Lespedeza Seed Oil. II.

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Introduction

IN a previous report[2] we presented a preliminary description of the properties of lespedeza seed oil. This data included an unusually low saponification number of 149. This value was regarded as tentative, and we wish to record data on further evaluation of the saponification characteristics of the oil at this time.

Discussion

The observation that originally clear lespedeza seed oil turns cloudy and deposits a solid on standing led us to suspect that some reaction with atmospheric oxygen was taking place. Other possible explanations for formation of this deposit such as separation of solid glycerides, waxes, or sterols were not consistent with available evidence. The amount of sterols, waxes, or unsaponifiable substances present is insufficient to reduce the saponification number as observed. Also, no evidence of separation of solid glycerides was observed on cooling.[3]

Experiments were designed to see if the formation of the precipitate was altered when the oil was stabilized with an antioxidant or stored under nitrogen. These experiments showed that the formation of this precipitate was slower when the oil was stored under nitrogen instead of air and much slower when hydroquinone was added even when stored under air.

With this information a series of experiments was designed to determine the saponification number on a series of samples of the oil after exposure to air for increasing lengths of time. These samples of oil were extracted from seeds ground under nitrogen and carefully protected from exposure to air during extraction. The samples were weighed into Erlenmeyer flasks and allowed to stand exposed to the air for increasing times whereupon the saponification number of the sample was determined. The data, summarized in Figure 1, show that the saponification number first decreases from 189 to a low of 163 and then increases to a value of 183 as time of exposure to air increases. This is interpreted as a preliminary absorption of oxygen and polymerization which increases the apparent molecular weight of the material and decreases the saponification number, followed by a rupture of the molecule with the formation of acidic fractions which increase the acidity of the sample and raise its saponification number. The final value of 183 reached in these experiments is in the C_{18} glyceride range. The initial low acid number which increases with time is consistent with this interpretation.

Another explanation[4] is that the oxidative changes occurring initially give products which cleave readily (with loss of carboxyl) during or before the alkali saponification whereas they do not do so during the original saponification. This result might come from too high temperatures in the alkali saponification or from unusual structures in the fat acid. It is known that α,β-unsaturated acids cleave with alkali at elevated temperatures. Indeed at 270°-300°C. the double bond in oleic acid is run down to the α,β-position and the molecule cleaved. If, during the oxidation of lespedeza seed oil, double bonds are shifted to a position more advantageous for subsequent shifting with alkali, a lower saponification equivalent might be obtained by the loss of carboxyl group during or before saponification. In any case a lower saponification value means that more vigorous conditions are needed in the saponification or some carboxylic acid group has been lost.

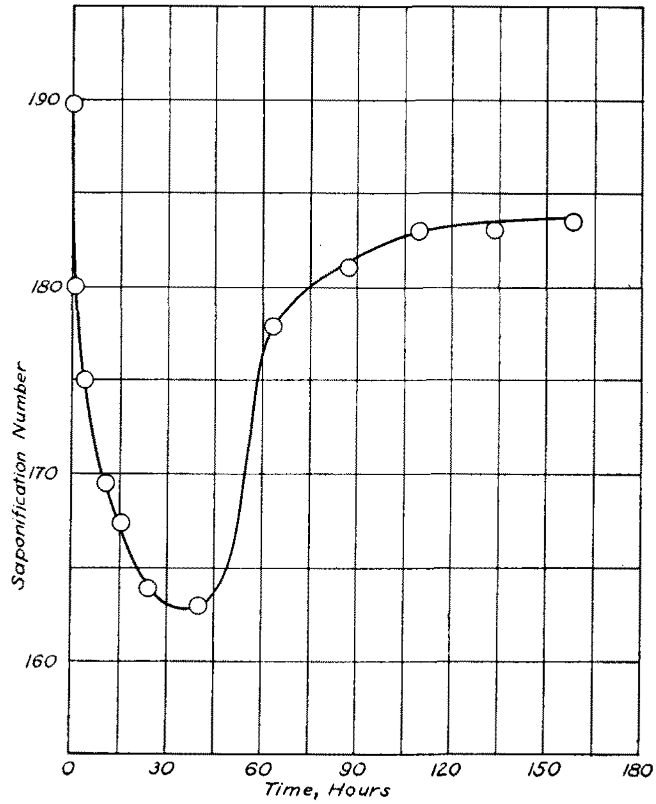

FIG. 1. Change of saponification number of lespedeza seed oil on exposure to air.

The fact that lespedeza seed oil absorbs oxygen from the air rapidly can be explained as due to the absence of natural stabilizers, such as tocopherol, or due to the presence of catalysts for the oxidation introduced in our samples either from the hulls, which were ground with the seed, or from iron, cobalt, or nickel salts formed by grinding our samples with stainless steel balls in a metal mill. Both of these factors are being investigated. It may also be attributed to a catalytic activity of the small but significant amount of conjugated triene present. Our earlier values were obtained on a sample which had been exposed to air and had, in view of information now available, undergone a reaction which altered the saponification number. The data now available show that the saponification number of this oil is not a satisfactory indication of the precise chain length of the acids in the glyceride.

