stearic acid or the analogous nitro-nitrite compound. Undoubtedly other side reactions take place concurrently with those shown above, but reversible free radical $\cdot NO_2$ addition to the double bond probably produces the *cis-trans* isomerization observed.

The rate of isomerization at 30C is sufficiently slow (Fig. 1, top) that a simplified kinetic analysis of the reaction can be made. If one assumes that during the initial stages only *cis* to *trans* isomerization occurs and the reverse reaction can be neglected, then the effect of catalyst concn on the reaction rate can be determined. The increase in *trans* content during the first 15 min of the reaction is plotted against the amt of catalyst used (expressed as the theoretical g HNO_2/100 g oleic acid) in Figure 6. A straight line is obtained passing close to the origin, indicating that reaction rate is directly proportional to catalyst concn (first order reaction).

If the isomerization rate has a first order dependence on catalyst concentration, this must mean that the transfer of $\cdot NO_2$ from the water phase to the fatty phase is not the rate determining step. This agrees with our experimental results showing the rate of isomerization is not a function of agitation.

The use of HNO_3 for *in situ* generation of HNO_2 gave faster isomerization rates than H_2SO_4, HCl, H_3PO_4 or CH_3COOH. The superiority of HNO_3 might possibly be due to its ability to convert the by-product NO into additional NO_2 by the reaction:

$$2\,NO + H_2O + HNO_3 \rightleftarrows 3\,HNO_3$$

Abel et al. (43) and Klemanc and Klima (44) have shown that this equilibrium reaction takes place at room temp. H_3PO_4 and CH_3COOH were probably less effective than the strong acids because of their lower pK_a values.

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Characterization and Evaluation of Some Rapeseed Oils[1]

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Abstract

Rapeseed oil is used mostly in edible products. Four rapeseed oils, brown sarson and toria oils from West Pakistan, a Swedish oil and a Canadian oil, were characterized and examined relative to their suitability as edible oils. The various analytical data obtained are reported. The hydrogenated oils have consistency characteristics and plastic ranges which make them suitable for use as plastic fats.

Introduction

MOST OF THE WORLD PRODUCTION of rapeseed oil is consumed as an edible oil in the countries in which it is produced, principally China and India. Of the total area in West Pakistan devoted to growing oilseeds (not including cottonseed), 80% is occupied by the *Brassica oleiferous* group. Rapeseed oil is a fairly important food oil in Europe. In the U.S. only relatively small amt of the oil have been used, mostly in nonedible products. However, in Canada there is an increasing production of rape to obtain an edible vegetable oil and a replacement crop for wheat. This effort to establish rape in Canada is supported by an extensive research program (2,3,5,9–16).

The objective of the present investigation was to examine and characterize two samples of rapeseed oil produced from the major varieties of rape grown in West Pakistan and to obtain additional data on these and other rapeseed oils relative to their suitability as edible oils.

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Source and Purification of the Oils

Two of the rapeseed oils examined were pure, representative samples obtained by the cold pressing of brown-seed sarson *(Brassica campestris,* L. var. *dichotoma watt)* and toria (*Brassica campestris,* L. var., *toria,* D. and F.). The seeds were supplied by the Oilseeds Section of the Agricultural Research Institute, Lyallpur, West Pakistan, and the actual extraction of the oil was carried out in West Pakistan.

The brown sarson oil was refined by AOCS Method Ca 9a-52 for peanut oil. The average refining loss of 30.9% was high owing to the formation of soft soap, which interfered with the clean separation of neutral oil. When the refining was repeated, except that the oil and soapstock were separated by centrifuging, the loss decreased to 8.6%.

The refined, brown sarson oil was bleached with 4% neutral, activated clay by heating the mixture of oil and clay for 5 min at 110C and filtering.

