

21. Berger, A. Long term variation of daily insolation and Quaternary climatic changes. *J. Atmos. Sci.* **35**, 2362–2367 (1978).
22. Raynaud, D. *et al.* The ice record of greenhouse gases. *Science* **259**, 926–934 (1993).
23. LIGA members. The last interglacial in high latitudes of the northern hemisphere: Terrestrial and marine evidence. *Quat. Int.* **10–12**, 9–28 (1991).
24. Sánchez Goñi, M. F., Eynaud, F., Turon, J. L. & Shackleton, N. J. High resolution palynological record off the Iberian margin: direct land-sea correlation for the last interglacial complex. *Earth Planet. Sci. Lett.* **171**, 123–137 (1999).
25. Leclainche, Y. *et al.* Diagnostic versus thermodynamic sea ice models in global coupled ocean-atmosphere simulations. *Clim. Dyn.* (submitted).
26. Rahmstorf, S. Bifurcation of the Atlantic thermohaline circulation in response to changes in the hydrological cycle. *Nature* **378**, 145–149 (1995).
27. Ives, J. D., Andrews, J. T. & Barry, R. G. Growth and decay of the Laurentide ice sheet and comparison with Fenno-Scandinavia. *Naturwissenschaften* **2**, 118–125 (1975).
28. Andrews, J. T. & Mahafy, M. A. W. Growth rates of the Laurentide ice sheet and sea level lowering (with emphasis on the 115,000 B.P. sea level low). *Quat. Res.* **6**, 167–183 (1976).
29. Mangerud, J. in *Klimageschichtliche Probleme der letzten 130,000 Jahre* (ed. Frenzel, B.) 307–330 (Fisher, Stuttgart, 1991).
30. Schmitz, W. J. & McCartney, M. S. On the North Atlantic circulation. *Rev. Geophys.* **31**, 29–49 (1993).

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**Late Jurassic salamanders from northern China**

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With ten extant families, salamanders (urodeles) are one of the three major groups of modern amphibians (lissamphibians)<sup>1–6</sup>. Extant salamanders are often used as a model system to assess fundamental issues of developmental, morphological and biogeographical evolution<sup>6–11</sup>. Unfortunately, our understanding of these issues has been hampered by the paucity of fossil evidence available to assess the early history of the group<sup>5,6,12</sup>. Here we report the discovery of an extraordinary sample of salamander fossils, some with rare soft-tissue impressions, from the Upper Jurassic of China<sup>13–16</sup>. With over 500 articulated specimens, this assemblage documents the morphological diversity of early urodeles and includes larvae and adults of both neotenic and metamorphosed taxa. Phylogenetic analysis confirms that these salamanders are primitive, and reveals that all basal salamander clades have Asian distributions. This is compelling evidence for an Asian origin of Recent salamanders, as well as for an extensive and early radiation of several major lineages. These discoveries show that the evolution of salamanders has involved phylogenetic and ecological diversification around a body plan that has remained fundamentally stable for over 150 million years.

- Amphibia Linnaeus, 1758
- Lissamphibia Haeckel, 1866
- Caudata Scopoli, 1777
- Urodela Dumeril, 1806
- Family incertae sedis

*Sinerpeton fengshanensis* gen. et sp. nov.

