V. THE OIL FROM TROPOEOLUM MAJUS.

With N. R. Damle.

According to Gadamer (*Arch. Pharm.*, 1899, **273**, 471) the oil from *Tropœolum majus*, Linn. consists of nearly pure trierucin. He found that the oil (iodine value 73·8) which had been extracted from the seeds by ether, solidified on cooling and when pressed between paper gave a product melting at 30·5° and on hydrolysis yielded erucic acid of melting point 34°. He concluded that the oil consists mainly of trierucin as the iodine value of this compound is not very different from that of the oil.

As no other data—not even the yield—regarding the oil appear to be recorded, we have prepared about 50 grams of the oil and have determined some of the common constants, and have also attempted to prepare from the erucic acid pure behenic acid.

The seed used was imported seed obtained through the Empress Gardens, Poona, and after crushing was extracted with ether. Using 375 grams of seed the weight of oil obtained was (*a*) 26 9 and (*b*) 27·3 grams, or a yield of only 7·2 per cent. The constants of the oil are given in Table I, and those of the fatty acids free from unsaponifiable matter in Table II.

TABLE I.

Analytical data for Tropœolum Oil.

Sp. gr. at 15·5	0·9092
Saponification value	172·6
Iodine value	77·5
Refractive index at 40°	1·4568
Unsaponifiable matter (per cent.)	1·1

TABLE II.

Fatty acids from Tropœolum Oil (free from unsaponifiable matter).

Hehner number	95·1
Iodine value	72·9
Mean molecular weight	312·8
Per cent. solid acid	45·7
Per cent. liquid acids	54·3
Iodine value of solid acids	72·9
Mean molecular weight of solid acids	330·0
Iodine value of liquid acids	72·6
Mean molecular weight of liquid acids	298·0

The method adopted for separating solid and liquid acids was the one due to Twitchell and as with the acids from rape, mustard and jamba seeds erucic acid is present in both the solid and liquid acids.

The oil itself has a distinct green colour, but the fatty acids have a brown tinge. It is noticeable that the iodine value of the oil is higher than that of the free fatty acids, whereas the reverse is usually the case.

The saponification value of the oil proves that it is by no means pure trierucin, as this has a saponification value of 160. The iodine value and molecular weight of the solid acids prove that these are nearly pure erucic acid as this has an iodine value of 75 and a molecular weight of 338. In addition to erucic acid there must be present small quantities of an acid with a lower molecular weight.

It is remarkable that the iodine value of the liquid acids is below that of erucic acid and as the molecular weight is considerably below that of erucic, it is probable that the liquid acids contain a certain amount of a saturated acid of low molecular weight.

The quantity of oil was not sufficient to make an exhaustive study of it, as our main object was to isolate trierucin and reduce it to tribehenin.

Trierucin.—When placed in ice-cold water the oil solidified and was then filtered with the aid of a Buchner funnel, a small amount of green oil was collected and the solid left on the funnel melted at 25°. It was crystallised from light petroleum (b. p. 40–60°); by cooling the solution with a freezing-mixture, the melting point rose to 28°, but the yield was only 35 per cent. of the original oil, and the melting point was not raised by further crystallisation from the same solvent; but on crystallisation from a mixture of benzene and chloroform the melting point rose to 30·5–31·0° corresponding with the melting point given by Reimer and Will (*Ber.*, 1887, **20**, 2386). This was hydrogenated at 180° by means of 5 per cent. of nickel deposited on kieselguhr and tribehenin melting at 80–81° isolated. After three crystallisations from benzene and subsequent crystallisation from chloroform the melting point remained constant at 81·0–81·5° and when saponified with alcoholic potash the glyceride gave a behenic acid melting at 79·5–80·0° and the melting point was not raised by two crystallisations from alcohol.

