Chemical Investigation of Oil of the Seed of "White Todri" (*Matthiola incana*, R.Br.)

AZIZ-UR RAHMAN and M. SAMI KHAN, Universidad Nacional del Sur, Bahia Blanca, Argentina

The fixed oil from the seeds of "White Todri," *Matthiola incana*, R.Br. *(Cruciferae)*, of Indian origin, has been studied for its component acids. The fatty acid composition was found to be myristic (2.60%), palmitic (4.73%), stearic (4.37%), arachidic (2.50%), lignoceric (?) (0.73%), oleic (32.17%), linoleic (21.70%), linolenic (10.70%), erucic (13.10%), and resin acids (7.40%).

MATTHIOLA INCANA (L.), R.Br., commonly known as "Todri" in Hindi and further designated as "White Todri" (10) in order to distinguish it from the other two varieties, *viz.*, "Red Todri" (*Cheiranthus cheiri* L.) and "Yellow Todri" (no botanical equivalent has been reported), belongs to the *Cruciferae*. Although not indigenous, it is cultivated in the gardens of northern India. The seeds are described as of medicinal value and find general application as stimulant, expectorant, and aphrodisiac (4,9,10,14).

A review of the literature indicates that the seed oil of this plant has not been examined, at least for its fatty acid composition. The present work describes the component acids of oil obtained from the seed. The analysis of oils of most of *Cruciferae* seeds so far made shows that the component acids are of the same general type with about 40–50% of erucic acid as the main component. Oleic, linoleic, and occasionally linolenic acids are also major components and account for all but about 5% of the remaining fatty acids, which include small proportions of palmitic and still smaller quantities of higher saturated acids.

As will be apparent from the results of the present investigation, this general pattern of the composition of the seed oil of the *Cruciferae* is not followed by "White Todri" or by the seed oils of the red and yellow varieties of "Todri" (11,12).

Methods and Results

The dried and finely powdered seeds on extraction with petroleum ether (b.p. 40–60°C.) gave a yield of 10% of a transparent yellow oil with the following characteristics:

Specific gravity, 30°C.	0.9344
Refractive index, 30°C.	1.3790
Saponification value	187.2
Iodine value, Hanus	139.4
Thiocyanogen value (3)	102.6
Acid value	2.72
Ester value	184.5
Unsaponifiable matter	2.18%

The oil on saponification and subsequent hydrolysis, after removal of unsaponifiable matter, yielded 92.6% free fatty acids which were still contaminated with some nonfatty matter of resinous character. The resin acids were estimated by Twitchell's gravimetric method and found to be 7.4% of the total acids. The mixed fatty acids were then resolved into their solid and liquid components by Hilditch's modification of Twitchell's lead-salt-alcohol method and were found to be composed of 30.6% solid and 69.4% liquid acids. The percentage of the saturated acids as obtained by Bertram's method (2) was nearly the same as obtained from the total percentage of the solid acids by subtracting that of erucic acid; the latter was separated by Holde and Wilke's method (7). Further, erucic acid was separated from the liquid unsaturated acids by fractional precipitation of the lead salts. This was accomplished by the initial addition of half of the quantity of lead acetate normally added to the alcoholic solution of total mixed fatty acids for separation into solid and liquid acids by Twitchell's method, which resulted in the separation of only the saturated acids as the insoluble salt, leaving the total unsaturated acids, including erucic in the filtrate. The additional half of the usual quantity of lead acetate was then added to precipitate the lead salt of erucic acid. This method for resolving the saturated acids, erucic acid, and the remaining unsaturated liquid acids was satisfactory, at least in the present case, as observed from the fact that the values for the amount of the saturated acids as determined by Bertram's method (2) and that of erucic acid as obtained by Holde and Wilke's method (7) agreed fairly well.

Oleic, linoleic, and linolenic acids were estimated by bromination (5) as well as by oxidation (6) of the fatty acids derived from the lead salt soluble in alcohol. A quantitative determination of these acids was made, on the one hand by bromination according to the method of Eibner and Muggenthaler (5), and on the other by thiocyanometric method. The composition of liquid acids as obtained by these two methods agrees fairly well. Myristic, palmitic, stearic, arachidic, and lignoceric (?) were identified in the specific fractions of the hydrolyzed solid methyl esters. The percentages of the individual saturated acids in each fraction were calculated according to the method of Baughman and Jamieson (3).

