R E S U M E

The work described in this thesis consists of two parts. Part - I deals with the chemical investigation of herbaceous seed oils.

Part - II concerns with the reactions of cis and trans epithio acids with dimethyl sulphoxide (DMSO), dioxan, and methanol in the presence of BF_3-etherate.

P A R T - I

Chemical Investigation of Herbaceous Seed Oils

The continuing shortages of edible and non-edible oils within the country have led to survey the widely distributed uncultivated oilseeds. Keeping this in view a programme has been underway in this laboratory to investigate the herbaceous oilseeds.

1. Herbaceous Seed Oils

The oils from the seeds of fifteen species representing eleven families have been examined by various chromatographic and spectroscopic techniques to determine their fatty acid

composition. The gas-liquid chromatographic (GLC) analysis revealed the presence of conventional fatty acids in varying proportions. The amount of total saturated acids present in the seed oils ranges from 14.8–52.9%. Oils of *Ruellia tuberosa* and *Martynia diandra* contained a very high content of total saturated acids (>50%) and hence can fulfil the demand for solid fats similar to cocoa butter.

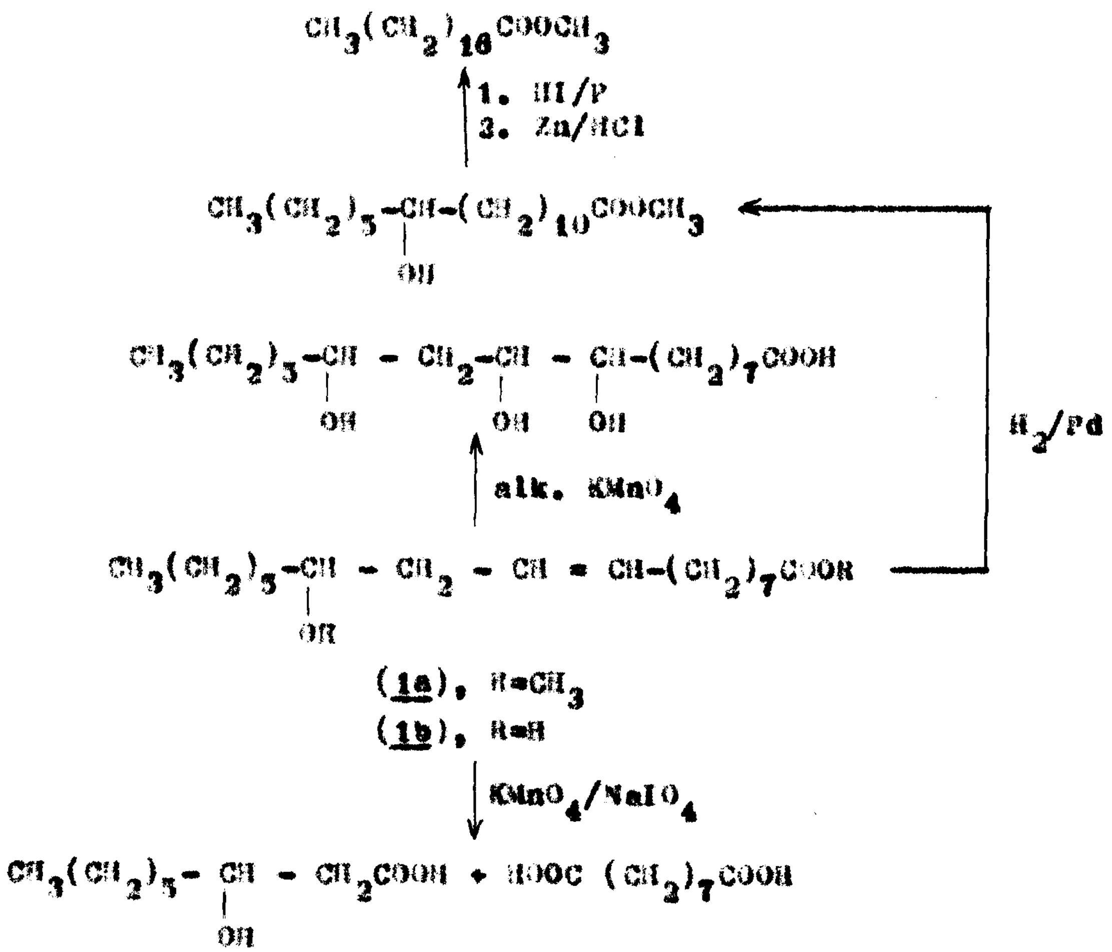
All the seed oils exhibit good sources of C18-unsaturated acids (>50%). Oils of *Withania somnifera*, *Trianthema monogyna*, *T. pentandra*, and *Hyptis suaveolens* were found to contain a high amount of linoleic acid (>60%) and hence classified as 'linoleic rich drying' oils. The combined contents of oleic-linoleic acids were found major (>80%) in six species, out of which *Withania somnifera* and *Hyptis suaveolens* seed oils may serve as 'semi-drying' type of oils; whereas *Zizyphus rotundifolia*, *Martynia diandra*, and *Amarantus spinosus* seed oils contain about 35% or less of linoleic acid and are classified as 'non-drying' oils.

