• *Short Communication*

Stability of Crude Sunflower Oils to Autoxidation and to Seed Aging

Abstract

Crude seed oils of Russian sunflower varieties, Armavirec and VNIIMK 8931, are somewhat more stable to gross autoxidation than crude oils of two commercial U.S. varieties, Arrowhead and Mingren. Small amounts of oxygenated fatty acids found previously in sunflower seed oils have been shown to be produced during seed storage.

Earlier work revealed that some sunflower (*Helianthus annuus*) seed oils contained small amounts of oxygenated fatty acids, but that seed oils from selected high-oil Russian varieties were essentially devoid of these acids (1). We now wish to report results of a study designed to compare the stability of crude oils from Russian oilseed sunflower varieties, Armavirec and VNIIMK 8931, with that of oils from two established United States varieties, Arrowhead and Mingren, which are used for birdseed and confections. In addition, two oil samples derived from plant introductions were included. One of these oils (freshly extracted) represented sunflower seeds introduced from Turkey in 1956 (Plant Introduction Number, PI 173 704) and stored since then, and the second oil sample was from a crop obtained by a 1966 planting of that stored seed at the North Central Regional Plant Introduction Station, Ames, Iowa. Seeds of the Russian (1966 crop) and Arrowhead varieties were furnished by Cargill, Inc., and seeds of Mingren variety were supplied by Dahlgren Co., Inc.

Ground seed kernels (hulls removed) were extracted overnight with petroleum ether (bp 30–60 C) in a Soxhlet apparatus. Solvent was removed on a rotary evaporator at 40 C. The linoleic acid content of these oils ranged from about 50% for the two PI 173 704 samples to 68% for Arrowhead, Mingren and Armavirec and 71% for VNIIMK 8931.

Samples of each oil (5 g) were placed in 50 ml beakers covered with watch glasses and the beakers were stored at room temperature away from direct sunlight. Once a day, and also just before sampling, the oils were stirred thoroughly. Ultraviolet (UV) analyses of the oils dissolved in cyclohexane were performed periodically in the 220–330 mμ range. In addition, the oils were titrated with HBr in glacial acetic acid according to the procedure of Durbetaki (2) to determine whether there was any correlation between HBr uptake and the UV absorption. Since oxidized oils are known to interfere with HBr titrations of epoxides and cyclopropenes (3), we felt that this method might be helpful in determining the extent of autoxidation in oils with no endogenous HBr-absorbing constituents. The reaction rate of HBr with these autoxidized oils at room temperature was relatively slow, but a reasonably stable end point could be attained in about 10 min. Enhancement of the reaction rate and a corresponding clarification of the end point could probably be achieved by performing the titrations at 55 C (3).

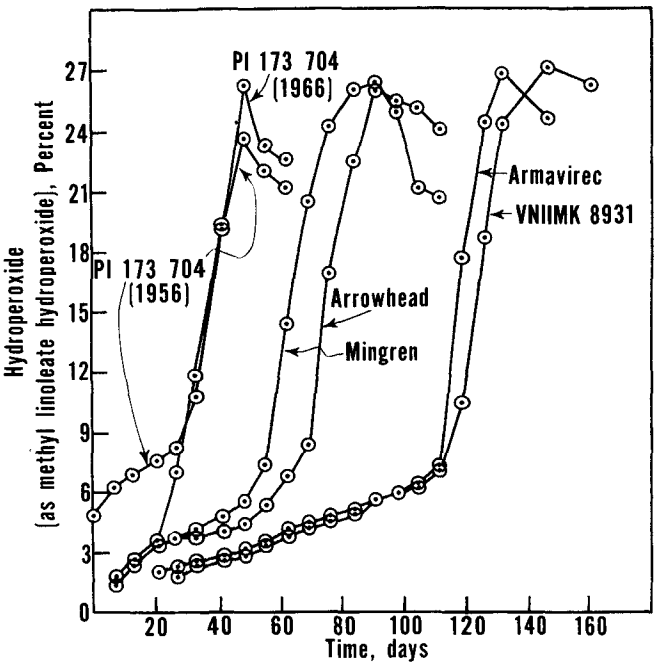

FIG. 1. Hydroperoxide content of autoxidized sunflower seed oils as calculated from UV absorption data.