A sample of refined Swedish rapeseed oil was used without further processing. A quantity of Canadian crude rapeseed oil of commercial origin was refined in the laboratory by the procedure used for the brown sarson oil. Both oils were spot samples and not necessarily typical for these countries. It should be recognized, of course, that some characteristics of an oil are markedly affected by the quality of the seed and the methods of processing.

Characteristics and Composition

Analytical data on the two crude oils from West Pakistan and on one of these oils after refining and bleaching were determined. The data obtained are recorded in Table I.

Colors as determined by the Wesson method using Lovibond glasses and by the spectrophotometric method did not agree very well. The rapeseed oils contained relatively small amt of red pigments and the ratio of yellow to red apparently was quite different from that of the domestic oils used in developing the spectrophotometric method of determining color.

The visible spectrum of the crude brown sarson oil exhibited absorption peaks at 669,610,533,472,433 and 415 mμ. Some of these peaks are attributed to the presence of pheophytin and carotene. The UV spectra of the refined and bleached oil indicated the presence of only trace amt of diene and triene conjugation.

The fatty acid composition was determined by gas chromatography for the Swedish oil and for refined and bleached samples of the brown sarson and Canadian oils. The oils were converted into methyl esters by a mild methanolysis catalyzed by sodium methoxide. The crude ester-methanol solution was diluted with water, the methyl esters were extracted with petroleum ether and then the latter was removed from the esters by stripping with an inert gas at a low temp. The analysis was made with 6 ft by 0.125 in. OD column packed with 80–100 mesh acid washed Celite coated with 10% diethylene glycol succinate polyester. Column temp was 180C. The sweep gas was argon and a tritium detecter was used. The data obtained are recorded in Table II. The refined and bleached brown sarson oil also was analyzed by a commercial processor of fats and oils and the data obtained conformed with that recorded in Table II.

The fatty acid compositions agree in general with those taken from the literature and recorded by Eckey (6), except that no traces of arachidic, behenic, lignoceric and docosadienoic acids were found. It is possible that the procedure used failed to separate any minor amt of these acids if they were present. A trace of palmitoleic acid was found in only one sample.

TABLE I

Analytical Data on the Oils from West Pakistan[a]

Property	Oil		
	Toria, crude	Brown sarson, crude	Brown sarson, refined and bleached
Free fatty acids, as oleic, %	1.51	1.06	0.07
Iodine value	103.9	101.7	101.7
Saponification value	174.2	173.6	174.7
Unsaponifiable matter, %	0.78	0.69	0.55
Linoleic acid, %	15.0	13.1	12.9
Linolenic acid, %	9.34	9.08	9.08
Specific gravity at 25C	0.910	0.910	0.908
Refractive index at 40C	1.4658	1.4657	1.4650
Color, Lovibond	.....	140Y 10R	35Y 6.7R[b] 35Y 1.0R
Color, spectrophotometric	.....	24.7	8.6[b] 2.1
Kinematic viscosity,[c] centistokes			
30C	65.1	65.7	65.5
40C	44.6	45.1	45.1
50C	31.9	32.4	32.3
60C	23.8	24.0	24.0
Cloud point,[d] °F	.....	.....	24
Pour point,[d] °F	.....	.....	6
Melting point, °C	ca. 5.8	ca. 5.8	ca. 5.8

[a] Determined by AOCS Official and Tentative Methods unless otherwise noted.
[b] Refined only.
[c] Measured with a Cannon-Fenske-Ostwald type viscometer.
[d] Determined by method for mineral oils, ASTM Method D97-57, except that the sample was examined at 2° instead of 5° intervals.