The present work revealed that the species rich in oils as well as in specific acids could be further subjected to agronomic evaluation.

2. Hydroxy Fatty Acid in Seed Oil of *Phyllanthus niruri* (Euphorbiaceae)

Seed oil of *Phyllanthus niruri* was found to contain hydroxy fatty acid (1.2%) in addition to the normal fatty acids. The hydroxy ester (**1a**) was isolated by column chromatography and characterised by its spectral behaviour and chemical transformations (Chart I) as methyl 12-hydroxy-*cis*-9-octadecenoate (ricinoleate).

Chart I



3. Cyclopropenoid Fatty Acids in Seed Oil of *Sida rhombifolia* (Malvaceae)

Sida rhombifolia seed oil, not studied previously, responded to Halphen test for the presence of cyclopropenoid fatty acids (CPFA). The estimation and characterisation of individual cyclopropene acids were achieved by the GLC analysis of the silver nitrate-methanol treated methyl esters using *Sterculia foetida* esters as a reference standard. GLC analysis showed it to contain malvalic (2.0%) and sterculic (10.8%) acids, other than normal fatty acids. Quantitation of total cyclopropenoid material by the method of HBr-titration was found in close agreement with that obtained by GLC. This method of GLC analysis was found most suitable to estimate the low level of CPFA in seed oils. Further, this method has the advantage of not reacting with the other unsaturated acids present in the seed oils.

