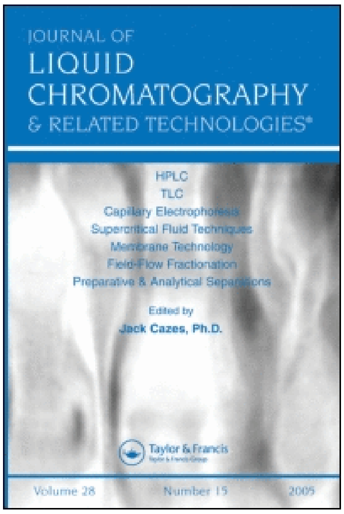

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Study of the Reaction of Antioxidant 1010 of One-Step Synthesis by RP-HPLC with Gradient Elution

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STUDY OF THE REACTION OF ANTIOXIDANT 1010 OF ONE-STEP SYNTHESIS BY RP-HPLC WITH GRADIENT ELUTION

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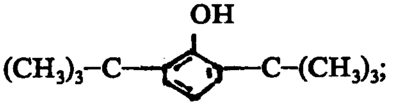
ABSTRACT

In this paper, the reaction of antioxidant 1010 of one–step synthesis had been studied by RP–HPLC with gradient elution, and 11 characteristic peaks of its components were obtained. The content of 1010 in the reaction product was over 85%. The quantitative analysis was carried out satisfactorily by internal and external standards. The recoveries, the sensitivities and variation coefficients of the method were 94.51–100.82%, 0.49–3.21μg and 0.80–1.91%, respectively. The method was rapid, accurate and sensitive.

INTRODUCTION

Antioxidant 1010 possessed the properties of nontoxicity, constant colour, thermal stability, antioxygenic activity, etc, and was an excellent antioxidant of polyalkene plastics, synthon and food in industrial production. In this paper, antioxidant 1010 was obtained by one–step synthesis. The mechanism of reaction was the following: In the presence of catalyst, the reaction of 2,6–di–tert.–butylphenol (1) with methyl propenoate (2) produced intermediate product of β–(3,5–di–tert.–butyl–4 –hydroxylphenyl) propionate (3), which directly transesterifized with pentaerythritol (4) to obtain the main product of antioxidant 1010 and by–products. The structures of all reactants and main product were the following:

1:



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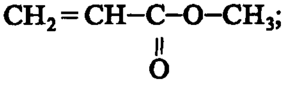
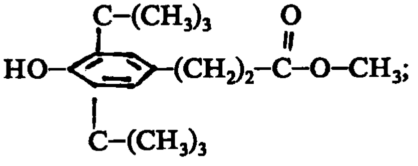


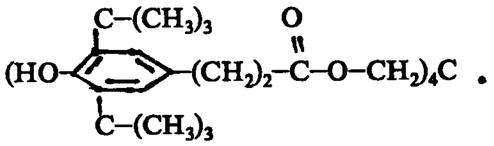
$\mathrm{CH_2{=}CH{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}O{-}CH_3}$;

3:



4: $(CH_2OH)_4C$;

1010:



In order to obtain success of antioxidant 1010 of one–step synthesis, it was necessary to set up rapid control and evaluation method of the main product, by–products, excess reactants and some impurities. In this paper, 11 components could be separated by RP–HPLC with gradient elution in 30 minutes. These components were very similar or very different in molecular polarity. The internal and external standard could be applied to routine analysis of antioxidant 1010 in industrial process.

EXPERIMENTAL

APPARATUS

Chromatographic experiments were performed with a Model Gilson HPLC system equipped with two 303 piston pumps, a HM UV–VIS detector, an Apple II computer (704 HPLC system manager with data analysis), a 620 data master and NEC printer.

REAGENTS AND STANDARD SAMPLES

The standard samples of 1, 2, 3, 4, 1010, 2,4,–di–tert.–butylphenol (5), 2,4,6–tri–tert.–butylphenol (6)were obtained from the Organic Factory of Lanzhou Chemical Industry Company. The chemical reagent of dioxane was purchased from Lanzhou Reagent Company and their aqueous solutions were prepared in redistilled water.

