While lesser amounts of skin-substantive agents (0.5%) may give relatively equivalent degerming action on the hands, it is reasonable to suppose that the advantages of skin-substantivity are largely overshadowed by the gross pick-up of soap in the underarm areas. Thus any agent at higher levels (1.0 to 2.0%) in soap yields greater accumulation and greater deodorant activity than at the 0.5% level.

It would therefore appear that the best measure of the deodorant capacity of a soap is a deodorant evaluation study rather than a bacteriological evaluation by means of controlled handwashing.

Toxicology. The complete toxicity picture was developed for the antibacterial synergist system hexachlorophene/T.C.C. in soap.

These studies indicate that soap containing this combination is neither a primary skin irritant nor a skinsensitizing agent. The acute oral toxicity for dogs lies above 16 g. per kilo which rates as "practically nontoxic."

#### Summary

It has been shown that mixtures of hexachlorophene and trichlorocarbanilide or bithionol and trichlorocarbanilide in soap show a marked synergism with respect to antibacterial properties. In both cases the approximate ratio of 50/50 of the two components represents an optimum.

Nonionic detergents enhance the antibacterial activity of trichlorocarbanilide in vitro when present at relatively low levels. At higher levels of nonionic the antibacterial agent is neutralized and loses its effectiveness.

The antibacterial activity of the pair hexachlorophene-trichlorocarbanilide extends over a wide spectrum of micro-organisms, and synergism is shown with each test organism.

High antibacterial activity of the synergistic pairs in soap is shown both in *in vivo* handwashing studies and in subjective deodorant tests. On the other hand, it is shown by way of several examples that in vivo observations do not necessarily correlate with in vitro bacteriological screening tests.

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## Search for New Industrial Oils. III. Oils from Compositae

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THE COMPOSITAE are the largest family of flowering plants and include about 900 genera and more than 13,000 species. Two species, safflower and sunflower, are grown for oil production on a commercial scale. In addition to these, some two dozen species have been studied sufficiently, with respect to oil composition, to be reported in reference works on oils. Linoleic and oleic acids are the major component acids found in the oils reported, with linoleic acid usually in the greater amount. Linolenic acid is reported in amounts up to 4% in some oils but is absent from others (5). Only Vernonia anthelmintica (6, 7), Calendula officinalis (9), and Chrysanthemum coronarium (10) have been reported to deviate from the pattern.

Among the first 87 oils studied in our extensive search (4) for new industrial oils were 16 from seeds of different species of the Compositae. Out of these 16, two are reported in the comprehensive compendia by Eckey (5) and Hilditch (7).

#### Materials and Methods

The seeds used as sources of oils, like those for Part I (4) of this series, were provided by the New Crops Research Branch, Agricultural Research Service, U.S. Department of Agriculture. Methods used are the same as those described in Part I. Their primary purpose is to permit selection of oils of unusual and potentially useful composition rather than to give positive identification of any acids. They probably give an adequate representation of most of the oils although unsuspected interferences in some crude oils may cause them to give inconclusive or erroneous results.

#### **Results and Discussions**

Results of screening analyses are presented in Table I. The range in iodine value from 102 to 147 is typical of the family (5). The low value for Vernonia anthelmintica is related to the high proportion of monoene while the low value for Cosmos bipinnatus results from the high proportion of saturated acids. The highest iodine value is found in the oil from Rudbeckia bicolor, which contains the largest proportion of apparent linoleic acid.

