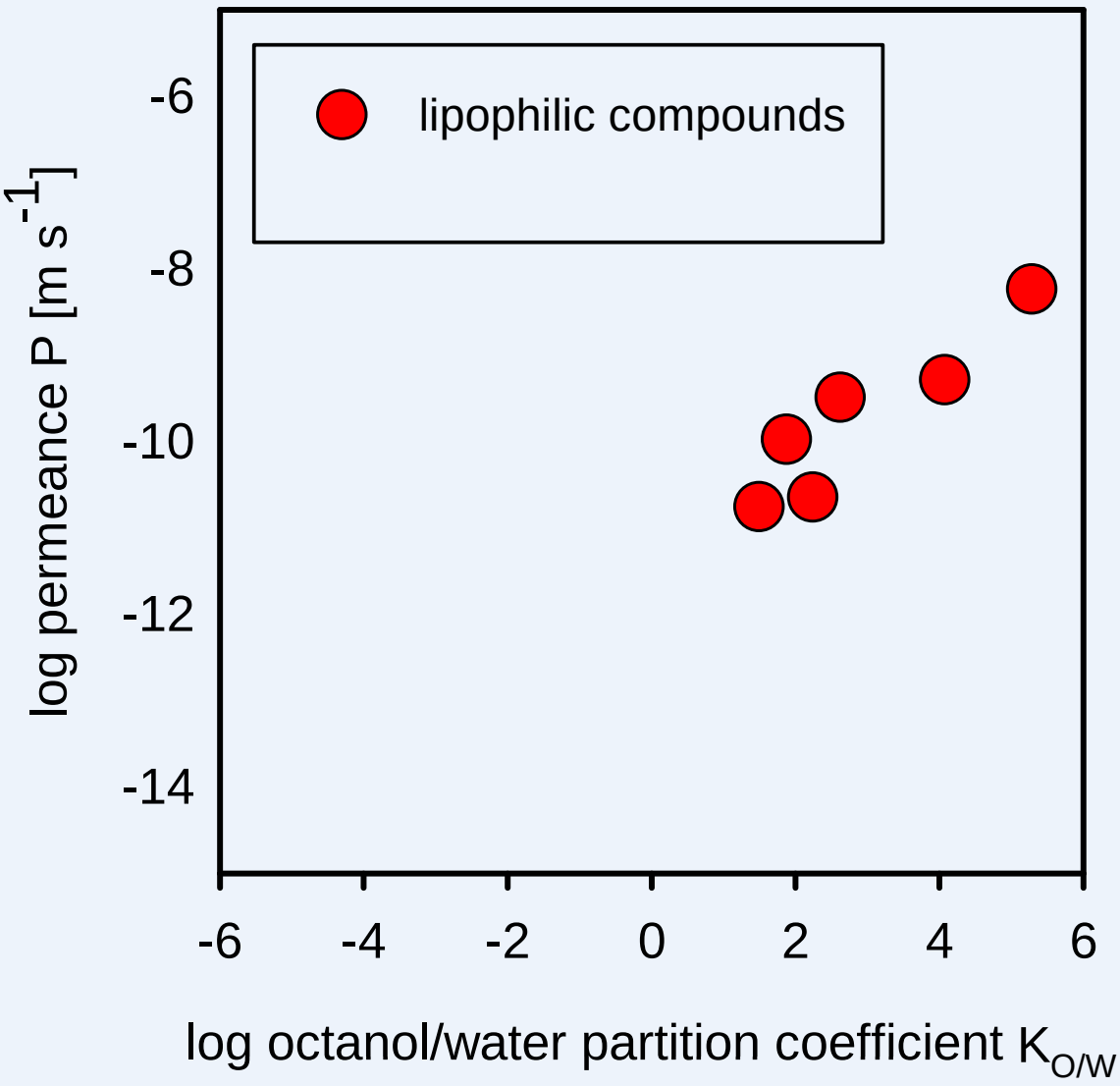
(Data from Kerler, Riederer and Schönherr)