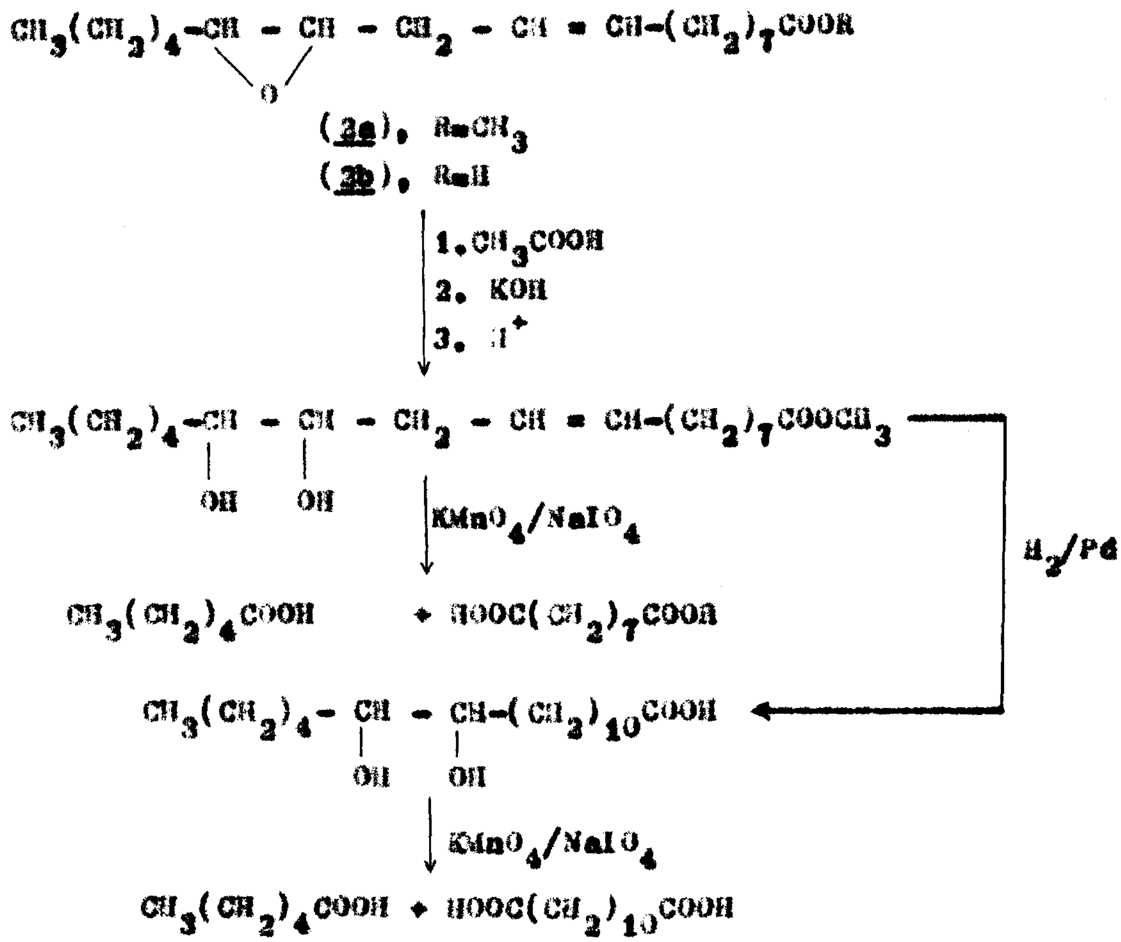
4. Epoxy Fatty Acid in *Mucuna pruriens* (Leguminosae) Seed Oil

The present analysis of the seed oil of *Mucuna pruriens* showed it to contain HBr-reactive acid as epoxyoleic in an amount of 1.3%. Acetylation of the oil, followed by saponification and separation of the fatty acids, gave 12,13-dihydroxyoleic acid. From this and other evidence it is concluded that cis-12:13-epoxyoleic (vernolic) acid is present as a constituent of the glycerides. The presence of small amount of epoxy acid in this seed oil might affect adversely on its stability and nutritional properties as *M. pruriens* is cultivated in some parts of the country for the sake of its brown velvety legumes, which are cooked and eaten as vegetable.