CHROMATOGRAPHIC CONDITION

An analytical column (Whatman 250 x 4.6 mm, 5μm, ODS–3) was used; Mobile phase was redistilled water (A) and dioxane (B); Flow rate was 0.5 ml / min; Wavelength of detection was 272 nm; Gradient elution was 75% B (0–14 min), 75% B–90% B (14–16 min), 90% B (16–24 min), 90% B – 75% B (24 – 26 min). Then equilibrium was 9 minutes under 75% B.

RESULTS AND DISCUSSION

According to the reports of T.A. Руσцовα(1,2), the choice of solvent was carried out by a trial and error method on the basis of TLC tests. The results showed that on the silica gel chromatographic column (YWG–80–5μm, 200 x 4mm), using dioxane / n–heptane (5:95 v / v) as mobile phase, a good separation was obtained, but the retention time of the 1010 and by–products were very long (90 mins), and had overlap, long tail; On whatman 250 / 4.6 mm, 5 μm ODS–3 column, using water / dioxane (25 : 75 v / v) as mobile phase, the separation of all constituents was very good, but the retention time of the 1010 was too long (78 mins). Through repeated tests, the optimum chromatographic condition was obtained in **EXPERIMENTAL** . Chromatogram of separation shown in Fig. 1 and Fig. 2.

The reaction mixture of 1010 of one–step synthesis were very complex. Their UV absorptions were different. The results showed that when wavelenth was 272 nm, the disturbance of some impurities was obated and the sensitivity of detection was enhanced.

In the qualitative analysis, in order to increase accuracy of their, not only using classic qualitatively of retention of time but also with reaction mixture and standard mixture separated under the same chromatographic

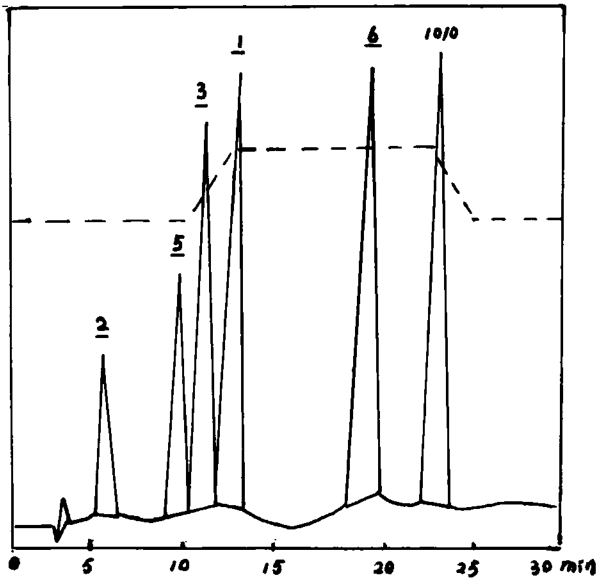


Figure 1. Integral graph of chromatogram of a standard mixture.

---- gradient line, —— integral line.