**Holotype.** GMV 1606, articulated skeleton including cranium and postcranium.

**Etymology.** *Sino* + *herpeton* (Greek, meaning creeping animal from China); fengshan (the type locality).

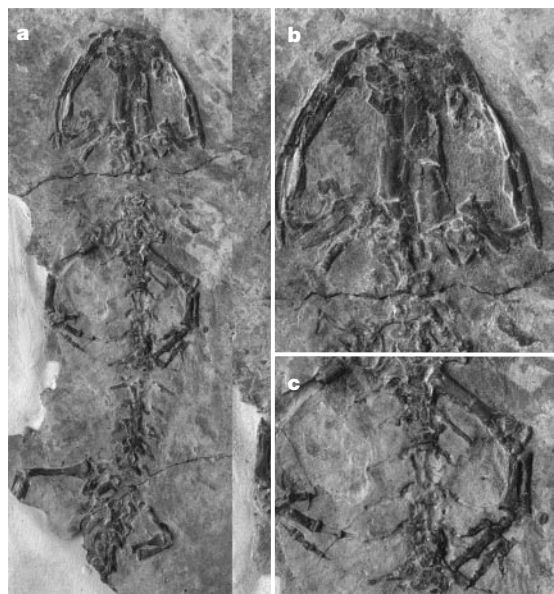
**Type locality and horizon.** Fengshan, Hebei Province, China; Late Jurassic fossil beds that overlay the Zhangjiakou Formation (Tithonian)<sup>13–16</sup>.

**Referred material.** GMV 1607–1610, and numerous unnumbered topotypic specimens.

**Diagnosis.** *S. fengshanensis* is a neotenic form that retains primitive urodele characters including: small dorsal processes on paired premaxillae; paired nasals articulated in midline; the presence of separate angular and coronoid; and a basale commune representing fused distal carpals 1+2 in the manus. It shares derived characters such as uncapitate ribs with cryptobranchoids, but differs from this group in having the following combination of characters: presacral vertebrae with laterally expanded zygapophyses; a single centrale; a greatly expanded metacarpal II in the manus; and phalangeal formulae of 1-2-3-2 in manus and 1-2-3-4-2 in pes.

The Fengshan assemblages include articulated specimens of both neotenic (*S. fengshanensis*; Figs 1, 2) and fully metamorphic salamanders (*Laccotriton subsolanus*; Fig. 3)<sup>17</sup>. The holotype of the new taxon *Sinerpeton* retains an ossified mesopodium and paired ossified ceratobranchials; the combination of these features suggests that this specimen represents a mature individual with external gills. The assessment of *L. subsolanus* as a metamorphic form is based on its high degree of ossification, particularly in the mesopodium, and apparent lack of external gills—ossified ceratobranchials are absent in adults (Fig. 3). Larvae are also present in the Fengshan sample. These specimens, some of which preserve impressions of the soft tissues of the external gills, have weakly ossified skeletons, are smaller than the metamorphosed individuals of *Laccotriton*, and retain the distinctive skull proportions seen in many larval salamanders (Fig. 3).

The 500-plus articulated salamander skeletons from the Fengshan locality were recovered from a small area of no more than 10 m<sup>2</sup>. The high concentration of fully articulated specimens in tuffaceous shales indicates catastrophic mass mortality during a pyroclastic eruption. The age of the fossil beds is probably mid-Tithonian or slightly younger, on the basis of radiometric dating and biostratigraphy. The underlying Zhangjiakou Formation yields an <sup>40</sup>Ar/<sup>39</sup>Ar



**Figure 1** Holotype (GMV 1606) of *S. fengshanensis*, gen. et sp. nov. **a**, Dorsal view of articulated skeleton including the cranium and postcranium. **b**, Enlarged skull. **c**, Enlarged pectoral girdle and forelimbs.

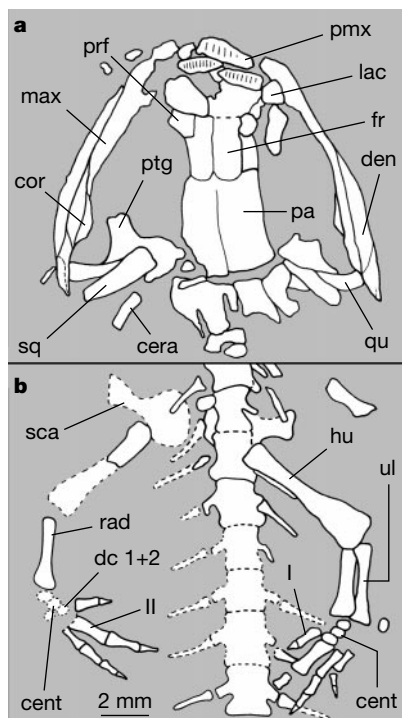
date of 151 million years BP (ref. 13). Biostratigraphic comparisons of the insect assemblage suggest a Tithonian age<sup>14</sup>, and analysis of conchostracans<sup>15,16</sup> suggests an age of Kimmeridgian. Therefore, the salamander fossils from Fengshan represent the earliest true urodeles that are known from fully articulated skeletons. In addition, some of these fossils have preserved rare soft-tissue impressions (Fig. 3a, b). Consequently, these early salamanders reveal pivotal anatomical details that are not available from other known fossils, and have fundamental evolutionary and biogeographic implications.