Chenopodium album + Bentazon



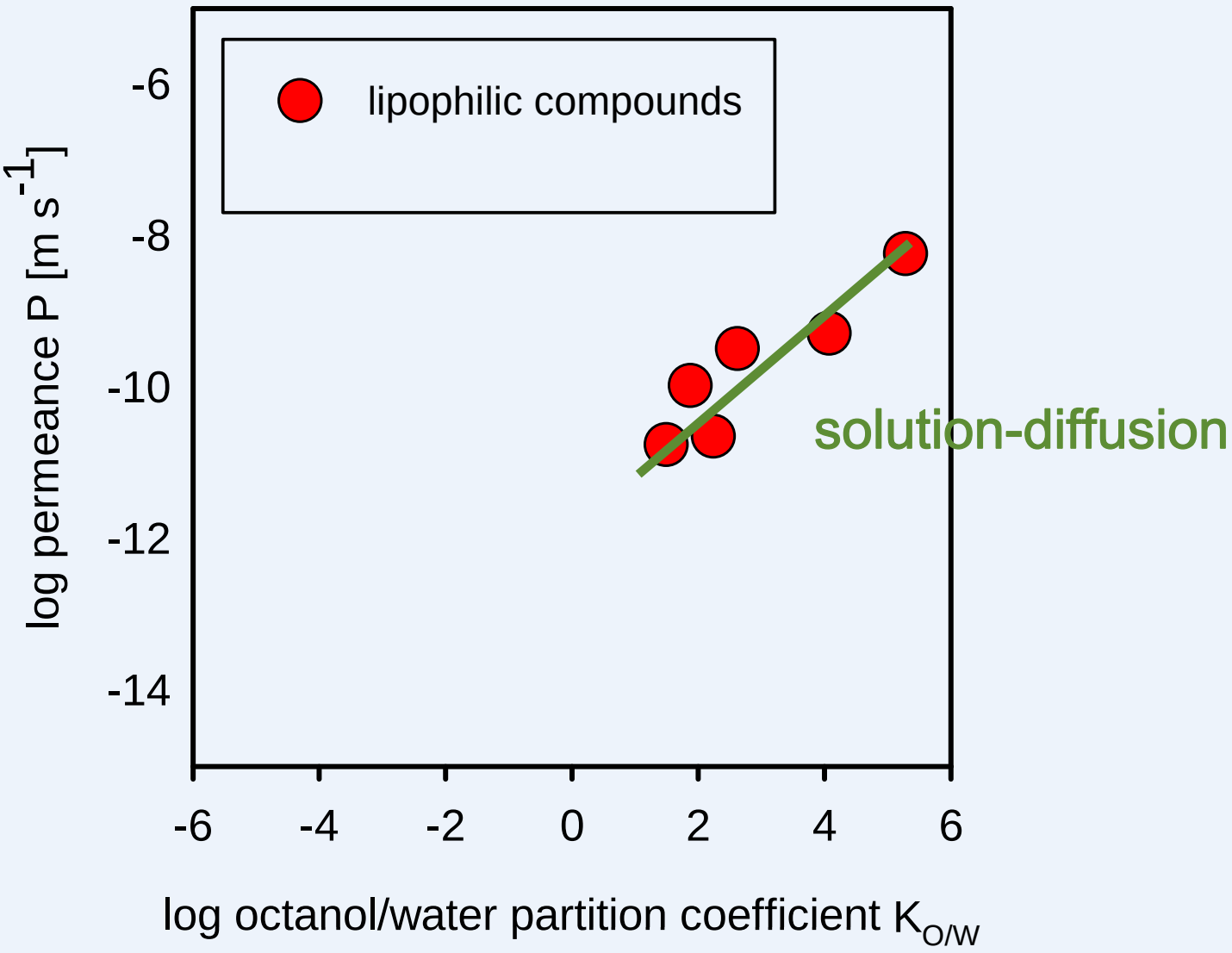
Energetic Yield of Photosystem II
(HAT, hours after treatment)

(Arand et al. unpublished)