According to data cited by Eckey (6), rapeseed oils contain 11-eicosenoic and 13,16-docosadienoic acids. Erucic acid is, of course, 13-docosenoic acid; and the oleic, linoleic and linolenic acids in the oils have their first double bonds in the 9-position. To established whether or not the brown sarson oil contained fatty acids having double bonds in positions other than those indicated, the refined and bleached oil was oxidized to cleave the double bonds and the mixture of dibasic acids obtained subsequently was analyzed by column chromatography. The oxidation and analyses were carried out essentially as described by Chahine et al. (4), except that the ozonides were cleaved by the procedure of Fore et al. (8). This method of analysis determines only the longer chain dibasic acids and their percentage in the mixture is calculated on the total wt of C_6 through C_{14} dibasic acids. The following data were obtained:

Dibasic acid	Wt found,%
C_{14}	None
C_{13}	54
C_{12}	None
C_{11}	10
C_{10}	Negligible
C_9	36
C_8	None

Therefore, the brown sarson oil apparently contained only those unsaturated fatty acids which have been found heretofore to occur in rapeseed oils, i.e., fatty acids having double bonds in the 9:10, 11:12 and 13:14 positions.

Suitability as a Salad Oil

None of the oils passed the AOCS cold test. When held at 0C for 3.5 hr, small crystals of solid fat appeared. Yet, for practical purposes the rapeseed oils were almost natural salad oils. Their melting points ranged between 4 and 5.8C. Conceivably, mayonnaise and similar products made from such oils could be stored in refrigerators without too great a breakage of the emulsion.

Because of the presence of linolenic acid, rapeseed oils would not be expected to exhibit a marked resist-

TABLE II

Fatty Acid Composition of Three Rapeseed Oils

Fatty acid	Percentage in indicated oil[a]		
	Swedish	Canadian	Brown sarson
Palmitic	2.7	1.7	0.6
Palmitoleic		0.1	
Stearic	0.6	0.7	0.8
Oleic	9.6	20.9	12.3
Linoleic	12.4	14.3	13.5
Linolenic	7.3	8.1	11.3
Eicosenoic	8.0	13.1	13.4
Erucic	59.4	41.1	48.1

[a] Calculated on a methyl ester basis by gas chromatography.

ance to oxidation. This was borne out by the stability tests (Table III). All of the oils tested possessed an undesirably high initial peroxide value. The brown sarson and Swedish oils were tested several months after refining, but the Canadian oil was tested only a few days after refining.

The refined Canadian oil was deodorized in a laboratory deodorizer (1) for 1 hr at 200C and a pressure of 1 mm of mercury. The oil was protected from light as much as possible. No color developed during the deodorization and the finished product was perfectly bland in flavor and odor. When a portion of the deodorized oil was poured into a 400-ml beaker to a depth of ca. 2 cm and exposed to light in a north window for 1 hr, a small amt of flavor definitely developed and could easily be detected by a panel of five individuals who compared the exposed oil with a sample which had been stored in the dark.

Hydrogenation and Hydrogenated Products

A sample of the refined Swedish oil was hydrogenated in a 2-liter reaction vessel at a temp of ca. 180C, a hydrogen pressure of approx 30 psig and a catalyst concn of 0.17% nickel. The catalyst was a commercially available, supported type prepared by electrolytic precipitation and dry reduction. The consistencies of the samples which were withdrawn as the hydrogenation progressed are represented in Table IV as coming from Run No. 1,

A cottonseed oil (I.V., 108.0) was hydrogenated in a similar run using the same operating conditions and reaction vessel. The samples obtained are described in Table IV as Run No. 2.

Two other series of hydrogenated samples were obtained by hydrogenating the refined Canadian rapeseed oil (Run No. 3) and another sample of the cottonseed oil (Run No. 4) under about the same operating conditions mentioned above, except that a reaction vessel of 16-pounds oil-capacity was used. Two samples of each of these runs are represented in Table IV.

The content of *trans* isomers was measured in each of the samples. For similar I.V., all samples contained approx the same percentage of *trans* isomers, calculated as trielaidin. When Runs No. 1 and 2 were compared, the samples of hydrogenated cottonseed oil possessed slightly more *trans* isomers than did comparable samples of the hydrogenated Swedish rapeseed oil. In Runs 3 and 4 the samples of hydrogenated cottonseed oil possessed a slightly lower content of *trans* isomers than did the comparable samples of hydrogenated Canadian rapeseed oil. The differences observed are not believed to be signficant.