5. *Vernonia roxburghii* (Compositae) Seed Oil: A New Source Rich in Epoxy Acids

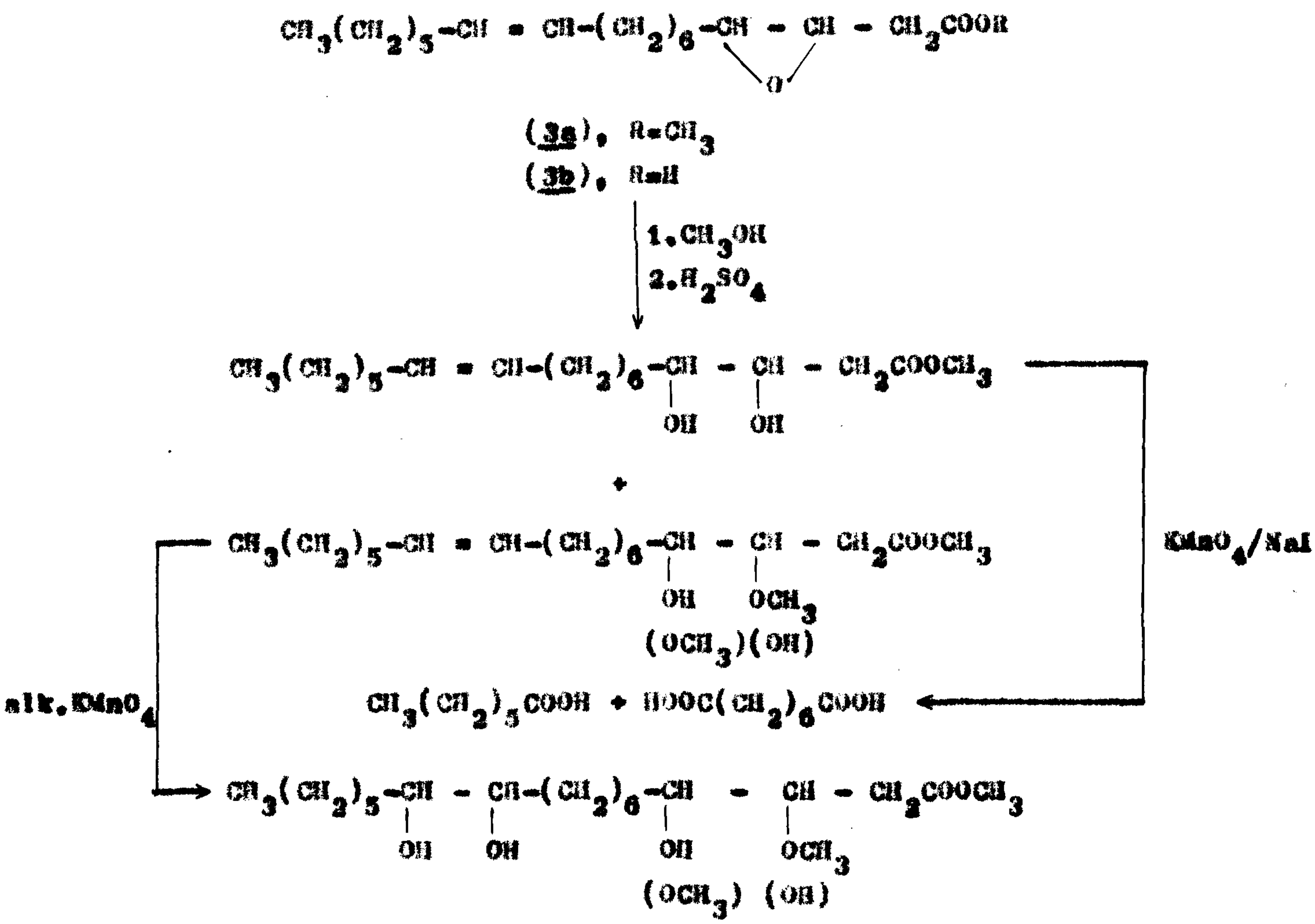
Seed oil of *Vernonia roxburghii* hitherto unexamined species was found to contain two epoxy fatty acids. Both the epoxy acids were isolated in pure form and characterised by spectral data as well as their chemical transformations. One of the epoxy acid is *cis*-12:13-epoxy-*cis*-9-octadecenoic (vernolic) acid (2b) present in an amount of 56.3%. The chemical reactions outlined in Chart II were performed to establish the structure.

Chart II



The other epoxy acid has been identified as *cis*-3:4-epoxy-*cis*-11-octadecenoic acid (3b, 17.4%). The following chemical reactions (Chart III) supported the above structure. This epoxy acid has been identified for the first time in naturally occurring seed glycerides.

Chart III


CH3(CH2)5-CH = CH-(CH2)6-CH - CH - CH2COOR
(3a), R=CH3
(3b), R=H
1. CH3OH
2. H2SO4
CH3(CH2)5-CH = CH-(CH2)6-CH - CH - CH2COOCH3
OH OH
+
CH3(CH2)5-CH = CH-(CH2)6-CH - CH - CH2COOCH3
OH OCH3
(OCH3)(OH)
KMnO4/NaI
alk. KMnO4
CH3(CH2)5COOH + HOOC(CH2)6COOH
CH3(CH2)5-CH - CH-(CH2)6-CH - CH - CH2COOCH3
OH OH OH OCH3
(OCH3) (OH)

