

RESEARCH PAPER

# Quantitative assessment to the structural basis of water repellency in natural and technical surfaces

P. Wagner, R. Fürstner, W. Barthlott and C. Neinhuis<sup>1</sup>

Botanisches Institut und Botanischer Garten, Rheinische Friedrich-Wilhelms-Universität Bonn, Meckenheimer Allee 170, D-53115 Bonn, Germany

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## Abstract

Many plant surfaces are water-repellent because of a complex 3-dimensional microstructure of the epidermal cells (papillae) and a superimposed layer of hydrophobic wax crystals. Due to its surface tension, water does not spread on such surfaces but forms spherical droplets that lie only on the tips of the microstructures. Studying six species with heavily microstructured surfaces by a new type of confocal light microscopy, the number, height, and average distance of papillae per unit area were measured. These measurements were combined with those of an atomic force microscope which was used to measure the exposed area of the fine-structure on individual papillae. According to calculations based upon these measurements, roughening results in a reduction of the contact area of more than 95% compared with the projected area of a water droplet. By applying water/methanol solutions of decreasing surface tension to a selection of 33 water-repellent species showing different types of surface structures, the critical value at which wetting occurs was determined. The results impressively demonstrated the importance of roughening on different length scales for water-repellency, since extremely papillose surfaces, having an additional wax layer, are able to resist up to 70% methanol. Surfaces that lack papillae or similar structures on the same length scale are much more easily wetted.

Key words: Confocal microscopy, epicuticular wax, plant cuticle, water-repellency.

## Introduction

The surfaces of plants, especially those of leaves, exhibit a great number of structural types that have been studied and classified in detail by scanning electron microscopy in the last 30 years (reviews in Baker and Parsons, 1971; Barthlott, 1981, 1990; Barthlott and Ehler, 1977; Barthlott and Wollenweber, 1981; Bukovac *et al.*, 1981; Holloway and Baker, 1974; Jeffree, 1986). Three general levels of structuring have been identified in this respect: the general cell's shape (primary-), cuticular folds (secondary-) and epicuticular wax crystals (tertiary-structure). Surface structures are also important in a functional respect. Water-repellency has been of particular interest because it is a major factor in spray application processes (Baker *et al.*, 1983; Boize, 1976; Bukovac *et al.*, 1979; Kadota and Matsunaka, 1986; Kuzych and Meggitt, 1983; Watanabe and Yamaguchi, 1991b; Wirth *et al.*, 1991; Zabkiewicz *et al.*, 1988). Therefore, the wettability of leaf surfaces has been studied in detail from the beginning of the last century (Boyce and Berlyn, 1988; Crisp, 1963; Engel, 1939; Fogg, 1947; Hall and Burke, 1974; Holloway, 1970; Linskens, 1950; Moilliet, 1963; Rentschler, 1971; Watanabe and Yamaguchi, 1991a; Ziegenspeck, 1942). From many studies it became apparent that a particular microroughness, especially due to epicuticular wax crystals, is the structural basis of extreme water-repellency of surfaces. Due to their surface tension water droplets form spheres lying only on the tips of the structures. The principal connections between surface roughness and water-repellency were worked out by Cassie and Baxter (1944), as well as Wenzel (1936). Later, the wetting properties of surfaces were subject to intensive studies in physics, as well as in biology, and reviewed several times

<sup>1</sup> Present address and to whom correspondence should be sent: Botanisches Institut, Technische Universität Dresden, D-01069 Dresden, Germany. Fax: +49 351 463 37032. E-mail: Christoph.Neinhuis@mailbox.tu-dresden.de

(Adam, 1963; Adamson, 1990; Bico *et al.*, 1999; de Gennes, 1985; Holloway, 1969, 1970). Nowadays, water-repellency has gained much interest because it represents the basis for a self-cleaning property of such surfaces called the 'lotus effect' (Barthlott and Neinhuis, 1997) which can also be transferred into technical applications (further informations see: [www.lotus-effect.com](http://www.lotus-effect.com)).

In an earlier study of about 300 plant species, Neinhuis and Barthlott (1997) showed that a wide range of different surface morphologies is suitable to serve as a basis for a water-repellent and self-cleaning surface. Although, intuitively, some species appeared to be more optimized to non-wetting (especially those with prominent epidermal papillae covered with an additional layer of wax crystals) conventional contact angle measurements did not allow any clear differentiation between individual morphologies. In addition, the real contact area between a water droplet and a rough surface has never been determined in an experimental approach, although it is generally accepted that the reduction in contact area and the enclosure of air between microstructures is the most important factor to induce non-wetting (Dettre and Johnson, 1964; Herminghaus, 2000; Holloway, 1970).

Therefore a new approach to address both questions was adopted. The first approach is based on the assumption that certain morphologies are better adapted to non-wetting, i.e. if the surface tension of a liquid is reduced, some species should be wetted more easily than others. To address this question, a range of species was tested against water–methanol mixtures with decreasing surface tension to determine the critical value at which wetting occurs.

In a second approach, an attempt was made to determine the contact area between a water droplet and a rough surface base compared with the projected area of the droplet. This was done by measuring and calculating the exposed area of differently structured surfaces combining confocal white light microscopy and atomic force microscopy, since the minimization of the contact area was supposed to be one of the major reasons for extreme water-repellency.

