304. *The Seed Fat of the Annual Nasturtium* (Tropaeolum var.).

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The seeds of the annual garden nasturtium resemble those of the perennial nasturtium, *Tropaeolum majus*, of tropical regions, in containing about 7—8% of a fat, the fatty acids of which are mainly erucic acid (82%) with oleic acid (16%) and very small quantities of linoleic and saturated (palmitic and behenic) acids. The fat probably contains nearly 40% of the simple glyceride trierucin, which separates from it as solid crystals on standing at room temperature, and which can be separated from it in the pure state by crystallisation from solvents. The large proportions of erucic acid in the mixed fatty acids, and the comparatively simple composition of the remainder of the acids (almost wholly oleic), cause nasturtium-seed fat to be the most convenient source of erucic acid, when this is required for experimental purposes.

Gadamer (*Arch. Pharm.*, 1899, **237**, 471) stated that the seed fat of the giant nasturtium, *Tropaeolum majus*, consists almost wholly of trierucin, and Sudborough, Watson, Ayyar, and Damle (*J. Indian Inst. Sci.*, 1926, **9**, *A*, 65) found that, whereas erucic acid formed by far the greater part of the mixed fatty acids, there were also present small quantities of unsaturated and saturated acids of lower molecular weight. These workers isolated 35% of trierucin from the seed fat by crystallisation from light petroleum and converted it into the isomeric tribrassidin and also, by hydrogenation, into the fully-saturated tribehenin. These observations show that the fat from seeds of *Tropaeolum majus* is far richer in erucic acid than rape- or mustard-seed oils and similar seed fats of the *Cruciferae* (which contain 40—50% of erucic acid). It was therefore of interest to make a quantitative examination of the component acids of the seed fat of the ordinary garden nasturtium.

The various forms of the annual garden nasturtium are cultivated varieties derived apparently from *T. minus* or *T. Lobbianum*, but some authorities refer the larger forms as varieties of *T. majus*, and it may be that the annual nature of the plant in this country is determined merely by its inability to withstand frost. The fat used in the present study was obtained from seeds from self-sown plants, originally of the dwarf double variety " Golden Gleam," which had mainly reverted to the ordinary single yellow and red flowered climbing types.

The air-dried seeds yielded 7—8% of fat on extraction with light petroleum. This fat resembled that described by Gadamer and by Sudborough *et al.* in its greenish colour, and in partly solidifying on keeping; the trierucin present in the liquid fat separated as a mass of crystalline needles. The fat had saponification equivalent 350·4, iodine value 75·1, acid value 4·0, and it contained 1·8% of unsaponifiable matter (from which a sitosterol was isolated, the acetate of which melted at 116°).

The fat (20 g.) was hydrolysed, and the mixed acids (freed from unsaponifiable matter) were converted into methyl esters, which were distilled under 0·1 mm. through an electrically-heated and packed fractionating column (Longenecker, *J. Soc. Chem. Ind.*, 1937, **56**, 199T), the following fractions being obtained.

Fractional distillation of methyl esters of nasturtium seed mixed fatty acids.

Fraction No.	Wt., g.	B. p.	Sap. equiv.	Iod. val.
1	2·14	108—125°	300·9	85·7*
2	2·60	125	334·5	77·9
3	3·24	125—140	344·0	72·7
4	2·06	140	349·6	72·0
5	1·80	140—142	350·2	72·0
6	6·07	Residue	352·5	71·6

* Thiocyanogen value of fraction 1, 76·3.

The acids from fraction 1 were oxidised with ice-cold dilute alkaline permanganate (Lapworth and Mottram, J., 1925, **127**, 1628). The product was a mixture of a small quantity of saturated (mainly palmitic) acid with 9 : 10-dihydroxystearic acid (m. p. 130°, mixed m. p. 129—130°), the latter proving the presence of ordinary Δ^9-oleic acid in the seed fat.

The combined acids from fractions 4 and 5 readily yielded, on crystallisation from aqueous alcohol, pure erucic acid (m. p. 34·0°; mixed with erucic acid from rape-seed oil, m. p. 33·7—34°).

The acids from the residual esters (no. 6) were similarly oxidised, and furnished in good yield 13 : 14-dihydroxybehenic acid (m. p. 129—130°) which, when mixed with the corresponding acid prepared from erucic acid of rape-seed oil, showed no depression in m. p.

The components of each ester fraction were calculated from their analytical values, in accordance with the foregoing qualitative characterisation, as follows: Fraction 1, as palmitic, oleic, linoleic, and erucic esters; fraction 2, as oleic and erucic esters; fractions 3, 4, and 5, as erucic, oleic, and saturated (as behenic) esters; fraction 6, as erucic and behenic esters. The final composition of the mixed fatty acids was found to be approximately as follows:

	% (wt.).	% (mol.).
Palmitic	0·2	0·3
Behenic	0·8	0·8
Oleic	16·0	18·5
Linoleic	1·2	1·4
Erucic	81·8	79·0

The main components of the fat are clearly erucic and oleic acids, the former constituting about 80% of the total fatty acids. If the glycerides are assembled on the lines almost invariably observed in seed fats, it is probable that the mixed glycerides present will contain for the most part two erucyl groups and one minor component acyl group; the fat will consist of over 50% of oleodierucin and nearly 40% of the simple glyceride trierucin.

It has been mentioned that Sudborough *et al.* (*loc. cit.*) recorded the isolation of 35% of trierucin by crystallisation from light petroleum. We also isolated the pure triglyceride by crystallisation from alcohol, benzene, and finally from alcohol at 0°; the trierucin melted at 31·5—32°, the transition points of the vitreous and the α-form being 5° and 25° respectively. Its *X*-ray spectrum was also examined; a long spacing of 51·3 A. was obtained for the stable crystalline modification, the associated side spacings being 5·28, 4·60, 4·02, 3·84, and 3·70 A.

The following data have been obtained for synthetic trierucin (M. G. R. Carter, unpublished observation): transition and melting points, 6°, 25°, 32·5°; *X*-ray long spacing, 51·1 A.; side spacings, 5·24, 4·60, 4·03, 3·84, 3·70 A. This group of side spacings is characteristic of trierucin and has not been found to occur in any other saturated or unsaturated glyceride.

The high content of erucic acid in seed fats of *Tropaeolum* species distinguishes them from any other seed fats yet investigated. Ordinary nasturtium seeds are, indeed, the most convenient source of erucic acid, in consequence of the relatively small concurrent proportions of oleic or other acids; these are readily removed, either by direct crystallisation of the erucic acid, or, better, by distillation of the esters of the mixed acids. The first table shows that fractional distillation of about 20% of the esters of the mixed fatty acids leaves a residue consisting almost wholly of methyl erucate. The fat-content of the seeds is much less than that of rape or mustard seed, but the isolation of the 80% of erucic acid present therein is a simple process, compared with the much more difficult separation of the mixture, encountered in the *Brassica* seed fats, of erucic and oleic (or linoleic) acids in approximately equal proportions.

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