

Although in this case the eruption followed application of a phenylbutazone-containing injection liquid, primary sensitization to Tanderil cannot be excluded with certainty. The primary sensitization to Tanderil supports the observations of Krook (1975), who concluded that Butazolidine does not induce cross-sensitivity to Tanderil, but Tanderil may induce cross-sensitivity to Butazolidine. Tanderil is a hydroxylated metabolite of Butazolidine and must be regarded as the active product of Butazolidine.

Topically applied creams with Butazolidine or Tanderil should be prescribed with caution; in cases of sensitization, systemic eczematous eruptions may occur following injections, tablets or application of suppositories containing one of the compounds.

Cross-sensitivity to other pyrazolone compounds could not be established in our patient but has to be kept in mind.

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A simple method for extracting crude sesquiterpene lactones from Compositae plants for skin tests, chemical investigations and sensitizing experiments in guinea pigs

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Sesquiterpene lactones are characteristic constituents of the Compositae family (Yoshioka et al. 1973). Numerous cases of contact dermatitis due to Compositae species have been reported (Mitchell 1969) and most of the allergens which have been isolated so far could be identified as sesquiterpene lactones (Hausen & Schulz 1976, Mitchell & Dupuis 1971). The usually performed chemical procedures of extracting sesquiterpene lactones from Compositae plants take a long time and are associated with the yield of numerous by-products which then must be separated from the allergic active fractions.

For this reason a method was sought by which more pure active extracts could be obtained without great expenditure of work. The studies were based on the following reflections.

Some authors described a dermatitis of the unclothed parts of certain patients and sup-

posed that the sensitization might have been caused by contact with airborne pollen or other airborne particles from Compositae species (Burry et al. 1973, Epstein 1960, Lonkar et al. 1974, Rook 1962). Studies of Rodriguez et al. (1976) showed recently that the Parthenium weed (*Parthenium hysterophorus* L.), which has been identified as the cause of severe airborne contact dermatitis in India (Lonkar et al. 1974), contains the highest concentration of its allergenic sesquiterpene lactones in the glandular trichomes of the upper and lower leaf surfaces, phyllaries and achenes. The question whether in other cases of airborne contact dermatitis the dry trichomes or other parts of the plants (e.g. pollen, fruit) are responsible for the transport of allergens through the air, is still open and has to be investigated by further experiments.

Experiments

Therefore in the following investigations the whole plant was extracted with different organic solvents (diethyl ether, benzene (50–70°C), acetone, chloroform, ethyl acetate, ethanol). Examination by thin-layer chromatography indicated the presence of high amounts of compounds in the ether extract which gave positive color reactions to a sesquiterpene lactone reagent (Geissman & Griffin 1971, Hausen & Schulz 1976). Further experiments were made by extracting the whole plants only with ether for 30 seconds, 1, 2, 15, and 30 min. In all cases the 30-second ether-extract yielded the same compounds with positive color reactions to the sesquiterpene lactone reagent as did the 30-min extract. The only difference was that the 30-min extract contained a greater amount of yellow and green by-products of which the majority are chlorophylls.

Hence it may be inferred that by this simple, short, external washing with ether the active compounds of Compositae species are almost completely obtained.

In the flora of northern West Germany and Denmark, about 170 wild Compositae species are known, of which 40 species were introduced from other countries and/or cultivated as ornamental plants. About 25 wild species are very common and generally considered as weeds (e.g. camomile, yarrow, mugwort, daisy, dandelion).

A screening study for allergenic constituents was performed by dipping 30 different species of the more common plants for 30 seconds into diethyl ether. Examination by thin-layer chromatography indicated that in all plants compounds were detectable which gave positive color reactions to a sesquiterpene lactone reagent. Sensitizing experiments in guinea pigs with the same extracts were started which showed that the main amount of the active allergens must be in these quickly made short extracts.

Some of these extracts were also tested by epicutaneous application to the skin of known Compositae-sensitized patients (e.g. *Chrysanthemum* spp., *Matricaria chamomilla*, *Arnica montana*). The positive skin responses revealed too that the allergens were obtained by the short external washing.

