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Short Communication

Chromatographic behaviour of the antidegradant ethoxyquin and its transformation products

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ABSTRACT

An antidegradant, 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline (ethoxyquin) and the products formed during its oxidation, hydrolysis or reduction were analysed by thin-layer and high-performance liquid chromatography. Attention was concentrated on the stability of the compounds during analysis.

INTRODUCTION

6-Ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline (ethoxyquin, EQ, compound **1**) is used as an antioxidant and antiozonant for rubber and as a feed additive. A number of transformation products of EQ have been reported [1], some of which have been investigated chromatographically [2], although a thorough reviw of the chromatographic properties of such compounds has not yet been performed.

This study considered compounds **1**–**12** shown in Fig. 1. Phenetidine (**2**) is a frequent impurity in technical EQ; the other compounds (**3**–**12**) are oxidation products of EQ under various conditions [1] and leucoforms of these compounds.

EXPERIMENTAL

Materials

Chromatographically pure compounds were used in the analyses. EQ, a light brown oil, was obtained by the repurification [1] of Vulkanox EC (Bayer, Leverkusen, Germany). Phenetidine (**2**) was obtained from Fluka. 2,2,4-Trimethyl-6-quinolone (**3**) (lemon yellow crystals, m.p. 56–57°C) was prepared [1,3] by the oxidation of compound **4** with silver (I) oxide. 6-Hydroxy-2,2,4-trimethyl-1,2-dihydroquinoline (**4**) (white crystals, m.p. 179–182°C with partial decomposition) was prepared [1,3] by the hydrolysis of EQ with hydrogen bromide. 2,2,4-Trimethyl-6-quinolone-N-oxide (**5**) (ochre yellow crystals, m.p. 94–95°C) was prepared [1] by the oxidation of compound **3** with *m*-chloroperbenzoic acid. 6-Ethcxy-2,2,4-trimethyl-1,2-dihydroquinoline-N-oxyl (**6**) (dark brown to violet crystals, m.p. 70.5–71.5°C) ws prepared [1] by the oxidation of EQ with *m*-chloroperbenzoic acid. 6-Ethoxy-2,2,4-trimethyl-8-quinolone (**7**) (red crystals, m.p. 122–124°C) was prepared [1] by the oxidation of EQ with Fremy's salt. 6-Ethoxy-8-hydroxy-2,2,4-trimethyl-1,2-dihydroquinoline (**8**) (almost white crystals, m.p. 104–106°C) was prepared [1] by the reduction of compound **7** with $Na_2S_2O_4$. 2,4-Dimethyl-6-ethoxyquinoline (**9**) (almost white crystals, m.p. 87°C) was prepared [4] by the oxidation of EQ with oxygen. 8-(6-Ethoxy-2,2,4-trimethyl-1,2-dihydro-1-

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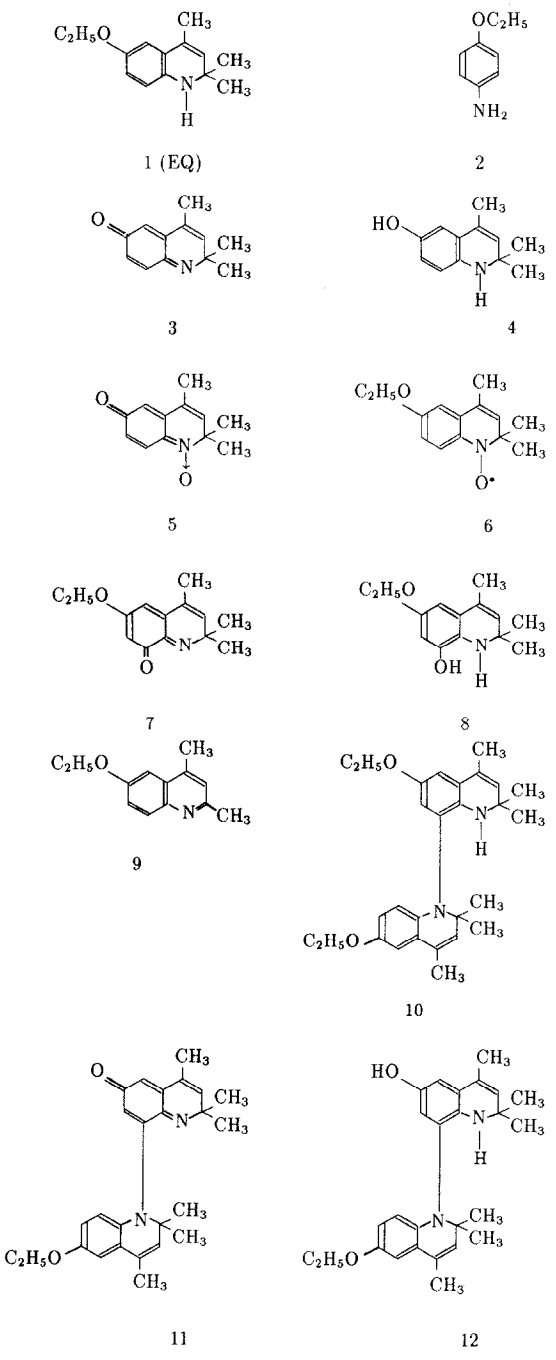