*Sinerpeton* and *Laccotriton* have cranial morphologies that are similar to those of extant hynobiids in having a lacrimal in the skull and a separate angular in the mandible. The retention of a well-defined coronoid along with other characters, however, indicates a more basal position of the two Late Jurassic taxa. In limb structure, an important trend in salamanders is the reduction in the number of mesopodial elements with derived limb patterns almost always involving the loss or fusion of bones<sup>9,10</sup>. This trend was underway by the Late Jurassic: both the neotenic and metamorphosed salamanders from Fengshan possess fused distal carpals 1+2 in the manus, and distal tarsals 1+2 in the pes. An Early Cretaceous salamander from Liaoning also shows a similar pattern<sup>18</sup>, although another salamander of the same age has unossified mesopodials<sup>19</sup>. Indeed, this character is one of the most diagnostic features of Recent salamanders and has remained remarkably stable for the past 150 million years in the evolution of urodeles.

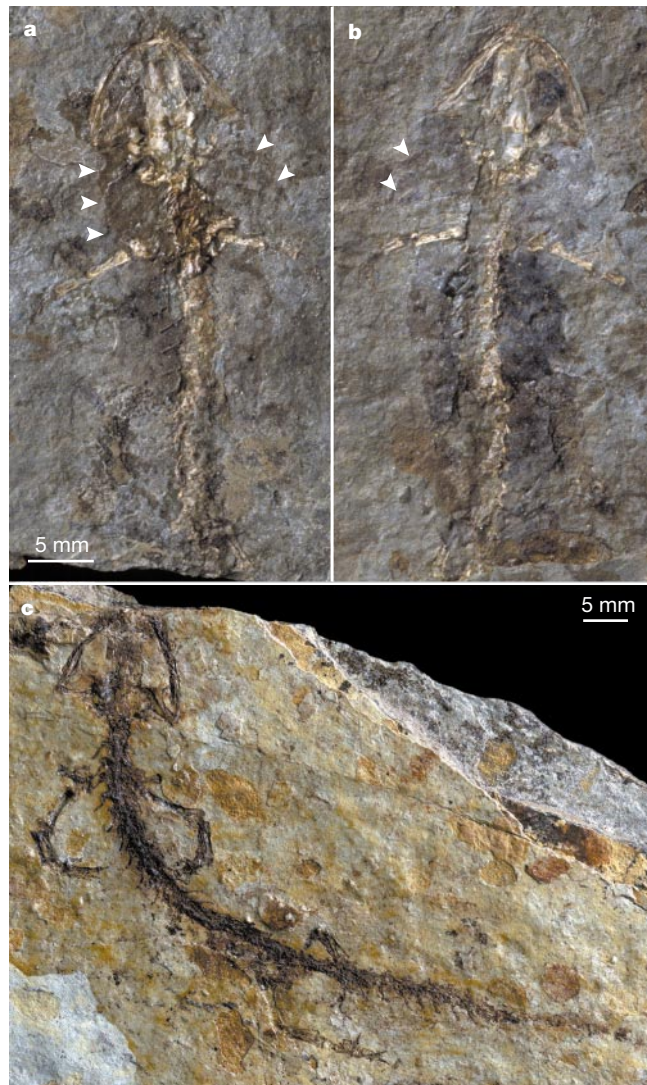
Inclusion of the Fengshan material in analyses of salamander phylogeny provides new insights into the relationships and biogeography of the main salamander clades. Most recent phylogenetic hypotheses recognize the neotenic family Sirenidae as representing the most basal extant salamanders<sup>1,3,20–23</sup>. Our analyses of morphological data independently and in combination with molecular data<sup>22</sup> suggest that sirenids are not basal but are most closely related

