Di-2-ethylhexyl Phthalate in Thermally Oxidized Corn Oil

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Abstract

A phthalate ester, recently isolated from thermally oxidized corn oil, has been identified as di-2-ethylhexyl phthalate.

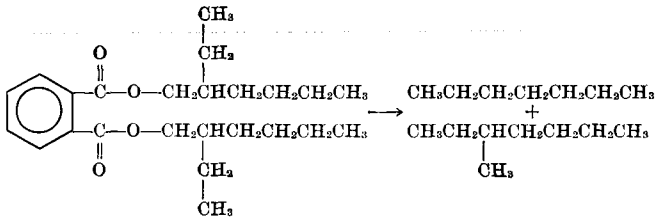
Introduction

COMPOUND A, ISOLATED BY PERKINS (1) from thermally oxidized corn oil, was characterized as "phthalic acid esterified with an eight-carbon alcohol, which is probably a mixture of branched- and straight-chain moieties." This report was of interest since an ester isolated from the mitochondria of bovine heart muscle by Nazir et al. (2) was shown to be di-2-ethylhexyl phthalate (DEHP). A sample of Compound A, supplied by Perkins, was therefore examined; it was found to be practically pure di-2-ethylhexyl phthalate.

Experimental Procedures and Results

In gas-chromatographic analysis the adjusted relative retention-times of DEHP and Compound A with diethyl phthalate as an internal standard were 3.08 and 3.10. When di-*n*-octyl phthalate (DOP) was used as an internal standard, the times were 0.829 and 0.817 respectively. In these analyses an 8-ft, ¼-in. O.D. copper column, containing 5% SE-30 on 60/80 mesh Gas-Chrom Q, was temperature-programmed at 13C/min from 150C to 250C and held at that temperature; the flow rate of the nitrogen carrier gas was 38 ml/min. An F & M Scientific Company gas chromatograph (Model 609 or 810), equipped with flame ionization detectors, was used.

Carbon skeleton chromatography (3) was conducted on Compound A with a neutral 1% palladium on Chromosorb P catalyst at 285C. The analytical column was a 15-ft, ¼-in. column, containing 5% squalane on 60/80 mesh acid-washed Chromosorb W at 80C; the flow rate of hydrogen was 30 ml/min. Products were normal heptane and a branched C_8 hydrocarbon. This latter compound was trapped and then identified by mass spectrometry as 3-methylheptane. A trace of toluene was also found. These results are consistent with the di-2-ethylhexyl ester of phthalic acid. Expected products from the alcohol moiety (parent and next lower homolog) are shown:



A small amount of Compound A was saponified with alcoholic KOH; after the addition of water, the alcohol was extracted with ether. The retention times of the alcohol were identical with those of authentic 2-ethylhexanol on two columns, a 10-ft, ¼-in. O.D. copper column containing 5% Carbowax 20M on 70/80 mesh Anakrom ABS at 120C and an 8-ft, ¼-in. copper column containing 5% SE-30 on 60/80 mesh acid-washed Chromosorb W at 100C (N_2 flow rate was 28 ml/min in both columns); retention times were 5.3 and 5.2 min respectively. Gas chromatography of equal amounts of the 2-ethylhexyl alcohol and the isolated alcohol gave a single peak on both the polar and nonpolar columns.

A mass spectrum of Compound A agreed with that of DEHP but not with that of DOP. A Consolidated Electrodynamic Corporation 21–110B high-resolution instrument was used.

Discussion

In the gas chromatography, di-*n*-octyl and di-2-ethylhexyl phthalates did not separate on an ethyleneglycol succinate column (1) but were readily separated on a nonpolar column (SE-30). On the latter column there was no evidence of any DOP in Compound A though it would have been easily visible on the chromatogram had it been present; neither was there any indication of an appreciable amount of any ester on the chromatogram other than the peak that matched DEHP in retention time. It was therefore concluded that Compound A is DEHP with minor amounts of impurities. These impurities were visible as peaks that appeared much stronger in the first mass spectrometric scan than in subsequent scans. When the diminishing peaks were deleted, as occurred for all practical purposes in the subsequent scans, the mass spectra of Compound A and DEHP were essentially identical. This comparison is shown in Fig. 1.

The fragments obtained in the carbon skeleton chromatography of Compound A left no doubt about the identity of the alcohol moiety. However Compound A was saponified, and the retention times of its alcohol on a polar and nonpolar column confirmed the presence of the 2-ethylhexyl alcohol moiety in Compound A.

Since DEHP is widely used (e.g., as a plasticizer in flexible plastic tubing and as a vacuum-pump oil), its derivation from biological materials is always suspect. Cerbulis and Ard (4) found 80 ppm DEHP in one milk sample and cited reports of phthalates in other materials. They discussed possible sources of dioctyl phthalate and its metabolism in man and animals. Nazir et al. (2) discussed the possible origin of DEHP in the mitochondria of bovine heart muscle. The concentration of 2.4% DEHP found in the thermally oxidized oil appears to be high enough to indicate that it is generated by the treatment rather than introduced.