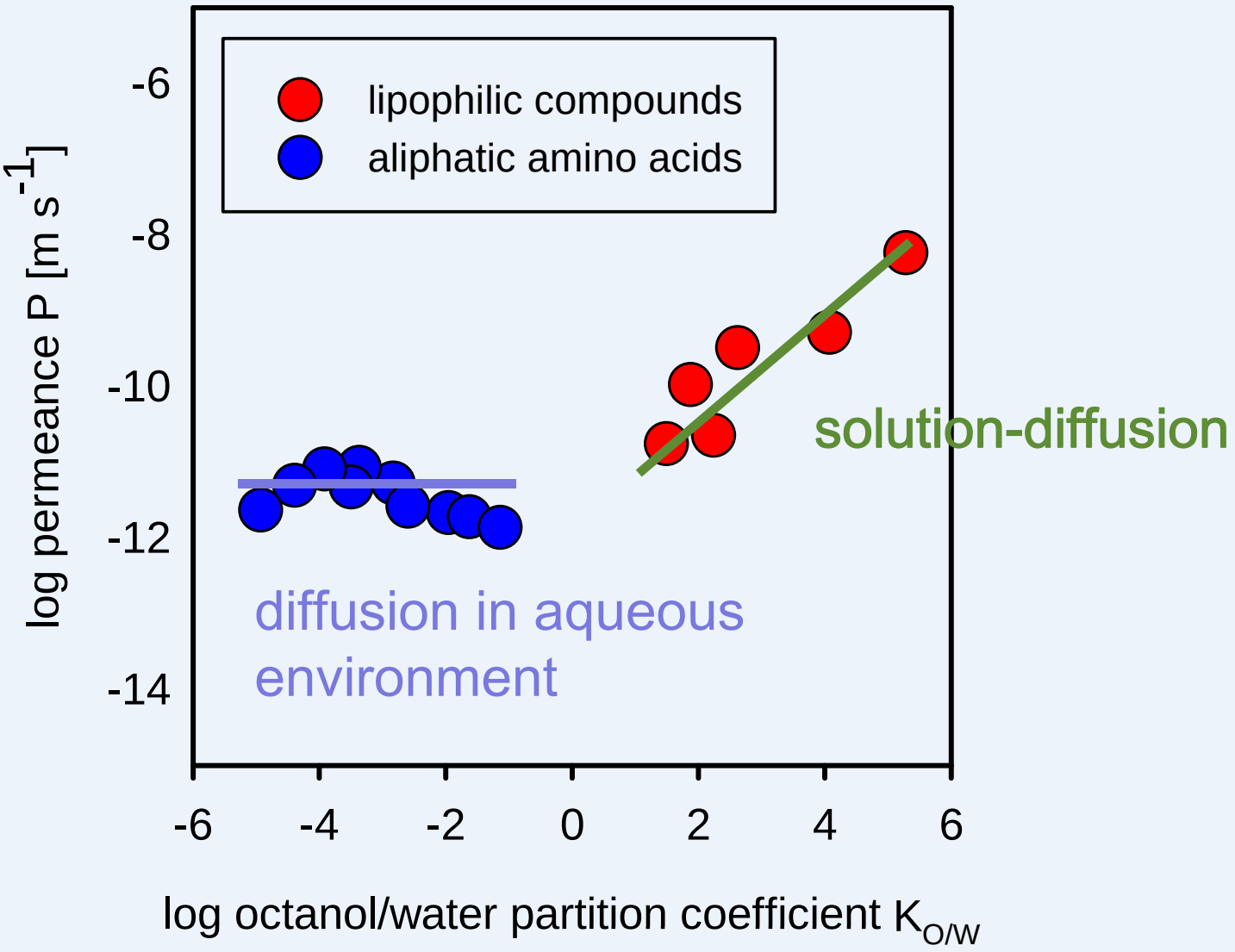


Lipophilicity