## Materials and methods

### Plant material

All plants were taken from the Botanical Garden of the University of Bonn (Germany) and represent a selection of microstructured plants (Table 1) based on the list published by Neinhuis and Barthlott (1997). For the combined investigation with confocal light microscopy (CLM) and atomic force microscopy (AFM) six species (marked in bold in Table 1) were chosen due to their prominent primary sculpture and extreme water-repellency (Fig. 1a–e). In total, 31 species were taken without further preparation for the wetting test with methanol–water mixtures.

### Artificial surfaces

In addition to the plant surfaces, several artificial microstructured hydrophobic surfaces were tested. They can be divided into (a) replicates of leaf surfaces (Fig. 1 f) and (b) technical surfaces made of metal with electrochemically deposited microstructures (Fig. 1g, h).

Replicates were made of a negative form worked out with a 2-component silicone moulding mass (President light body, Coltene, Switzerland). After drying, the negative is flexible and rubber-like. Into this a conventional lacquer (Acryllack, seidenmatt weiß, Karl Knauber, Germany) or a liquid polymer (polyether, ZK 2068-026, BASF, Germany) was filled, which resulted in an almost perfect replicate of a leaf's surface up to details in the range of 1 µm when dry. Epicuticular wax crystals could not be replicated because of their poor mechanical stability.

The metal surfaces used for the experiments are fabricated for printed electronic circuits representing copper-foils with a smooth upper surface and a heavily structured lower surface (Bolta, Germany, Circuit Foil, Luxemburg). The surfaces of some of these samples are strongly reminiscent of a microstructured leaf surface. Becromal (Frolyt, Freiberg, Germany) is an electrochemically microstructured aluminium surface used for condensator manufacturing.

Both replicates and metal foils were gold sputtered for 40 s and hydrophobized with 1-hexadecanethiol (Merck-Schuchard, Hohenbrunn, Germany)/heptane (Carl Roth, Karlsruhe, Germany). The metal surfaces were additionally hydrophobized with Dynasilan (Sivento, Rheinfelden, Germany) or Antispray (Dr Tillwich, Horb-Ahldorf, Germany), both are fluorinated agents. In Dynasilan a SiO-group adheres to the surface while the molecule's F<sub>3</sub>C-end is exposed to the air. Antispray polymerizes on the surface. Hexadecanethiol is a non-fluorized agent, which the SH-group binds to the gold atoms of the surface while exposing the hydrophobic CH<sub>3</sub>-group.

### Specimen preparation

Samples of the leaf surfaces were cut into 5×5 mm in size avoiding the leaf's veins, dehydrated and fixed according to the liquid-substitution method (Ensikat and Barthlott, 1993), allowing long-term investigation of the prepared plant specimens with CLM or AFM. In addition, SEM investigation of the same sample is possible for more than 30 min.

The samples were fixed to microscope-slides for CLM-investigation or an AFM-specimen holder using 2-component epoxide-gluue (UHU plus schnellfest, UHU, Bühl, Germany), sputter-coated (SCD 034, Balzers Union, Wiesbaden, Germany) with gold of approximately 10 nm thickness in order to increase electrical conductivity (SEM) or light reflection (CLM).

### Wetting with water–methanol solutions

In order to find out differences between surfaces that are water-repellent (contact angles >150°), but show differently microstructured surfaces, water–methanol mixtures were applied. Methanol is a suitable medium because it is miscible with water in any concentration, lowers the surface tension (Fig. 2) and does not alter the wax ultrastructure, which has been demonstrated earlier (Neinhuis and Edelmann, 1996). The specimens have been fixed to a tilted surface (θ=25°) with double-sided adhesive tape to allow droplets to bounce off the surface. A single use syringe (vol=10 ml) has been attached to a tripod in a way that the tip of the drain tube (inner diameter: 0.70 mm; Braun Sterican Gr. 12, 0.70×30 mm) was fixed 10 mm above the specimen surface. The methanol was added to distilled water, weight in mass-percentage, in steps of 5%. Values of the critical surface tension were taken as follows: individual droplets of water–methanol mixtures (approximately 10 µl) were dropped onto the test

**Table 1.** list of plants (accession numbers of the Botanical Garden, Bonn, are given) treated with water–methanol mixtures

\*, Abaxial leaf side only; bold, measured with the CLM and AFM; (+), plant has been grown for this investigation.