to another neotenic clade, the proteids (Fig. 4). To move sirenids to a basal position involves the addition of 26 and 16 steps to the morphological and combined trees, respectively. The analyses also reveal that Asian taxa lie at the base of caudate phylogeny: both *Sinerpeton* and *Laccotriton* are placed at the base of Urodela clade together with Cryptobranchoidea. As hynobiids are almost exclusively Asian in distribution, and cryptobranchids have a combined Asian/North American distribution, the most parsimonious hypothesis is that the basal salamanders initially radiated in Asia, and later spread to North America and Europe. This new hypothesis is further supported by the presence of a basal caudate, *Karaurus*, in Late Jurassic deposits of Kazakhstan<sup>24</sup>, and a younger record of salamanders from the Early Cretaceous of both Europe and Asia<sup>12,18,19</sup>. All other Jurassic records of salamanders consist of isolated elements and are either taxonomically equivocal or not amenable to phylogenetic analysis<sup>25,26</sup>.

Analyses of salamander phylogeny are plagued by both morphological conservatism and homoplasy of major characters. The study of the new Fengshan material suggests that these phylogenetic difficulties reflect the biological realities of the salamander cladogenesis. Phylogenetic analysis of fossil evidence strongly supports the hypothesis that major extant salamander families have been

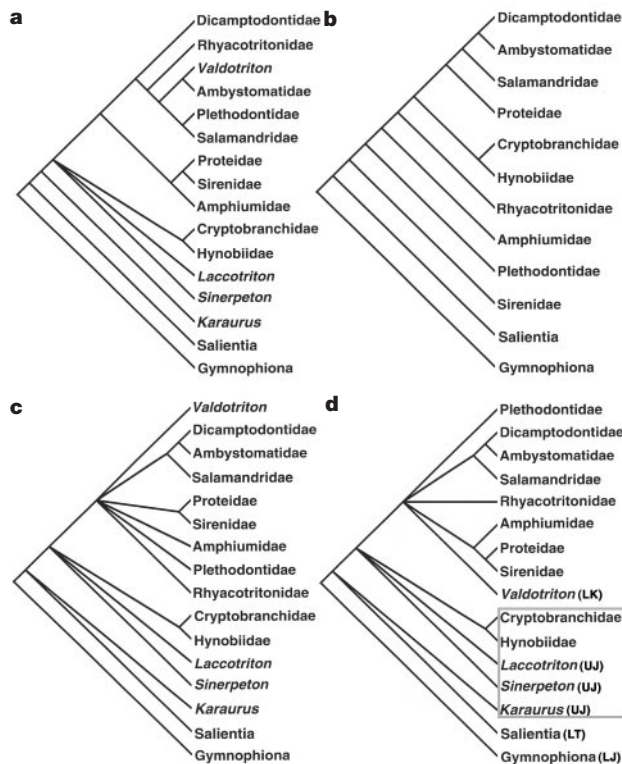


**Figure 2** Line drawing of the holotype of *S. fengshanensis*, gen. et sp. nov. **a**, Dorsal view of skull. **b**, Pectoral girdle and forelimbs. cent, centrale; cera, ceratobranchial; cor, coronoid; dc, distal carpal; den, dentary; fr, frontal; hu, humerus; lac, lacrimal; max, maxilla; pa, parietal; pmx, premaxilla; prf, prefrontal; ptg, pterygoid; qu, quadrate; rad, radius; sca, scapulocoracoid; sq, squamosal; ul, ulna.



**Figure 3** *L. subsolanus*. **a, b**, Part and counterpart of a juvenile specimen (GMV 1603) with arrows pointing to impressions of external gills. **c**, GMV 1602 (holotype), nearly complete cranial and postcranial skeleton and impressions.





