Search for New Industrial Oils. VII.[1]

F. R. EARLE, I. A. WOLFF, and C. A. GLASS, Northern Regional Research Laboratory,[2] Peoria, Illinois; and QUENTIN JONES, Crops Research Division[3] Beltsville, Maryland

Abstract

Seed oils from 37 plant species in 18 families have been analyzed for fatty acid composition by the isomerization method. The variability encountered is evidenced by the range in content of component acids: from 0–23% for apparent linolenic acid, from 8–74% for apparent linoleic acid, and from 2–88% for apparent oleic acid. Dimorphecolic acid has been found to the extent of approximately 60% in a second species of *Dimorphotheca, D. pluvialis* (L.) Moench, and in the closely related species, *Osteospermum ecklonis* (DC.) T. Norl. *O. spinescens* Thunb. contained instead 30% of a conjugated triene, presumably the same as the 8,10,12-octadecatrienoic reported from the related *Calendula officinalis* L. Oils rich in monoenoic acids are mostly in the Umbelliferae and Araliaceae and presumably contain petroselinic acid as well as oleic.

Introduction

IN CONTINUATION of our search for useful new oils, analyses have been performed on seed oils of 37 species in 18 plant families. Fatty acid composition was reported previously for only six of these oils, although selected characteristics have been published for several more.

Sample procurement and methods of analysis were as described in Parts I (4) and IV (3) of this series.

Results and Discussion

Analytical data on the seed samples and derived oils are listed in Table I.

Conjugated Trienes and Hydroxy Dienes. Oils of greatest chemical interest in this group are from four closely related species of Compositae. Oils from *Dimorphotheca pluvialis* [31][4] and *Osteospermum ecklonis* [34] contain a conjugated diene, react with HBr, and show infrared absorption due to hydroxyl. They apparently contain dimorphecolic acid, previously isolated from *Dimorphotheca sinuata* DC. (*D. aurantiaca* Hort.) and characterized as 9-hydroxy-*trans,trans*-10,12-octadecadienoic acid (11). Oils from *Osteospermum spinescens* [35] and *Calendula officinalis* [29] contain conjugated triene rather than diene, show no infrared absorption for hydroxyl, and react with only minor amounts of HBr. The triene in calendula oil has been reported to be 8,10,12-octadecatrienoic acid (2,8). Dimorphecolic acid dehydrates readily to give a conjugated triene, presumably with 8,10,12 unsaturation. The close botanical relationship between the three genera and the probable chemical relation between the diene and triene suggest that the conjugated triene in oil from *Osteospermum spinescens* will prove to be the same as the triene in calendula oil. Discovery that each of these acids occurs as a major component in more than one species provides a wider range of genetic material for developing plant types suitable for commercial production.

Other HBr-Reactive Acids. Many other oils react with hydrogen bromide under the conditions prescribed by the AOCS for determination of oxirane oxygen. *Matricaria capensis* L. [33], a composite, has 11% of HBr-absorbing acid (calculated as C_{18} epoxy acid). Since it also contains some conjugated diene structure, part of the HBr reaction is probably attributable to dimorphecolic acid, and the remainder, to epoxy acid. The occurrence of the two types of acids together has been demonstrated previously (9, 10). Oil from *Malva parviflora* L. [11] contains 13% of HBr-reactive acids. It gives a positive Halphen test, and the reactive acids are presumed to be primarily cyclopropenoid (10,12) although there may be epoxy acids present as in other mallows (7).

Other Hydroxy Acids. Oil from an *Ipomoea* [20] of an unidentified species shows hydroxyl absorption in the infrared. Chemical analysis of the methyl esters from the oil indicates hydroxyl equivalent to 40% of a C_{18}-hydroxy acid. Characterization of the hydroxy components is in progress.

Trienoic Acids. The highest concentration of "apparent linolenic" acid (ca. 23%) in the oils reported here occurs in a legume, *Brongniartia alamosana* Rydb. [5]. The 11% apparent linolenic acid in oil from *Matricaria capensis* [33], Compositae, is unusually high for this family.

Dienoic Acids. "Apparent linoleic" acid occurs in three oils in concentrations above 70% [4,13,27]. These oils show evidence of only traces of linolenic acid. *Anthemis tinctoria* L. [27] oil contains 6% of HBr-absorbing acids.

Monoenoic Acids. Five oils contained more than 65% monoenoic acid. That from *Melia azedarach* L. [8] has been reported previously (1,5,6) to contain oleic acid, but the percentage in this sample is much higher than in earlier samples. The other four oils [14–16,18] occur in the families Araliaceae and Umbelliferae, which are known to produce petroselinic acid. Of these, oil from *Hedera helix* L. has been reported to contain 62% of petroselinic acid and 20% of oleic acid, and that from *Pastinaca sativa* L. to contain, respectively, 46% and 32% (5,6). The monoenoic acid reported here probably consists of both oleic and petroselinic acids, but the analytical methods used do not differentiate between them. Our analyses indicate marked variability in *Pastinaca* oils [17,18].

