COMMUNICATION

Determination of Isomer Content of Butylated Hydroxyanisole

The isomer content of butylated hydroxyanisole has been determined quantitatively by nuclear magnetic resonance spectroscopy and by gas liquid chromatography. The *tert*-butyl groups of the 2- and 3-*tert*-butyl-4-hydroxyanisole appeared at τ 8.72 and τ 8.63, respectively, in the NMR spectrum. Peak area or peak height was used as a measure of isomer content. Also, gas chromatography of BHA gave two distinct peaks, whose relative areas were used for quantitative determination.

The isomer content of butylated hydroxyanisole (BHA) is important because the antioxidant properties of the two isomers (3-*tert*-butyl-4-hydroxyanisole and 2-*tert*-butyl-4-hydroxyanisole) differ (Whetsel *et al.*, 1957).

The presently available method for the determination of isomer content (Whetsel *et al.*, 1957; Food Chemicals Codex, 1965) is based on quantitative infrared spectroscopy. The method suffers from the disadvantage that relatively large amounts (about 1 gram) of the pure isomers are needed to construct a standard reference curve. Relative isomer content is then calculated from the infrared spectrum of the sample using the reference curve.

The authors now report two simple, fast, and accurate methods which are economical and do not necessarily require reference standard materials.

In the first method, the NMR spectrum of the sample was obtained in carbon tetrachloride. Comparison of the peaks at τ 8.63 and τ 8.72 gave the relative ratios of the 3-isomer of BHA and the 2-isomer, respectively.

In the second method, the sample in chloroform was subjected to gas chromatography. The isomers appeared as two separate peaks, the relative areas of which gave the isomer ratio.

Experimental

Samples. Ten mixtures of the 2- and 3-isomers of BHA containing 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100% by weight of the 2-isomer, respectively, were made from authentic components obtained from Eastman Chemical Products, Inc. (Kingsport, Tenn.). The stated purity was: 3-isomer, 100%; 2-isomer, 98.5%.

Method 1. NMR Spectroscopy. A Varian A60 NMR spectrometer was used. The NMR spectrum of 100 mg. of pure 3-*tert*-butyl-4-hydroxyanisole in 1 ml. of carbon tetrachloride was obtained at 60 Mc. per second in the usual way. The spectrum of pure 2-*tert*-butyl-4-hydroxyanisole was similarly obtained.

The 100-mg. sample of BHA to be analyzed was dissolved in 1 ml. of carbon tetrachloride and its spectrum obtained. The relative isomer content was obtained by measuring the peak heights due to the *tert*-butyl groups at τ 8.72 (2-isomer) and at τ 8.63 (3-isomer). The ratio of these heights gave the isomer ratio. Integrals of these peaks also may be used (Table I).

Method 2. Gas-Liquid Chromatography. The gas chromatograph was an F and M Model 609 with a flame ionization detector.

An aluminum column (7 feet × 1/4 inch) containing

Table I. Comparison of the Results Using NMR and GLC to Determine the Isomer Content of BHA

Sample	% 2-BHA Theoretical	% Found by NMR		% Found by GLC	
		Integral	Peak height	Uncorrected	Corrected
1	0	0	0	0	0
2	10	11.0	11.4	8.1	9.8
3	20	20.4	21.5	16.8	19.9
4	30	29.3	30.8	25.4	29.7
5	40	38.8	40.6	34.4	39.4
6	50	49.0	49.5	44.8	50.0
7	60	59.4	59.5	55.3	60.4
8	70	68.6	68.5	65.9	70.5
9	80	78.0	78.4	76.4	80.0
10	90	88.5	89.1	88.3	90.3
11	100	100	100	100	100

Table II. Positions of NMR Signals of BHA Isomers Relative to Tetramethylsilane (τ 10.0)

Group	NMR Signals	
	2-Isomer	3-Isomer
$C(CH_3)_3$	8.72	8.63
OCH_3	6.25	6.29
Aromatic H	3.40, 3.29	3.52, 3.21
OH	4.44	5.30

Carbowax 20M (20%) on Chromosorb W (80 to 100 mesh) was used.

The chromatography conditions were as follows. Column temperature 215° C., injection port temperature 280° C., detector temperature 260° C., and attenuation 6400×.

The 100-mg sample was dissolved in 1 ml. of chloroform, and 2 μl. of the solution was injected into the chromatograph. The retention times of the 3-*tert*-butyl-4-hydroxyanisole peak and the corresponding 2-isomer were 25 and 29 minutes, respectively. The peak areas were integrated by triangulation.

Results and Discussion

The 10 samples were analyzed by both methods. Results are presented in Table I.

The positions of the NMR signals due to the *tert*-butyl, methoxyl, and aromatic protons are outlined in Table II. The signals due to *tert*-butyl were sufficiently sharp to allow using the peak height as a quantitative measure.

In the case of the GLC method, the chromatographic response was not the same for each isomer. Comparison of the theoretical and experimental values for each of the 10 mixtures gave an average correction factor of 1.235. (This factor would vary with the instrument.) When this factor was applied to the peak areas of the 2-isomer, the results closely approached theory.

Literature Cited

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