

strain shadows, shattering, cloudy appearance, fractured and displaced lamellae, undulose extinction, etc. (Figures 3c, d and 4b). Type A shows subophitic to ophitic texture. Type A rock also shows some other fragments looking like xenoliths. One xenolith shows microcrystalline equigranular structure (Figure 4d), another encloses few pyroxene grains in a thick opaque background (Figure 4e). The third xenolith consists of granular pyroxene filling the

spaces between the rosettes of laths of plagioclase (Figure 4f).

The specific gravity of one of the pieces of the Pipliya-1 meteorite is 2.78 (mercury displacement method). There is no perceptible radioactivity as detected by scintillometer in any fragment of the meteorites.

1. Frost, M., *Meteoritics*, 1969, 4, 217-232.
2. Krinov, E. L., *Acad. Sci. URSS*, 1953, 92, 503-505.

V. K. VAYA
D. S. MEHTA*
P. C. BAFNA*
M. S. SISODIA
K. L. SHRIVASTAVA

*Department of Geology,
J.N.V. University,
Jodhpur 342 005, India*

**Department of Mines and Geology,
Khanij Bhawan,
Jodhpur 342 011, India*

The expanding world of 2-acetyl-1-pyrroline

2-Acetyl-1-pyrroline (2AP) was first reported in 1982 as the principal component of the pleasant aroma of fragrant varieties of rice¹. Such a common source of fragrance was discovered so late, probably because of the unstable nature of the molecule and the general fact that even the comparatively blunt human nose is more sensitive than the sophisticated instruments of analytical chemistry.

Unexpected newer sources of 2AP are now being revealed. I first followed the trail of this elusive molecule (Figure 1) thirty-odd years ago when George Schaller had undertaken the first long-term study of the tiger and brought to the notice of scientists the musky, milky fluid sprayed upwards by tigers and tigresses, presumably to leave communicatory signals². With Schaller I noticed at Kanha, Central India, the smelly signal of a tiger, uncontaminated by the polluting odour of unclean zoos. In 1976 I had the opportunity of closely studying the fluid of a pet tigress and the odour of fresh sprayings seemed to be surprisingly similar to the aroma of

basmati and other fragrant rice (Figures 2, 3). Since then my colleagues and I have been studying the tiger fluid and we have established that the volatile smelly molecules are a number of amines, aldehydes, free fatty acids, etc., but the most elusive of them is a molecule similar to 2AP (refs. 3-7). Rice aroma and tiger aroma turned out to be identical in the course of investigations utilizing paper chromatography and gas-liquid chromatography but for lack of 'sniff GLC' (where one part of the test material is led to the flame ionization detector and the other, to the nose for sniffing) the latter set of experiments was not conclusive. Further confirma-

tion has now been obtained as described below.

Synthesis

Following the initial attempt of Buttery *et al.*¹, Schieberle⁸ succeeded in finding a simple method for synthesizing 2AP. Proline and a sugar (sucrose, fructose or glucose) form 2AP at 170°C. In our hands the procedure led to the production of two different fragrant substances *S*₁ and *S*₂. *S*₂ seemed to be identical to the tiger aroma and rice aroma⁷. At first we had the impression that *S*₁, the major component, was 2AP (ref. 7) but recently by