Species	Family	Acc. no.	Primary structure	Epicuticle wax type
<i>Acacia dealbata</i> Link	Mimosaceae	00146	papillose	tubules
<i>Alchemilla mollis</i> (Buser) Rothm.	Rosaceae	10092	trichomes	rodlets
<b><i>Alocasia macrorrhiza</i> (L.) G. Don.</b>	Araceae	01194	papillose*	waxfilm
<i>Apocynum cannabinum</i> L.	Apocynaceae	06118	convex	platelets
<i>Argemone mexicana</i> L.	Papaveraceae	03318	convex	tubules
<i>Berberis gagnepainii</i> Schneid.	Berberidaceae	04155	convex	tubules
<i>Berberis julianae</i> Schneid.	Berberidaceae	01914	convex	tubules
<i>Berberis verruculosa</i> Hemsl. & Wils.	Berberidaceae	12285	convex	tubules
<i>Brassica oleracea</i> L.	Brassicaceae	+	smooth	dendritic rodlets
<i>Chondrilla juncea</i> L.	Asteraceae	03411	trichomes	platelets
<b><i>Colocasia esculenta</i> (L.) Schott.</b>	Araceae	04069	papillose	platelets
<i>Coronilla coronata</i> L.	Fabaceae	03151	convex	tubules
<i>Crambe maritima</i> L.	Brassicaceae	03333	smooth	polymorph
<i>Daphniphyllum humile</i> Maxim.	Daphniphyllaceae	00515	papillose	tubules
<i>Dicentra formosa</i> (Haw.) Walp.	Fumariaceae	03303	convex	tubules
<i>Drimys winteri</i> Forst. & Forst.	Winteraceae	00768	convex	tubules
<i>Eucalyptus macrocarpa</i> Hook	Myrtaceae	00612	convex	tubules
<i>Euphorbia atropurpurea</i> Brouss.	Euphorbiaceae	13695	convex	platelets
<i>Euphorbia characias</i> L.	Euphorbiaceae	14076	convex	platelets
<b><i>Euphorbia myrsinites</i> L.</b>	Euphorbiaceae	08048	papillose	platelets
<i>Ginkgo biloba</i> L.	Ginkgoaceae	01894	convex	tubules
<i>Hebe albicans</i> (Petrie) Ckn.	Scrophulariaceae	00728	papillose	platelets
<i>Iris japonica</i> Thunb.	Iridaceae	00283	convex	platelets
<b><i>Liriodendron chinense</i> (Hemsl.) Sarg.</b>	Magnoliaceae	15354	papillose*	transv. ridged rodlets
<i>Marsilea drummondii</i> A.Br.	Marsileaceae	00225	convex	platelets
<b><i>Nelumbo nucifera</i> (Willd.) Pers.</b>	Nelumbonaceae	11705	papillose	tubules
<i>Neptunia plena</i> (L.) Benth.	Mimosaceae	15656	papillose	platelets
<i>Oryza sativa</i> L.	Poaceae	08616	papillose	platelets
<i>Papaver atlanticum</i> (Ball) Coss.	Papaveraceae	03315	papillose	tubules
<i>Thalictrum flavum</i> (Desf.) Battand.	Ranunculaceae	02700	convex	tubules
<i>Tropaeolum majus</i> L.	Tropaeolaceae	+	convex	tubules
<b><i>Xanthosoma nigrum</i> (Vell.) Mansf.</b>	Araceae	16126	papillose*	platelets
<b><i>Xanthosoma spec.</i></b>	Araceae	01070	papillose*	platelets

surface according to Fig. 3 and (a) bounced off if the critical surface tension was not reached or (b) partially wetted the test surface and got stuck if the critical surface tension was reached. Those values are presented in Fig. 7. Convergently to the surface tension, the overall mass of the droplets decreased from 10.4 µg (pure distilled water) to 3.8 µg (solution with about 90% methanol) due the lower density of methanol. The experiments have been carried out at room temperature (approximately 23 °C). On the basis of preceding tests contact angles were not measured because methanol evaporates too fast from small droplets and therefore no standardized conditions could be established.

### Microscopy

The CLM used is a recently developed new type of white light confocal microscope (µ-surf, NanoFocus, Duisburg, Germany) which has been designed specifically for the 3D-investigation of microstructures (Fig. 4). The digital images were analysed by NanoFocus software. More detailed information is given by Jordan *et al.* (1998).