As this paper was being written, a publication by R. G. Taborsky (5) appeared in which one of three components isolated from bovine pineal gland was identified as DOP. The published NMR spectrum matches that of DEHP much more closely than that of DOP. A noteworthy feature is the absence of the triplet of DOP at 4.3 ppm and the presence in its place of a doublet at 4.25 ppm, which indicates that only one proton (presumably owing to alkyl substitution) is located in the 2-position of the alcohol moiety. Taborsky's finding of 10 methyl protons per molecule in the NMR spectrum agrees better with the 12 methyl protons in DEHP than with the six in DOP. The published infrared spectrum of the isolated oil is likewise more consistent with the spectrum of DEHP than with that of DOP. The most striking features are the ratio of CH_3 to CH_2, based on the

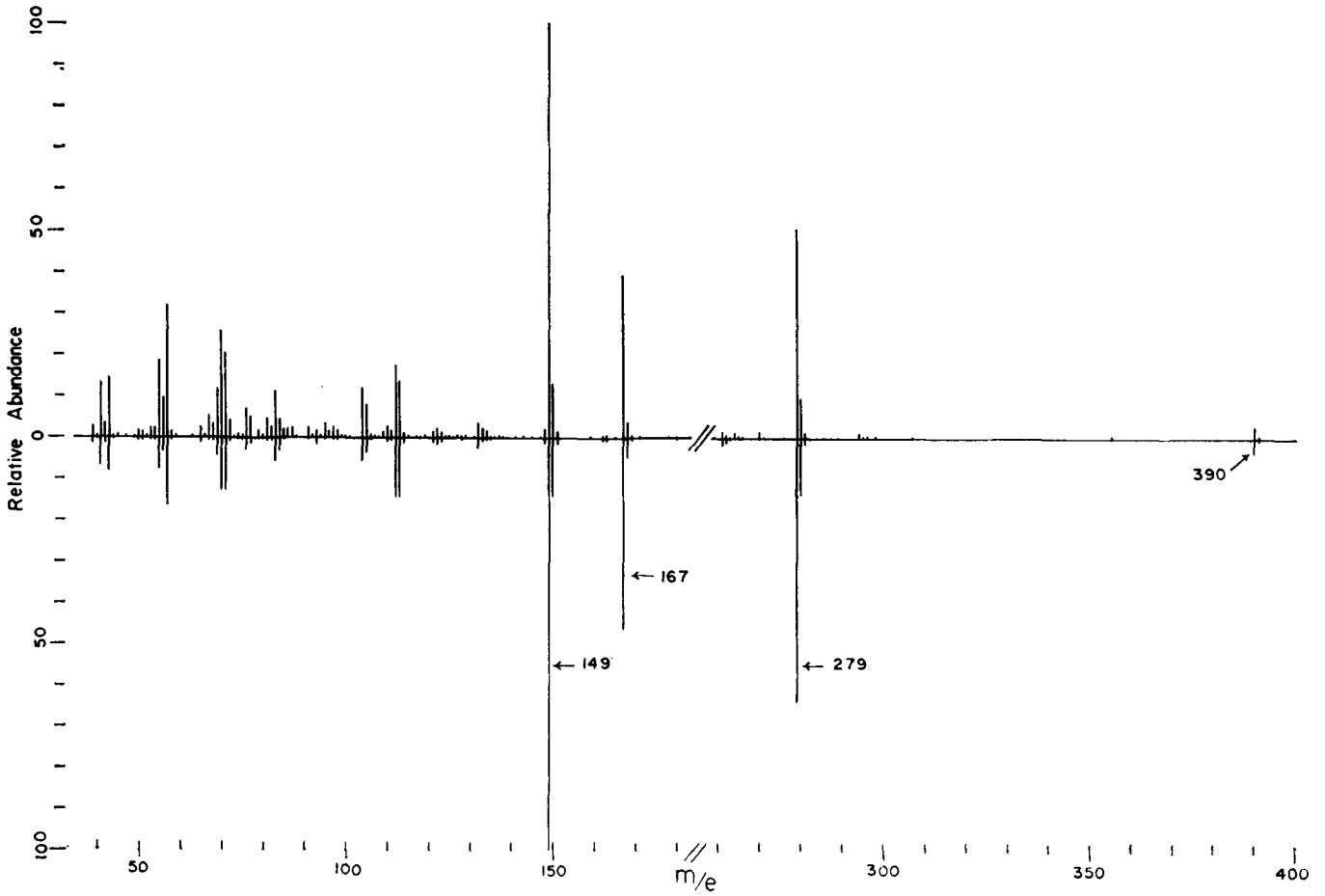


FIG. 1. Mass spectra: upper, Compound A; lower, di-2-ethylhexyl phthalate (DEHP).

C–H deformation bands at 6.9 μ and 7.3 μ respectively, and the pattern of the C–H stretching bands in the 3.4 μ region. Thus Taborsky's data indicate that his isolated product is more likely DEHP than DOP. Since DEHP has two centers of asymmetry, the lack of optical activity in the isolated product, if it is indeed DEHP, favors its exogenous origin.

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