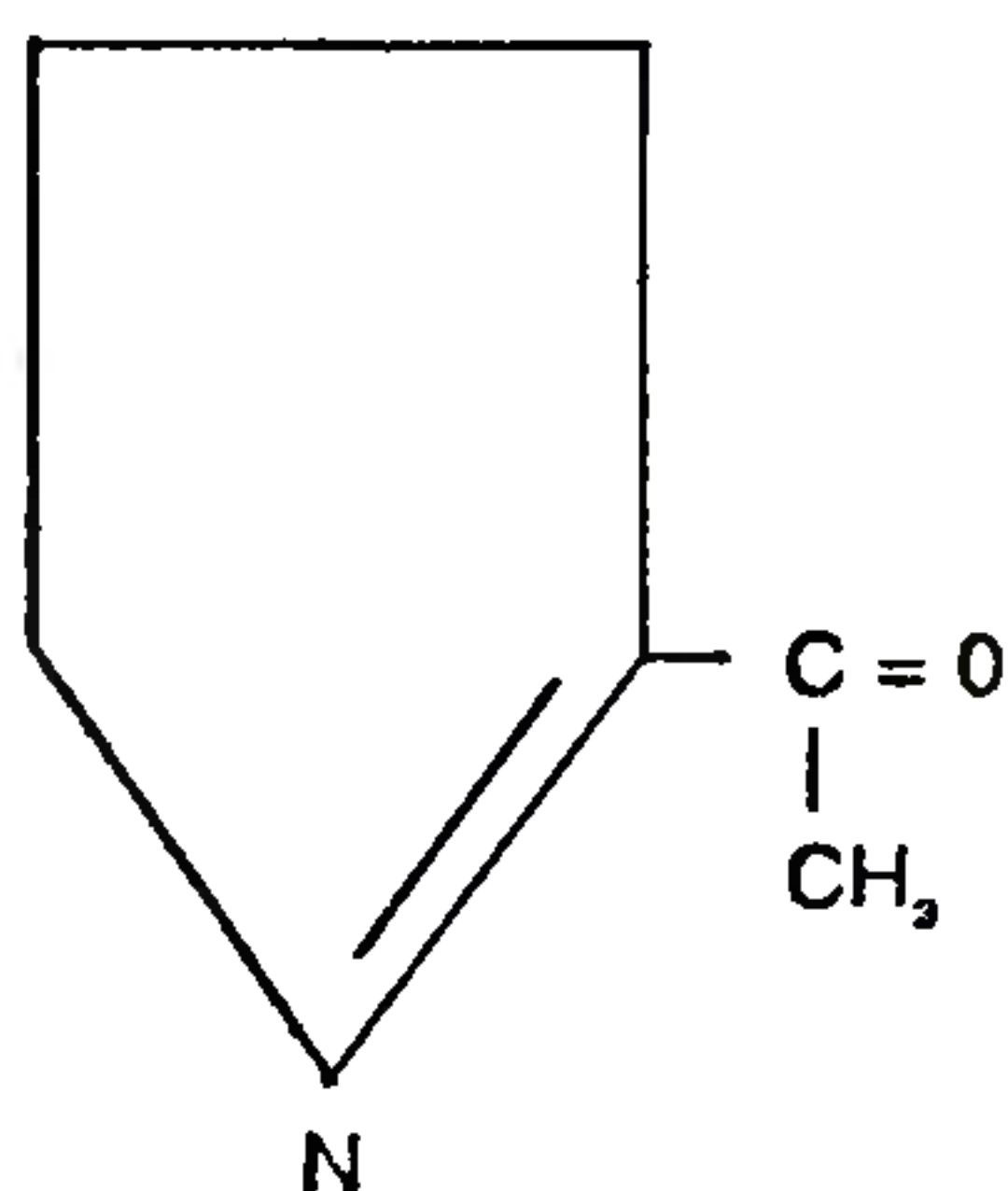


Figure 1. Structure of 2AP.



Figure 2. The raised tail of a tiger indicates that it is ready to spray a fluid containing 2AP.



Figure 3. Rice – A source of 2AP.

comparing authentic synthetic 2AP from Schieberle's laboratory we have established that S_2 of our first synthesis, rice aroma, tiger aroma and 2AP are identical as established by paper chromatography and GLC (squalane column).

In another synthesis we succeeded in obtaining a large amount of S_2 (2AP) but under the anhydrous conditions of Schieberle⁸ we usually obtained variable results. A slight modification using an aqueous solution of proline and sugar led to more uniform production of 2AP (ref. 9). The temperature of the solution inside the container was later measured and found to be between 105°C and 110°C. The temperature range for 2AP production is narrow; 2AP is not formed even at 103°C, but at 105°C the first whiff of the pleasant aroma is unmistakable.

As the quality of aroma in compounds like carvone and limonene is known to depend on the chirality of the molecule, we synthesized 2AP with both L-proline and D-proline. The quality of 2AP-aroma turned out to be independent of the chirality of proline.

Sources of '2AP-like aroma'

Fragrant rice, tiger and leopard produce this aroma which is absent in the African lion and almost absent in a cheetah I studied in Namibia. People in both England and India have described rice aroma as mousey. It is worth investigating whether certain strains of mice at certain times produce this odour. I have also smelt this fragrance in a certain breed of dog and, rarely, in human

sweat. A bintaurong in a clean zoo, at night, spread a very sweet odour which seemed to me to be exactly like that of the freshest, best-quality fragrant rice. It is to be noted, however, that civetone, which has a different chemical structure smells like 2AP as asserted by many people.

