COMPARATIVE STUDY OF ANETHUM GRAVEOLENS AND ANETHUM SOWA

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ABSTRACT

The seeds of A. graveolens and A. sowa exhibit definite differences in their chemical components in regard to dill-apiole, commarins and flavonoids. The first two can be used for quick distinction using small quantities of seeds. Dill-apiole, characteristic of A. sowa, could be detected by gallic acid- H_0SO_4 reaction for methylene dioxy group and also by IR spectrometry, the two characteristic frequencies being 940 and 1040 cm⁻¹. Commarins found in A. graveolens exhibit fluorescence on t.l.c. plates. Both these seeds contain petroselinic acid triglyceride and β -sitosterolglucoside.

THE genus Anethum belonging to the family Umbelliferae has two important species which yield the "dill oil" used in medicine. A, graveolens is indigenous to S. Europe and A. sowa to India. Both are reputed for their medicinal properties because of their content of essential oil which had been studied already 1-6 in detail and they are good aromatic carminatives, specially useful for flatulence in children and in adults. The Indian dill oil differs in having higher sp. gr. and the heavier fr. Jon consists chiefly of dill-apiole which is not present in European dill oil. Since these two seeds are morphologically similar, there nas been need to differentiate between them chemically in as easy a manner as possible. This is important because A. graveolens is far more costly and is the one recognised by Indian pharmacopoea. Therefore a comparative study of the chemical constituents of the two seeds has now been carried out.

A. graveolens.—The seeds (2 kg) were stracted successively with pet, ether, acetone and alcohol. The pet, ether extract, after complete removal of solvent, was subjected to steam distillation. Steam volatile part contained essential oil which did not give methylene dioxy test and the non-volatile portion when repeatedly extracted with ether, the solvent removed, the residue taken up in the minimum quantity of pet, ether and kept for a few weeks, deposited a solid (0.2%). It was filtered and the mother liquor was marked The solid, m.p. 35°, showed in (L). its IR spectrum, a sharp peak at 1740 cm⁻¹ (Saturated ester), 1470 and 1380 cm⁻¹ (C-CH₃). NMR spectrum had a singlet (9 H) at $0.85 \, \delta$. a broad singlet (66 H) at 1.35, a multiplet (18 H) between $1.9-2.3 \delta$, a triplet (4 H) at 4.15δ and a multiplet (7 H) around 5.25δ . These NMR spectral data7 indicated that it was

a triglyceride of a C₁₈-unsaturated acid. On saponification with 10% aqueous alkali it gave an acid whose, m.p. was 33·4°; IR and NMR spectra showed that it was petroselinic acid8. The neutral part of the saponification product was identified as glycerol by paper chromatography⁹, thus leading to the identification of the non-volatile solid as the triglyceride of petroselinic acid. The mother liquor (L) when chromatographed over silica gel yielded a solid, m.p. 187-88°, identified as bergapten from its spectral data and also by comparing with an authentic sample.

The acetone extract of the defatted seeds when subjected to chromatographic separation yielded bergapten, m.p. $187-88^{\circ}$ and umbelliprenin, m.p. $62-63^{\circ}$, which have been already reported¹⁰ and β -sitosterolglucoside, m.p. 230-31°. Their identification was done by m.m.p., t.l.c. and IR.

