FOOD ADDITIVE MEASUREMENT

Rapid Detection and Determination of Mineral Oil on Dried Fruit by Thin Layer Chromatography

FERDINAND RADLER and M. V. GRNCAREVIC

Commonwealth Scientific and Industrial Research Organization, Horticultural Research Section, Merbein, Victoria, Australia

A rapid method for the detection and determination of mineral oil on dried grapes, previously dressed with oil to prevent stickiness, is described. The oil is extracted with cold chloroform, then separated and detected by thin layer chromatography. The smallest detectable amount is 0.5 μg. of oil on the chromatogram or 0.01% on the dried fruit.

DRIED GRAPES tend to become sticky during storage and transport, mainly because of the harsh mechanical treatment necessary for cleaning and destemming. To avoid this unwanted stickiness, oils are added to the dried fruit as a final dressing. As vegetable and animal oils eventually become rancid, paraffin oil is the preferred dressing oil for dried fruit.

Some countries, for health reasons, limit or prohibit the use of paraffin oil as a fruit additive (*1*, *2*), so that a quick and reliable method is required for its detection and estimation on dried grapes. This is particularly necessary as the total amount of oil remaining on the fruit after aerosol spraying or aqueous emulsion wash is often not known.

Of the available methods, the determination of the total material extractable by solvents is of little use as natural waxes, paraffin oil, or other oils cannot be distinguished from one another. The accurate quantitative method for paraffin determination on dried grapes by column chromatography (*4*) and the general method for the determination of mineral oil on foods (*8*) have the disadvantage of being cumbersome and time-consuming. The determination of mineral oil as the unsaponifiable matter of the lipid extract (*3*, *7*) has the same disadvantages.

This paper describes a method for the detection and semiquantitative determination of paraffin oil on dried fruit by thin layer chromatography. The method can be carried out in less than 1 hour.

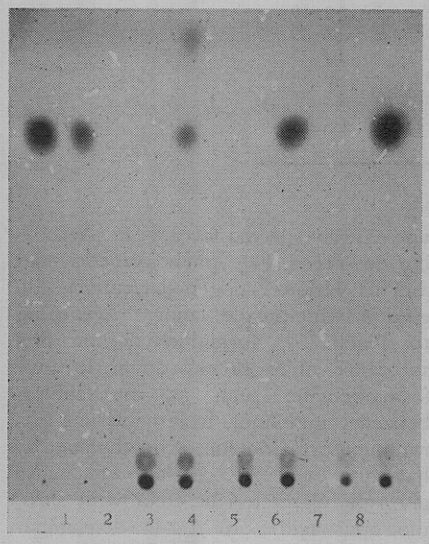

Figure 1. Chromatogram of natural and paraffin-treated dried fruit

(1) 10 μg. paraffin oil; (2) 2.5 μg. paraffin oil; (3) currants, untreated; (4) currants, 0.05% paraffin oil; (5) sultanas, untreated; (6) sultanas, 0.1% paraffin oil; (7) raisins, untreated; (8) raisins, 0.3% paraffin oil

Experimental

Reagents and Apparatus. Samples of dried grapes were obtained from the experimental vineyards of the C.S.I.R.O.'s Horticultural Research Section, Merbein, Victoria, and from local packing houses. Samples of paraffin and other oils which could be used for treating dried fruit were obtained from commercial sources or from the producers. Reagents were of analytical grade, and solvents were redistilled before use.

The technique and equipment for thin layer chromatography according to Stahl (*9*) were used for the separation and determination of paraffin oil. Silica gel G served as supporting material, plates (200 × 200 mm.) being prepared according to the standard method (thickness of the layer, 0.25 mm.; activation, 30 minutes at 110° C.). Petroleum ether, b.p. 60° to 70° C., was used as solvent. For the development, chromic sulfuric acid (5 grams of $K_2Cr_2O_7$ in 100 ml. of 40% H_2SO_4) was used as spray reagent. After the solution was heated for 20 minutes at ca. 200° C., permanent dark spots developed.

Extraction. The extraction of paraffin oil from the grapes was performed with chloroform at room temperature; 25 grams of fruit were shaken twice for ca. 1 minute with separate 25-ml. portions of chloroform. The decanted and combined extracts were used for chromatography without further treatment, unless a high content of suspended organic or inorganic particles made filtration or centrifugation necessary.

Semiquantitative Determination. Ten microliters of the extracts were chromatographed for the semiquantitative determination of the paraffin oil content of the fruit. The size and intensity of the spots were compared visually with those of known amounts of paraffin oil similarly applied as a chloroform solution to the same plate.

Table I. Maximum R_f Values of Constituents of Possible Grape Dressing Oils and Grape Wax on Thin Layer Silica Gel Plates Using Petroleum Ether as Solvent

Substance	Max. R_f Value
Mineral oil	85–91
Mineral grease	85–95
Animal and vegetable oils and acetylated glycerides	0
Dipping oil	0–7
Grape wax	0–10

Table II. Content of Paraffin Oil in Commercial and Experimental Samples of Dried Fruit and the Efficiency of Extraction with Cold Chloroform