P A R T - II

Preparations and Reactions of cis and trans-13:14-Epithio-docosanoic Acids

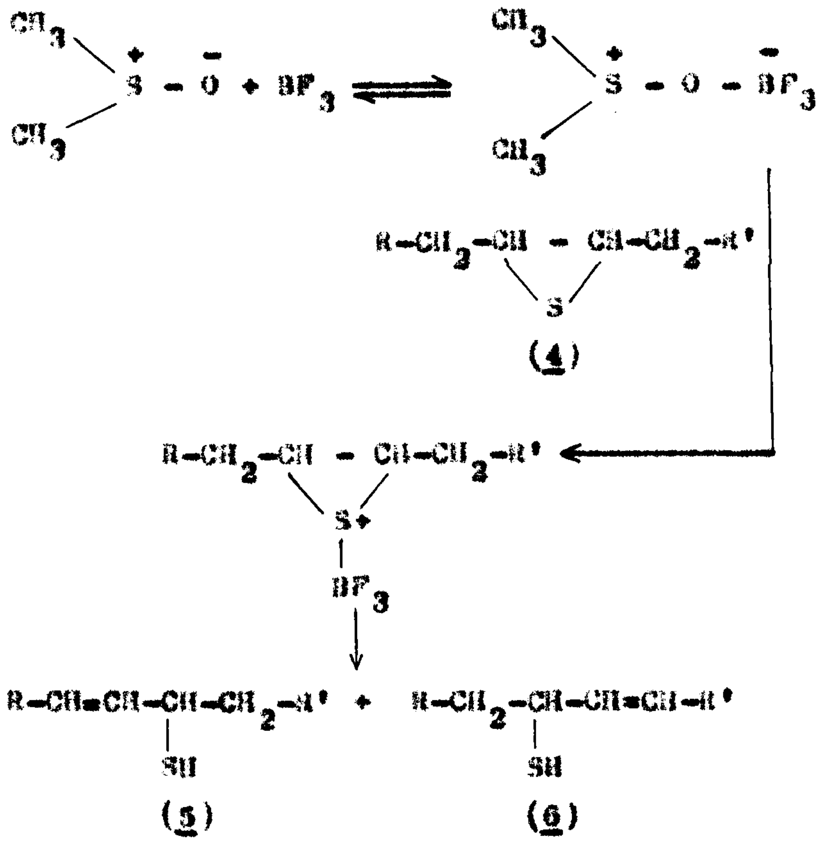
cis-13,14-Docosenoic (erucic) acid has been isolated from *Brassica campestris* (Cruciferae) seed oil by urea fractionation method. Stereomutation of erucic acid gave *trans*-13,14-docosenoic (brassidic) acid. The erucic and brassidic acids were epoxidised with perbenzoic acid and subsequently converted to the corresponding epithio acids by treatment with thiourea solution. The structures of *cis* and *trans*-13:14-epithiodocosanoic acids were established by spectral and elemental analyses.

1. *Reaction of trans-13:14-epithiodocosanoic acid with BF_3-DMSO:*

It was observed that the reaction of *trans*-13:14-epithiodocosanoic acid (4) with BF_3-etherate in DMSO as the solvent yielded 13-mercapto-*trans*-14,15-docosenoic and/or 14-mercapto-*trans*-12,13-docosenoic (5 and/or 6, ca. 94%) acid (Chart IV).

The formation of 13-mercapto-*trans*-12,13-docosenoic and/or 14-mercapto-*trans*-12,13-docosenoic acid clearly showed that epithio fatty acid behaved differently, though not unexpectedly, from the epoxy fatty acid. In the case of epoxide,

<u>Chart IV</u>



$R=CH_3(CH_2)_6$; $R'=(CH_2)_{10}COOH$

the main product is usually α-hydroxy ketones. It was anticipated that analogous reaction of epithio acid with BF_3-DMSO should produce α-mercapto ketones. A mechanism is proposed to account for the unusual product formed from the epithio acid.