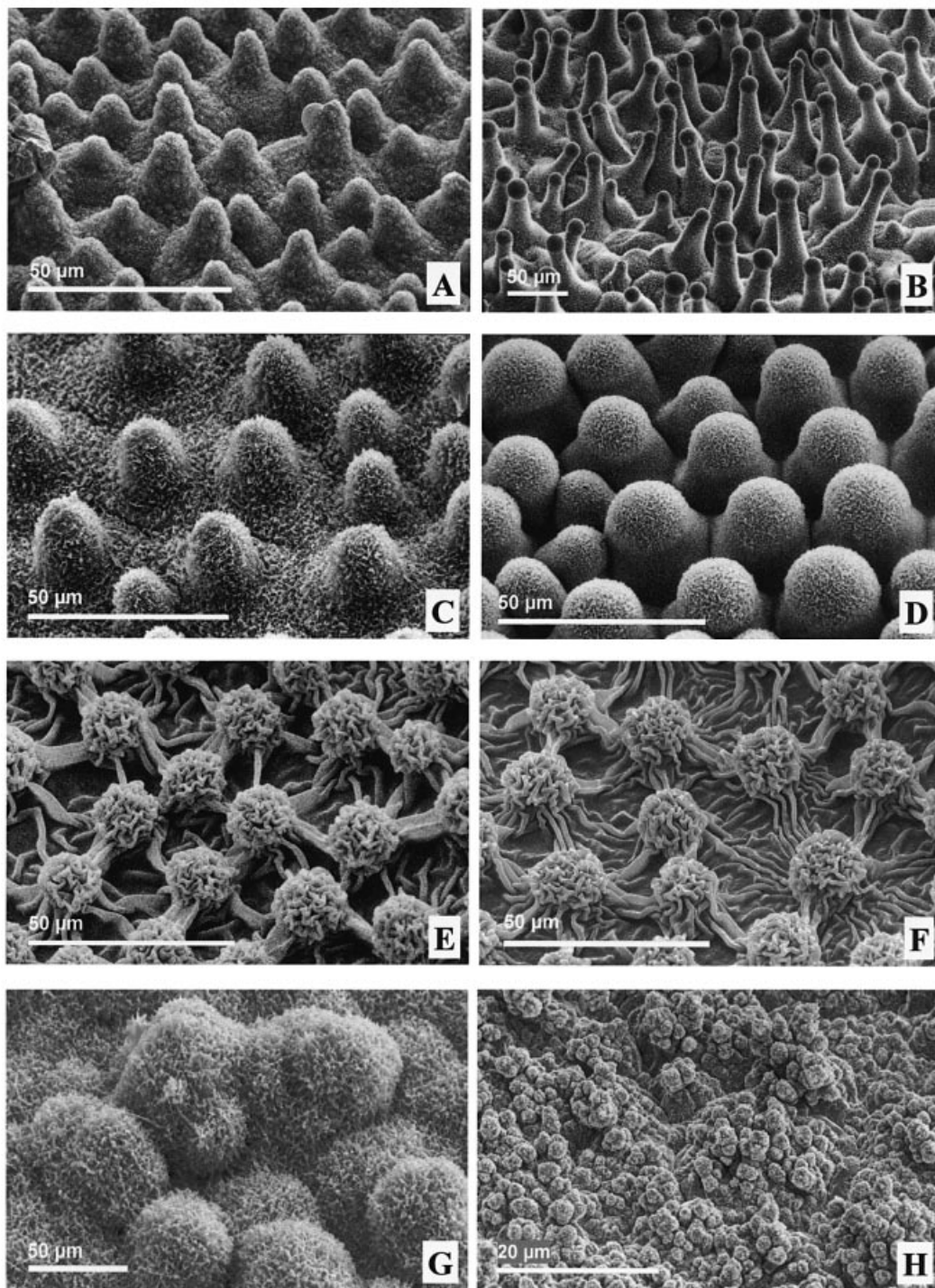
A standard AFM (NanoScope IIIa, Digital Instruments, Mannheim, Germany) was used applying the tapping-mode. The needles used were one-piece and made of silicon, type: Nanoprobe SPM™, TESP, L=125 µm,  $F_0=298\text{--}312$  kHz.

All specimens have been additionally investigated by SEM (Cambridge Stereoscan 200, Oxford, UK; LEO 440, LEO, Oberkochen, Germany).

### Measurement techniques

In order to measure the surface's primary sculpture from a leaf by CLM usually 10 (20 on *Alocasia macrorrhiza*) epidermal papillae have been selected and surveyed in X-, Y- and a diagonal direction over the papilla's centre. Each survey results in a 2D profile, which has been used for measuring the papilla's height from top to bottom. From each species two digital images have been surveyed. The results of 20 individual papillae have been statistically averaged and the standard deviation (sd) has been calculated. To investigate the papillae's lateral distances a free survey-line has been laid from top to top, for example, the highest point in the image. About five to eight neighbouring cells surrounding a central papilla have been measured and the results have been statistically calculated as mentioned above. From *A. macrorrhiza* only one digital image was available, so 20 epidermal papillae were surveyed from this image. Each sample of the other species has been measured as described above.

A square of usually 20 µm has been scanned by AFM (Fig. 5). These images have been analysed using the bearing-application included in the microscope's software (NanoScope IIIa, vers. 4.23r3). Bearing analysis reveals which area of an investigated surface lies above or below any arbitrarily chosen height. A level of 1.0 was chosen, 0.5 µm below the top of the papillae: these two heights—or better depths—were chosen according to the presumed elastic deformation of a virtual water droplet of two different masses. Such a water droplet lying on a few tips of a microstructured surface is deformed by its own weight, but held in shape by its surface

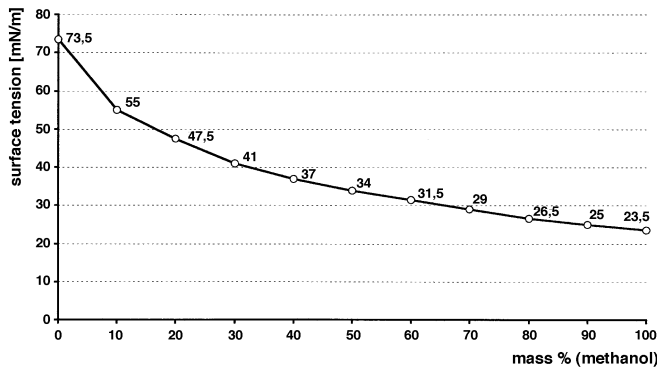


**Fig. 1.** SEM photographs of microstructured water-repellent surfaces. (A) *Nelumbo nucifera* adaxial leaf surface (ad), (B) *Liriodendron chinense* abaxial leaf surface (ab), (C) *Euphorbia myrsinites* ad, (D) *Colocasia esculenta* ad, (E) *Alocasia macrorrhiza* ab, (F) replicate of *A. macrorrhiza*, (G) copper-foil Bolta 18 µm B0, (H) copper-foil circuit foil 35 µm NT-TO.

