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The determination of the geometrical configuration of epoxides

The determination of the configuration of epoxy groups present in organic compounds, *i.e.* whether they are *cis* or *trans*, is of considerable interest, not only from an academic point of view but also because of the industrial importance of such compounds as plasticizers and stabilizers. Several methods are available for the quantitative determination of epoxides but these give no information as to the configuration of the epoxy groups being determined. Such methods are generally based on acid cleavage of the oxiran ring by hydrogen chloride or hydrogen bromide followed by back-titration of the unreacted acid[1,2] and require relatively large samples. Perhaps the most sensitive and specific method described is that of MORRIS AND HOLMAN[3], using near infrared spectrophotometry. It depends on the measurement of the absorption band at 2.795 μ which is due to chlorohydrins produced from any epoxy compounds present in the sample by treatment with anhydrous ethereal hydrogen chloride solution. This method was developed for the quantitative estimation of *cis*-epoxy fatty acids in seed oils but, again, it is not suitable for distinguishing *cis* from *trans* isomers because the absorption maxima of the *threo*- and *erythro*-chlorohydrin derivatives, 2.795 μ and 2.752 μ respectively, are too close together.

The *cis*- and *trans*- isomers of epoxy compounds exhibit different mobilities on thin-layer chromatography (TLC) on silica gel[4]. However, it is sometimes rather difficult to obtain satisfactory and definable separations when both geometrical isomers are present simultaneously, particularly if positional isomeric and/or unsaturated epoxy esters are also present[4,5]. The identification of compounds on the sole basis of TLC migration behaviour is, in any case, rather unsatisfactory. With the development of TLC adsorbents containing glycol-complexing agents such as boric acid or sodium arsenite[6,7], on which *erythro*- and *threo*-dihydroxy isomers are clearly separated, an indirect method for the identification of *cis*- and *trans*-epoxy compounds is now available. The epoxy compound must first be specifically hydrated to the corresponding diol which can then be characterised by TLC on, say, boric acid impregnated silica gel.

Diols are normally obtained from epoxy compounds by acetolysis, followed by alkaline hydrolysis of the hydroxy, acetoxy products so formed[8]. This is a time-consuming method and is not ideal for work on a milligram scale. With the new macroreticular resins such as Amberlyst XN-1005, however, epoxy compounds can be converted very easily, quickly and cleanly to diols in a single step and on only a milligram or, if necessary, a microgram scale.

We have verified that Amberlyst XN-1005 resin catalyses a geometrically specific cleavage of epoxy compounds in such a way that a *cis*-epoxide only gives a *threo*-diol and a *trans*-epoxide only gives an *erythro*-diol. Although this method is not completely quantitative, due presumably to the establishment of an equilibrium, this does not detract from its value in structure determinations because any residual epoxy compound does not interfere in the subsequent chromatographic separation and identification of the diols formed. The position of the original epoxy group, of course, can also be readily determined or verified by permanganate–periodate cleavage[9] of sub-milligram amounts of the diol isolated from the thin-layer chro-

matogram and characterisation of the cleavage fragments by gas–liquid chromatography.

Materials

The resin used, Amberlyst XN-1005 (Rohm and Haas, Philadelphia, Pa., U.S.A.), is converted to the hydrogen form as follows: The resin is placed in a chromatographic column and washed with distilled water until the column eluate is colourless. The resin is then successively and thoroughly extracted with methanol and with ethanol in a Soxhlet extractor. The resin is again placed in the chromatographic column and washed with 3 *N* hydrochloric acid, 50 ml being sufficient to transform 25 ml of resin. The excess acid is removed by eluting the column with bis-deionized water until the eluate no longer gives a precipitate with silver nitrate solution, 100 ml of water normally being sufficient for each 25 ml of resin. The resin is then dried at 50° under vacuum (50 mm Hg).