**Figure 4** Phylogenetic relationships of major salamander families. **a**, Strict consensus of the nine most parsimonious trees derived from morphological data (length, 109; consistency index (CI), 0.629; retention index (RI), 0.713). **b**, Single tree (length, 258; CI, 0.578; RI, 0.579) from molecular data in ref. 22. **c**, Strict consensus of 21 trees (length, 402; CI, 0.549; RI, 0.537) derived from combined analysis of morphological and molecular data with insertion/deletion events coded as a fifth state. **d**, Strict consensus of nine trees (length, 297; CI, 0.556; RI, 0.584) from combined analysis with insertion/deletion events coded as missing data. LJ, Lower Jurassic; LK, Lower Cretaceous; LT, Lower Triassic; UJ, Upper Jurassic.

evolving separately since at least the Early Cretaceous (Fig. 4). Extant salamander families are characterized by a diversity of life-history strategies. Neoteny, in particular, has been a key component in the generation of salamander diversity; over 40 species in 9 different families show this evolutionary strategy<sup>20</sup>. The Fengshan salamanders reveal that this major mode of urodele evolution was already established by the Late Jurassic. The early and independent occurrences of neoteny in Mesozoic and Recent salamander groups make parallel evolution of numerous morphological features a long-standing factor of salamander history. □

**Methods**

**Phylogenetic analyses**

We used PAUP version 3.1.1 to analyse the data sets (see Supplementary Information) and Branch-and-Bound search algorithm to identify most parsimonious trees. We treated all characters unordered and equally weighted, and rooted the trees using *Karaurus*, Salientia and Gymnophiona as successive outgroups. We did not include the Early Cretaceous *Liaoxitriton* and *Jeholotriton* in this analysis because the preliminary description of these taxa did not provide sufficient character information to evaluate their placement in a phylogenetic framework.

**Description of *Sinerpeton***

The holotype is a well-preserved skeleton with a snout-vent length of 47 mm. The maxilla contacts both a small lacrimal and a reduced prefrontal dorsally. The frontals are short, having an essentially transverse anterior suture with the nasals and a roughly W-shaped posterior suture with the parietals. The parietals lack an anterolateral extension, and form the medial border of the orbit with the frontals. The squamosal in dorsal view forms a transverse bar that contacts the parietal medially. The pterygoid is primitively tri-radiate and boomerang-shaped. The mandible has five separate elements, including the dentary,

prearticular, angular, coronoid and articular.

The vertebral column consists of 16–17 presacrals, a sacral and more than 20 caudals. A pair of spinal nerve foramina penetrates the atlas laterally, but these are not present in other vertebrates. The presacrals have laterally expanded zygapophyses, differing from the unexpanded condition in cryptobranchoids. Ribs are unicipitate with an expanded head. Up to four anterior caudals are also rib-bearing. In the manus, the distal carpals are well ossified, and possess the standard urodele fusion of distal carpals 1+2. The phalangeal formulae are 1-2-3-2 in the manus, and 1-2-3-4-2 in the pes.

**Redescription of *Laccotriton***

*Laccotriton* is a metamorphic form, having a well-ossified mesopodium but lacking ossification of the ceratobranchials. It shares with cryptobranchoids derived characters such as unicipitate ribs with a broadened base, but differs from this group in having more than three pairs of caudal ribs, and the absence of spinal nerve foramina on presacral and caudal vertebrae. It differs from neotenic *Sinerpeton* in having two centralia in the manus, and phalangeal formulae of 2-2-3-2 in the manus and 2-2-3-4-2 in the pes.

The skull of *Laccotriton* retains a small lacrimal anterolateral to the prefrontal. The frontals are short, lacking the anterior extension seen in cryptobranchids, sirenids and amphiumids. The squamosal is a transverse bar that connects the parietal to the quadrate. The vomers are paired and triangular, with vomerine teeth forming a short arcade that runs mediolaterally. The pterygoid is triradiate, lacking the anteromedial process seen in cryptobranchids. As in *Sinerpeton*, five separate mandibular elements are present (dentary, prearticular, angular, coronoid and articular).