Fig. 1 shows the progression of autoxidation as determined by UV absorption at 232–234 mμ. The maximum during the early stages is at 234 mμ, but it gradually shifts to 232 mμ; this shift reflects an increase in the ratio of *trans,trans*-diene to *cis,trans*-diene. No measurements were recorded until a definite maximum was observed in the spectrum. When the hydroperoxide content is 3–5%, the oils have a rancid odor, and their yellow color fades until they are nearly colorless by the time the hydroperoxide content reaches 7–9%. At this point viscosity begins to increase noticeably and the UV absorption rises rapidly. The eventual drop in UV absorption indicates that conjugation is disappearing faster than it is being formed. In order to obtain the last points shown in Figure 1, the oils had to be warmed with cyclohexane to get them into solution.

The data in Figure 1 indicate that age of the seeds before oil extraction has no effect on the rate of oil oxidation. For example, PI 173 704 oil from the 1966 planting deteriorates as rapidly as that from the 1956 crop although during the early part of the test the 1956 oil has UV absorption three times greater than the 1966 seed oil. This high absorption is due to conjugated dienol fatty acids already incorporated in this oil before extraction (1). Oils from the Arrowhead and Mingren seeds, which are commercial U.S. varieties, apparently oxidize considerably faster than oils of the Russian varieties, Armavirec and VNIIMK 8931. Specific factors that could affect the autoxidation rates of these crude oils during the early stages, such as variations in the phosphatide and tocopherol content, have not been investigated. However, since the more highly un-

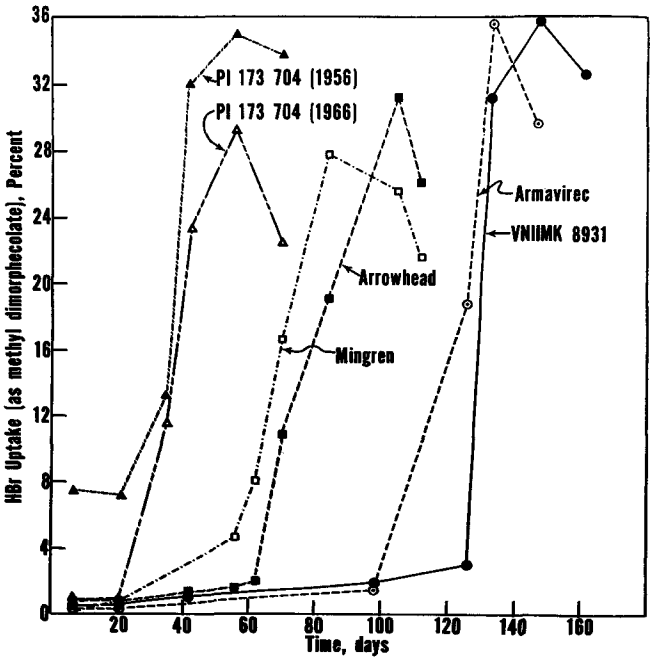

FIG. 2. HBr uptake of autoxidized sunflower seed oils.

saturated oils in this study are more stable to oxidation, it is evident that factors other than fatty acid content are contributing to their stability. These factors might also affect the stability of refined oils from these same seed varieties (not available for testing), even though the oxidation levels reported here are far greater than those associated with edible oils.