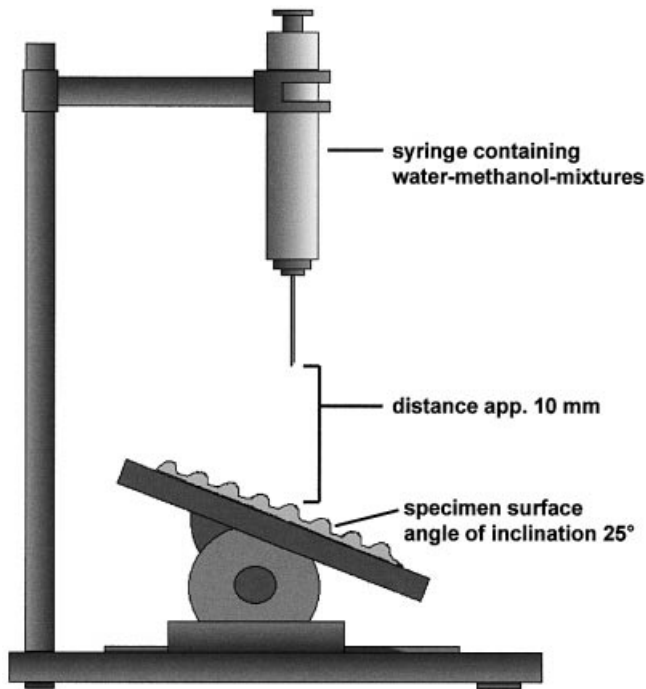
tension. So it bulges its lower part to a certain depth into the microstructure (Fig. 6), lying on the secondary or tertiary structure of the epidermal papillae. According to this deformation the contact area was calculated according to the two different bearing heights.

## Results and discussion

The results of the wetting tests with methanol–water mixtures are given in Fig. 7. Depending on the amount of

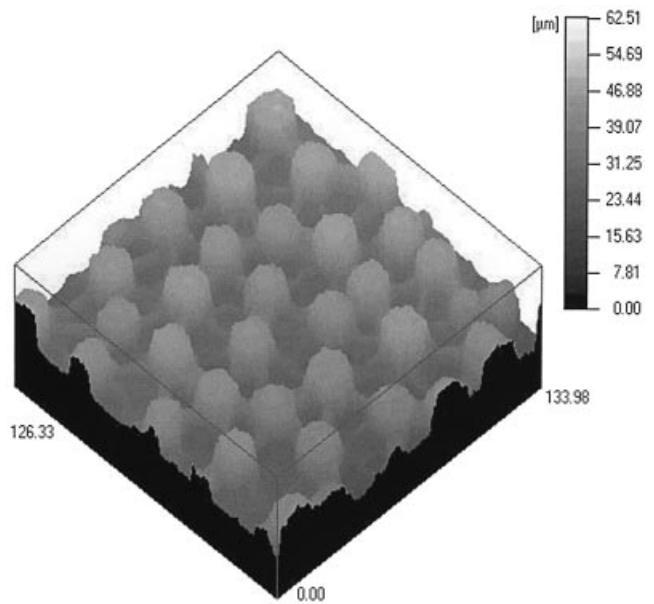


**Fig. 2.** Surface tension of water–methanol mixtures. Increasing the mass-percentage of methanol in water the surface tension of the mixtures is reduced by about 66%.

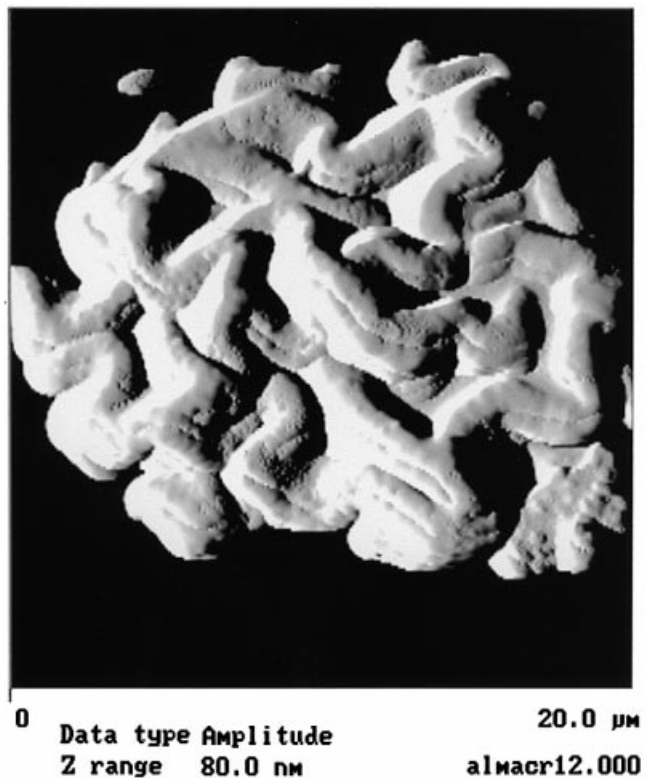


**Fig. 3.** Testing device for the application of individual droplets of water–methanol mixtures on different plant and technical surfaces.