The presence of erucic acid was ascertained by the isolation of a solid acid (m.p. 33–34°C.) by repeated crystallization of the solid acids from 96% alcohol at 0 to −5°. It was also isolated in a fairly pure state by a slight modification of Twitchell's lead salt method, as described above. Erucic acid was further detected in the mixed acids by selective oxidation with dilute alkaline permanganate according to the method of Kaufmann and Fiedler (8), which yielded dihydroxybenhenic acid [m.p. and mixed m.p. (12), 130–132°C.]. An attempt was also made to isolate erucic acid by the application of Bertram's method (1) for the separation of oleic acid from saturated acid as reported by J. Van Loon (14) by using mercuric acetate. Although some erucic acid was obtained by this method, it was found that it was not free from the saturated acids.

The mixed saturated acids were converted into methyl esters. The esters were systematically fractionated by vacuum distillation. The percentages of the individual esters in each fraction, calculated from the iodine value and saponification equivalent figures

TABLE I

Fractions	Wt./g.	B.P./ 2 mm.	I.V.	S.E.	Myristate	Palmitate	Stearate	Arachidate	Lignocerate	Unsat. esters
					g.	g.	g.	g.	g.	g.
S_1	3.70	150–55°	1.02	256.86	1.69	1.98	.....	.....	.....	0.03
S_2	1.77	155–60°	1.52	280.28	.....	1.10	0.65	.....	.....	0.02
S_3	3.06	160–65°	2.51	308.81	.....	.....	1.78	1.22	.....	0.05
S_4	0.84	165–71°	2.69	311.21	.....	.....	0.42	0.41	.....	0.02
S_5	0.68	.....	3.94	364.66	.....	.....	.....	.....	0.49	0.19
Loss	0.35	.....	.....	.....	.....	.....	.....	.....	.....	.....
Total	10.40	.....	.....	.....	1.69	3.08	2.85	1.63	0.49	0.31
% as esters	.....	.....	.....	.....	16.87	30.66	28.36	16.23	4.87	3.01
% as acids	.....	.....	.....	.....	16.87	30.66	28.36	16.23	4.87	3.01

(3) in conjunction with the qualitative examination data of the fractions, are given in Table I.

The unsaponifiable matter obtained prior to the liberation of the mixed fatty acids, when crystallized from methyl alcohol, gave colorless needles, m.p. 130–131°. This appears to be a sitosterol.

From the data obtained in the manner outlined, the composition of the total fatty acids in the seed oil of "White Todri" was calculated to be as follows:

Resin acids	7.40%
Saturated acids:	
Myristic	2.60%
Palmitic	4.73%
Stearic	4.37%
Arachidic	2.50%
Lignoceric (?)	0.73%
Unsaturated acids:	
Oleic	32.17%
Linoleic	21.70%
Linolenic	10.70%
Erucic	13.10%

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The Selective Hydrogenation of Linolenic Acid[1]

JOHN G. WILLARD[2] and MARIA LUISA MARTINEZ, Southwest Research Institute, San Antonio, Texas

The hydrogenated samples were analyzed by ultraviolet spec- conditions produced mostly nonselective hydrogenation. The variables of catalyst, catalyst concentration, solvent, temperature, and pressure had very little effect on the selectivity. Large differences were found in the relative reactivities of the three double bonds in methyl linoleate. It appears that the initial reaction strongly favors the 12 position assuming a limited amount of shifting of double bonds during hydrogenation. The solvent has an appreciable effect on this selectivity, but the other variables have only minor effects.

The hydrogenated samples were analyzed by ultraviolet spectroscopy. Efforts to identify the location of the double bonds by oxidative methods were unsatisfactory. Preliminary studies on the possible use of nuclear spin resonance as an analytical method in fatty acid analysis look promising.

THE OBJECT of this investigation was to find experimental conditions that would favor the conversion of linolenic acid (9,12,15-octadecatrienoic acid) to linoleic acid (9,12-octadecadienoic acid) with the limited formation of other unsaturated acids. Such a reaction would be expected to find industrial application in the hydrogenation of several vegetable oils, such as linseed oil. To accomplish such a reaction it is necessary to find conditions which will favor the reaction of the number 15 double bond in linolenic acid over the 9 and 12 positions and also favor the hydrogenation of the trienoic acid over less unsaturated acids. Both of these aspects of selectivity are considered in the present investigation.

Each of the three double bonds in linolenic acid has been reported at one time or another to be the most reactive. Hilditch and Vidyarthi (9) reported (1929) that the rate of reduction of an ethylenic bond is greater the farther it is removed from the carboxyl group. This would indicate selectivity at the 15 position in linolenic acid. On the other hand, Bauer and Ermann (3) have claimed (1930) that linolenic acid is first reduced at the 9 position. van der Veen (20) (1931) and more recently (1946, 1949) Bailey and Fisher (1,2) find that the number 12 double bond is the first to be reduced.

It has been established that under the conditions of hydrogenation the double bonds in linolenic acid do not remain stationary but rather migrate to ad-

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[2] Present address, Jefferson Chemical Company, Austin, Tex.