Short Communication

⁂Participation of Cyclopropenoid Fatty Acids in the Tortelli-Jaffe Reaction with Bromine

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ABSTRACT

The Tortelli-Jaffe reaction of ditertiary double bonds with bromine in the presence of formic acid occurred with cyclopropenoid fatty acid-containing oils after prior bromination of other alkenes in the oil. The blue-colored (650 nm) cyclopropene-bromine complex appeared a basis for colorimetrically assaying cyclopropenoid fatty acids in vegetable oil.

INTRODUCTION

In 1915, Tortelli and Jaffe (1) reported a bromine-based color test for detecting fish oils in other oils. It was later shown that the reaction was due to the presence of steroids, specifically those that contain, or isomerize to, a ditertiary double bond in the ring system (2). Since cyclopropenoid fatty acids (CPFA) consist of such a system, the participation of CPFA in the Tortelli-Jaffe (TJ) reaction was of interest. Furthermore, the reaction of CPFA with bromine has never been reported. In this communication, we report the reaction of CPFA in the TJ system, forming a basis for analysis of CPFA in plant oils.

EXPERIMENTAL PROCEDURES

Corn oil was purchased locally; *Sterculia foetida* oil was a gift of G. S. Fisher of this laboratory; peanut and glandless cottonseed oils were extracted from seeds with hexane. Oils were dissolved in hexane (ca. 20% oil, w/v) and passed through columns of basic alumina (4 g of alumina per 1 g of oil). Hexane was removed in vacuo and weighed samples were dissolved in dichloromethane. Addition of zeolite NaA pellets or 4A molecular sieve beads to dichloromethane (used for both oil and bromine solutions) shortly before use removed water and ethanol.

Three-mL samples of corn, peanut, cottonseed and mixtures of corn and *S. foetida* oils containing a total of 13-14 mg of oil in dichloromethane were titrated with 4% bromine in dichloromethane (v/v) until a faint yellow color persisted. (Samples of highly unsaturated oils required more bromine. Utmost caution should be exercised when working with bromine. One can be (and has been) burned by fumes without realizing it—the burning is painless and blisters appear hours after contact.) The bromine solution was added dropwise very slowly with mixing (swirling) between drops. At no time was a large excess of bromine present during titration. Then 3-6 drops excess of 4% bromine were added, followed immediately by 5 drops of 99% formic acid. A blue color developed after 10-30 min and was stable for several hours.

RESULTS AND DISCUSSION

The original Tortelli-Jaffe reaction (1) for detection of fish oil in other oils employed chloroform and acetic acid, for which we substituted dichloromethane and formic acid, respectively, as suggested by Tosonotti as reported by Bigoni (3,4). Figure 1 shows a spectrum of *S. foetida* oil with the modified test. Corn and peanut oils yielded negative tests, whereas cottonseed and *S. foetida* oils were positive with color intensity proportional to the amount of oil. The *S. foetida* oil we used contained ca. 50% CPFA, yielding a molar absorptivity at 650 nm of ca. 600 L mol^{-1} cm^{-1}. We found that one of the three following references (zero absorbance) sufficed: corn oil; an identical sample of CPFA-containing oil under analysis but without formic acid; an identical sample under analysis but with a large excess of 4% bromine needed for the persistent yellow color. The blue color (650 nm) did not develop with a large excess of bromine, showing that care must be taken to reach the persistent yellow color, which occurred after bromination of alkenes. Rather than formation of colorless brominocyclopropanoid by radical addition (5), the reaction of CPFA with bromine in acid apparently involved the cyclopropenium ion (6,7).

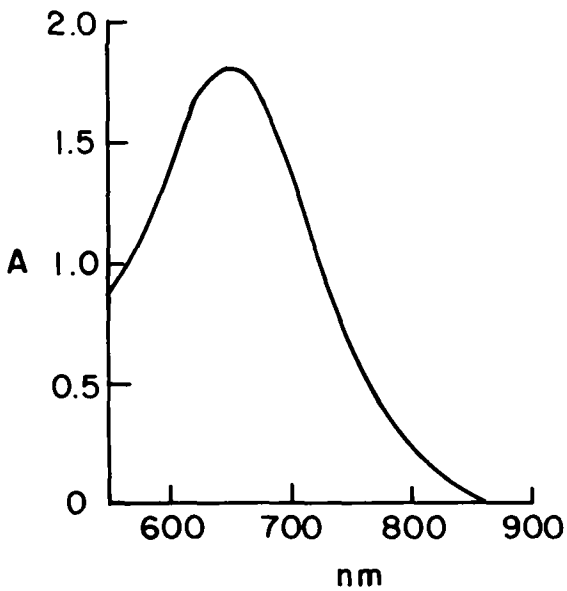

FIG. 1. Spectrum of product from the Tortelli-Jaffe reaction with *Sterculia foetida* oil. Ordinate is absorbance at wavelengths given on abscissa.

We also report the participation of CPFA in the TJ reaction for possible employment in a quantitative colorimetric assay for CPFA in vegetable oils. Adaptability of the reaction as a rapid spot test, similar to that for certain steroids (2), should also be of interest.

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REFERENCES

1. Tortelli, M., and E. Jaffe, Chem. Ztg. 39:14 (1915).
2. Fieser, L.F., and M. Fieser, Steroids, Reinhold Publ. Corp., New York, 1959, p. 114.
3. Bigoni, G., Olii Miner. Grassi Saponi Colori Vernici 32:193 (1956).
4. Bigoni, G., Olearia 11:16 (1957).
5. Rosie, D.A., and G.G. Shone, J. Chem. Soc., Perkin Trans. I. 1972:1750.
6. Breslow, R., and J.T. Groves, J. Am. Chem. Soc. 92:984 (1970).
7. Breslow, R., and H. Hover, Ibid. 82:2644 (1960).

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