Fig. 1. Structures of compounds **1**–**12**.

quinolyl)-6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline (**10**) (almost white crystals, m.p. 110°C) was prepared [1] by the oxidation of EQ with silver (I) oxide. 8-(6-Ethoxy-2,2,4-trimethyl-1,2-dihydro-1-quinolyl)-2,2,4-trimethyl-6-quinolone (**11**) (almost black needles, m.p. 152–153°C) was prepared [1] by the oxidation of EQ with lead (IV) oxide. 8-(6-Ethoxy-2,2,4-trimethyl-1,2-dihydro-1-quinolyl)-6-hydroxy-2,2,4-trimethyl-1,2-dihydroquinoline (**12**) (light coloured glassy substance) was prepared [1] by the reduction of compound **11** with $Na_2S_2O_4$.

Procedures

Thin-layer chromatography (TLC) was carried out on precoated silica gel plates (Silufol UV 254 with a luminescent indicator). The neutral mobile phases were: M_1, benzene–diethyl ether (9:1, v/v); M_2, benzene–diethyl ether (4:1, v/v); M_3, benzene–diethyl ether (1:1, v/v); M_4, diethyl ether; and M_5, benzene–acetone (1:1, v/v). The basic mobile phases were freshly prepared each time by shaking the following solvents with concentrated aqueous ammonia: M_6, benzene; M_7, benzene–diethyl ether (9:1, v/v); M_8, benzene–diethyl ether (1:1, v/v); and M_9, diethyl ether. An acid permanganate solution was obtained by dissolving 8 g of $KMnO_4$ in 500 ml of water and adding 1.5 ml of concentrated sulphuric acid; the excess of the reagent was removed with water after the plate had been sprayed.

Liquid chromatography took place on a silica gel column (two columns 150 × 3 mm connected in series, packed with Separon SIX, 5μm; Laboratory Instruments, Prague, Czechoslovakia). The neutral mobile phases were mixtures of hexane containing isopropyl alcohol in the following amounts: 0.1, 0.5 and 4% (v/v) (phases M_{10}, M_{11} and M_{12}); the basic mobile phases were mixtures of hexane with 0.1% (v/v) triethylamine, again containing isopropyl alcohol at 0.1, 0.5 and 4% (v/v) (phases M_{13}, M_{14} and M_{15}). The flow-rate of the mobile phases was 1 ml/min; the pressure was 140 bar. The temperature of the column was 24°C. All compounds were detected by a differential UV detector operating at 254 nm.

RESULTS AND DISCUSSION

Information on the composition of unknown mixtures containing the transformation products of EQ can be obtained by TLC. In this study compounds **1**–**12** were analysed using precoated silica

TABLE I

R_F VALUES IN TLC IN NEUTRAL (M_1–M_5) AND BASIC (M_6–M_9) MOBILE PHASES

Compound	R_F								
	M_1	M_2	M_3	M_4	M_5	M_6	M_7	M_8	M_9
1	0.37[a]	0.51	0.63	0.81	0.73	0.28	0.48	0.62	0.92
2	0.10[a]	0.13[a]	0.24[a]	0.33[a]	0.44[a]	0.08	0.17	0.29	0.56
3	0.08	0.15	0.33	0.51	0.60	0.05	0.17	0.37	0.65
4	0.10[a]	0.21[a]	0.40[a]	0.65[a]	0.63	0.02	0.05[c]	0.21[c]	0.52[c]
5	0.07	0.11	0.23	0.33	0.58	0.03	0.12	0.25	0.42
6	0.28[c]	0.40[c]	0.56[c]	0.73[c]	0.70[c]	0.19	0.39	0.54	0.80
7	0.01	0.02	0.05	0.08[a]	0.33[a]	0.00	0.01	0.05	0.11
8	0.16[a]	0.32[a]	0.59	0.75	0.63	0.00	–[c]	–[c]	–[c]
9	0.04	–[b]	–[b]	–[b]	–[b]	0.04	0.15	0.31	0.58
10	0.68	0.73	0.77	0.92	0.81	0.57	0.73	0.77	0.96
11	0.26	0.42	0.60	0.75	0.76	0.14	0.38	0.58	0.82
12	0.36	0.51	0.64	0.83	0.70	0.07	0.25	0.51	0.79

[a] Spot is slightly elongated towards the start.
[b] Spot is strongly elongated.
[c] Compound undergoes chemical changes during measurement.

gel plates with detection at 254 nm (Table I). Neutral or basic mobile phases were used. It is known that in TLC on a silica gel medium, basic compounds form asymmetrical spots with the tail orientated towards the initial position. In these instances R_F depends on the amount of compound initially present. This unfavourable behaviour is suppressed in the basic system. Ammonia was chosen because in two-dimensional TLC the neutral mobile phase can be used again in the second direction after the ammonia has evaporated.