3. <u>Reaction of *trans*-13:14-epithiodocosanoic acid with BF_3-dioxan:</u>

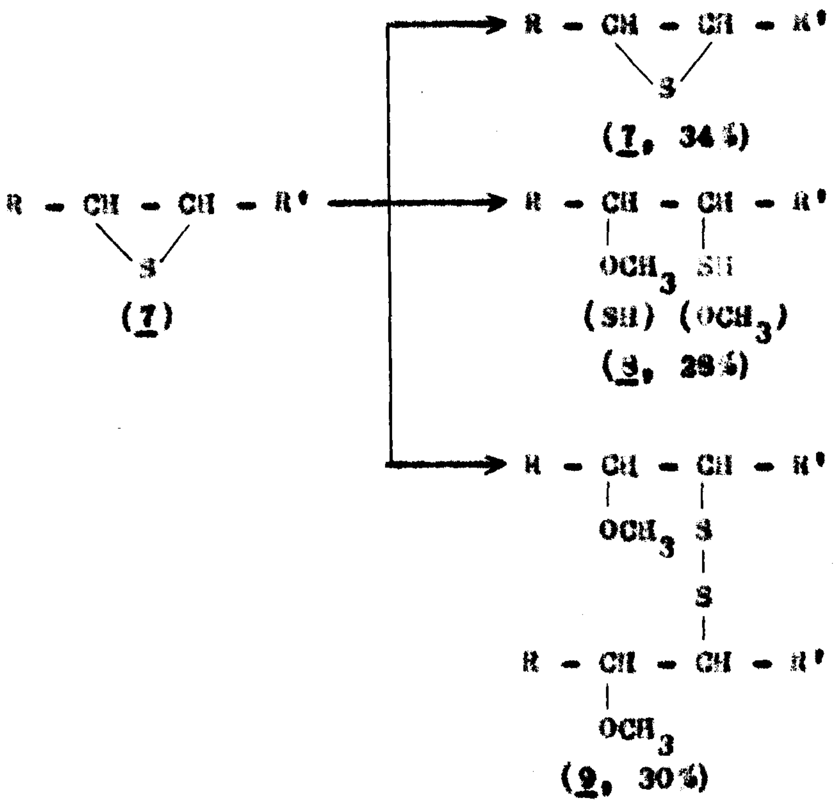
trans-13:14-Epithiodocosanoic acid (**4**) on treatment with BF_3-etherate in dioxan again gave 13-mercapto-*trans*-14,15-docosenoic and/or 14-mercapto-*trans*-12,13-docosenoic (**5** and/or **6**, ca. 94%) acid following the path depicted in Chart IV. However, the epoxides are known to isomerise to ketones upon their reaction with BF_3-dioxan. The formation of thioketones from epithio acids, parallel to epoxy acids, was anticipated. But due to the reluctance of sulphur to form normal $p\pi - p\pi$ (double) bond with carbon or other elements, the formation of thioketones from epithio acid was not observed.

It is interesting to note that the cis epithio acids did not afford any reaction product on treatment with BF_3-etherate either in DMSO or in dioxan. This may be accounted for due to the formation of comparatively stable BF_3-complex by the cis epithio acid which retards further reaction to yield the final product.

3. Reaction of methyl cis-13:14-epithiodocosanoate with BF_3-methanol:

The reaction of methyl cis-13:14-epithiodocosanoate (7) with BF_3-etherate in methanol gave unreacted component (7, ca. 34%), methyl 13(14)-mercapto-14(13)-methoxydocosanoate (8, ca. 28%), and the dimer (9, ca. 30%). Literature scanning revealed that epoxy acids on treatment with BF_3-methanol gave hydroxy-methoxy derivatives as the sole product. Following similar course of reaction, the epithio acid forms the mercapto-methoxy derivatives. The formation of an additional compound (dimer) from epithio acid may be attributed to the ability of sulphur to unite with itself to form polysulphides. The above reaction is outlined in Chart V.

Chart V



R = $CH_3(CH_2)_7$; R'=$(CH_2)_{11}COOCH_3$

It may be added that the behaviour of cis and trans epithio acids in their reactions with BF_3-etherate in DMSO/dioxan was found reversed in their reaction with BF_3-methanol. The cis epithio smoothly reacted with BF_3-methanol while the trans epithio, however, failed to react with BF_3-methanol combination. An explanation has been advanced based on the steric grounds. The cis epithio-BF_3 complex being less hindered is easily attacked by methanol acting as a nucleophile. On the other hand the trans epithio-BF_3 complex is more sterically crowded and hence the nucleophilic attack of methanol is not facilitated.