The rapeseed oils hydrogenated at ca. one-half the rates observed for the cottonseed oil when the rates were compared at equal I.V. This was not unexpected. The mol wt and viscosities of the rapeseed oils were greater than those of the cottonseed oil.

The consistency of various samples of the hydrogenated rapeseed and cottonseed oils and of their mixtures was determined by a micropenetration technique (7). The data obtained are recorded in Table IV.

When the all-hydrogenated samples are compared at about equal I.V., it is evident that the hydrogenated rapeseed oils were harder at the lower temp and softened more slowly as the temp increased. The all-hydrogenated rapeseed oils possessed a longer plastic range than did the all-hydrogenated cottonseed oils.

The same conclusion can be drawn when a shortening-type mixture composed of highly hydrogenated and unhydrogenated rapeseed oil is compared with a similar mixture composed of highly hydrogenated and unhydrogenated cottonseed oil.

It should be noted that rapeseed and cottonseed oils hydrogenated to the same I.V. do not have the same monoene content. Below I.V. of ca. 60, the hydrogenated rapeseed oil will contain ca. 10% more monoenes.

TABLE III

Stability of Rapeseed Oils[a]

Oil	Original peroxide value	Hr to reach peroxide value of 100
Refined brown sarson	33.0[b]	5.5
Refined Swedish	38.0[b]	7
Refined Canadian	<4.7[c]	12
Crude brown sarson	<4.7	18.5
Crude toria	<4.7	19
Crude Canadian	<4.7	20

[a] Determined by AOCS Method Cd 12-57.
[b] Determined several months after refining.
[c] Determined several days after refining.

TABLE IV

Consistency of Hydrogenated Samples

Type of oil or mixture	No. of hydrogenation run	Iodine value	*Trans* isomers,[a] %	Micropenetration, mm/10, at								
				10C	15C	20C	25C	30C	35C	40C	45C	50C
Swedish rapeseed	1	81.4	19.1	117	352							
	1	64.7	34.7	10	11	22	43	145	369			
	1	47.5	36.3	3	6	6	6	12	21	52	157	369
	1	30.8	27.5	5	5	5	5	5	6	10	14	41
Cottonseed	2	79.9	24.0	26	45	117	267	407				
	2	66.9	34.4	14	15	43	92	202	392			
	2	52.6	40.6	6	8	9	16	17	62	191		
	2	38.4	32.2	5	6	7	10	11	13	23	83	337
Canadian rapeseed	3	64.9	37.0	12	15	15	32	52	195	382		
Cottonseed	4	68.7	25.2	40	64	107	272					
Canadian rapeseed	3	55.0	37.6	6	8	9	9	15	33	116	396	
Cottonseed	4	56.4	29.3	15	20	23	36	62	194			
10% Hydrogenated rapeseed oil, I.V. 1.5, plus 90% Swedish rapeseed oil				84	62	69		94	139	205	222	262
10% Hydrogenated cottonseed oil, I.V. 3.9, plus 90% cottonseed oil				22	29	38	61	104	169	219		
10% Hydrogenated rapeseed oil, I.V. 1.5, plus 90% Swedish rapeseed oil				45	59	55	67	72	93	127	154	202
10% Hydrogenated cottonseed oil, I.V. 3.9, plus 90% cottonseed oil				68	76	92	92	121	159	216		

[a] Calculated as trielaidin.

The addition of 10% of either highly hydrogenated rapeseed or cottonseed oils to nonhydrogenated rapeseed oil gives a product with harder consistency than when the corresponding hydrogenated oils are added to nonhydrogenated cottonseed oil. Linteris and Thompson (12) in experiments with somewhat similar mixtures came to the conclusion that the presence of long-chain fatty acids and a suitable diversity of fatty acids in the constitutent triglycerides promoted the precipitation of fine crystals and helped subsequently in aeration during the mixing of cake batters.

