Gas chromatographic examination of an essential oil of Santolina chamaecyparissus L.

By L. N. Misra, M. S. Siddiqui, and S. K. Srivastava Central Institute of Medicinal and Aromatic Plants, Lucknow, India,
and B. P. Dimri, C.I.M.A.P. Regional Centre, Bangalore, India

Santolina chamaecyparissus L. (fam. Compositae) or "Lavender cotton" as it is more commonly known (Husain), which is native to southern Europe, can also be found as a garden border plant. Over the years, *S. chamaecyparissus* has become naturalized in the Kodaikanal region of India where it is grown as a hedge plant because of its attractive foliage and odour. In Europe, *S. chamaecyparissus* is reputed to have antispasmodic and anthelmintic properties and, as a result, it has been used in rural herbal medicines. The oil from *S. chamaecyparissus*, which has a strong and penetrating odour, has been the subject of some investigations. For example, a number of workers (cited in Guenther 1952) have determined the physicochemical properties of oils obtained from different geographical origins. A summary of these properties can be seen in Table I.

Many years ago, it was reported (Anon 1911, cited in Guenther 1952) that a sample of Italian *S. chamaecyparissus* which was taken just prior to flowering contained 0.47% essential oil. This oil was found to have an odour reminiscent of tansy and wormwood. In addition, the yield compared favorably, with the 0.41% and 0.33% reported by Pellini and Morani (cited in Guenther 1952) for Sicilian *S. chamaecyparissus*.

The chemical composition of *S. chamaecyparissus* oil has not been the subject of systematic study. For example, it has been reported (Guenther 1952) that the oil probably contained a terpene, a phenol ether, camphor (?) and two unsaturated ketones ($C_{10}H_{16}O$) which were given the trivial names α- and β-santolinenones. Neither of these ketones were actually obtained in pure form and hence their suggested formulae remain in doubt.

Experimental

S. chamaecyparissus which was found growing in Mysore as a hedge plant, was collected, air-dried, chopped, and hydrodistilled to produce a dark-coloured essential oil (0.4-0.5% yield), which was found to have a penetrating tansy-davana-like odour.

Table I. Comparative physicochemical properties of Santolina chamaecyparissus oil

Properties	Sicilian Oils		African Oil	French Oil	Indian Oil
Sp. Gr. at 15°C	0.8868	0.9060	0.9275	0.9546	0.9065
Refractive Index at 20°C	1.4769	1.4807	1.4632	1.4908	1.50040
Opt. Rotation at 20°C	+24°38'	+20°27'	-5°50'	-6°26'	Too dark
Acid number	7.2	13.6	5.64	9.12	16.4
Ester number	--	--	114.4	22.41	--
Esters	2.52	4.76	--	--	--
Ester value (after acetylation	33.2	56.1	164.4	126.25	74.2
Total alcohol content	9.27	15.82	51.56	--	--
Solubility at 25°C	Sol. in 0.37 vol. 90% alcohol	--	Sol. in 3 vols. 70% alcohol	Sol. in 0.1 vol. 95% alcohol	Sol. in 0.5 vol. 90% alcohol

0272-2666/81/0002-2501$02.00/0

(See Table I for physicochemical properties.) It was felt, by the authors, that because of its odour characteristics, Indian S. *chamaecyparissus* oil might have a useful application in the essential oil industry. Hence, the oil was submitted to analysis. Initially, the oil was redistilled because the odour of the essential oil was dissimilar to the odour of the fresh herb. It was the considered opinion of the authors that the off-notes of the oil were probably present in the higher boiling constituents, and consequently the oil was redistilled prior to analysis. During redistillation, only the lower boiling 2/3 of the oil were considered to possess a characteristic odour, and as a result only this early boiling (2/3) fraction was subjected to gas chromatography (10% SE-30 column). It was found by retention time studies that the largest peak in the oil was p-cymene. As a result, the relative retention times of the other constituents were determined against it. Identification of the constituents of the oil was made by the serial dilution technique and the relative retention times were compared with those of authentic reference compounds. Percentage composition of each constituent was calculated using the Sigma method (Smith and Levi 1961, Bartlet and Smith 1962).

Results and discussion

An Indian oil of S. *chamaecyparissus* analyzed as described above was found to produce a gas chromatogram as shown in figure 1. A summary of the chemical composition and the relative retention times of the individual constituents of this oil can be seen in Table II.

It is the considered opinion of the authors that in view of the good growth habits of S. *chamaecyparissus*, an oil could be obtained economically from this plant. However, because of its odour similarity with tansy oil, the oil would probably only be used in compositions where tansy oil has been used. Because there is no composition known to the authors in which tansy oil is a major component, the authors feel that potential exploitation of S. *chamaecyparissus* oil for commercial use is probably limited.

