

a small part of the total odor complex. Nevertheless it appears to accompany the odor very closely. The relationship between malonaldehyde, other carbonyls, and odor, in distillates from pure fatty acids, is under investigation at the present time in an effort to throw light on these questions.

Summary

An improved distillation method is described for the quantitative determination of malonaldehyde in foods containing oxidized fats. The procedure is compared with other methods in current use for the determination of malonaldehyde. A high correlation of TBA numbers with rancid odor in cooked meats was established.

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Search for New Industrial Oils. II. Oils with High Iodine Values

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AMONG THE FIRST 87 samples of seed oils analyzed in a program to find new oils of industrial importance (1), 12 were found to have iodine values above 180.

Only three plant families, the *Cruciferae*, *Euphorbiaceae*, and *Labiatae*, are represented, and all three have previously been known (2,5) to contain members producing oils with high iodine values. Eight of the 12 species however have not had oil composition reported. Failure of other plant families to appear in this tabulation of oils with iodine values above 180 may result partly from the limited number of samples thus far analyzed. It may be expected that additional oils with high iodine values will be discovered and that other plant families will be represented as additional seed materials are examined.

The *Cruciferae* (mustard family) include some 300 genera and 3,000 species (3). The rapeseed and mustard seed oils from this family are familiar items of commerce. Oil composition has been reported in the literature for some 30 species of *Cruciferae*, and the presence of erucic acid is characteristic of the family. The two representatives of the family in this report belong to *Hesperis* and *Matthiola*, genera which contain some 25 and 50 species, respectively. The only previously analyzed oil from these genera was from *H. matronalis*. There are almost 75 other species which may be explored with the expectation of finding some with improved oil composition, increased seed yield, more desirable plant form, and wider climatic adaptability.

The *Euphorbiaceae* (spurge family) are a large family of some 280 genera and 8,000 species. The plant types are quite varied, ranging from prostrate herbaceous weeds to cactus-like trees. The best known commercial oils from this group are tung and castor oils, which have special value because they contain structures not present in the more common oils. Only about 60 species from the entire family and about 15 of the 1,000 species in the genus *Euphorbia* have been analyzed for oil composition.

The *Labiatae* (mint family) include some 3,000 species, of which about 60 are grown in gardens in this country as ornamentals or as kitchen herbs. Perilla is the principal representative of the family among industrial seed oils, but published analyses for some 15 other species (2,5) indicate that several should produce oils of similar drying quality.

Materials and Methods

The source of seeds, the method of preparing oils, and the methods of analysis have been described previously (1). Methods presented by Gardner (4) were used to determine film hardness and drying time. Films of oil modified by the addition of 0.015 g. of mixed drier (24% lead, 6% cobalt, and 6% manganese naphthenates) were put on microscopic slides. Those for the drying-time test were touched repeatedly with the finger to determine when the film had set to touch. The films for the hardness test were aged two days, then tested with a series of drawing pencils of graduated hardness to determine the softest one which would scratch the film. Viscosities were determined by using the Gardner-Holdt Bubble Viscometer.

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TABLE I
 Analytical Data on Seeds and Derived Oils

Source	Common name	Seed analysis		Iodine value	Saponification value	Refractive index n_D^{40}	Fatty acid content of oil				Viscosity, Gardner-Holdt	Drying time Set to touch	Pencil hardness
		Oil content	Protein content $N \times 6.25$				Nonconjugated triene, as linolenic	Nonconjugated diene, as linoleic	Monoene, as oleic	Saturated			
<i>Cruciferae</i>		% DB	% DB				%	%	%	%		hrs.	
<i>Hesperis matronalis</i>	Dame's rocket	32	25	186	186	1.4737	46	21	26	3	A2	3.0	F
<i>Matthiola bicornis</i>	Evening stock	29	35	196	192	1.4748	59	9	20	8	A1	2.5	H
<i>Euphorbiaceae</i>													
<i>Euphorbia marginata</i>	Snow-on-the-mountain	32	21	198	185	1.4761	57	14	17	8	A2	2.5	2H
<i>Euphorbia heterophylla</i>	Painted-spurge	37	25	200	188	1.4754	55	22	10	8	A4	2.5	2H
<i>Labiatae</i>													
<i>Majorana hortensis</i>	Sweet marjoram	40	32	199	188	1.4753	55	20	16	5	A	2.2	4H
<i>Monarda fistulosa</i>	Wild bergamot	32	27	210	192	1.4756	58	18	19	0	A1	2.1	3H
<i>Nepeta mussinii</i>	25	22	200	184	1.4749	55	18	17	6	A2	1.8	H
<i>Ocimum basilicum</i>	Sweet basil	24	21	191	188	1.4742	50	22	15	8	A1	2.1	2H
<i>Perilla frutescens</i>	Perilla	42	32	189	185	1.4734	55	11	21	9	A3	2.8	H
<i>Salvia columbariae</i>	California chia	34	20	198	188	1.4748	56	16	18	5	A1	2.8	3H
<i>Satureja hortensis</i>	Summer savory	42	24	214	184	1.4765	62	18	12	4	A2	2.2	4H
<i>Thymus vulgaris</i>	Thyme	37	28	208	189	1.4772	62	13	18	3	A	2.2	4H
<i>Linaceae</i>													
<i>Linum usitatissimum</i>	Linseed	40	26	184	49	14	22	11	A3	3.0	F