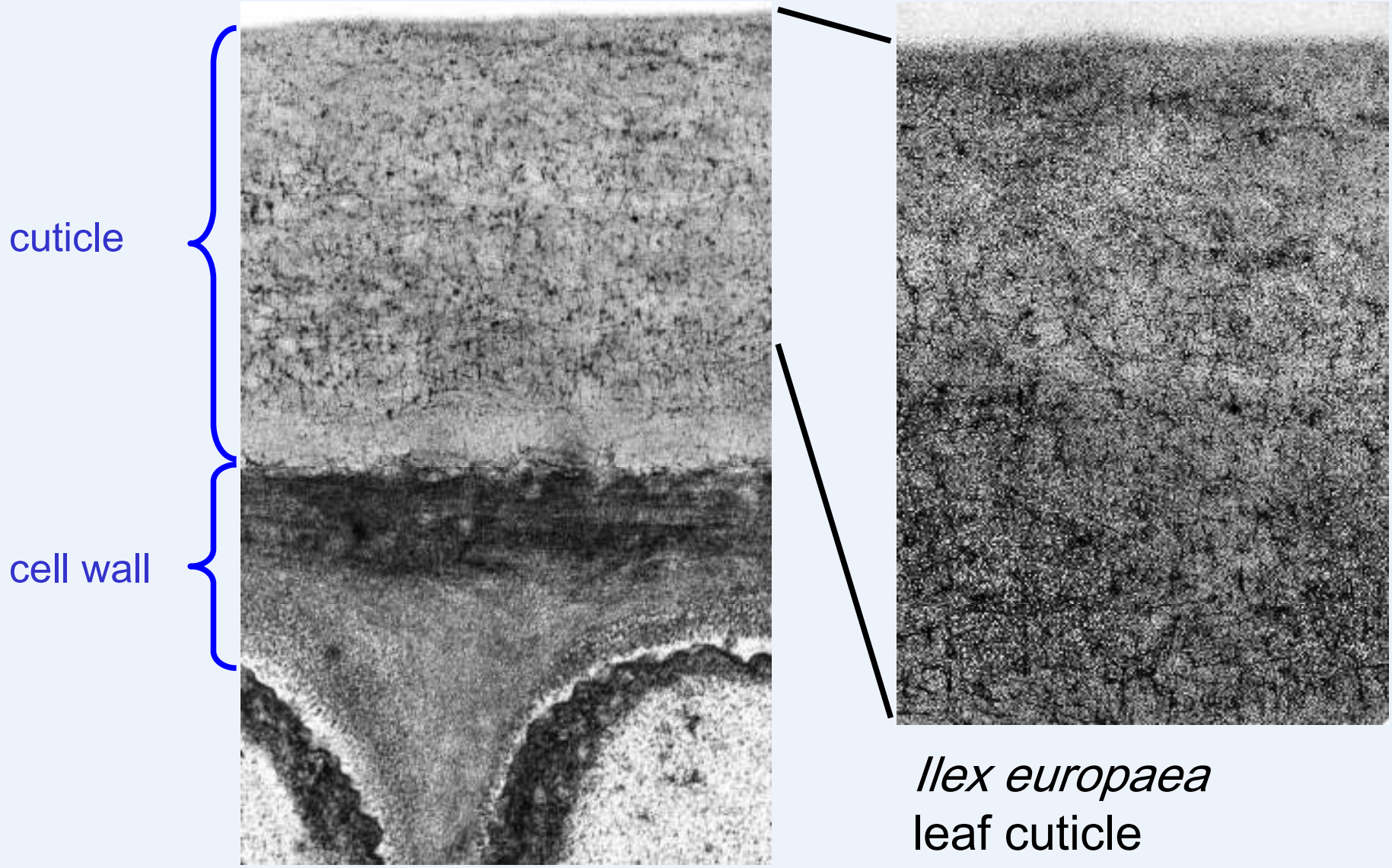
Arand K et al. (2010) J Exp Bot 61: 3865-3873