The vertebral column comprises 16 presacrals, a single sacral and more than 20 caudal vertebrae. No spinal nerve foramina are identifiable in the vertebrae. All of the presacrals but the atlas carry short and rod-like ribs, with a unicipitate and slightly expanded proximal head. At least five anterior caudals bear free ribs.

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- Milner, A. R. in *Amphibian Biology* (eds Heatwole, H. E. & Carroll, R. L.) 4, 1412–1444 (Surrey Beatty & Sons, Chipping Norton, Australia, 2000).
- Trueb, L. & Cloutier, R. in *Origins of the Higher Groups of Tetrapods: Controversy and Consensus* (eds Schultze, H. -P. & Trueb, L.) 223–313 (Cornell Univ. Press, Ithaca, London, 1991).
- Cannatella, D. C. & Hillis, D. M. Amphibian relationships: phylogenetic analysis of morphology and molecules. *Herpetol. Monogr.* 7, 1–7 (1993).
- Feller, A. E. & Hedges, B. Molecular evidence for the early history of living amphibians. *Mol. Phylog. Evol.* 9, 509–516 (1998).
- Estes, R. *Handbuch der Paläoherpologie. Teil 2. Gymnophiona, Caudata* (Gustav Fischer, Stuttgart, 1981).
- Milner, A. R. in *Evolution, Time and Space: the Emergence of the Biosphere* (eds Sims, R. W., Price, J. H. & Whalley, P. E. S.) 431–468 (Academic, London, 1983).
- Wake, D. B. & Larson, A. Multidimensional analysis of an evolving lineage. *Science* 238, 42–48 (1987).
- Wilbur, H. M. & Collins, J. P. Ecological aspects of amphibian metamorphosis. *Science* 182, 1305–1314 (1973).
- Shubin, N. & Wake, D. B. Phylogeny, variation, and morphological integration. *Am. Zool.* 36, 51–60 (1996).
- Shubin, N., Wake, D. B. & Crawford, A. J. Morphological variation in the limbs of *Taricha granulosa* (Caudata: Salamandridae): evolutionary and phylogenetic implications. *Evolution* 49, 874–884 (1995).
- Wake, D. B. Homoplasy: the result of natural selection or evidence design limitations? *Am. Nat.* 138, 543–567 (1991).
- Evans, S. E. & Milner, A. R. A metamorphosed salamander from the Early Cretaceous of Las Hoyas, Spain. *Phil. Trans. R. Soc. Lond. B* 351, 627–646 (1996).
- Luo, X. & Li, P. A study on the boundary age between Jurassic and Cretaceous. *Acta Geol. Sinica* 18, 242–247 (1997).
- Ren, D., Yin, J. & Huang, B. Preliminary research on Late Mesozoic insect communities and ecostratigraphy of Fengning, Hebei Province. *Geol. Sci. Tech. Inform.* 18, 39–44 (1999).
- Chen, P. Nonmarine Jurassic strata of China. *Mus. North. Arizona Bull.* 60, 395–412 (1996).
- Wang, S. Correlation of the continental Jurassic in the north of China to the paralic Jurassic in northwest Scotland, United Kingdom. *Acta Geol. Sinica* 72, 11–21 (1998).
- Gao, K., Cheng, Z. & Xu, X. First report of Mesozoic urodeles from China. *Chin. Geol.* 248, 40–41 (1998).
- Dong, Z. & Wang, Y. A new urodele (*Liaoxitriton zhongjiani* gen. et sp. nov.) from the Early Cretaceous of western Liaoning Province, China. *Vert. PalAsiat.* 36, 159–172 (1998).
- Wang, Y. A new salamander (Amphibia: Caudata) from the Early Cretaceous Jehol Biota. *Vert. PalAsiat.* 38, 100–103 (2000).
- Duellman, W. E. & Trueb, L. *Biology of Amphibians* (McGraw-Hill Book Company, New York, 1986).
- Larson, A. in *Evolutionary Biology* (eds Hecht, M. K., Wallace, B. & MacIntyre, R. J.) 25, 211–277 (Plenum, New York, 1991).
- Larson, A. & Dimmick, W. W. in Amphibian relationships: Phylogenetic analysis of morphology and molecules. (eds Cannatella, D. & Hillis, D.) *Herpetol. Monogr.* 7, 77–93 (1993).
- Sever, D. M. Comparative anatomy and phylogeny of the cloacae of salamanders (Amphibia: Caudata). *Herpetologica* 47, 165–193 (1991).
- Ivachnenko, M. F. Urodelans from the Triassic and Jurassic of Soviet Central Asia. *Paleontol. J.* 12, 362–368 (1978).
- Evans, S. E., Milner, A. R. & Mussett, F. The earliest known salamanders (Amphibia: Caudata): a record from the Middle Jurassic of England. *Geobios* 21, 539–552 (1988).
- Evans, S. E. & Milner, A. R. in *In the Shadow of the Dinosaurs* (eds Fraser, N. C. & Sues, H.-D.) 303–321 (Cambridge Univ. Press, Cambridge, 1994).