structuring, individual plant surfaces repel mixtures containing up to 75% methanol, in a single measurement of *C. esculenta* up to 80% (not indicated in the figure). There is a gradient in the cell shape directly related to the repellency from left to right. While all *Berberis* species as well as *Alchemilla mollis* exhibit flat or only slightly convex outer epidermal cell walls (apart from the layer of wax crystals that was present in all species), those species with high methanol repellency (for example, *Nelumbo nucifera*, *Colocasia esculenta*) are characterized by very pronounced papillae (Fig. 1a, d). On the other hand there is no evidence that high methanol resistance depends on a specific wax chemistry and micromorphology. The grey



**Fig. 4.** Confocal light microscopic picture of the abaxial leaf surface of *Alocasia macrorrhiza* used for measuring average distance and height of epidermal papillae. The numbers in the corners indicate the length scale, the grey scale indicates the height of papillae.

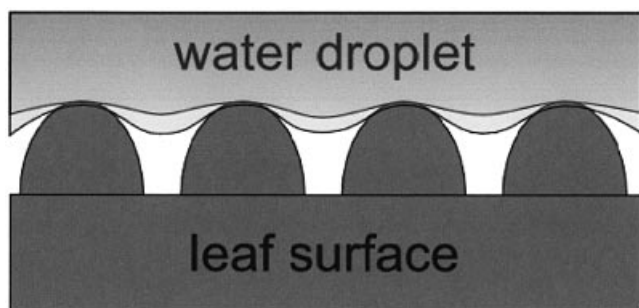


**Fig. 5.** Atomic force microscopic picture of the tip of an individual papilla of *Alocasia macrorrhiza* leaves showing the fine structure based on cuticular folds.

columns indicate the occurrence of small wax tubules composed of the secondary alcohol nonacosan-10-ol

which are found among surfaces characterized by different amounts of structuring at the cell level and therefore of different methanol resistance.

In addition to the plant surfaces some artificial surfaces have been tested. The percentage values up to which a water–methanol droplet was repelled from the surface are shown in Table 2. The very high values of Bolta 18  $\mu\text{m}$  BO-foil (Fig. 1g), which show a methanol-tolerance of up to 90%, are remarkable, in that only almost pure methanol wets the surface. The results of the other artificial surfaces are within the range of the tested plants. However, although the artificial hydrophobization should be more



**Fig. 6.** The drawing visualizes schematically the contact lines of two virtual water droplets with different masses on a papillose surface used to calculate the actual contact areas in relation to the projected areas of the droplets.

**Table 2.** Methanol resistance of hydrophobic technical surfaces

Note that the Bolta copper surface shows very high values while replicates of the lower leaf surface of *Alocasia macrorrhiza* are considerably lower than the original leaf surface independent of the type of hydrophobization.

	Gold Thiol	Antispread	Dynasilan	
CF 35 $\mu\text{m}$ NT-TO	25%	–	30%	
CF 35 $\mu\text{m}$ NT-TW HTE	25%	50%	20%	
Becromal CD888F 86V	25%	–	20%	
Bolta 18 $\mu\text{m}$ BO	70%	$\geq 90\%$	80%	
Replicate made of Polyether BASF ZK 2068-026	–	–	–	30% <sup>a</sup>
Replicate made of Knauber acryllaquer	30%	–	–	

<sup>a</sup>Not hydrophobized due to the hydrophobic nature of the polymer.

**Table 3.** Average number of papillae  $\text{mm}^{-2}$  and the calculated remaining contact area

The calculated contact area of a virtual water droplet of two different masses, modelled by the two bearing depths, is given in (%) in relation to a smooth surface of  $1 \text{ mm}^2$ . All values are average (except *A. macrorrhiza*).

Species	Papillae on $1 \text{ mm}^2$	Contact area (%) according to a depth (d) of	
		(d)=1.0 $\mu\text{m}$	(d)=0.5 $\mu\text{m}$
<i>A. macrorrhiza</i>	2002	5.13	1.50
<i>C. esculenta</i>	2662	7.20	1.71
<i>E. myrsinites</i>	1265	2.74	0.41
<i>L. chinense</i>	737	4.88	1.44
<i>N. nucifera</i>	3431	6.95	1.77
<i>X. spec</i>	967	6.40	1.12

effective, the replicate of the leaf surface of *A. macrorrhiza* shows a considerably lower methanol resistance as compared to the natural surface (30% versus 70% of the leaf).

In earlier papers dealing with water repellency, the surface roughness has attracted much attention, because it is obviously the reason for contact angles close to  $180^\circ$  (Bico *et al.*, 1999; Busscher *et al.*, 1984; Cassie and Baxter, 1944; Dettre and Johnson, 1964; Holloway, 1970; Wenzel, 1936). In these papers the actual kind of roughness has been recorded only as long as they were periodic, for example, grids or columns or were supposed to be fractal (Onda *et al.*, 1996; Shibuichi *et al.*, 1996, 1998). Natural surfaces rarely show periodic structures, some have been regarded as self-affine, but generally they exhibit a random distribution of structures on different length scales. On the other hand, investigations of water-repellent surfaces that included a detailed description of the structures, were not correlated with the wetting properties since contact angle measurements of the water droplets did not allow differentiation between individual topologies (Holloway, 1970; Neinhuis and Barthlott, 1997). The results presented here show the effectiveness of combined structures which have been theoretically postulated earlier (Herminghaus, 2000). In particular, the formation of papillae is a good design to increase water-repellency. This may be due to the fact that waxes in general are not very hydrophobic because of many hydrophilic functional groups (e.g.  $-\text{OH}$ ,  $-\text{COOH}$ ,

