The "henna stone" myth

Sir,

Black henna does not exist naturally; it is obtained by adding para-phenylenediamine (PPD) to natural henna[1] in order to yield a dark brown to black color and to accelerate the process of tattooing. In Turkey and in the Middle-East countries, however, a solid product named "henna stone" or "German stone" is sold by local herbal sellers as a natural source of black henna claimed to be obtained from some rocks. To the best of knowledge, it has not been analyzed chemically before. In this study, a chemical analysis

was performed in order to investigate the presence of PPD and identify its concentration in various samples of commercially available "henna stones."

Six samples of henna stones [Figure 1] were collected from local herbal sellers. Henna samples were analyzed using gas chromatography-mass spectrometry (GC-MS).[2] Before analyzing any sample, PPD standard was prepared with pure PPD substance (Sigma-Aldrich™) and was first tested to determine its MS spectrum and retention time.

In GC chromatograms, the PPD standard peak emerged at a retention time of 9.93 min, and the characteristic ions produced from the analyte had m/z values: 54.07, 64.02, 80.04, and 108.07 in the MS spectrum corresponding exactly to the molecular weight of PPD.

The MS spectra of all of the six commercial henna stones demonstrated a major peak at an m/z ratio of 108.06 and 108.07, whereas the retention time for the samples ranged between 9.93 and 9.95 min, showing perfect consistency with that of the PPD standard.

Figure 1: Six samples of whitish grey to purplish brown and black "henna stones" collected from local herbal sellers in Turkey

PPD was found in all of the six samples of "henna stones" at concentrations ranging between 84.89 and 90.90% [Table 1].

Among the well-known commercially available forms of black henna such as powder, paste, or ink, there is also a lesser-known solid form named "henna stone" or "German stone" in some countries. They are sold as "natural stones" at herbal sellers. It is advised to crush the stone into powder first and then to mix it with natural henna, water, and hydrogen peroxide.

Interestingly, the whitish grey to purplish brown and black color of henna stones [Figure 1] was reminiscent of the color of PPD powder which is white to light purple that darkens on exposure to air via oxidation, turning first red, then brown, and finally black.[3] In this study, PPD was found in all of the six samples of the so called "henna stones" at concentrations ranging between 84.89 and 90.90% that was significantly higher than previously reported PPD concentrations ranging between 2.35% and 64% in black henna samples.[3-5] The physical appearance, the easy crushability with a pestle into powder as well as the very high PPD content of "henna stones" suggested that these stones might be the compressed form of PPD powder in real.

This study appears to be the first to confirm the presence of PPD in "henna stone" at very high concentrations by qualitative and quantitative chemical analyses. "Henna stones" which are usually sold as "natural stones" at herbal sellers are in fact not henna itself, but contain high concentrations of PPD. Therefore, these stones should be regarded among important sources of allergic contact dermatitis (ACD) from PPD. Indeed, patients with ACD from henna stone powder mainly used for hair dyeing are occasionally seen in our dermatology clinic (unpublished data). We further propose that henna stone is the compressed form of PPD powder in real and not a natural product obtained from some rocks.

Table 1: Para-phenylenediamine percentage of six different henna samples obtained by gas chromatography-mass spectrometry method

Sample number	Sample weight (g)	Mean values of the obtained peak areas	C_{PPD} (results obtained from *calibration curve) ×4 (ppm)	PPD (%)
1	0.0050	9657653	10.67×4=42.68	85.36
2	0.0052	10549568	11.27×4=45.08	86.69
3	0.0055	12379542	12.50×4=50	90.90
4	0.0052	11023715	11.59×4=46.36	89.15
5	0.0054	10839872	11.46×4=45.84	84.89
6	0.0055	11184570	11.69×4=46.76	85.01

*The calibration curve between *Peak Area* and concentration (C): *Peak Area* = $1.49 \times 10^6 C_{PPD} - 6.24 \times 10^6$ (regression coefficient = 0.9989)

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