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[2] Wiley and Cagle, J. Amer. Oil Chem. Soc., *27*, 34 (1950).

[3] Farmer and Paice, J. Chem. Soc., *1935*, 1630. These authors observed a separation of a solid from Telfairia oil, which they assumed to be stearin.

[4] The authors are indebted to J. C. Cowan, Northern Regional Research Laboratory, Peoria, Ill., for this interpretation of the data.

Experimental

Extraction of the Oil Under Nitrogen. Grinding of the seed was carried out in a one-gallon capacity, steel ball mill containing 50% of capacity of ½″ stainless steel balls. A minimum of 12 hours was allowed for reducing the seed to a pulverized state. The ground seed was separated from the balls under nitrogen. This was done in a cardboard container covered with a plexi-glass top and fitted with one opening for the introduction of nitrogen and two openings, cut in the sides, for hands. The ground sample was stored under nitrogen prior to extraction in a 500-ml. capacity Soxhlet extractor with petroleum ether. Care was exercised to prevent exposure to air during the extraction process. The solvent was removed under vacuum at 15°C. and the crude oil was placed under nitrogen and stored in the dark. Oxygen was removed from the nitrogen used throughout the experiment by washing with Fieser's solution.

The freshly extracted Korean lespedeza seed oil was a clear, yellow-green oil. A yield of 7.5% of oil was obtained. This oil had a saponification number of 189.3, an acid number of 1.2, and a refractive index of $N^{D}_{20^\circ} = 1.4770$.

Determination of the Change of Saponification Number With Exposure to Air. Samples of approximately one g. of lespedeza seed oil obtained as above were weighed into 125-ml. Erlenmeyer flasks and exposed to sunlight and air. The saponification number of the oil was determined by A.O.C.S. Official Method Cd3-25 on duplicate samples at the following hourly intervals: 0.167, 1, 4, 10, 16, 24, 40, 64, 88, 110, 134, and 158. The data obtained are shown in Figure 1.

Rate of Formation of Cloudiness Under Nitrogen and in Presence of Hydroquinone. To each of three 3-in. test tubes was added a one-g. sample of clear Korean lespedeza seed oil. The first tube was stoppered after adding 0.1 g. hydroquinone. The second tube was flushed with oxygen-free nitrogen and stoppered, and the third tube was stoppered under air as a control. The tubes were observed at intervals for formation of cloudiness or a precipitate. After three hours the control had turned cloudy. The sample under nitrogen was clear for six days and cloudy on the seventh day. The sample stabilized with hydroquinone was clear for 13 days and on the 14th became cloudy. All deposited a precipitate a few days after cloudiness was first noted.

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The Buffalo Gourd, a Potential Oilseed Crop of the Southwestern Drylands[1]

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THE Buffalo gourd, *Cucurbita foetidissima* H.B.K., is a wild gourd that is native to the Great Plains, the Southwestern United States, and Northern Mexico. It was first described from growing specimens by Edward James in 1820, who stated that it was found in "arid and sandy wastes, along the base of the Rocky Mountains from the confluence of the Arkansa, the Boiling Spring Fork, to the sources of the Red River" (7). It is now known to be growing wild in South Dakota, Nebraska, Kansas, Missouri, Oklahoma, Texas, New Mexico, Colorado, Utah, Arizona, Nevada, and California; and in Mexico as far south as Guanajuato (8).

This gourd is a long-lived perennial with dull green or gray stems and leaves. The stems and leaves are harsh to the touch, and the crushed foliage emits a fetid odor. After midsummer this odor disappears, but at the time of wheat harvest or cultivation of summer growing crops the odor is very pronounced when the plants are cut or bruised. The trailing vines grow to be 8 to 10 feet long, and a single plant in a good location can occupy 300 square feet of land area. Twenty or more vines usually emerge from a single root. The roots grow to great size, and roots six feet long and 12 inches in diameter are not unusual. The plants persist for many years. The leaves are heart-shaped and as large as a man's hand and are numerous enough to cover the ground completely. The sulfur-yellow flowers are numerous and conspicuous.

The gourds are usually about the size of a tennis ball, and two or three green fruits will weigh a pound. There is an abscission layer, at which the fruits separate from the vines at maturity. Pioneer women used the fruits as darning balls. When green, the fruit is hard and bitter to the taste and the seeds are attached to a mat of tough, coarse fibers. In the spring when the fruits are dry, they crush easily and the seeds separate readily from the fibrous mass. The flat, oval-shaped seeds, which resemble melon seeds, are about ½-inch long and about 5/16-inch wide. The fruits are eaten by cattle and horses, and the seeds are eaten by rodents. The literature contains many references relative to the use of the seeds for food by the American Indian. Curtis (9a) and Ault *et al.* (1a) have recently pointed out the potential value of the seeds of perennial cucurbits as a source of vegetable fat and protein.

Although this gourd has a wide natural geographic distribution, the plants are usually sparsely distributed on uncultivated land. The plants were very conspicuous in the short-grass territory, and before the South Plains area of Texas was put into cultivation 40 years ago, single isolated plants could be seen at the rate of two or three to each section (square mile)

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