Results

Characteristics and composition of the oils, as indicated by the tests applied, are presented in Table I. The proportion of apparent linolenic acid varied from 46 to 62%. Apparent linoleic acid varied from 9 to 22% and the total of "linolenic" and "linoleic" from 66 to 80%. The oils containing the highest concentration of "linolenic" acid are from *Satureja hortensis* and *Thymus vulgaris*. Those highest in total "linolenic" plus "linoleic" acids are from *S. hortensis*, *E. heterophylla*, and *Monarda fistulosa*.

Several oils apparently contain minor components other than the usual saturated and unsaturated acids. Those from *T. vulgaris* and *Matthiola bicornis* reacted with HBr in the oxirane oxygen test to an extent corresponding to about 1% of a C_{18} epoxy acid. *T. vulgaris* oil shows a trace of preformed conjugation, but the amount, 0.5%, is probably insignificant for any industrial use of the oil. Oil from *Monarda fistulosa* is indicated to be free of saturated acids and, by gas chromatography, to contain 4% of some component moving more slowly than the usual C_{18} acids. Oil from *Matthiola bicornis*, the only other oil to be analyzed by gas chromatography, shows no indication of acids longer than C_{18} .

Measured characteristics of the films and the viscosity of the crude oils are also shown in Table I. The linseed oil included as a reference material was extracted from seed of variety B-5128 obtained from a commercial seed distributor. Its iodine value, 184, is slightly above the mode shown by Hopper and Nesbitt (6) in their study of 1,485 samples ranging in iodine value from 144 to 196 but is within the range of good commercial oils.

Viscosity of the various oils ranged from A (Gardner-Holdt) to A4. Oils from *Majorana hortensis* and *T. vulgaris* were the most viscous of the group. That from *E. heterophylla* was the only one less viscous than linseed. The iodine value of the oil from *H. matronalis* was the lowest in the group and was essentially the same as that of the linseed oil used for comparison. These last two oils were the slowest to dry and produced the softest films in the series. *Nepeta mussinii* dried faster than the other oils although it does not have the highest iodine value.

Discussion

The oils reported in this work are, on the basis of iodine value, very similar to each other and to linseed oil. None of them deviate markedly from the regression line (Figure 1) calculated from iodine value and refractive index data on 70 oils (1) including these 12, or from lines published for soybean (8), linseed (6, 9, 10), and perilla (7) oils. The agreement with the line suggests that the oils contain primarily the common fatty acids, and the data in Table I are in agreement with this suggestion. Similarly infrared examination of the oils reveals no unusual components. While the present data include no proof, it seems reasonable to assume that the diene and triene are the common linoleic and linolenic acids.

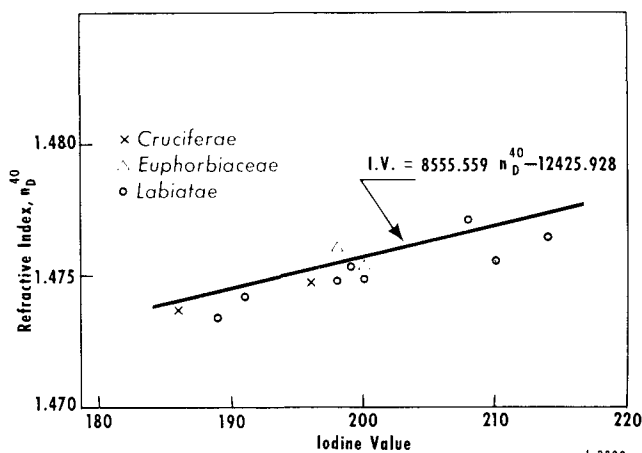


FIG. 1. Relation between iodine value and refractive index.

