brief communications

dissolving lead shavings in vinegar⁸. Stannic oxide would have been an acceptable substitute, with supplies being available through the Cornish tin industry. The Romano–British chemists probably believed that they were using a new source of cerussa, so confused were their encyclopaedias in distinguishing lead from tin.

None of the surviving Greco–Roman medical corpora suggest that tin had pharmaceutical value⁹. Although organic tin compounds are now well known for their toxicological properties, inorganic forms seem to be largely inert¹⁰. Hence, unless SnO₂ was added owing to some hitherto unrecognized medicinal attribute, we must conclude that its function was solely as a pigment. The non-toxic properties of SnO₂ would also have been desirable, because by the second century AD the dangers of lead were becoming recognized⁹.

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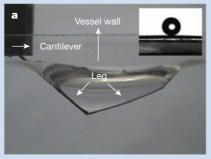
- 1. Durrani, N. Curr. Archaeol. 192, 540-547 (2004).
- 2. Beagrie, N. Britannia 20, 169-191 (1989).
- Copley, M. S. et al. Proc. Natl Acad. Sci. USA 100, 1524–1529 (2003).
- Ralph, J. & Hatfield, R. D. J. Agric. Food Chem. 39, 1426–1437 (1991).
- Blakeney, A. B., Harris, P. J., Henry, R. J. & Stone, B. A. Carbohyd. Res. 113, 291–299 (1983).
- PDF-2 Powder Diffraction Database (International Centre for Diffraction Data, Pennsylvania, 1999).
- Cert, A., Lanzón, A., Carelli, A. A., Albi, T. & Amelitti, G. Food Chem. 49, 287–293 (1994).
- 8. Pliny Natural History (ed. Rackham, H.) **9** (Loeb Classical Library, Cambridge, Massachusetts, 1944).
- Riddle, J. M. in *Dioscorides on Pharmacy and Medicine* 153–154 (Univ. of Texas Press, 1985).
- Toxicological Profile for Tin and Tin Compounds (Agency for Toxic Substances and Disease Registry, US Public Health Service, 2003).
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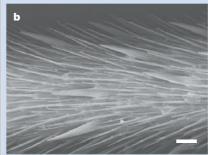
Biophysics

Water-repellent legs of water striders

ater striders (*Gerris remigis*) have remarkable non-wetting legs that enable them to stand effortlessly and move quickly on water, a feature believed to be due to a surface-tension effect caused by secreted wax¹⁻³. We show here, however, that it is the special hierarchical structure of the legs, which are covered by large numbers of oriented tiny hairs (microsetae) with fine nanogrooves, that is more important in inducing this water resistance.

We used a high-sensitivity balance system to construct force—displacement curves for a water strider's legs when pressing on the





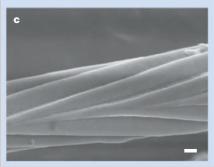


Figure 1 The non-wetting leg of a water strider. **a,** Typical side view of a maximal-depth dimple $(4.38\pm0.02 \text{ mm})$ just before the leg pierces the water surface. Inset, water droplet on a leg; this makes a contact angle of $167.6\pm4.4^{\circ}$. **b, c,** Scanning electron microscope images of a leg showing numerous oriented spindly microsetae (**b**) and the fine nanoscale grooved structures on a seta (**c**). Scale bars: **b,** $20 \mu \text{m}$; **c,** 200 nm.

water surface (for methods, see supplementary information). Surprisingly, the leg does not pierce the water surface until a dimple of 4.38 ± 0.02 mm depth is formed (Fig. 1a). The maximal supporting force of a single leg is 152 dynes (see supplementary information), or about 15 times the total body weight of the insect. The corresponding volume of water ejected is roughly 300 times that of the leg itself, indicating that its surface is strikingly water repellent.

For comparison, we made a hydrophobic 'leg' from a smooth quartz fibre that was similar in shape and size to a strider's leg. Its surface was modified by a self-assembling monolayer of low-surface-energy heptadecafluorodecyltrimethoxysilane (FAS-17), which makes a contact angle of 109° with a water droplet on a flat surface⁴. Water supports the artificial leg with a maximal force of only 19.05 dynes (see supplementary information), which is enough to support the strider at rest but not to enable it to glide or dart around rapidly on the surface.

This finding suggests that the force exerted by the strider's legs could be due to a 'superhydrophobic' effect (that is, the contact angle with water would be greater than 150°). We verified that this was indeed the case by sessile water-drop measurements, which showed that that the contact angle of the insect's legs with water was $167.6 \pm 4.4^{\circ}$ (Fig. 1a, inset).

The contact angle of water made with the cuticle wax secreted on a strider's leg is about 105° (ref. 5), which is not enough to account for its marked water repellence. Knowing that microstructures on an object with low surface energy can enhance its hydrophobicity⁶, we investigated the physical features of the legs.

Scanning electronic micrographs revealed numerous oriented setae on the legs. These are needle-shaped, with diameters ranging from 3 micrometres down to several hundred nanometres (Fig. 1b). Most setae are roughly 50 μ m in length and arranged at an inclined angle of about 20° from the surface of leg. Many elaborate, nanoscale grooves are evident on each microseta, and these form a unique hierarchical structure (Fig. 1c).

According to Cassie's law for surface wettability, such microstructures can be regarded as heterogeneous surfaces composed of solid and air⁷. The apparent contact angle θ_1 of the legs is described by $\cos \theta_1 = f_1 \cos \theta_w - f_2$, where f_1 is the area fraction of microsetae with nanogrooves, f_2 is the area fraction of air on the leg surface and θ_{w} is the contact angle of the secreted wax. Using measured values of θ_1 and θ_w , we deduce from the equation that the air fraction between the leg and the water surface corresponds to $f_2 = 96.86\%$. Available air is trapped in spaces in the microsetae and nanogrooves to form a cushion at the leg-water interface that prevents the legs from being wetted.

This unique hierarchical micro- and nanostructuring on the leg's surface therefore seems to be responsible for its water resistance and the strong supporting force. This clever arrangement allows water striders to survive on water even if they are being bombarded by raindrops, when they bounce to avoid being drowned. Our discovery may be helpful in the design of miniature aquatic devices and non-wetting materials.

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- Caponigro, M. A. & Erilsen, C. H. Am. Midland Nat. 95, 268–278 (1976).
- 2. Dickinson, M. Nature 424, 621–622 (2003).
- 3. Hu, D. L., Chan, B. & Bush, J. W. M. Nature **424**, 663–666 (2003).
- Tadanaga, K., Katata, N. & Minami, T. J. Am. Ceram. Soc. 80, 1040–1042 (1997).
- 5. Holdgate, M. W. J. Exp. Biol. 32, 591–617 (1955).
- 6. Feng, L. et al. Adv. Mater. 14, 1857–1860 (2002).
- 7. Cassie, A. B. D. & Baxter, S. *Trans. Farad. Soc.* **40**, 546–551 (1944). **Supplementary information** accompanies this communication on *Nature's* website.

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