

a: $x = 0$
 b: $x = 1$
 c: $x = 2$

EXPERIMENTAL

Chemicals

Compound Ia, m.p. 104–105°C, 2,2'-sulphinylbis(4,6-di-*tert.*-butylphenol) (Ib), m.p. 146–147°C and 2,2'-sulphonylbis(4,6-di-*tert.*-butylphenol) (Ic), m.p. 172–173°C were prepared according to ref.²). Compound IIa, m.p. 125.5–126.5°C, 4,4'-sulphinylbis(2-methyl-6-*tert.*-butylphenol) (IIb), m.p. 180°C and 4,4'-sulphonylbis(2-methyl-6-*tert.*-butylphenol) (IIc), m.p. 239.5–241.5°C were prepared according to ref. 3.

The solvents used in chromatography were analytical grade.

Thin-layer chromatography (TLC)

TLC was carried out on silica gel precoated aluminium foils Silufol UV 254 (Kavalier, Votice, Czechoslovakia). Samples of the antioxidants were dissolved in chlorobenzene. Chloroform–acetone–ammonia (50:25:1) (S_1) and chloroform–acetone (10:1) (S_2) were used as the eluents. Detection was performed with a UV lamp at 254 nm, acidic $KMnO_4$ or ferricyanide reagent.

Liquid chromatography (LC)

The analyses were performed with an LC Chrom 50 chromatograph (Laboratory Instruments, Prague, Czechoslovakia) provided with a differential flow UV detector operated at 254 nm (Development Workshop of the Czechoslovak Academy of Sciences, Prague). The antioxidants were injected as chlorobenzene solutions. (Chlorobenzene was used as solvent in kinetic studies.) The columns used were: (a) glass, 300 × 4 mm, packed with a special fine-grain silica gel SG-10 (Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences), eluent, isopropanol–hexane (1:9), flow-rate 80 ml/h, pressure 1 MPa, chart speed 120 mm/h., (b) stainless steel, 250 × 6 mm, packed with silica gel Separon SI VSK 54610 (Laboratory Instruments), eluent isooctane–ethyl acetate–methanol (100:10:12), pressure 2–4 MPa, flow-rate 43 ml/h, chart speed 300 mm/h.

RESULTS

Melt stabilizers Ia and IIa were previously used in the investigation of the mechanism of antioxidant action in the non-radical decomposition of *tert.*-butyl hydroperoxide, under conditions modelling processes involved in the processing of polyolefins^{2,4}. Changes in the hydroperoxide content were examined by titrimetry and consumption of sulphides and formation of sulphoxides and sulphones were investigated chromatographically. IR spectroscopy did not give satisfactory results,

but TLC made possible a qualitative observation of the changes which take place during the antioxidant action. Along with sulphoxides and sulphones which give primary and secondary oxidation products, other products were detected the structure of which has not yet been elucidated. A liquid chromatography procedure was worked out for the determination of sulphides, sulphoxides and sulphones, which made possible a graphic treatment of the complicated quantitative relations existing in the system hydroperoxide-sulphide-sulphoxide-sulphone^{2,4}.

In this paper we report details of the LC chromatography. It should be pointed out that both isomers Ia and IIa are never employed simultaneously in the stabilization of hydrocarbon polymers. Hence, in practical applications, systems can be used with advantage which have proven to be optimal for each type of sulphide and derived transformation products.

Various combinations of elution systems were tested in TLC in order to achieve separation of the original sulphides (Ia, IIa) and of the products of their oxidation at sulphur (Ib.c; IIb.c). None of these combinations was universal for both groups of isomeric compounds. In some systems the compounds either remained at the start (benzene, heptane) or all had almost identical R_F values (system S_2 or heptane-ethyl acetate-methanol, 10:1:1). In the system S_1 , compounds Ia-c could readily be separated, while IIa-c had very similar R_F values. On the contrary, in the system S_2 , compounds IIa-c could be perfectly separated, but compounds I had very close R_F values (Table I).

TABLE I

R_F (TLC) VALUES ON SILUFOL UV 254 PLATES

For solvents S_1 and S_2 see Experimental.

Compound	R_F	
	S_1	S_2
Ia	0.88	0.82
b	0.16	0.79
c	0.47	0.83
IIa	0.69	0.63
b	0.53	0.17
c	0.59	0.35

Similarly, the separation of these compounds by LC also required the testing of many elution systems and the use of various column packings because of the difficulties involved in the fractionation of this mixture. Compounds II could be separated by using isopropanol-hexane (1:9). Only the resolution between IIb and IIc was difficult to accomplish. These two compounds slightly overlap in the chromatograms (Fig. 1).

Great difficulties were encountered in the separation of compounds I. In elution systems containing isopropanol and hexane in various ratios, the peak of chlorobenzene overlapped those of Ia, Ic or all the three compounds. In hexane-chloroform (10:1), sulphide Ia and sulphone Ic were separated from chlorobenzene, but sulphoxide Ib was retained. In hexane-chloroform containing small amounts of *n*-bu-

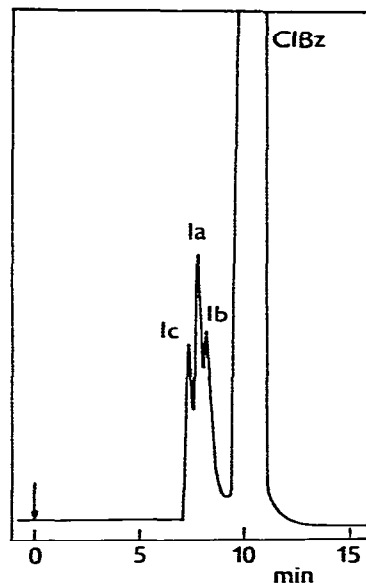
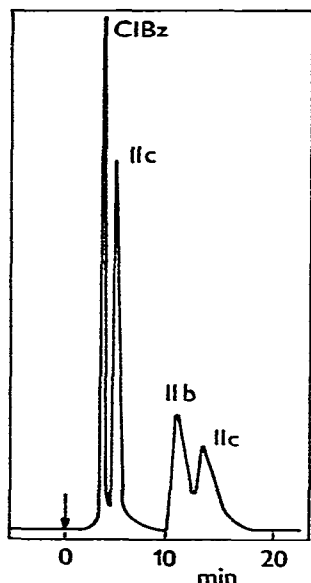


Fig. 1. LC of a mixture of compounds II in chlorobenzene (CIBz). Column: SG-10. Eluent: isopropanol-hexane (1:9). For other conditions see Experimental.

Fig. 2. LC of a mixture of compounds I in chlorobenzene (CIBz). Column: Separon SI VSK 54610. Eluent: isooctane-ethyl acetate-methanol (100:10:12). For other conditions see Experimental.

tanol or isopropanol, Ia and Ic could not be separated, whereas in heptane-ethyl acetate-methanol (10:1:1), they were separated, but Ib coincided with chlorobenzene. Some other ratios between these solvents were also tested; at 100:10:8, Ib could partly be separated, but the overall resolution was unsatisfactory. Satisfactory results were obtained when heptane was replaced with isooctane. The best results were obtained with the system isooctane-ethyl acetate-methanol (100:10:12), in which all three compounds I were separated both from each other and from chlorobenzene (Fig. 2). No further improvement of separation could be achieved by changes in the elution system, only by a decrease in the flow-rate. This prevents a major overlapping of the peaks, and the chromatographic record can be optimized for a quantitative resolution by using a curve resolver.

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