Oils from the two *Cruciferae*, *H. matronalis* and *Matthiola bicornis*, are not typical of the oils produced by the family. *H. matronalis* has been reported (5) to contain no erucic acid, and the present work shows that the oil from *M. bicornis* likewise contains none. Linolenic acid is common in *Cruciferae* oils, but the high level in these two species is unusual. The previous report on oil from *H. matronalis* (46% linolenic acid and 35% linoleic acid) is in good agreement with the "linolenic" acid content shown in

Table I but is 14% higher in linoleic acid. The presence of 1% of apparent epoxy acid in the present sample of *M. bicornis* is based only on HBr absorption and is not conclusive.

The compositions of the two *Euphorbia* oils are similar to each other and to the composition of several *Euphorbia* oils reported earlier (2, 5). The *E. marginata* oil reported here differs significantly however from the literature report of 45% linolenic acid and 45% linoleic acid. This discrepancy may be resolved, or the variability of the species may be revealed more clearly as additional samples are analyzed in the screening program.

Oils of the eight *Labiatae* in this study are similar in composition to other *Labiatae* oils with high iodine values. Only two of these oils are reported by Hilditch (5), and the composition of the present samples are distinctly different. The earlier sample of *Ocimum basilicum* was reported to have 21% linolenic acid and 60% linoleic acid in contrast to 50% "linolenic" and 22% "linoleic" acid found in the present sample. Similarly the previous report shows *Perilla frutescens* (*P. acymoides*) oil to contain 63 to 70% linolenic acid and from 0 to 16% linoleic acid whereas the present sample contains only 55% "linolenic" acid and 11% "linoleic" acid. Regardless of the discrepancy, which may result from differences in the sources of samples, the composition of the eight *Labiatae* oils are sufficiently similar to suggest that they would all serve in applications where perilla oil has been used in the past; several of them are probably superior to perilla oil of average composition.

The minor amounts of apparent epoxy acid and of conjugated unsaturation in *Thymus vulgaris* oil have no value and for most applications probably would not be detrimental. The absence of saturated acids from the oil of *Monarda fistulosa* may perhaps indicate the presence of some component which responds abnormally to either the iodine value procedure or the alkali isomerization in the determination of polyunsaturated acids, or it may result from the chance accumulation of errors in the procedures. Complete absence of saturated acids would be most unusual, but such a result is often within the accepted precision of the method. The 4% of material in this same oil moving more slowly than the C_{18} acids has not been identified but might be arachidic acid, which has been reported in several oils of the *Labiatae* (2, 5).

The tests of drying time and film hardness, while

not precise, support the generality that oils with higher iodine values dry more rapidly and produce harder films. The oil from *Nepeta mussini* is anomalous in that it dries more rapidly than three oils of higher iodine value but produces a softer film than five oils of comparable or lower iodine value. This behavior may indicate greater or lesser amounts of trace constituents which affect the rate or extent of oxidation and polymerization in the drying film.

In general, the analyses reported in Table I suggest that all these oils should be equal or superior to linseed oil as drying oils. They should receive serious consideration if any can be produced more economically, if any are especially adapted to areas of the country which require an alternative crop, if they are sufficiently good to permit performance equal to linseed after dilution with a cheaper oil, or if over-all demand for drying oils should increase sufficiently to justify production of additional ones.

Extensive study of any of the species reported in this paper may reveal that the sample tested is not typical but may be better or worse than the average. Until proved otherwise, it must be assumed in a screening program that the sample analyzed is sufficiently representative to serve as a guide to further study of oils for specific uses.

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ABSTRACTS . . . R. A. REINERS, Editor

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• Fats and Oils

ESTIMATION OF CATALYST ACTIVITY FOR HYDROGENATION OF FATS. I. Kaganowicz. *Prace Inst. i Lab. Badawczych Przemysłu Spożywczego* **8**(4), 33-44 (1958). A nickel catalyst was prepared by heating nickel formate in rapeseed oil at $245 \pm 4^\circ$ for 2 hours. When this catalyst was used in the hydrogenation of rapeseed oil, the rate of change of the iodine number of rapeseed oil was proportional to the catalyst activity. The activity of the catalyst was determined by means of the formula

$A = (I_i - I_f) \times 88.25/at$, where I_i and I_f are the iodine numbers of the oil before and after hydrogenation, a is the amount of catalyst in weight % based on the oil, t is time in minutes, and 88.25 is the number of ml. of hydrogen corresponding to an iodine number unit. (*C. A.* **53**, 19410)

THE APPLICATION OF ION-EXCHANGE RESINS TO THE PURIFICATION OF FATS. A. Ollero Gómez and A. Soto Cartaya (Univ. Seville). *Grasa y aceites* (Seville, Spain) **9**, 296-301 (1958). Ion-exchange resins may be used for neutralization of fats, removal of trace elements, and analysis of trace elements. The