Sample No.	Estimated Paraffin Content, %	Soxhlet-Extractable Paraffin in Residue (25 G. Dried Fruit), mg.	Total Paraffin not Extracted with Cold Chloroform, %
Sultana, Untreated			
1	0	0	0
Sultana, Commercial Sample from Australia			
2	0.05	1	<10
3	0.05	1	<10
4	0.1	2	8
5	0.1	2.5	10
6	0.1	3	12
7	0.15	2.5	8
8	0.2	3	6
9	0.2	5	10
10	0.25	10	16
11	0.4	5	5
Sultana, Sample from U. S. A.			
12	0	0	0
Currants, Commercial Sample from Australia			
13	0.05	<1	10
14	<0.05	<1	10
15	<0.02	0.5	10
Raisins, Commercial Sample from Australia			
16	0.1	0.5	2
17	0.1	4	16
Raisins, Deseeded, Commercial Sample from Australia			
18	0.3	7	10
Raisins			
19	0.6	10	8
Raisins, Sample from U. S. A.			
20	0	0	0

Table III. Estimation of Amounts of Paraffin Added to Dried Fruit

Amount Added, % (W./W.)	Paraffin Recovered from: Currants, In 10-µl. extract, µg.	Currants, In dried fruit, %	Sultanas, In 10-µl. extract, µg.	Sultanas, dried fruit, %	Raisins, In 10-µl. extract, µg.	Raisins, dried fruit, %
0	0	0	0	0	0	0
0.005	0	0	0	0	0	0
0.0125	Trace	0.01	0.5	0.01	Trace	0.01
0.025	1	0.02	1	0.02	1	0.02
0.05	2–3	0.05	2–3	0.05	2–3	0.05
0.1	5–7	0.1	5	0.1	5	0.1
0.2	10–12	0.2	10	0.2	12	0.2
0.4	20–25	0.4–0.5	20	0.4	20	0.4

Results and Discussion

Australian dried grapes—sultanas, currants, and raisins—contain about 0.2 to 0.3% natural wax, residual dipping oil (if used), and a varying amount of the oils used for final dressing. All of these may be found in chloroform extracts of dried fruit (*6*). The technique of thin layer chromatography appeared to be the most convenient way of separating paraffin oil from the chloroform extract.

In several trials with different solvents, petroleum ether, b.p. 60° to 70° C., gave a satisfactory separation of paraffin and other mineral oils from grape waxes and dressing oils of animal or plant origin. The chromatogram can be run in 15 minutes. The R_f value of the nonpolar paraffin oil is well above that of all other components which stay close to the starting point (Table I).

Grape wax itself contains a small amount of hydrocarbons, probably nonacosane and hentriacontane (*5*). However, the concentration of components in grape wax which gives R_f values similar to that of paraffin oil seems to be very low, obviously not more than 1 to 2% of the grape wax. Only a very faint spot corresponding to hydrocarbons can be detected when 50 µg. of grape wax is applied to the chromatogram. The smallest detectable amount of paraffin oil is about 0.5 µg.

For the subsequent detection of mineral oil on dried grapes, the method of extraction is most important. Chloroform is a good solvent for waxes, and two extractions with cold chloroform usually removed more than 90% of the mineral oil from the fruit (Table II).

By using 2 ml. of chloroform for each gram of dried grapes and applying 10 µl. of this extract to the chromatogram, the amount of paraffin on the fruit could be approximated. Five micrograms of paraffin oil on the chromatogram corresponds to 0.1% oil on the fruit. The smallest detectable amount of paraffin oil is about 0.5 µg.; this value corresponds to 0.01% on the fruit.

The amounts recovered were in good agreement with the amounts of paraffin oil applied to the fruit (Table III). In this test, the paraffin oil was added as an emulsion in an aqueous solution of 0.5% oleic acid and 2.5% K_2CO_3 (similar to commercial practice). To increase the emulsion stability, ca. 2.5% of triethanolamine was added.

Figure 1 gives an example of the chromatographic detection of paraffin oil on dried fruit. It also shows that the small content of hydrocarbons in the natural grape wax does not interfere with the method used.

The results of the estimation of the paraffin oil content in some commercial and experimental samples of dried grapes are presented. Sultanas had an average content of ca. 0.1 to 0.2% of paraffin oil, with a maximum of 0.4%. Currants contained less paraffin oil (ca. 0.05%). The highest content was found in seeded raisins (0.6%).

The method described here may be generally applicable to the detection of mineral oil in other dried fruits and similar products.

Acknowledgment

The authors are indebted to A. A. Gregory of the Department of Primary Industry for supplying samples of dried fruit, and to N. Permezel for help in the preparation of the manuscript.

Literature Cited

(1) Diemair, W., *Lebensmittelrecht und-kunde* **33,** 1 (1960).
(2) Food Standards Committee Report on Mineral Oil in Food, p. 4, Min. Agr. Fish & Food, London, 1962.
(3) Jacobs, M. B., "The Chemical Analysis of Food and Food Products," p. 387, Van Nostrand, Princeton, N. J., 1958.
(4) Krummel, G., *Deut. Lebensm. Rundschau,* **58,** 36 (1962).
(5) Markley, K. S., Sando, Ch. E., Hendricks, S. B., *J. Biol. Chem.* **123,** 641 (1938).
(6) Martin, R. J. L., Stott, G. I., *Australian J. Agri. Res.* **8,** 444 (1957).
(7) "Official Methods of Analysis," p. 372, Assoc. Offic. Agr. Chemists, Washington, D. C., 1960.
(8) Silverberger, H. D., *J. Assoc. Offic. Agr. Chemists* **45,** 241 (1962).
(9) Stahl, E., "Dünnschicht-Chromatographie," p. 5, Springer, Berlin-Göttingen-Heidelberg, 1962.

Received for review June 17, 1963. Accepted August 9, 1963.