Separate examination of different parts of five common Compositae weeds (pollen, fruits, flowers, leaves, stems, roots) by two-dimensional thin-layer chromatography established

that equal components giving a positive color reaction to a sesquiterpene lactone reagent could be detected in the pollen as well as in the fruit, stems and leaves of the same species. In some species there was no difference between the sesquiterpenoid compounds of the airborne fruit and stems or leaves (e.g. in *Senecio vulgaris* L.).

These results should not be used as an explanation that possibly the airborne fruits of some Compositae species may be the cause of contact dermatitis, but they show that

- a) finally the whole plant should be extracted (until we know which parts contain the highest amount of allergens)
- b) the active compounds are situated at the surface of the plants and therefore are very easily accessible.

Method

Fresh plants (whole or cut into suitable parts) are dipped for 30–60 seconds into highly purified peroxide-free diethyl ether (max. 0.1 % water); (test for peroxides, e.g. by Merckoquant® ether-peroxide test).

The ether extract is dried over Na₂SO₄ for 8 h (about 80 g/l) and then evaporated at room temperature by a rotary evaporator to dryness (water pump vacuum).

After determination of the dry weight, different solutions for further investigation purposes can be made:

- a) 1 % in petrolatum for epicutaneous skin tests
- b) 10 % solution in acetone or ethanol for guinea pig sensitization
- c) different solutions for analytical and preparative chromatography.

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Chromate and cobalt eczema due to magnetic tapes

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A man 45 years of age had worked as a telegraphist on ships for 20 years. For 4 years he had been in charge of TV-tasks, which involved daily handling of magnetic tapes in a TV-recorder. He had suffered from dermatitis of the hands for 1 year and of the feet for 7 months. Patch testing with a standard series showed positive reactions to chromium, cobalt and nickel. He also reacted to the coated side of a magnetic tape used in his work.

Magnetic tapes of a high-energy type used for sound or television contain chromium dioxide, cobalt- or nickel-oxides (Akashi et al. 1972). Some of the tapes are labelled "chromium dioxide tapes" or "chrome tapes". The content of chromium dioxide is reported to be about 1 mg/cm² (DuPont 1976) and cobalt-ferrite up to 25 mg/cm² (3M 1976).

Chromium dioxide (Cr^{IV}O₂), a black powder, was kindly provided by DuPont Inc. in the US. Soluble six-valent chromium, cobalt and nickel have been determined with the aid of atomic absorption spectrophotometry after chelation and extraction by an organic solvent. The concentration of six-valent chromium was high enough to be detected also with diphenyl carbazide.

From CrO₂ powder soaked in water for 24 h, 1.0 µg Cr^{VI}/mg was released. CrO₂ powder washed with water for 12 h still released 0.4

µg Cr^{VI}/g. The remaining six-valent chromium indicates that such chromium is constantly produced. The explanation is that the four-valent CrO₂ undergoes a slow disproportionization to form six-valent CrO₃ and three-valent CrOOH in the presence of water (DuPont 1976). Philips VCR-tape and BASF CrO₂-tape, soaked in synthetic sweat (pH 6.5) for 5 days released 0.4 µg Cr^{VI}/cm², Sonab-tape 0.6 µg/cm² and DuPont-tape 0.1 µg/cm². Cr^{VI} was not released from eight other tapes examined.

Tapes containing CrO₂ soaked in synthetic sweat for four periods of 6 days and rinsed in water for 1 day still contained six-valent chromium. As in the experiment with the CrO₂ powder, this indicates that six-valent chromium is constantly formed in the presence of water.

Soluble cobalt was found in 3M 461 tape (0.5 µg/cm²) and in 3M VC 30-tape (0.6 µg/cm²) when soaked in synthetic sweat. After heating these two tapes in 7 M nitric acid the total amount of cobalt was found to be 14.4 µg/cm² and 18.4 µg/cm² respectively. Nickel was not found in any of the tapes examined.

The patient brought a piece of cotton used for cleaning the play-back head of the TV-recorder from dust given off by the tape. It contained 0.4 µg six-valent chromium but no cobalt or nickel.

Ten individuals sensitive to chromium were