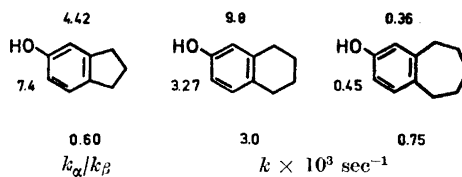


## Short Communications

## Tritium Exchange in Specifically Labeled 7-Hydroxybenzocycloheptane\*

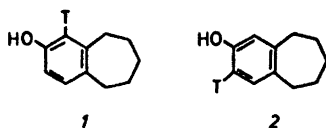
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Scheme 1.

We have previously determined the rate of detritiation of specifically labelled xylenols, indanols, and tetrahydronaphthols in anhydrous trifluoroacetic acid.<sup>1</sup> We have now extended this study to the detritiation of the specifically labelled 7-hydroxybenzocycloheptanes 1 and 2.



The syntheses of the tritiated compounds were carried out using the methods previously outlined for the preparation of specifically labelled phenols.<sup>2</sup>

The detritiation was carried out in anhydrous trifluoroacetic acid. The first order rate constants obtained are given against the appropriate positions in Scheme 1. For comparison, the rate of detritiation of specifically labelled 5-indanol and 6-tetralol, determined under identical conditions, are included in Scheme 1. This Scheme also shows the ratio between the rate constants ( $k_{\alpha}/k_{\beta}$ ) for the position *ortho* to the hydroxyl group.

\* Part XIII of "The directing effect of annelated rings in aromatic systems". Part XII: K.-G. Svensson and J. L. G. Nilsson, *Acta Pharm. Suecica*. In press.

The ratio  $k_{\alpha}/k_{\beta}$  can be used as a measure of the directing effect of the annelated ring. This ratio is smaller than 1, for 5-indanol and 7-hydroxybenzocycloheptane indicating an *ar-β* directing effect of the five- and the seven-membered annelated rings. However, for 6-tetralol the ratio  $k_{\alpha}/k_{\beta} = 3$  indicating, analogous to the result of earlier bromination studies,<sup>3</sup> that only the six-membered annelated ring has an *ar-α* directing property.

It is of interest to note that in 7-hydroxybenzocycloheptane the rate constants are approximately ten times smaller than those of the other phenols in Scheme 1. The reason for this difference is presently not understood.

*Experimental.* Melting points were determined with calibrated Anschütz thermometers in an electrically heated metal block. Infrared absorption spectra were measured on a Perkin-Elmer 237 spectrophotometer. Nuclear magnetic resonance spectra were measured in  $\text{CDCl}_3$ -solutions with a Varian A 60 spectrometer. Chemical shifts are expressed in  $\delta$  ppm relative to tetramethylsilane. Mass spectra were obtained with an AEI MS-30 instrument at 70 eV. Thin layer chromatography was performed as previously described.<sup>2</sup>

The radioactivity of the synthesized compounds was determined by liquid scintillation counting (Nuclear Chicago Mark II) after purification to constant specific activity. The chemical identity was determined by spectral and chromatographic comparison with authen-

tic samples. Exchange rate measurements were carried out in anhydrous trifluoroacetic acid at  $20 \pm 0.1^\circ$  as previously described.<sup>2</sup>

*8-Bromo-7-methoxybenzocycloheptane.* 8-Bromo-7-hydroxybenzocycloheptane<sup>3</sup> was methylated using dimethyl sulphate in alkali<sup>4</sup> to yield the title compound in 75% yield, m.p.  $54-55^\circ$  (from light petroleum). NMR:  $\delta = 7.05$  and  $6.46$  ppm (s, 1H each, ArH);  $3.74$  ppm (s, 3H,  $-\text{OCH}_3$ );  $2.8-2.4$  ppm (m, 4H, ArCH<sub>2</sub>-) and  $1.9-1.3$  ppm (m, 6H, aliphatic ring protons). The mass spectrum showed prominent peaks at *m/e* (rel. int. %) 257(9), 256(100), 255(10), 254(100), 215(8), 213(8), 175(22), 146(19), 115(13), and 91(11).

*7-Hydroxybenzocycloheptane-6-(<sup>3</sup>H)* (1). This compound was obtained from 8-bromo-7-hydroxybenzocycloheptane using the method described for 6-tetralol-7-(<sup>3</sup>H) in Ref. 2. Spec. act.  $0.7 \mu\text{C}/\text{mmol}$ .

*7-Hydroxybenzocycloheptane-8-(<sup>3</sup>H)* (2). 8-Bromo-7-methoxybenzocycloheptane (1.5 g; 5.9 mmol) was converted to a Grignard reagent which was hydrolysed using tritiated water (1 ml; 19 mC/ml) as described for 3,4-dimethylanisole-6-(<sup>3</sup>H) in Ref. 2. The crude product was demethylated using BBr<sub>3</sub> as described for 3,4-dimethylphenol-6-(<sup>3</sup>H) in Ref. 2. This afforded a mixture of 8-bromo-7-hydroxybenzocycloheptane and 7-hydroxybenzocycloheptane-8-(<sup>3</sup>H). The radioactive compound was separated by preparative TLC affording 140 mg (15%). Spec. act.  $0.9 \mu\text{C}/\text{mmol}$ .

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1. Selander, H. and Nilsson, J. L. G. *Acta Chem. Scand.* **25** (1971) 1182.
2. Selander, H. and Nilsson, J. L. G. *Acta Chem. Scand.* **25** (1971) 1175.
3. Nilsson, J. L. G., Selander, H., Sievertsson, H., Skånberg, I. and Svensson, K.-G. *Acta Chem. Scand.* **25** (1971) 94.
4. *Org. Syn. Coll. Vol. 1* (1946) 58.

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## Lanthanide-Induced PMR Chemical Shifts in Triglycerides

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High resolution proton magnetic resonance (PMR) spectroscopy is a valuable tool in research on fats and oils, isolated<sup>1</sup> or in single seeds.<sup>2</sup> The present investigation was initially concerned with the evaluation of pig fat quality and of a method for more rapid selection among turnip rape genetic crosses. The latter project has so far been hampered by poor spectral resolution. As illustrated by Fig. 1, detailed information

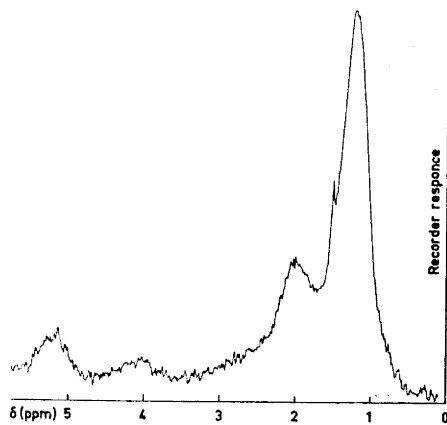


Fig. 1. 100 MHz PMR spectrum of a 5 mg turnip rape kernel, immersed in CCl<sub>4</sub>. The resolution did not improve appreciably on drying the kernel.

such as the iodine or saponification number cannot readily be obtained from the PMR spectrum.

For isolated fats, the situation has improved greatly with the advent of "shift

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