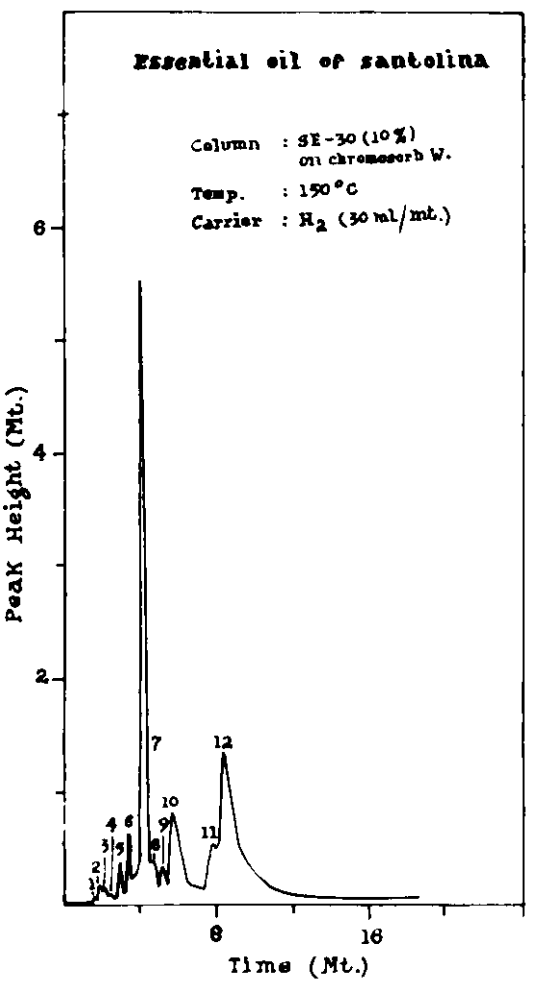
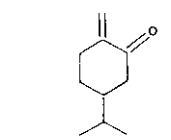
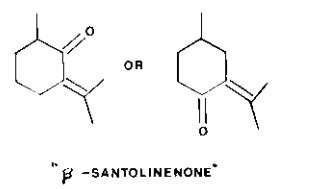


Figure 1.





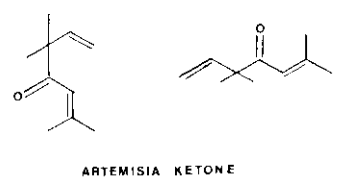


Figure 2.

Table II. Chemical composition of Santolina chamaecyparissus oil

Peak No.	Constituent	RRT	Percentage (W/W)
1.	alpha-pinene	0.37	0.10
2.	sabinene	0.46	0.50
3.	beta-pinene	0.48	0.50
4.	limonene	0.61	trace
5.	gamma-terpinene	0.71	1.80
6.	2-heptanol	0.83	3.40
7.	p-cymene	1.00	33.00
8.	methyl heptenone	1.10	3.60
9.	uncharacterized	1.26	3.00
10.	linalool	1.37	10.00
11.	alpha-thujone	1.91	7.50
12.	beta-thujone	2.03	24.00

Acknowledgement

The authors are grateful to Dr. Akhtar Husain, Director, C.I.M.A.P. Lucknow for his keen interest in this work. The authors are also grateful to Dr. M. C. Nigam, Head of Phytochemistry Division, C.I.M.A.P., for guiding this work.

References

A. Husain, unpublished work
E. Guenther, The Essential Oils, Vol. V, 475, D. Van Nostrand, Inc., New York (1952)
D. M. Smith and L. Levi, J. Agric. Food Chem. **9** 230 (1961)
J. C. Bartlet and D. M. Smith, Can. J. Chem. **40** 2083 (1962)

Addendum by Editor, Natural Flavor and Fragrance Materials

In 1964, Zalkow and coworkers decided to examine the chemical composition of an oil of *S. chamaecyparissus* (whole plant) for the purpose of elucidating the structures of the previously reported α-santolinenone and β-santolinenone (see figure 2 for reported structures). The authors found that the oil contained one major constituent (65%) and three minor ones (4%, 15%, and 10% respectively). This major constituent was found to be 3,3,6-trimethyl-1,5-hepta dien-4-one or artemisia ketone (on a typical monoterpene in which the tail of one isoprene unit is linked to one of the central carbon atoms in the other isoprene unit, see figure 2). The minor components were not identified.

That same year, Thomas and Willhalm (1964) obtained an oil from the steam distillation of *S. chamaecyparissus* flowers collected at around 1200 m. in Sardinia. Using a combination of GC, MS and IR, the authors positively identified α-thujene, α-pinene, β-pinene, β-phellandrene, myrcene, limonene, p-cymene, ar. curcumene, cryptone, phellandral, terpinen-4-ol, and α-terpineol. Thomas and Willhalm also found a hydrocarbon of novel structure in the early boiling fraction of the oil. This compound, which was found to have the same retention time as α-pinene and α-thujene on polar and nonpolar (packed) columns, was characterized spectroscopically as 2,5-dimethyl-3-vinylhexa-1,4-diene.

Four years later, Waller and coworkers (1968) examined the biosynthesis of monoterpenoids in *S. chamaecyparissus* oil. In this study, the authors used retention time data to identify the presence of α-pinene, β-pinene, myrcene and artemisia ketone.

References

L. H. Zalkow, D. R. Brannon, and J. W. Uecke, On the occurrence of the santolinenones. Terpenes XV. J. Org. Chem. **29**, 2786-2787 (1964)
A. F. Thomas and B. Willhalm, Oil of Santolina Chamaecyparissus. A new nonisoprenoid C_{10} hydrocarbon. Tet. Lett. 49, 3775-3778 (1964).
G. R. Waller, G. M. Frost, D. Burleson, D. Brannon, and L. H. Zalkow, Biosynthesis of monoterpenoids by Santolina chamaecy parissus L. Phytochem **7**, 213-220 (1968)