When iodine value is plotted against refractive index, oils of the Compositae are in agreement with the regression line calculated for oils of 71 species (4) with four exceptions, those from Dimorphotheca aurantiaca, Vernonia anthelmintica, Artemisia absinthium, and Chrysanthemum leucanthemum. Data for six additional oils are perhaps far enough from the line to suggest a need for further study. The probable reason for the divergence of V. anthelmintica oil is its high content of epoxyoleic acid (6). D. aurantiaca and A. absinthium oils are shown by tests, discussed later, to contain conjugated unsaturation. The reason for the deviation of C. leucanthemum oil is not apparent. The oil has complex absorption in the ultraviolet and an unusual reddish color. It is not suitable for analysis by the A.O.C.S. method for polyunsaturated

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TABLE I Analytical Data on Compositae Seeds and Derived Oils

	Common name	Seed Analysis <sup>a</sup>					Fatty Acid Content of Oil						
Source		Oil content % DB	Protein content N×6.25 % DB	Iodine value	Saponi- fication value	Refrac- tive index n <sup>40/D</sup>	Noncon- jugated triene as linolenic %	Noncon- jugated diene as linoleic %	Mono- ene as oleic %	Conju- gated triene %	Conju- gated diene %	Satu- rated %	Oxirane oxygen as epoxy- oleic %
Ageratum houstonianum	Ageratum	31.4	24.4	144	190	1.4689	13.0	53.0	$(-3.0)^{b}$	1.3	0		<1.0
Ageratum houstonianum	Ageratum	30.8	25.2	141	186	1.4685	10.0	53.0	19.0	0	0	13.0	0
Artemisia absinthium	Wormwoood	33.4	25.8	118	186	1.4711	0	45.0	24.0	.6	8.2	18.0	23.0
Centaurea cyanus	Cornflower	23.6	15.8	143	182	1.4686	.4	67.0	22.0	0	0	6.0	0
Chrysanthemum													
leucanthemum	Ox-eye daisy	23.4	24.3	145	186	1.4753	0	62.0	36.0	0	0	$(-3.0)^{5}$	2.0
Chrysanthemum	Garland chrys-												
coronarium	anthemum	22.0	13.2	133	181	1.4701	1.3	59.0	24.0	.2	.5	11.0	16.0
Cosmos bipinnatus	Cosmos	20.2	19.0	107	181	1.4657	.2	49.0	14.0	.2	2.4	30.0	7.0
Cynara cardunculus	Cardoon	42.2	27.1	115	188	1.4680	.3	42.0	32.0	0.2	4.8	16.0	12.0
Dimorphotheca	0010001	10.0	21.1	110	100	1.1000		15.0	01.0	v	1.0	10.0	12.0
aurantiaca	Cape marigold	34.0	37.8	124	177	1.4864	0	10.0	4.0	3.9	48.0		52.0
Helichrysum bracteatum		0 =											00
var. monstrosum	Strawflower	24.2	21.9	142	190	1.4708	32.0	33.0	$(-7.0)^{b}$	.2	1.2		2.0
Heliopsis helianthoides	Orange sun-						1						
	flower	22.6	18.9	131	187	1.4700	1.	56.0	22.0	0	5.2	13.0	13.0
Liatris spicata	Gayfeather	35.9	35.6	128	186	1.4692	.2	54.0	32.0	0	.6	8.0	0
Rudbeckia bicolor	l												
var. superba	Cone flower	32.0	29.1	147	185	1.4697	.2	76.0	8.0	.1	1.0	10.0	1.0
Vernonia				100		1.4742						10.0	
anthelmintica	Ironweed	26.5	18.1	$\begin{array}{c} 102 \\ 139 \end{array}$	$175 \\ 192$	1.4742 1.4687	0 1.0	$\begin{array}{c} 27.0 \\ 63.0 \end{array}$	59.0	0	0	$10.0 \\ 7.0$	68.0
Vernonia baldwini	Ironweed		26.9	$139 \\ 141$	206	1.4087 1.4676	1.0	63.0	$\begin{array}{c c} 25.0 \\ 33.0 \end{array}$	0	0	2.0	0
Vernonia baldwini	Ironweed	$26.1 \\ 21.5$	26.9 23.4	$131 \\ 133$	181	1.4670 1.4699	1.2	57.0	30.0	0	0	8.0	$2.0 \\ 1.0$
Vernonia missurica	Ironweed	41.5		199	101	1.4033	1.2	57.0	<u>  av.u  </u>	U		0.0	1.0

<sup>a</sup> Analysis based on materials as cleaned.
 <sup>b</sup> Obviously incorrect results in parentheses indicate inapplicability of the analytical method.

acids (1) because the calculations result in negative figures for saturated acids. Possibly the components responsible for these features also result in a high refractive index relative to iodine value.