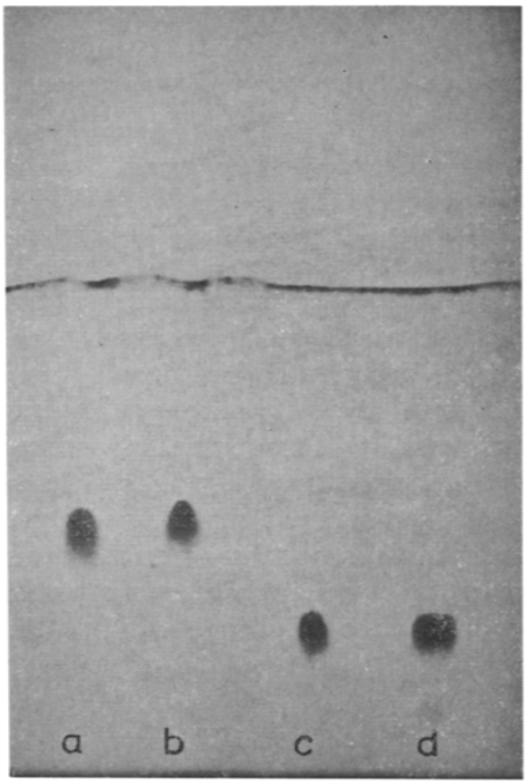
Methyl *cis*- and *trans*-9,10-epoxystearate were prepared by the method of GREENSPAN AND GALL[10] using sulphuric acid as catalyst. Each ester was purified by column chromatography on a mixed adsorbent (8:2, by weight) of Mallinckrodt silicic acid (100 mesh) and Celite. The product were completely pure as judged by TLC.

Methyl *erythro*- and *threo*-9,10-dihydroxystearates were prepared by hydroxylation of oleic and elaidic acids with dilute alkaline permanganate[11] and subsequent esterification of the hydroxy acid products. The esters were purified by crystallisation from ethyl acetate.

Methods and results

A few milligrams of epoxy ester are weighed into a Gorbach flask[12] and about ten times that weight of resin and 0.5 ml of solvent (benzene or hexane) are added. The mixture is stirred magnetically and after 30 min enough epoxy ester is converted to the diol for TLC analysis. The product solution is decanted or filtered from the resin which is then washed with ether to recover any adsorbed product. The combined solutions are concentrated and the dihydroxy ester product is purified, if desired and if sufficient material is available, by preparative TLC on silica gel. The purified diol can then be characterised by TLC on boric acid impregnated silica by comparison with authentic *threo*- and *erythro*-diol standards. Alternatively, a portion of the supernatant solution from the reaction flask may be directly applied to the boric acid–silica thin-layer plate. The impregnated thin-layers consist of Silica Gel G containing 10 % by weight of boric acid[7]. They are developed with an ether–hexane (1:1) mixture and the spots are visualised by charring after spraying with 50 % sulphuric acid.

Fig. 1 illustrates the TLC separation of the purified dihydroxy products obtained from methyl *cis*-9,10-epoxystearate (sample *a*) and methyl *trans*-9,10-epoxystearate (sample *c*), by treatment with the resin as described. Authentic samples of *threo*- and *erythro*-9,10-dihydroxystearates (samples *b* and *d*, respectively) are also included. In Fig. 2, sample *b* shows the thin-layer chromatogram of 10 μl of the supernatant 30 min after reaction of 0.7 mg of *trans*-epoxystearate with 10 mg of resin in 50 μl of benzene (*i.e.* 140 μg of diol plus unchanged epoxy ester), no preliminary isolation or purification of the product having been carried out. Standard samples of *threo*- and *erythro*-9,10-dihydroxystearate are again included (samples *a* and *c*, respectively).



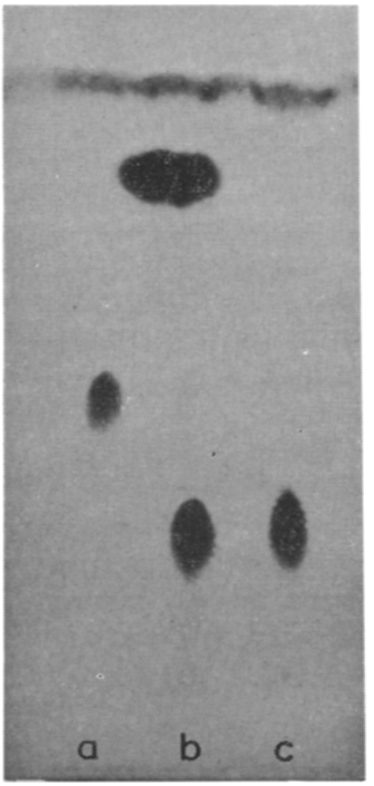


Fig. 1. Thin-layer chromatogram showing the separation of the dihydroxy products obtained from methyl *cis*-9,10-epoxystearate (*a*) and methyl *trans*-9,10-epoxystearate (*c*) after treatment with resin; *b* and *d* are authentic samples of *threo*- and *erythro*-9,10-dihydroxystearates.

Fig. 2. Sample *b* corresponds to 10 μl of the reaction mixture of 0.7 mg of *trans*-epoxystearate; *a* and *c* are standard samples of *threo*- and *erythro*-9,10-dihydroxystearates, respectively.

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