In general, close correlation exists between the percentage of hydroperoxide plotted in Figure 1 and the HBr uptake shown in Figure 2. After rapid autoxidation begins, the HBr uptake (calculated as per cent methyl dimorphecolate) is higher than the per cent hydroperoxide calculated from the UV absorption [assuming $\epsilon = 22{,}000$ (4)]. During early stages of oxidation, the HBr titration remains relatively constant and is useless as an analytical method. The gradual increase in UV absorption during this period indicates formation of products that do not react with HBr. It is only after the UV absorption begins to increase sharply that HBr uptake rises correspondingly. This behavior may be related to the observation (5) that autoxidized oils show UV absorption before hydroperoxides can be detected.

As already mentioned, our earlier work (1) demonstrated that aged samples of sunflower seeds yielded oils containing about 7–10% of oxygenated fatty acids, whereas oils from recently harvested seeds contained insignificant amounts of these acids. Since the source and prior history of the two sets of samples were quite different, one cannot exclude genetic or environmental factors as causes of the observed differences in fatty acid composition. Therefore, a group of seed samples—including three of those in the autoxidation study and one additional Russian variety, Peredovik—were aged in the laboratory. Whole, undamaged seeds were stored in capped bottles at room temperature. Periodically, samples of these seeds were dehulled and ground and the oils were extracted with petroleum ether. Titration of the oils with HBr, as previously described, gave the results shown in Figure 3. The HBr titration for all four oils increased steadily throughout the aging period,

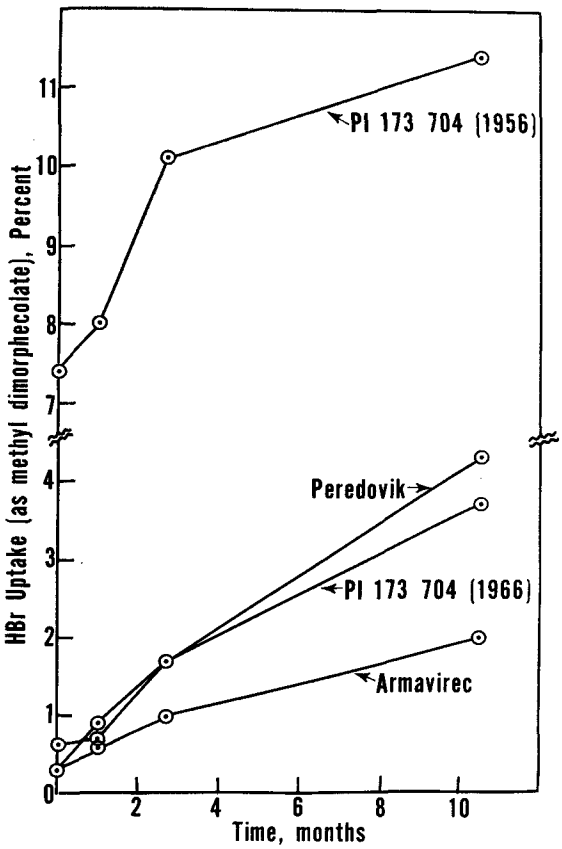

FIG. 3. HBr uptake of oils from aged sunflower seeds.

although the relative rates differed somewhat. It should be mentioned that titration of the oxidized oils with HBr was, presumably, measuring hydroperoxides or secondary oxidation products; in the case of the oils from aged seeds the products being measured are probably oxygenated fatty acids formed enzymatically in the intact seeds. UV analysis of the oils also showed a pattern of increasing absorption during the aging period. This behavior demonstrates that the presence of oxygenated fatty acids in sunflower seed oils is the result of seed aging and is not perceptibly influenced by genetic or environmental factors. The unusually high level of oxygenated fatty acids isolated previously from sunflower seed oil (1) was due to prolonged (10 yr) storage of the seed. Whether or not a very active lipoxidase system (6) in sunflower seeds is involved in this synthesis remains to be determined.

K. L. MIKOLAJCZAK
C. R. SMITH, JR.
I. A. WOLFF
Northern Regional Research Laboratory
Agricultural Research Service
U.S. Department of Agriculture
Peoria, Illinois 61604

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