The fresh flowers of *Bassia latifolia* emit a smell which resembles the fragrance of rice and has also been described as mousey by a European. Paper-chromatography of this flower extract and synthetic 2AP suggest that the flower aroma is 2AP (ref. 10). Further work with GLC and HPLC may establish the contention and in that case this may be the first example of 2AP traced in the scent of flower.

Biosynthesis

The biosynthesis of 2AP is not clear. It may be enzymatic or, simply, a Maillard reaction, a principle described about 80 years ago but which is now evoking renewed interest¹¹. A Maillard reaction involving an amino-acid and a sugar may yield numerous products at very many different temperatures. In our attempts the lowest temperature that yields 2AP is 105°C, but in the rice plant this process occurs in the temperature gained from autumn sunshine (~30°C) and in *Bassia* flower, at dawn or evening or night in the spring season and therefore, at a much lower temperature. In some export-quality basmati rice, the sweet 2AP smell is not present in the unboiled grain. Boiling rice leads to further Maillard reaction and production of 2AP.

Unstable molecule

2AP decays very quickly, a fact that may explain why most urban people have no concept of the excessively sweet smell of freshly husked rice grains of many indigenous fragrant varieties. This smell disappears very quickly but even relatively old rice, on boiling, produces 2AP once again, presumably due to Maillard reaction. Buttery *et al.*¹ succeeded in keeping the synthetic molecule (as a hydrochloride) intact for 3 months. We note that the picrate is stable even up to 2 years. In a recent experiment, we found good stability as a citrate salt after 6 months and we hope to test again after one year of preservation.

Utility of 2AP for the plant

We enjoy the aroma of 2AP and probably the tiger uses it as a component of its pheromonal, communicatory signal but what good does this perfume do to the rice plant itself? This, at present, is anybody's guess but recently jasmonic acid and methyl jasmonate, the fragrant molecules of jasmine have been found to be useful as arsenals of the plant for fighting bacterial, viral and fungal attack¹². A fragrant rice variety in West Bengal has recently been noticed to be unusually fungus-resistant¹³. The role of 2AP, if any, in protecting the rice plant may be studied in future.

1. Buttery, R. G., Ling, C. and Juliano, B. O., *Chem. Ind.*, 1982, 958–959.
2. Schaller, G., *The Deer and the Tiger*, Chicago University Press, 1967.
3. Brahmachary, R. L. and Dutta, J., *Am. Nat.*, 1981, **118**, 561–567.
4. Brahmachary, R. L. and Dutta, J., in *Tigers of the World* (eds Tilson, R. L. and Seal, U.), Noyes, 1987.
5. Brahmachary, R. L., Poddar-Sarkar, M. and Dutta, J., *Nature*, 1990, **344**, 26.
6. Brahmachary, R. L., Poddar-Sarkar, M. and Dutta, J., *Mammalia*, 1990, **55**, 150.
7. Brahmachary, R. L., Poddar-Sarkar, M. and Dutta, J., in *Chemical Signals in Vertebrates VI* (eds Doty, R. L. and Mueller-Schwarze, D.), Plenum, 1992.
8. Schieberle, P., *Getriede. Mehl. Brot.*, 1988, **42**, 334–335.
9. Poddar-Sarkar, M., De Sarkar, N., Dutta, J. and Brahmachary, R. L., *Int. Rice Res. Newsl.*, 1992, **17**, 9.
10. Midya, S. and Brahmachary, R. L., in preparation.
11. Ledl, F. and Schleicher, E., *Angew. Chem. Int. Ed. Engl.*, 1990, **26**, 565–594.
12. Special issue *Proc. Natl. Acad. Sci. USA*, 1995, **92**.
13. Deb, D., *Sustainable Agriculture and Folk Rice Varieties*, Mimeo production, WWF, Calcutta.

ACKNOWLEDGEMENT. I thank Drs M. Poddar-Sarkar, J. Dutta, P. Bhattacharya, S. Midya and E. Ali for cooperation and P. Schieberle and P. Bhargav for gifts of 2AP and D-proline, respectively.

R. L. BRAHMACHARY

Flat 10, 21 B Mati Jheel,
Calcutta 700 074, India