Highly hydrogenated rapeseed oil is probably the highest melting and most viscous fat which may be incorporated in food products. The Swedish oil when hydrogenated to an I.V. of 1.5 had the following viscosity:

Temp, °C	Viscosity, centistokes
65	30.8
70	26.5
75	23.0
80	20.2
85	17.9
95	14.2

The fat had a melting range of 69.3–70.6C, but it solidified at 57–58C when cooled rapidly.

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Gas Liquid Chromatographic Analysis of Hydroxy Fatty Acids, as Their Trimethylsilyl Ether Derivatives[1]

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Abstract

A quantitative method is described for the rapid gas liquid chromatographic analysis of mono- and polyhydroxystearates as their trimethylsilyl (TMS) ether derivatives. The TMS derivatives of the hydroxy esters are formed rapidly and quantitatively at room temp. The retention times of ricinoleic acid as the methyl ester, acetylated derivative and the TMS derivative are compared. Purified diastereoisomers of di-, tri- and tetrahydroxystearates and their mixtures were analyzed on three different columns. Gas liquid chromatographic analysis of methyl mono-, di-, tri- and tetrahydroxysteartes were shown to give quantitative results as TMS derivatives. Analyses were carried out on a diethylene glycol succinate polyester (DEGS) packed column and on large-bore capillary columns of DEGS and Apiezon L. The elution order of the TMS derivatives of the hydroxy esters from the DEGS large-bore capillary column was not the same as that obtained from the DEGS packed column. The unusual elution pattern of the large-bore capillary column is discussed.

Introduction

THE QUANTITATIVE DETERMINATION of long-chain mono- and polyhydroxy fatty acids by gas liquid chromatography (GLC) is presently unsatisfactory. Their high polarity and low volatility gives rise to undesirably long retention times.

Methyl ether derivatives of hydroxy acids have been used by Kishimoto and Radin (1) to increase their volatility. Downing and co-workers (2,3) reported that α-hydroxy acids can be reduced to their corresponding 1,2-diols from which a more volatile isopropylidene derivative may be prepared and analyzed by gas chromatography. The former method is nonquantitative and laborious, while the latter can only be used for vicinal dihydroxy or α-hydroxy acids. Acetylated hydroxy acids have been used by Kishimoto and Radin (4), and more recently by O'Brien and Rouser (5), with some success, but still have undesirably long retention times, especially on polar liquid phases. The gas chromatographic analysis of long-chain dihydroxy acids is nonquantitative and limited (6–8), while the analysis of long-chain tri- and tetrahydroxy acids by this method has not been reported, to the authors' knowledge.

The use of the TMS ether derivatives of hydroxy compounds has opened new areas in which GLC can be used for their analysis. Some of the areas where the use of the TMS derivative has been proven to be successful have been reviewed recently (9).

This report describes the quantitative analysis of mono- and polyhydroxy long-chain fatty acids using this technique.

TABLE I

Quantitative Determination of Hydroxy Acids as Their TMS Derivatives by GLC Analysis[a]

Hydroxy acid	Actual[b]	Found[c]
	%	%
12-hydroxystearic acid	14.07	14.06
Threo-9,10-dihydroxystearic acid	21.87	22.47
Threo-9,10-12-trihydroxystearic acid	27.91	27.97
Erythro-9,10-*erythro*-12,13-tetrahydroxystearic acid	36.14	35.50

[a] Analysis was carried out on 3 ft x ¼ in. column packed with 20% DEGS on 80–100 mesh Chromosorb W at 215C. A typical chromatogram of this mixture is shown in Figure 4 (middle).
[b] Prepared by weighing out purified acids.
[c] Values derived by measuring the area under the peaks with a planimeter.

[1] Presented at the AOCS Meeting in New Orleans, 1964.