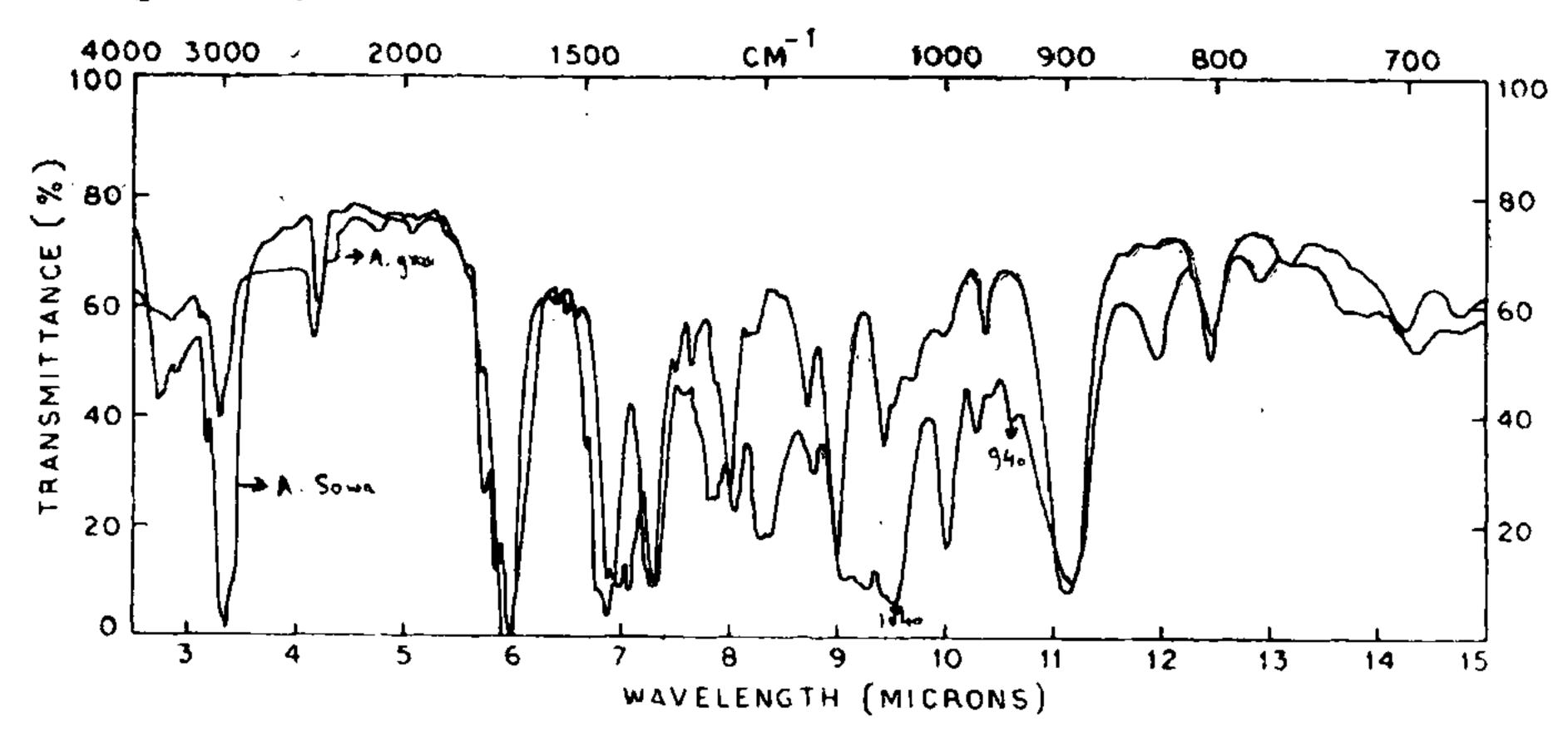
The alcohol extract of the seeds were concentrated and chromatographed over silica gel column. It afforded β -sitosterolglucoside, m.p. 230-31° and two flavonoid compounds, designated as I and II in extremely poor yield. Compound I, m.p. 270-72°, gave violet colour with FeCl₃ and pink colour with Mg/HCl; $\lambda_{\rm max}^{\rm EtOH}$ 270 and 360 mm. Compound II gave a single spot on t.l.c. greenish-violet colour with FeCl₂ but it could not be crystallised even after repeated chromatography. It was then boiled with 7% H₂SO₄ for 2½ hrs. The sugar part was identified as glucose by paper chromatography and the aglycone came as yellow needles, m.p. 229–30°; M⁺ 380, λ_{max}^{EtOH} 270 and 360 m μ and \(\lambda_{\text{max}}^{\text{EtOH/A}\text{ICl}_3}\) 285 and 360 m μ . Due to paucity of both the compounds, their identification could not be done.

Anethum sowa.—The seeds (2 kg) were successively extracted with petroleum ether, acetone and alcohol. The pet ether extract,

after steam distillation, gave triglyceride of petroselinic acid but no coumarin derivatives. The volatile oil gave marked test for methylene dioxy group and the IR contained the frequencies 940 and 1040 cm⁻¹.

The acetone extract after chromatography yielded β -sitosterolglucoside and the alcohol extract gave β -sitosterolglucoside and some fractions which showed greenish-violet spots with FeCl₃ on t.l.c. but did not give flavonoid test. These fractions after rechromatography gave insignificant yields.

the most convenient method is the test for the presence of dill-apiole in A, sowa. It comes in the pet, ether extract and after steam distillation, the steam volatile part gives green colour with con. H_2SO_4 and gallic acid (test for methylene dioxy group), but A, graveotens is free of dill-apiole and hence its steam volatile portion does not give the test. Further in the IR of the steam volatile part the absorption due to methylene dioxy group at 940 and $1040~\rm cm^{-1}$ is present in the oil of A, sowa and absent in A, graveolens (see chart).



The results of the above chemical examination of the seeds of A. graveolens and A. sowa can be tabulated as in Table I.

Table I

Comparison of A. graveolens and A. sowa

	Chemical componen	A. graveolens	A. 50700	
1.	Dill-apiole		— ve	+ve
2.	Coumarins	• •	+ ve	−ve
3.	Flavonoids		+ ve	- ve
•	Petroselinic acid triglyceride		+ ve	+ ve
5.	β-sitosterolglucoside		+ ve	+ve

As will be clear from Table I, there are definite points of difference between the two seeds. Since the flavonoids are found only in very minor amounts, the colour reaction of flavonoids cannot be carried out and hence this method is not suitable for their identification. The fluorescence due to the coumarins can be easily observed with the pet ether and acetone extracts using the colour reaction. But

Recently it has been reported that there are two varieties of Indian dill, namely A. ghoda and A. vareli¹¹. Examination of the extracts of both the varieties by t.l.c showed that they do not differ chemically.

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