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Note

Quantitative high-performance liquid chromatographic analysis of 12-oxododeca-4,8-dienoic acid and its by-products in the nylon 12 process

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In the first step of the nylon 12 process according to Snia Viscosa patents[1–3], 12-oxododeca-4,8-dienoic acid is obtained by ozonolysis of 1,5,9 (*cis*, *trans*, *trans*)-cyclododecatriene followed by transposition of the monozonide, using a blend of acetic acid and vaseline oil as the solvent (Fig. 1).

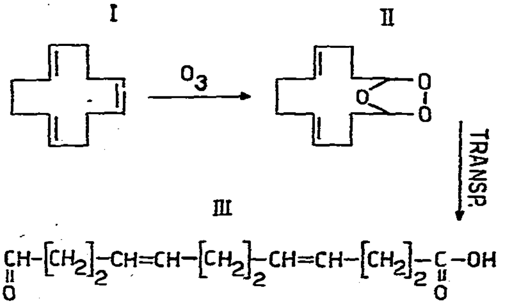

Fig. 1. Reaction scheme. Compound I = 1,5,9(*cis*,*trans*,*trans*)-cyclododecatriene; II = 1,5,9-cyclododecatriene monozonide; III = 12-oxododeca-4,8-dienoic acid.

In this paper, we describe a method for the quantitative determination of the reagents and the main products by high-performance liquid chromatography (HPLC). Gas–liquid chromatography is not suitable as some compounds are high boiling and thermally unstable.

EXPERIMENTAL AND RESULTS

Reagents and standards

The reagents used were dioxane (R.P.), *n*-hexane (R.P.) and acetic acid (R.P.) (Carlo Erba, Milan, Italy). The following standards were double distilled or recrystallized (purity 99%): 1,5,9(*cis*, *trans*, *trans*)-cyclododecatriene, 12-oxododeca-4,8-dienoic acid, vaseline oil, dodeca-4,8-diene-1,12-dioic acid, dodeca-4,8-diene-1,12-dial and benzophenone (internal standard).

Apparatus

A Hewlett-Packard Model 1010-B liquid chromatograph was used, equipped with a differential refractometric detector (Hewlett-Packard Model 1031) connected with a stainless-steel column (50 × 0.3 cm) packed in our laboratory with LiChrosorb Si-60, particle size 10 μm (Merck, Darmstadt, G.F.R.) by the slurry-packing technique[4,5]. The injector was a Rheodyne Model 7120.

Method

The mobile phase was dioxane–*n*-hexane–acetic acid (74.6:25:0.4). The flow-rate was 1 ml/min, the column temperature 48° and the pressure 25 atm. The presence of acetic acid is necessary in order to prevent tailing of the peaks of acidic compounds.

Samples obtained from different process steps were weighed with the internal standard and dissolved in a solvent with the same composition of the mobile phase. The injector loop volume was 20 μl. The maximum detector sensitivity utilized was × 8 and the solution concentration was about 4%.

The five compounds and the internal standard were completely separated, as can be seen from the chromatogram of a standard mixture (Fig. 2). Retention times are given in Table I.

Calibration graphs were obtained by plotting the ratio of the peak heights against the amounts of the compounds (Fig. 3).

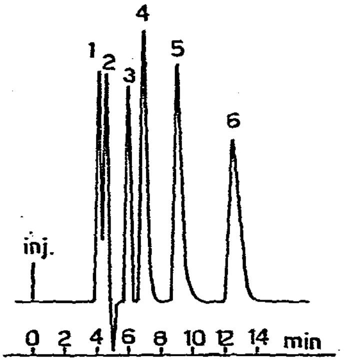

Fig. 2. Chromatogram of standard mixture. Peaks as in Table I.

TABLE I

RETENTION TIMES OF COMPOUNDS EXAMINED

*No.**	*Compound*	*Retention time (min)*
1	Vaseline oil	4.0
2	1,5,9(*cis,trans,trans*)-Cyclododecatriene	4.4
3	Benzophenone (internal standard)	6.0
4	Dodeca-4,8-diene-1,12-dial	6.8
5	12-Oxododeca-4,8-dienoic acid	9.5
6	Dodeca-4,8-diene-1,12-dioic acid	12.8

* Peak Nos. in Fig. 1.

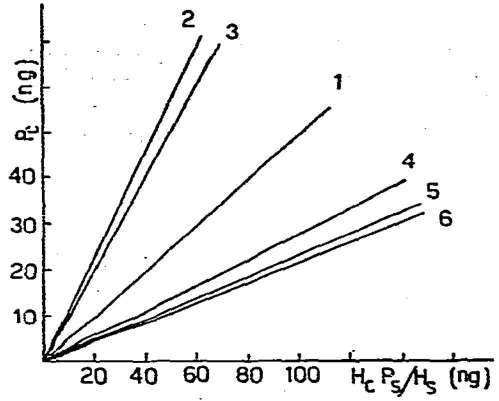

Fig. 3. Calibration graphs for the compounds listed in Table I. H_c = peak height of compound (mm); H_s = peak height of standard (mm); P_c = amount of compound (ng); P_s = amount of standard (ng).

Sensitivity and error

The minimum detectable amount when using this method is between 10 ng [1,5,9(*cis, trans, trans*)-cyclodocatriene] and 50 ng (12-oxododeca-4,8-dienoic acid). The standard deviation is between 0.5% and 1.5% for the same two compounds, respectively.

Some of the samples contained 10% of water which was not completely mixed with the eluent, but this had no effect on the calibration graphs. Variations in the flow-rate, if less than 2%, do not change the calibration graphs to an appreciable extent.

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