Keto Acids. A qualitative test for carbonyl was positive for 10 of the seed oils [3,5,7,14–18,29,30]. Quantitative colorimetric analyses and calculation as a C_{18}-keto acid showed, however, only 4% in [29],

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[2] A laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U.S.D.A.
[3] Agricultural Research Service, U.S.D.A.
[4] Numbers in brackets identify oils in Table I.

TABLE I

Analytical Data on Seeds and Derived Oils

Source	Common name	Component analyzed		Oil content % D.B.	Protein content (N×6.25) % D.B.	I.V. wijs.	Saponification value	Refractive index n_D^{40}	Fatty acid content of oil						
		Plant part (see key)	wt./1,000, g.						Triene as C_{18} acid		Diene as C_{18} acid		Monoene as oleic, %	Saturates, %	HBr uptake as C_{18} epoxy acid, %
									Nonconj., %	Conj., %	Nonconj., %	Conj., %			
Liliales															
Liliaceae															
1. *Nolina texana* S. Wats.		A	12	20	16	130	185	1.4664	0	0	54	1	34	7	2
2. *Yucca peninsularis* McKelvey		A	30	28	15	131	187	1.4678	0	0	56	2	29	8	2
Urticales															
Moraceae															
3. *Humulus scandens* (Lour.) Merr.	Hop	D	18	31	24	146	192	1.4696	13	0	54	0	15	14	0.5
Rosales															
Saxifragaceae															
4. *Deutzia scabra* Thunb.		A	0.1	34	26	148	190	1.4688	0.6	0	74	0	13	8	0.3
Leguminosae															
5. *Brongniartia alamosana* Rydb.		A	10	34	27	129	166	1.4726	23	0	15	3	37	18	0.5
6. *Coursetia glandulosa* A. Gray	Baby bonnets	A	16	17	56	106	186	1.4652	1	0	50	0	13	31	1
7. *Willardia mexicana* (S. Wats.) Rose		A	20	34	26	137	175	1.4735	21	0	15	4	50	5	0.4
Geranisles															
Meliaceae															
8. *Melia azedarach* L.	Chinaberry	A	21	45	30	93	....	1.4669	0	....[4]	17	....[4]	70	9	0.3
Sapindales															
Anacardiaceae															
9. *Rhus radicans* L.	Poison sumac	B	16	22	11	53	214	1.4546[1]	0.4	0	24	0	10	62	0.2
Malvales															
Malvaceae															
10. *Abutilon incanum* (Link) Sweet		A	4	15	24	122	197	1.4676	0	0	59	0	17	19	2
11. *Malva* cf. *parviflora* L.		B	29	11	16	124	172	1.4668	0.8	0.1	53	0	29	13	13
Myrtales															
Thymelaeaceae															
12. *Daphne mezereum* L.	February daphne	C	3	65	24	123	184	1.4668	2[2]	0	42	0	46	6	0.2
Onograceae															
13. *Godetia amoena* (Lehm.) G. Don		A	0.6	33	32	134	179	1.4679	0.7	0	71	1	2	21	0.3
Umbellales															
Araliaceae															
14. *Acanthopanax spinosum* Miq.		A	3	37	31	98	184	1.4648	0.2	0	15	0	78	2	0.8
15. *Hedera helix* L.	English ivy	A	20	35	16	97	184	1.4630	0.6	0	8	0	88	—2[4]	0.4
Umbelliferae															
16. *Trachymene caerulea* (DC.) R. Grah.	Blue laceflower	A	2	37	22	87	182	1.4632	0.2	0	8	0	80	7	0.2
17. *Pastinaca sativa* L.	Parsnip	B	2	27	16	119	200	1.4680	0	....[4]	47	....[4]	38	11	0.2
18. *Pastinaca sativa* L.	Parsnip	B	....	22	15	93	204	1.4671	0	....[4]	18	....[4]	68	10	0.4
Gentianales															
Apocynaceae															
19. *Thevetia thevetioides* (H.B.K.) K. Schum.		C	1800	62	18	83	187	1.4611	0	0	14	0	64	17	0.3
Polemoniales															
Convolvulaceae															
20. *Ipomoea* sp.		A	144	18	26	84	190	1.4674[3]	12[2]	0	17[1]	0	20[1]	46[4]	3
Polemoniaceae															
21. *Phlox paniculata* L.	Phlox	A	9	24	41	121	173	1.4676	2[2]	0	34	0.9	55	2	1
Solanaceae															
22. *Datura metel* L.		A	14.1	19	13	109	188	1.4662	0.5	0	30	0	59	6	0.3
23. *Solanum nodiflorum* Jacq.		A	0.8	25	14	138	180	1.4688	0.8	0	65	0	20	10	0
Bignoniaceae															
24. *Tabebuia palmeri* Rose	Trumpet tree	C	113	36	23	68	176	1.4601	0.4	0	18	0	39	38	2
Martyniaceae															
25. *Proboscidea altheaefolia* (Benth.) Decne.		A	20	36	26	115	178	1.4650	0	0	36	0	55	4	0
Campanulales															
Compositae															
26. *Actinomeris alternifolia* (L.) DC.		A	5	39	43	127	176	1.4676	0.4	0	56	0.9	27	12	1
27. *Anthemis tinctoria* var. *Kelwayi*	Golden camomile	B	1	23	16	153	186	1.4699	0.4	0	73	2	18	2	6
28. *Bidens frondosa* L.		A	3	34	34	128	176	1.4669	0.3[2]	0.1	62	0	17	16	0.7
29. *Calendula officinalis* L.	Pot marigold	A	3	42	33	154	189	1.4998	....[4]	43	....[4]	0	....[4]	....[4]	4
30. *Coreopsis lanceolata* L.		B	2	15	15	128	189	1.4689	0	0	56	3	22	14	6
31. *Dimorphotheca pluvialis* (L.) Moench	Rain daisy	A	0.8	36	38	....	....	.....	....[4]	2	....[4]	60	....[4]	....[4]	35
32. *Doronicum caucasicum* Bieb.	Leopards bane	A	0.8	38	21	135	187	1.4728	1	0	60	0	26	9	1
33. *Matricaria capensis* L.	Wild camomile	B	1	27	26	133	180	1.4709	11	0.2	45	6	11	22	11
34. *Osteospermum ecklonis* (DC.) T. Norl.		A	4	50	31	....	....	.....	....[4]	0.2	....[4]	69	....[4]	....[4]	41
35. *Osteospermum spinescens* Thunb.		A	3	43	40	....	....	.....	....[4]	29	....[4]	0	....[4]	....[4]	2
36. *Rudbeckia hirta* L.	Blackeyed susan	B	0.4	30	30	141	182	1.4702	0.2	0	67	4	14	11	7
37. *Tagetes erecta* L.	African marigold	B	4	20	24	118	162	1.4646	0.3	0.1	54	2	17	22	3
38. *Zinnia elegans* Jacq.	Mexican zinnia	A	7	28	38	78	174	1.4622	0.2	0	19	0	48	29	0.8