None of the saponification values are conspicuously different from those of the common oils. The lowest value in the group, that for V. anthelmintica, is in excellent agreement with the value reported by Gunstone (6). The highest value is also from a Vernonia, but the other tests reported here give no information in support of the high value.

Determination of polyunsaturated acids confirms previous reports on the pattern of composition of the Compositac. Rudbeckia bicolor, Vernonia baldwini, Chrysanthemum leucanthemum, C. coronarium, and Centaurea cyanus have high concentrations of dienoic acids; the R. bicolor is outstanding. These oils should be suitable for any present applications dependent on the reactions of linoleic acid. The presence of more than 10% apparent linolenic acid, as found in three oils, has not been reported previously in the Compositae.

The only oil containing sufficient monoene to be of probable interest for industrial use is that from Vernonia anthelmintica, which has previously been reported to contain a large proportion of vernolic acid (6). In other oils the negative results for monoene and the negative or obviously erroneous results for saturated acids indicate the presence of compounds or structures that interfere with determining either the iodine value or polyunsaturated acids. Oils giving such results should receive further study to identify the interfering components.

Preformed conjugation occurs in half the oils, but only in *Dimorphotheca aurantiaca* is the concentration high enough to be of interest for industrial use. The saponification value of this oil indicates that the constituent acids are primarily C<sub>18</sub> acids or larger. If present indications are confirmed by work now in progress, this oil will be the first found to contain a naturally conjugated diene in an acid longer than  $C_{12}$ . Its probable occurrence in the trans, trans form adds to its interest.<sup>3</sup> The indication of 8% of an acid con-

taining conjugated unsaturation in oil from Artemisia absinthium may serve as a lead to other species containing larger amounts and may be of direct interest when considered with other features of the oil.

Infrared analysis indicates significant amounts of hydroxyl in two oils, and chemical analysis provides confirmation. When calculated as an hydroxy C<sub>18</sub> acid, analyses show 20% in Artemisia absinthium and 70% in Dimorphotheca aurantiaca.

The A.O.C.S. method (1) for oxirane oxygen indicates the presence of epoxy compounds in most of the oils. Only in Vernonia anthelmintica (6) and Chrusanthemum coronarium (10) has their presence been established. The numerous indications of epoxy compounds in this survey and the reports of Gunstone (2, 6) and Hopkins (3, 8) suggest that epoxy acids may be much more widely distributed than hitherto expected.

Our infrared analysis does not support the chemical evidence for epoxy acids in D. aurantiaca. The proportion of hydroxyl and of conjugated diene found in the oil suggests strongly that the two structures must occur in the same acid. Possibly the combination results in the absorption of HBr, giving a false indication of oxirane oxygen.<sup>3</sup> Although the infrared absorption and the relative proportions of hydroxyl, epoxy acid, and conjugated diene in A. absinthium suggest that the oil might be like D. aurantiaca, no definite evidence is at hand. The only other oil showing unusual infrared absorption is Vernonia anthelmintica, which contains epoxyoleic acid.

Gas chromatography as applied to seven oils demonstrates three oils with components moving more slowly than the usual  $C_{18}$  acids. In V. anthelmintica the component is surely epoxyoleic acid. Cynara cardunculus has been reported (7) to contain  $C_{20}$  acids, and these may constitute the slow component found slowly and might also appear in the slow component. In D. aurantiaca we can assume, on the basis of present information, that the slow component is an hyin this sample. However the epoxyoleic acid and the

<sup>a</sup> Since this paper was presented, further work has shown that the oil contains 9-hydroxy-trans,trans-10,12-octadecadienoic acid (11).

conjugated dienoic acid reported here would travel droxylated conjugated diene. Chromatography showed no unusual components in Centaurea cyanus, Cosmos bipinnatus, Liatrus spicata, or Vernonia missurica.