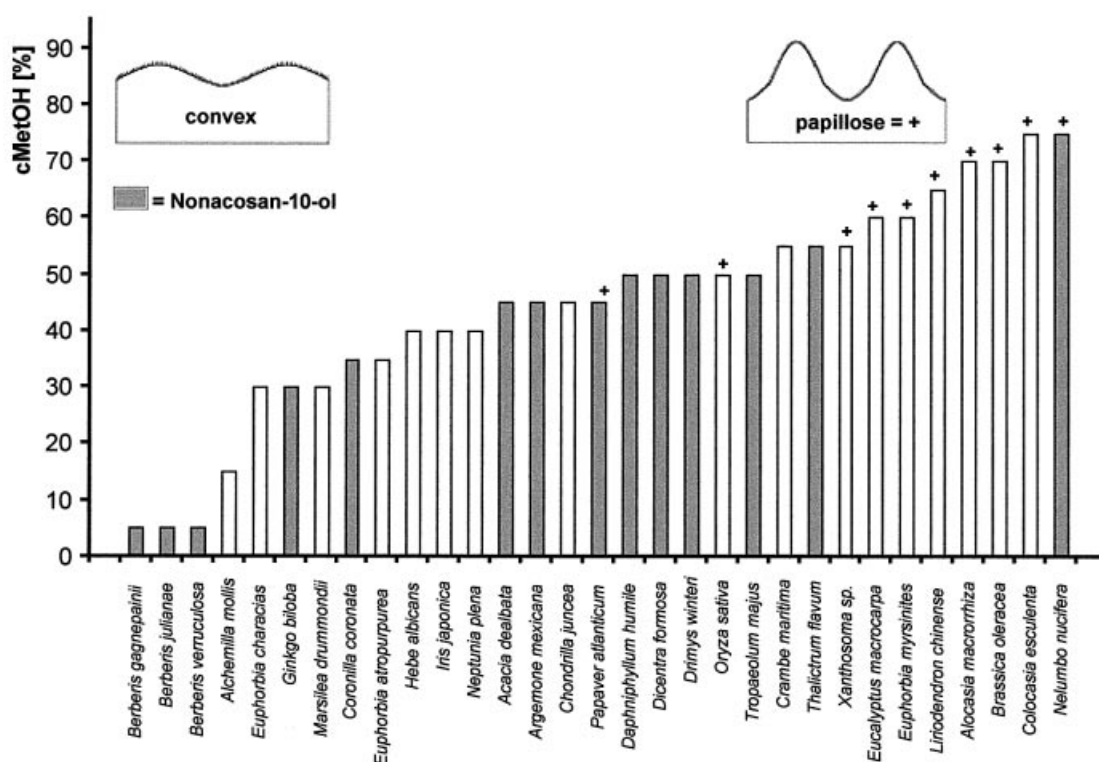
–CHO). As demonstrated by Herminghaus (2000), specific combinations of structures on different length scales can result in water-repellent surfaces (not ultra-phobic) although the intrinsic contact angle of a specific chemical on the surface is below  $90^\circ$ . From the biological point of view, an explanation for the evolution of such ‘over-optimized’ surfaces may be found in the fact, that plants (especially under wetland conditions) often have to deal with water that may be polluted with oily or amphiphilic substances. These substances originate from decaying organic matter and may decrease the surface tension. To achieve this goal, water-repellency caused by wax crystals in the range of  $0.5\text{--}5\ \mu\text{m}$  seems not to be sufficient, but needs an additional surface structure in the range of  $20\text{--}50\ \mu\text{m}$ , which is provided by the shape of the outer epidermal cell walls. Other reasons for developing water-repellent surfaces have been discussed by Neinhuis and Barthlott (1997).

The resistance of up to 90% methanol in the case of one of the copper foils may be explained by the combination of a highly effective surface structure that is hardly distinguishable from plant surface, together with a fluorinated hydrophobic chemical that minimizes the surface energy. As in the plant surfaces, the metals show a similar behaviour in that respect, that individual combinations of

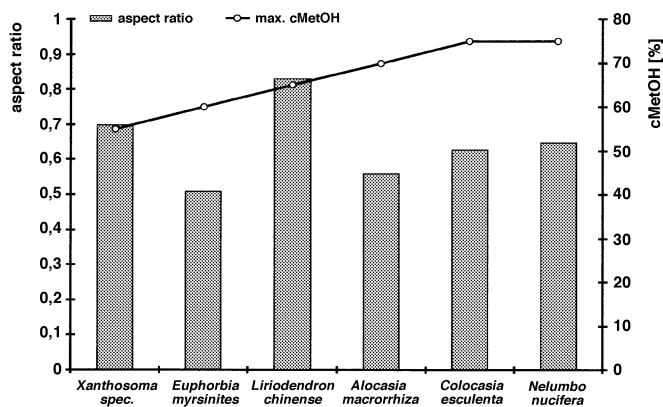
structures have an enormous influence on the wetting properties, which can be seen from those experiments where the same type of hydrophobic chemical has been applied. However, the contradictory behaviour of the replicates from leaves of *A. macrorrhiza* still remains to be explained.