[1] At 50C. [2] Less than 1% tetraene. [3] At 60C. [4] Method not applicable or questionable.

Key: A, Seed. B, Seed plus pericarp. C, Seed minus seed coat. D, Seed plus pericarp plus calyx.

2% in [18], and no more than 1% in the remainder.

Other Acids. At least nine oils are unsuited for analysis by the isomerization method. Four [29,31, 34,35] contain enough preformed conjugation to cast doubt on the measurement of conjugation after isomerization. Three [8,17,18] contain constituents that absorb ultraviolet light and prevent measurement of preformed conjugation. These constituents were lost during the high-temperature isomerization and may have been essential oils. One [15] gave a negative value for saturated acids. The final oil in this group is from the *Ipomoea* species [20] already mentioned.

Other listed oils not specifically discussed contain varying proportions, within the usual ranges, of the common fatty acids.

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Report of the Literature Review Committee

Annual Review of the Literature on Fats, Oils, and Detergents. Part II

V. MAHADEVAN, University of Minnesota, The Hormel Institute, Austin, Minnesota

DETERIORATION OF FATTY MATERIALS

The majority of papers published on this subject dealt with the theoretical and practical aspects of autoxidation and its prevention. A significant step was made in the elucidation of many of the products of autoxidation of various lipids subjected to different reaction conditions. Increased effort in the identification of reaction products, and in the development of the required isolation and analytical procedures, should result in a substantial clarification of the mechanisms and kinetics of autoxidation within the next few years.

Papers on the nutritional aspects of oxidized fats are not included, as this literature is adequately covered in the "Nutrition, Physiology and Biochemistry" section. This section is further restricted to edible materials except for those cases where the investigations and findings on similar materials were considered significant.

REVIEWS

General reviews appeared on the development and inhibition of oxidative rancidity in foods (Dugan, *Food Tech. 15*, 10), autoxidation and analysis of oxidized fats (Debrus, *Riv. ital. sostanze grasse 38*, 229), and recent problems in rancidity and oxidation of fats and oils (Shimamura, *Yukagaku 10*, 129). The following reviews were presented at a symposium on flavor chemistry (*Proceedings Flavor Chemistry Symposium - 1961.* Campbell Soup Company, Camden, New Jersey): Kummerow, "Introductory remarks - fats and oils"; Evans, "Chemical changes accompanying flavor deterioration of vegetable oils"; Privett, "Some observations on the course and mechanism of autoxidation and autoxidant action"; Chang, "Isolation and characterization of reversion flavor of soybean oil"; and Jacobson, "Some aspects of chemical assessment of fat and oil flavors." Another symposium devoted exclusively to the oxidative deterioration of food lipids was held at Oregon State University. Extensive consideration was given to the mechanisms and products of lipid oxidation, factors affecting lipid oxidation, autoxidation in foods, and the biological significance of autoxidized lipids. These proceedings will be published by the AVI Publishing Co., Inc., Westport, Conn.

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