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**TAS-method for the microanalysis of important constituents of saffron**

The principal pigments of Spanish saffron are the bitter-tasting picrocrocin, a 4-[glucopyranosido]-2,6,6-trimethyl-1-cyclohexene-1-aldehyde and the water-soluble orange-red carotenoid crocin, a digentiobioside of the aglycone crocetin, a heptaenedicarboxylic acid.

During detailed investigations<sup>1</sup> it was discovered that a "thermomicro separation" (by the so-called TAS-method; refs. 2-4) of the components is quite possible, and some new aspects of common interest were demonstrated.

At a temperature of 200° and a reaction time of 1 min, a definite fission of picrocrocin occurred, and the free aglycone, a 2,6,6-trimethyl-1,3-cyclohexadiene-1-aldehyde designated safranal, appeared immediately on the TLC plate. The orange-red carotenoids, however, remained in the stigma. After treating some milligrams of powdered saffron stigmas with an ethereal solution of diazomethane, fission of crocin occurred followed by methylation to the *trans*-dimethyl ester of crocetin, as shown by TLC. Using redried saffron powder in the TAS-oven at 200°, the compound described appeared on the plate as a yellow spot. The separation was accomplished by TLC on Silica Gel HF<sub>254</sub> using benzene-chloroform (80 + 20) under standard conditions. Under shortwave U.V. light a fluorescence-quenching spot appears at  $hR_F = 60$ , and a yellow spot was visible in daylight at  $hR_F = 45$ .

For further identification, the spectra were measured directly on the plate<sup>5</sup> (max. 240 and 280 nm = safranal and max. 456 and 480 nm = *trans*-dimethyl ester of crocetin). After the spectrophotometric determination the chromatogram was treated with antimony trichloride reagent. Even at low temperatures the safranal zone shows a yellow color which becomes green-yellow after heating for 10 min at 110°. The carotenoid undergoes the Carr-Price reaction turning blue.

The experiment described shows that the combination of the TAS-method with TLC is very useful for the indication of the characteristic constituents of saffron. This can be significant in view of the numerous adulterations. Further experiments with other  $\beta$ -glucosidic compounds not mentioned here showed that they can also be broken down in the same manner.

In addition to the esterification and cleavage, the synthesis of trimethylsilyl ethers can also be useful.

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