Sodium Borohydride Reduction of the Phenyl Ester of *cis,cis*-Octadeca-9,12-dienoic Acid (Linoleic Acid)

Jorge N. Chacon, George R. Jamieson, and Roy S. Sinclair

Chemistry Department, Paisley College of Technology, High Street, Paisley PA1 2BE, Scotland, U.K.

Phenyl *cis,cis*-octadeca-9,12-dienoate was found to be unstable to the effect of the mild reducing agent sodium borohydride; high pressure liquid chromatography (h.p.l.c.) analysis showed the generation of free phenol from the reduction of the fatty acid ester.

The study of oxidation products of unsaturated fatty acids has received considerable attention by chemists and biochemists over the past 40 years.[1—3]

Purification and isolation procedures are normally done by chromatographic methods but because of the problems associated with the behaviour of free acids, the studies and analysis are generally carried out using esters of the fatty acids which facilitate separation and detection and hence quantification; the methyl ester has nearly always been the first choice.[4—6] For stability reasons primary oxidation products, mainly hydroperoxides, are reduced to hydroxy compounds and for this conversion sodium borohydride is generally chosen as the reducing agent.

To improve detectability and hence quantification of oxidation products by h.p.l.c. using a u.v. detector, we have been using phenyl esters of fatty acids. Other workers in this field have also recently reported the use of such esters for the same reasons.[7,8] However, we found that following treatment of oxidation mixtures in methanol with $NaBH_4$ free phenol was generated; this was easily detected by h.p.l.c. at various wavelengths and identified by co-chromatography of authentic samples of phenol which were eluted with the same retention time. Methyl esters were stable under comparable conditions. The possibility that solvolysis of the phenyl ester group was produced by the basicity of the $NaBH_4$ solutions was tested by measuring the amount of phenol liberated when the system contained an equivalent quantity of NaOH. Only a small amount of free phenol was detected under these conditions (<20% of that with $NaBH_4$).

Figure 1 shows the chromatogram (h.p.l.c.) of oxidised phenyl *cis,cis*-octadeca-9,12-dienoate before (· · · ·) and after (——) reduction with $NaBH_4$, the position of the phenol peak being confimed by running the chromatogram (h.p.l.c.) of pure phenol under identical conditions. The instrument used

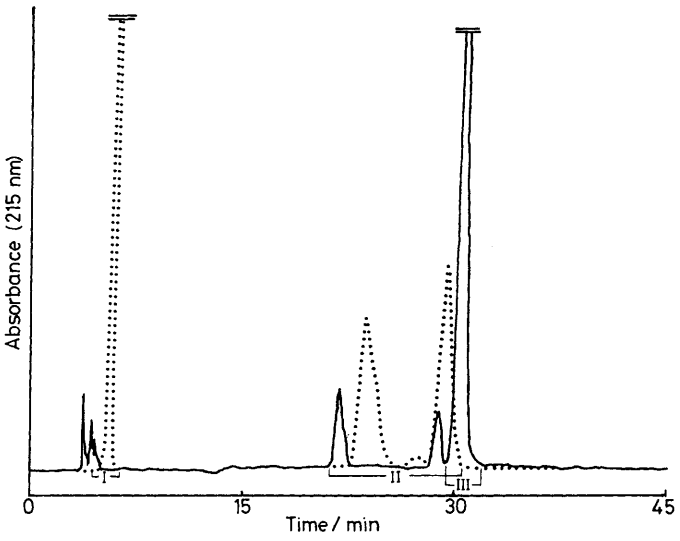

Figure 1. Chromatogram (h.p.l.c.) of oxidised phenyl *cis,cis*-octadeca-9,12-dienoate · · · · before reduction, —— after reduction with $NaBH_4$ (u.v. detector 215 nm, solvent system 0.5% ethanol in hexane, flow rate 1 cm^3 min^{-1}). I—Phenyl ester, II—oxidation products, III—free phenol.

was a Perkin-Elmer Series 3 liquid chromatograph coupled to a Perkin-Elmer Sigma 10 data station; a 25 cm × 4 mm silica column was used.

As far as we know, the only other report of a similar reaction was that made by Takahashi and Cohen in 1970 on the reduction of phenyl esters of 3-phenylpropioic acid using $NaBH_4$ in 1,2-dimethoxyethane.[9]

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