The following data have been obtained for the two glycerides together with some values for a sample of tribrassidin prepared from trierucin by the action of nitrous acid :—

	Trierucin.	*Tribrassidin.*	*Tribehenin.*
M. p.	30·5–31·0°	56–57°	81·0–81·5°
n_D^{40}	1·4630	—	—
n_D^{80}	1·4560	1·4547	1·4391 at 85°
n_D^{91}	1·4475		1·4375 at 89°

VI. THE PREPARATION OF PURE BEHENIC ACID.

With N. R. Damle.

As already pointed out (pp. 40, 49, 58 and 66) the behenic acid obtained from the hardened oils of rape, mustard, jamba and *Tropæoleum majus* seeds melts at 79·3°–79·8°. This does not agree with the melting point given by recent authorities and attempts have therefore been made to prepare behenic acid by different methods and see whether the melting points of different specimens of the acid melted much above 79·8°.

As early as 1846 Walter (*Annalen*, 1846, **60**, 271) gave the melting point at 52–53°, but in 1848 Völcker (*Ibid.*, 1848, **64**, 342) gave the value 76° and this was confirmed by Goldschmidt (*Wien Acad.*, 1874, **70**, 451). In 1894 Talanzeff (*J. pr. Chem.*, 1894, [II], **50**, 72) prepared the acid by the addition of hydrogen iodide to erucic acid and subsequent reduction in alcoholic solution with zinc and hydrogen chloride. The melting point is given as 84° in a capillary tube. Meyer, Brod and Skita (*Monatsh.*, 1913, **34**, 1128) prepared behenic acid by reducing pure erucic acid with hydrogen in the presence of nickel as catalyst and gave the melting point at 82–84°, but state that with a catalyst which has been used several times a product melting at 75° is obtained and that it is impossible to get a product melting at 84° from this. Flecker and Taylor (*J. Chem. Soc.*, 1922, **121**, 1102) used an acid melting at 81–82° and prepared by reducing erucic acid and subsequent crystallisation from alcohol, and Toyama (*J. Chem. Ind. Japan*, 1922, **25**, 1053) describes an acid obtained by the same method as melting at 81–82°.

It is thus clear that the acid obtained from the seeds melts at a lower temperature than the acid prepared by the reduction of erucic acid, although the values given for this reduced acid vary from 81–84°.

Behenic acid has been prepared by the following methods :—

1. The reduction of brassidic acid melting at 59·5–60·0° and with an equivalent weight 337 (theory) but unknown iodine value by three per cent. of nickel deposited on kieselguhr. After four hours at 180° the iodine value fell to 4 and the product was repeatedly crystallised from acetone. After two crystallisations the melting point was 79·3–79·8° and remained constant after further crystallisation.

2. Kahlbaum's pure erucic acid was twice crystallised from 95 per cent. alcohol and was once crystallised by cooling to 13° to remove saturated acids. About 10 per cent. of the product was precipitated as lithium salt, also with the object of removing saturated acids, and the residue was crystallised again from alcohol. The acid melted at 33·5–34·0° and had an equivalent 337. It was reduced at 180° using a nickel catalyst and on crystallisation from acetone gave a product melting at 79·3–79·8°.

3. Attempts were made to obtain from Kahlbaum's acid a product with the correct iodine value (75) by Holde's (*Angew. Chem.*, 1922, **35**, 290) method of fractional precipitation with lithium acetate. The iodine value obtained for the more soluble portions was only 71·5, and the behenic acid obtained from this by hydrogenation melted at 79·3–79·8°.

4. A fresh specimen of erucic acid obtained from Kahlbaum had the iodine value 75·4 and the solidifying point 33·0°. This was completely hardened, extracted with petroleum ether to remove nickel soap and the acid crystallised from 95 per cent. alcohol and acetone in succession. It melted at 80° and the solidifying point was 79·2°.

5. A sample of brassidic acid with an iodine value 73·8 (theory 75) and a melting point 59·5–60·0° gave on reduction an acid melting at 79·3–79·8° after two crystallisations from acetone.

6. As already stated, the acid obtained by hydrogenating trierucin to tribehenin, and subsequent hydrolysis melted at 79·5–80·0°.