In the second approach the surface structures of six of the most extremely water- and methanol-repellent plant surfaces have been investigated by CLM and AFM. The papillae representing a length scale of some  $10\ \mu\text{m}$  show an aspect ratio (height/distance) smaller than one (Fig. 8). Statistically tested, there is no correlation between this parameter and the resistance against high methanol concentrations (X versus Y scatter plot:  $r^2=0.0071$ ). Using the digital images of the CLM it was possible to calculate the average number of papillae  $\text{mm}^{-2}$  (Table 3). It is remarkable that, although all surfaces are water-repellent, the papillae density varies between 737 and 3431. At the same time, the aspect ratio does not show such a variation. In *X. spec.* and *L. chinense* with comparatively high skittle-like papillae ( $27.8$  and  $38.6\ \mu\text{m}$ ) the cells correspondingly have a greater lateral distance compared with those with lower papillae.

These results are in good accordance with the theoretical background about water-repellency of microstructured



**Fig. 7.** Resistance of leaf surfaces against wetting with water–methanol mixtures. Leaf surfaces without papillose epidermal cells (on the left) are more easily wetted than those with prominent papillae (right). Grey columns mark wax tubules composed of nonacosan-10-ol indicating that the high methanol resistance is independent of the individual fine structure of the wax layer but mainly depends on the sculpturing of the outer epidermal cell wall.



**Fig. 8.** Aspect ratio of the epidermal cells of six highly non-wettable plant surfaces compared to the highest repelled methanol-concentration showing no obvious correlation.

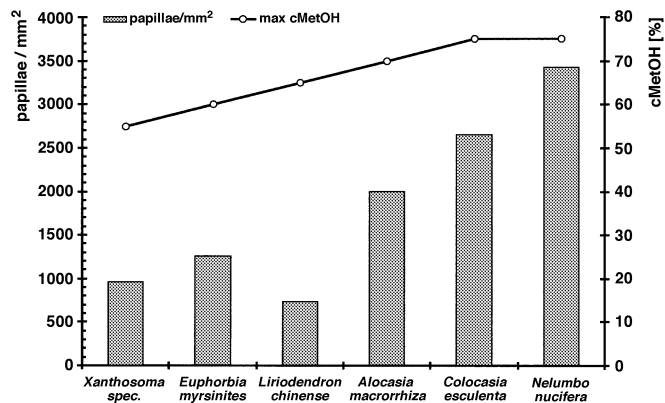
surfaces that has been discussed in detail elsewhere (Dettre and Johnson, 1964; Herminghaus, 2000; Holloway, 1970).

A very thin air-layer trapped in the depressions between the papillae is regarded to be the main reason for water-repellency. Increasing the distance between the papillae on the one hand increases the water/air contact area. At the same time, the water droplet may penetrate more easily into the depressions by its own weight, high impact velocity or due to a reduced surface tension and wets the surface. Increasing the height of the papillae decreases the risk because the droplet dramatically increases its surface before reaching the bottom between the papillae.

Looking at the number of papillae per unit area shows only a weak correlation ( $r^2=0.7213$ ) with the methanol resistance of a particular surface (Fig. 9) due to the small amount of data. However, a higher amount of smaller papillae seems to be more effective in terms of water-repellency than surfaces with larger but less numerous papillae.

Furthermore, the contact area of a water droplet on the tips of the epidermal papillae in relation to the projected area has been calculated. The outermost wax-crystals (or cuticular folds in the case of *A. macrorrhiza*) have been scanned by AFM and two wetting scenarios have been assumed as described above. In Table 3 the values for the calculated contact areas are given. In relation to a smooth surface the contact area of a 'larger water droplet' ( $D=1.0\ \mu\text{m}$ ) decreases by at least 92.80%. If a smaller droplet is suggested the contact area decreases by at least 98.33%.

By contrast to the assumption, that the minimization of the contact areas should result in optimized water-repellency, the results indicate that this is not the case. The moderately decreased contact areas of surfaces as in leaves of *C. esculenta* and *N. nucifera* seem to be more effective than those with lower contact areas such as *X. spec.* and *E. myrsinites*. This points to the conclusion



**Fig. 9.** Papillae density ( $1\ \text{mm}^{-2}$ ) in relation to methanol resistance. Surfaces with a high amount of smaller papillae show a better resistance than those with lower numbers. Note that *A. macrorrhiza* (wax film on heavily structured secondary structure) is equally resistant as those surfaces characterized by wax crystals.

that a well designed water-repellent surface is optimized only in a narrow range of aspect ratios and papillae densities. Individual morphologies of contributing structures are less important to achieve this goal as can be seen from the surface of *A. macrorrhiza*. Here, water-repellency is based on papillose epidermal cells and cuticular folds. The latter are covered by a thin amorphous wax film and not by wax crystals. The number of papillae as well as aspect ratios and the contact area are comparable to the other species and therefore the values for methanol resistance are in the same range.

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