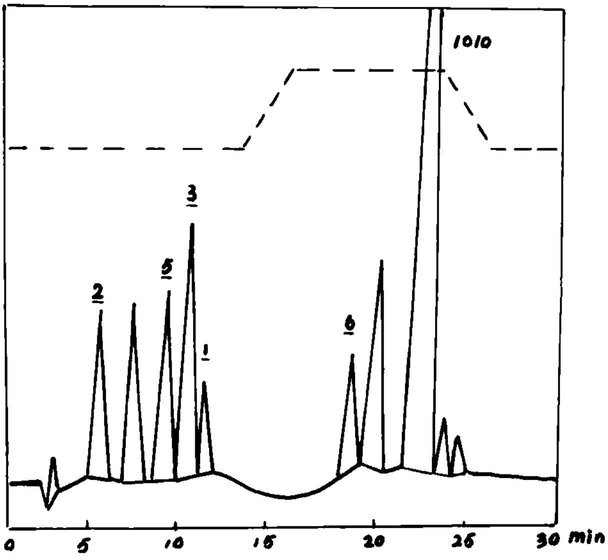


Figure 2. Integral graph of chromatogram of a sample solution

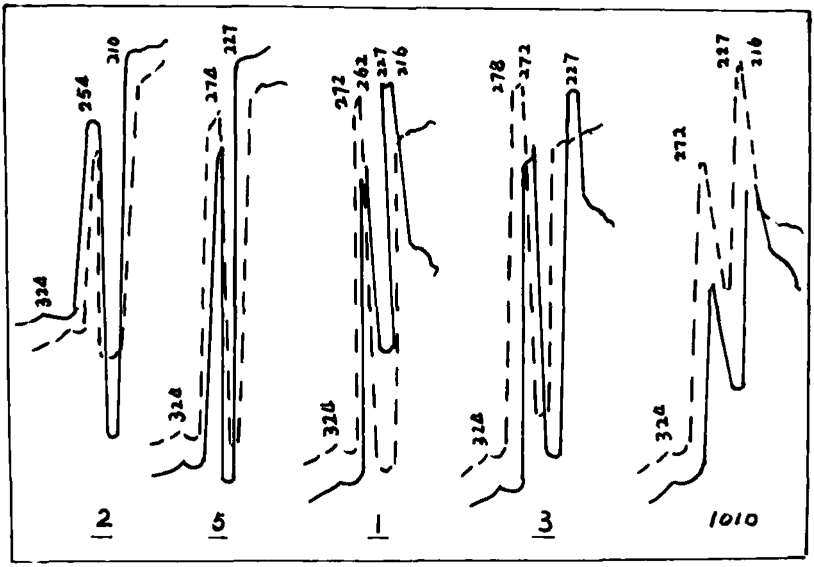


Figure 3. UV spectra

scanning condition:

range : 185 – 350 nm; scan speed : 60 nm / min; chart speed : 10 mm / min;
scale : % T ; slit : 0.4 nm; response : med.
– – – –spectra of standard, —— spectra of each component in a sample.

condition, respectively, two corresponding peaks with the same retention were scanned on–line with a fast scanning UV detector. The resultant UV spectra were identical(3)(see Fig. 3).

Under the same chromatographic condition, 6 was chosen as internal standard, the standard sample mixture solution, sample solution and sample solution which known amount of standard sample was added, were detected with an external and internal standard method of peaks′

areas, respectively. Then, the linear equations was acquired with least aquare method:

1: $y = -0.0079 + 0.0077\,x$; 2: $y = 0.0089 + 0.3556\,x$;
3: $y = -0.0088 + 0.0105\,x$; 5: $y = 0.0139 + 0.0067\,x$;
6: $y = -0.0262 + 0.0082\,x$; 1010: $y = -0.0321 + 0.0109\,x$.

Quantitative results were given in Table 1 and Table 2.*

It was indicated from Table 2 that two quantitative methods could satisfy the requirement of quantitative analysis in industry. If there was 6 in raw materials, the method of external standard could be used by sin-

Table 1. Quantitative results of sample solution

quantitative method	sample number	1(%)	2(%)	3(%)	5(%)	1010
external standard	9–6	0.01	0.80	6.69	0.03	82.73
	1–20	0.88	0.00	10.82	0.16	86.84
internal standard	9–6	0.04	0.86	5.78	0.05	81.26
	1–20	0.91	0.00	9.98	0.14	85.95

Table 2. Results of precision and accuracy test*

standard sample	external standard			internal standard		
	R(%)	CV(%)	CC	R(%)	CV(%)	CC
1	99.62	0.80	0.9999	98.35	1.12	0.9992
2	96.52	1.31	0.9996	94.51	1.27	0.9997
3	98.57	1.89	0.9997	100.82	1.91	0.9998
5	100.08	1.13	0.9998	99.23	1.12	0.9999
6	100.65	1.51	0.9998			
1010	98.97	1.34	0.9997	97.68	1.28	0.9995

* : R was recovery;

CV was coefficient of variation;

CC was correlation coeffictient;

The results in Table 1. and Table 2. were observed in five repeated tests.

gle point correction method(4). Conversely, the method of internal standard could be used, too. The methods could satisfy the control and evaluation of quality of 1010 of one–step synthesis of on–line production.

In this experiment, the trapezoid gradient elution curve was used and all components passed through the column in 30 mins. In order to ensure the repeatability of retention time of constituents and obtain the same injection condition of column system, it was necessary to eluate the column with initiatory mobile phase (75 % B, 30–35 min).

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