#### Summary

Screening analyses of oils from seeds of 16 species of the Compositae family reveal numerous indications of unusual component fatty acids or interferences with the application of standard methods. Epoxyoleic acid is indicated in amounts from 1% to 67%. Conjugated dienes equivalent to 5% to 48% of  $C_{18}$  acid appear in four oils. Hydroxyl groups are found in two oils in amounts corresponding to 20% and 70% of a  $C_{18}$  acid.

Of special interest is the oil from Dimorphotheca aurantiaca, which appears to contain some 50% of an acid with both an hydroxyl group and conjugated diene.<sup>3</sup>

Oil from Rudbeckia bicolor var. superba contains 76% of apparent linoleic acid and may rank among the richest sources of this acid.

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### • Letter to the Editor

# A Low-Cost Bench-Top Shortening Blender

CONVENIENT APPARATUS which would allow the preparation of small batches (300-500 g.) of blended shortening containing oil, emulsifier, antioxidant, water, etc., for evaluation and which could be constructed from equipment commonly available in the laboratory is desirable both from the standpoint of ease of use and for the lower cost involved in preparing pilot-batches.

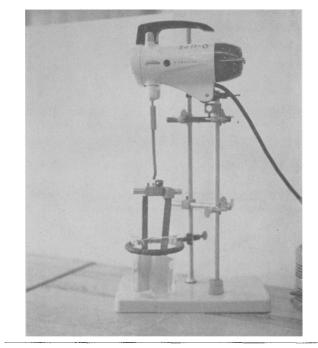
We wish to report an apparatus which we have found useful for screening fats, oils, and additives on a small scale. The apparatus consists of a stand having a rod supported parallel to the rod of the stand by means of clamp holders and two 51/2-in. sections of rod' at right angles to the two main rods.

To the supported rod, the mixer section of a commercial household mixer with an attachment rod at a right angle to the mixer blade is attached.

A scraper with an adjustable radius to accommodate beaker sizes from 600 to 3,000 ml. (this allows for the preparation of larger samples) is constructed by attaching two rubber bowl scrapers through the holes of two flexaframe connectors attached to a  $4\frac{1}{2}$ -in. rod and separated from each other by a third flexaframe connector. This scraper unit is connected to the mixer motor by means of a  $5\frac{1}{2}$ -in. piece of flat metal having a hook on the end<sup>2</sup>, which is inserted through the other opening in the center flexaframe connector.

This metal piece is, in turn, attached by means of a straight tubular chuck, having two set screws, to a shaft made by removing the blades from one of the mixer beaters, and the shaft is connected to the mixer in the usual way. The rate of stirring may be regulated either by means of the mixer control or by use of a powerstat.

The shortening blend is prepared by melting the vegetable oil or animal fat in a beaker of suitable size and adding the other components. The beaker is then transferred to a suitable container having a cooling medium (water, ice, etc.) and is supported by a standard laboratory support ring atached to the support stand. The beaker may be secured in this ring by means of a cork of suitable size cut lengthwise and placed between the beaker and ring. The rate of



solidification of the blend is governed by the medium in which the beaker is placed. Rapid stirring is continued until an extremely viscous product is obtained.

This procedure does not allow for a controlled incorporation of air. However it does provide an economical method for primary evaluation of shortening systems. It is felt that this method may also find application in fields other than that involving shortenings, such as slush freezing of fruit juices (using dry ice as a coolant) and blending of solid propellant compositions.

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<sup>&</sup>lt;sup>1</sup>These shorter sections may be conveniently prepared by sawing the clamp portion off extension clamps which, due to corrosion of the adjustment screws or other causes, are no longer functional. <sup>3</sup>The handle of a laboratory brush may be used here.