PHYTOCHEMICAL STUDIES ON FERULA MARMARICA

By

ADEL KAMEL YOUSSEF

B.Sc., 1967

Thesis Submitted
For
M. Sc. Degree
(Partial Fulfilment)

Biochemistry Department
Faculty of Science
Ain Shams University

1975

ACKNOWLEDGEMENT

The author wishes to express his profound gratitude to; Professor Dr. IBRAHIM RAOF SHIMI, Head of Biochemistry Department, Faculty of Science, Ain Shams University, Professor Dr. AHMED FOUAD SHALABY; Head of Botany Department, Faculty of Girls, Al-Azhar University and Dr. FAWZIA ABBASE FAHIM; Assistant Professor of Biochemistry, Faculty of Science, Ain Shams University, for suggesting the problem, their valuble criticism and sound advice.

Thanks are also due to Assisuant Professor Dr. MOHAMMED AHMED ETMAN; Head of Medicinal Plants Unit, Desert Institute and to Professor Dr. Mohammed ABD El MONEAM EL MAHDY; Director of Desert Institute for the facilities and encouragement which made this work possible.

" This dissertation has not previously been submitted for a degree at this or other universities.

The references in the text will show specificially the extent to which I have availed myself of the work of other authors".

A.K. Youssef

A.K. Youssef

C O N T E N T S

CONTENTS

Page

Chapter IV

Page

REVIEW OF LITERATURE

REVIEW OF LITERATURE

Asafoetida is the oleo-gum-resin obtained by incision of the roots and rhizomes of several Ferula species e.g. F. Asafoetida Linn., F. foetida Regal, F. rubricaulis Bois., F. brinefulia Linn., F. Linkii Webb. and Berth, F. nodiflora Guss, F. sancta Boiss, F. neopolitana Tenure, F. narthex Boiss, F. communis Linn., F. alliacea Boiss, F. foetida Linn., F. eurbesceas Boiss, F. galbanifolia Boiss, F. gummosa Boiss, F. persica Willd., F. schair Borz., F. scordosma Benth. U. Hook, F. Tingitana Linn. and other species of Ferula, Family Umbelliferae. (Chopra; (1933), Small; (1944), Ramstad; (1959), Wallis; (1960), Edward; (1961), Mohran; (1967).

Several pharmaceutical preparations of asafoetida were used in ancient centuries, still have their reputation in modern therapy.

Asafoetida is official since 1841 in pharmacopoeas, e.g. Pharmacopea Dublin Ireland (1807), Pharmacopoea Portugueza; (1876), British pharmacopoea; (1885) & (1914), Pharmacopoea Japan, (1907), British Pharmacopoea Codex; (1923, 34 & 49); Pharmacopoea Mexican (1925), Pharmacopoea Bilge, (1930), Pharmacopoea Espaneola; (1930), Pharmacopoea Helvetica, (1934), Pharmacopoea Estonica, (1937), National

Formularity Part IV, (1949), Egyptian Pharmacopoea, (1953) & Pharmacopoea Standard "Pakistan", (1961).

Asafoetida is an old drug. It was mentioned under the name "Hongu" is Sanskrit work (Gild-Meister & Hoffman (1910) and Trease, G.E. (1962)), of old Indians.

It has been imported from the East by the Arabian Physicians (Gathercoal & Wirth, (1949) and Trease; (1962)). after whom it was named as "ALHALTIT" and "ABUKABER".

Asafoetida was used in Europe during the middle ages as acurative agent for Wound-ulcers, burns, whooping, Cough and in Hysteria (Trease, 1962).

It was used also by old Persians & Sicilian for some purposes Goery (1898), Peach & Tracey (1955)).

In Afghanistan, the drug is called "Hingu" and "Anghuza" (Ibn Sina (1037)) and is used as purgative expectorant, antitussive and some cases of Hysteria.

Semmler (1891)(Peach & Tracey (1955)) was the first who analysed the drug & reported on the presence of α-pinene & asecondary butyl-propenyl-disulphide.

Later on, Harrison (1912) reported on the presence of the following constants for volative oil of asafoetida:

Specific gravity 25°C = 0.915;

Optical rotation : 10°58' to 17°3'

Refractive index at 20°C: 1.4942;

Sulphar content : 31.4%.

Glevenner, (1932) obtained a yeild of volatile oil ranging from 7.5 to 12 ml/100 gm from oleo-gum-resin with sulphar content 32%.

Igolen & Fresenius (1936) analysed asafoetida drug and found that it contained 20% volatile oil which might be extracted by water or separated by steam distillation, 25% gum and from 40-60% resin.

The resin consisted of asaresinotannol (A) and asaresinotannol (B), either free or combined umbelliferone with ferulic acid.

The same authors, when fractionated the volatile oil had obtained a high bioling point fraction, consisting mainly of organic disulphide e.g. secondary butyl-propanol disulphide & secondary butyl propyl disulphide to which the disagreable odour of the oil was attributed.

Fresenius (1936) also reported on the presence of a trisulphide $C_6 H_{10} O_3$ which might be diallyl trisulphide

in addition to another unknown oxygenated compound $(C_{10}H_{16}O)_n$ which gave cadenine when treated with sodium metal.

Koffler (1934), obtained vanillin by fractional microsublimation of the ether extract of the drug in the first fraction and ferulic acid in the second fraction and the lactone Umbelliferone in the third fraction.

Igolen (1936), determined the acid value; 3.08 and the ester value; 173.95, of the drug. Mannich; (1936), carried further study on the disulphide constituent of the oil and postulated the structure formula ($CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-S-S-CH_2-CH=CH_2$) for the disulphide present.

This compound on distillation with Zn dust gave butyl mercaptan having the structure $CH_3-CH_2-CH_2-SH$.

Also the same mercaptan might be obtained by reduction of disulphide with Al/Hg moisted with ether.

On the rectification of the produced mixture 2ry butyl mercaptan B.p. 83-4°C was obtained having the structure $CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-SH$ ($C_4H_{10}S$).