Supplementary information is available on Nature's World-Wide Web site (<http://www.nature.com>) or as paper copy from the London editorial office of Nature.

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**Caterpillar-induced nocturnal plant volatiles repel conspecific females**

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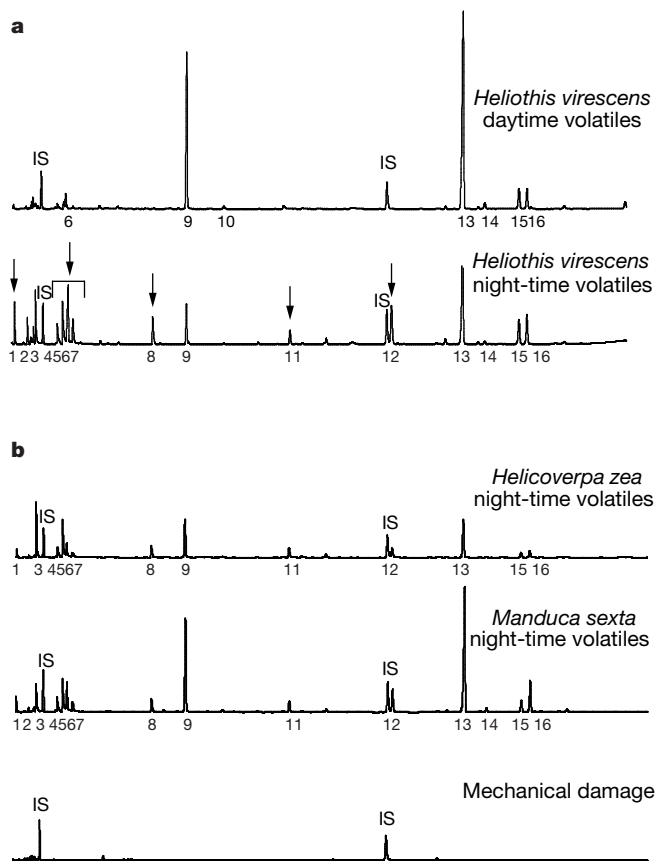
Plants respond to insect herbivory by synthesizing and releasing complex blends of volatile compounds, which provide important host-location cues for insects that are natural enemies of herbivores<sup>1–3</sup>. The effects of these volatile blends on herbivore behaviour have been investigated to only a limited extent<sup>4,5</sup>, in part because of the assumption that herbivore-induced volatile emissions occur mainly during the light phase of the photoperiod<sup>6,7</sup>. Because many moths—whose larvae are some of the most important insect herbivores—are nocturnal, herbivore-induced plant volatiles have not hitherto been considered to be temporally available as host-location cues for ovipositing females. Here we present chemical and behavioural assays showing that tobacco plants (*Nicotiana tabacum*) release herbivore-induced volatiles during both night and day. Moreover, several volatile compounds are released exclusively at night and are highly repellent to female moths (*Heliothis virescens*). The demonstration that tobacco plants release temporally different volatile blends and that lepidopteran herbivores use induced plant signals released during the dark phase to choose sites for oviposition adds a new dimension to our understanding of the role of chemical cues in mediating tritrophic interactions.