Arand K et al. (2010) J Exp Bot 61: 3865-3873

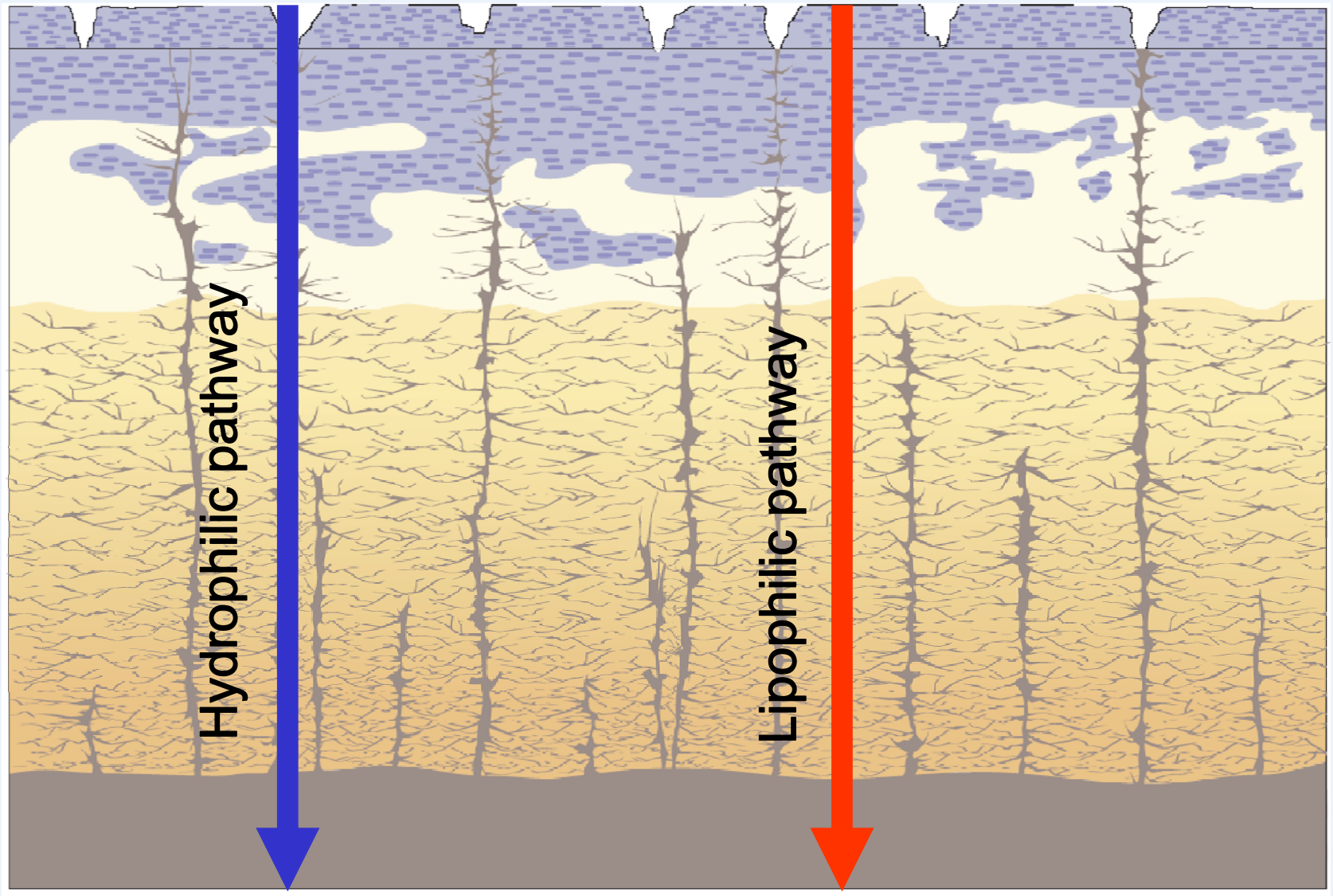


Arand K et al. (2010) J Exp Bot 61: 3865-3873



Ilex europaea
leaf cuticle

(Jeffree, in: Riederer & Müller: Biology of the Plant Cuticle, 2006)


Hydrophilic pathway
Lipophilic pathway

Deutsche Forschungsgemeinschaft DFG

syngenta Crop Protection

syngenta Seed Care

State of Bavaria

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Dr. Michael Riedel

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Thank you!