The basic system is necessary for the TLC separation of compound **9**, because in neutral mobile phases this compound either remains at the initial position (M_1, Table I) or forms a long band. The presence of ammonia favourably affects the separa-

TABLE II

DETECTION OF COMPOUNDS IN TLC

Compound	Colour of spot in neutral mobile phases			Colour of spot in basic mobile phases		Luminescence at 366 nm[a]	Acid $KMnO_4$
	Immediately after analysis	After 1 h	After 20 h	Immediately after analysis	After 1 h		
1	Colourless	Grey–yellow	Grey–brown	Colourless	Yellow–grey	Blueish	+
2	Colourless	–	Grey–brown	Colourless	Light brown	–	+
3	Lemon yellow	Lemon yellow	Grey–yellow	Light yellow	Grey, green–yellow	–	+
4	Colourless	Grey	Grey–brown	Colourless	Grey, green–yellow	Blueish	+
5	Yelow	Yellow	Yellow	Yellow	Yellow	–	+
6	Brown–red	Brown–orange	Grey, yellow–orange	Red	Brown	–	+
7	Red	Red	Red	Red–orange	Red	–	+
8	Colourless	Red–brown	Red–brown	–	–	Blue	+
9	Colourless	Colourless	Colourless	Colourless	Colourless	Intense blue	–
10	Colourless	Grey–pink	Grey red	Colourless	Grey–red	Blueish	+
11	Blue	Blue	Blue	Blue	Blue	–	+
12	Colourless	Light blue	Blue	Colourless	Blue	Blueish	+

[a] All compounds quench the luminescence of the indicator at 254 nm.

TABLE III

ELUTION TIMES IN HPLC IN NEUTRAL (M_{10}–M_{12}) AND BASIC (M_{13}–M_{15}) MOBILE PHASES

Compound	Elution time (min)					
	M_{10}	M_{11}	M_{12}	M_{13}	M_{14}	M_{15}
1	46	8	5	13	6	–
2	–	30	11	–	28	14
3	–	32	8	37	10	6
4	–	–	17	–	–	21
5	–	–	11	–	34	11
6	–	11	7	15	7	5
7	–	–	14	–	–	11
8	–	–	7	–	–	13
9	–	34	9	43	13	7
10	15	–	–	6	–	–
11	–	13	6	24	8	5
12	–	28	7	–	–	8
Benzene	4	4	4	4	4	4

tion of other compounds by causing them to form rounder spots (Table I). The basicity of most of the compounds studied is so low, however, that in these instances neutral mobile phases, which are more convenient, can be used successfully.

Another reason for the application of both neutral and basic mobile phases is the low stability of some of the compounds under investigation, which in some instances is more significant in one or the other of these phases. For example, compound **6** in contact with silica gel decomposes [1], with the formation of EQ (**1**), nitrone **5** and some other compounds. The decomposition takes place gradually in the TLC analysis in neutral mobile phases, whereas the decomposition is suppressed in basic mobile phases. The opposite behaviour is observed with compounds **4**, **8**, and **12**, which in the basic medium are readily oxidized in air. The ease of oxidation increases in the order compound **12**, **4**, then **8**. Compound **8** is also partly oxidized in neutral mobile phases.

The R_F values of the compounds under investigation are summarized in Table I and increase with increasing ether content in the mobile phase (series M_1–M_4 and M_6–M_9). In the basic systems, in which the silica gel surface has been partly deactivated with ammonia and moisture, the R_F values are higher than in neutral systems at the same diethyl ether content. The M_5 phase is qualitatively different.

Detection of the compounds under study proceeds without difficulty (Table II). Many of the compounds are coloured or become coloured when the chromatogram is stored in the laboratory under scattered light. This behaviour is characteristic for each compound. Compounds **5** and **9** are stable. All compounds can be identified by a UV detector. With the exception of compound **9**, all can also be detected using an acid permanganate solution. Compound **9** has a characteristic intense light blue luminescence at 366 nm.

Similarly to separation by TLC, liquid chromatographic analysis was also performed using both neutral and basic mobile phases (triethylamine, Table III). The basic mobile phases are not absolute necessary for the compounds investigated in this study, although knowledge of their chromatographic behaviour is useful because basic conditions may be required by the presence of other compounds in the analysis of more complicated mixtures.

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