Feeding by insect herbivores induces plants to release chemical signals that serve as important foraging cues for parasitoids and predators, and thus enhance the plants' defence<sup>1–3,8–10</sup>. Synthesis and release of these chemical signals is an active physiological process triggered by substances in the oral secretion of herbivores<sup>11,12</sup>. The recent discovery that plant volatiles can transmit herbivore-specific information that allows natural enemies to identify particular herbivore species demonstrated that chemically mediated plant–insect interactions are more sophisticated and complex than was previously appreciated<sup>13</sup>. However, the role of chemical signals in plant–herbivore interactions remains largely unexplored. Some researchers have examined the effects of constitutive plant volatiles and herbivore-induced daytime volatiles on conspecific herbivores<sup>4,14–17</sup> including some lepidopterans<sup>18</sup>, but the effect of herbivore-induced plant volatiles on moths that are active at night has been neglected. The fact that several major terpene components of herbivore-induced plant volatiles have high emissions during the periods of maximal photosynthesis<sup>6,7</sup> may explain why little attention has been paid to the importance of these volatiles to female moths searching for oviposition sites at night. To our knowledge, this study represents the first demonstration that plants emit herbivore-induced volatile blends that exhibit systematic temporal variation, that some volatile compounds are released exclusively at

night, and that female moths exploit these specific night-time signals to avoid oviposition on previously damaged plants.

Gas chromatographic analysis of volatiles collected in two-hour intervals continuously for seven days revealed consistent differences in the composition of volatile blends released by *H. virescens*-infested tobacco plants ( $n = 6$ ) during the light and dark phases of the photoperiod (Fig. 1a). Visual and auditory observations confirmed that larvae fed during both the light and dark phases. Seven major compounds were consistently released during both light and dark phases, but usually in lesser amounts during the dark phase (Fig. 1a). In addition, five compounds ((*Z*)-3-hexenyl butyrate, (*Z*)-3-hexenyl isobutyrate, (*Z*)-3-hexenyl acetate, (*Z*)-3-hexenyl tiglate, and one unidentified compound) were produced only during the dark phase. Others—(*E*)-2-hexenal and three unidentified compounds—were produced in significantly larger amounts during the dark than the light period. Thus, the qualitative and quantitative composition of volatile blends emitted by tobacco plants in response to feeding by *H. virescens* larvae can differ significantly between night and day.

Repetition of our analysis using two other species of lepidopteran larvae ( $n = 6$  per species), *Manduca sexta* and *Helicoverpa zea*, provided further evidence of induced volatile release from tobacco plants during the dark period (Fig. 1b). Although the volatile



**Figure 1** Gas chromatographic analysis of induced plant volatiles. **a**, Diurnal and nocturnal profiles of volatiles released from tobacco plants during a 2-h interval after 48 h of feeding by *H. virescens*. Arrows represent volatiles that are present only (or in significantly larger amounts) in the nocturnal profile. **b**, Nocturnal profiles of volatiles released from tobacco plants during a 2-h interval after 48 h of feeding by *H. virescens*, *H. zea* or *M. sexta* compared with mechanical damage. Represented are: 4, (*E*)-2-hexenal; 5, (*Z*)-3-hexen-1-ol; 8, (*Z*)-3-hexenyl acetate; 9, (*E*)- $\beta$ -ocimene; 10, linalool; 11, (*Z*)-3-hexenyl butyrate; 12, (*Z*)-3-hexenyl tiglate; 13,  $\beta$ -caryophyllene; 14,  $\alpha$ -humulene; 15, (*E,E*)- $\alpha$ -farnesene; 16, unidentified sesquiterpene; compounds 1–3, 6, 7 are unidentified compounds; IS, internal standards (*n*-octane and *n*-nonyl-acetate).