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GAS-LIQUID CHROMATOGRAPHY OF TERPENES

PART VIII. THE VOLATILE OIL OF TANACETUM VULGARE L.^{1, 2}

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ABSTRACT

The chemical composition of the commercial oil of tansy and of that obtained from a local tansy species was determined by means of gas-liquid chromatography. Both oils contained *d*-isothujone as the major component (68.5%, 58%). The commercial oil contained fairly large amounts of *l*-camphor (13.9%), whereas that from local plants had only traces of camphor and 19.8% of *l*-thujone. The minor components isolated and identified in both oils were *l*- α -pinene, *l*-camphene, *d*-sabinene, *d*-limonene, 1:8-cineole, γ -terpinene, *p*-cymene, *d*-terpinen-4-ol, *l*-carvotanacetone, and *l*-borneol. Small amounts of α -thujene, β -pinene, α -terpinene, terpinolene, neoisothujyl and isothujyl alcohols, and dihydrocarvone were identified by retention characteristics only. Car-4-ene, isomeric alloocimenes, and carvomenthone may also be present. An unknown, crystalline monoterpene alcohol with a terminal methylene group was isolated in small amounts. A sesquiterpene (3.7%) was obtained from the oil of local plants.

Prefractionation of these oils by fractional distillation resulted in extensive isomerization of isothujone to *dl*-carvotanacetone. Such a rearrangement was not encountered during prefractionation by preparative gas-liquid chromatography.

An accurate qualitative and quantitative analysis of the volatile oil of the common tansy (*Tanacetum vulgare* L., fam. Compositae) was required for a biochemical study. Several early investigations have been reported (1), but no analysis with more modern techniques appears to have been published. Only two recent papers deal with this oil, Schenk and Heim (2) reporting that the highest oil content is found in the flowers shortly after opening (up to 1.42% of the dry weight of the plant) and Ionescu *et al.* (3) finding it to contain *d*-isothujone (60%, $[\alpha]_D +68.3^\circ$), a mixture of terpenes (10%), and a camphor (20%, $n_D^{15} 1.4570$, $[\alpha]_D +24^\circ$, oxime m.p. 141°C) which was not further characterized.

Semmler (4) was the first to recognize that the major constituent of the oil of tansy is thujone and Wallach (5) showed this to be dextrorotatory β -thujone (*d*-isothujone (6)). Persoz (7, cf. ref. 1) and Vohl (8, cf. ref. 1) found camphor which was later shown to be the rare *l*-form (9, cf. ref. 1). Small amounts of borneol appear to be present (9) and Bruylants (10) thought it likely that thujyl alcohol was a constituent of this oil. None of the terpene hydrocarbons have been isolated and identified.

In previous papers of this series (11, 12) the analysis of other thujone-containing oils by means of gas-liquid chromatography (GLC) has been reported. When this technique was applied to the analysis of the oil of tansy considerable difficulty was encountered in the complete separation and identification of the minor oxygenated monoterpenes. Since some of these components may have biochemical significance an attempt was made to improve the present technique, using temperature-programmed GLC, to a point where complete analysis may become possible. Two samples of the oil of tansy were investigated, one being of commercial origin, the other being obtained by steam distillation of local wild tansy plants.

EXPERIMENTAL

Isothermal GLC chromatograms were obtained as described previously (11-13). Temperature-programmed experiments were carried out with an Aerograph Autoprep model A-700 chromatograph (Wilkins

¹For Part VII, see *Can. J. Chem.*, **41**, 1 (1963).

²Issued as N.R.C. No. 7354.

Instrument and Research Inc., Walnut Creek, Calif., U.S.A.). This instrument is equipped with an automatic injector (0.03- to 2-ml capacity) and an automatic collector. Temperature programming was non-linear and the single-column technique was used. Fractions were automatically collected in 5-ml glass traps (ice-cooled) by a trip-switch which was actuated by the recording pen and which may be set for any particular peak height. Analytical runs were carried out on 4 mm I.D. (1/4 in. O.D.) coiled copper or stainless steel columns, and preparative runs on similar ones of 6-mm I.D. (3/8-in. O.D.).

Melting points were determined with a Leitz hot-stage microscope. Optical rotations were measured at 22–25° C in chloroform (1–5% solution) or, in case of the derived oximes and semicarbazones, in ethanol. The rotation of each oil sample was obtained with the undiluted material. Infrared spectra were recorded with a Perkin-Elmer model 21 double-beam spectrophotometer, liquid samples being mounted as films between sodium chloride plates and solid ones by the KBr-disk method.

Materials

The commercial oil (Fritzsche Bros. Inc., New York) had n_D^{24} 1.4590, $[\alpha]_D +39.7^\circ$. Steam distillation of the leaves and flowers of locally growing wild tansy plants (11.7 kg fresh weight), harvested near Saskatoon during September 1962, gave a light yellow oil (24.3 g) with n_D^{24} 1.4615, $[\alpha]_D +19.3^\circ$. Reference compounds were either commercial samples (purified by GLC where necessary) or those obtained from other plant sources (11–13). The four isomeric thujyl alcohols were prepared by reduction of *l*-thujone or *d*-isothujone with lithium aluminum hydride. Dihydrocarvone, carvotanacetone, and carvomenthone were obtained by reduction of *l*-carvone (14–17). A detailed description of these reductions and of the isolation of the individual products will be reported elsewhere.

The liquid phases used in the GLC columns were commercial products, except for adipate and azelate polyethylene glycol polyesters, which were kindly donated by Dr. B. M. Craig. The solid support was Chromosorb W (60–80 mesh) in the analytical columns, and Gas Chrom P (60–80 mesh) in most of the preparative columns. The ratio of liquid phase to solid support was 1 to 6, except in the 20-ft preparative polyethylene glycol column supplied with the Aerograph instrument (3/8 in. O.D. aluminum), which had 30% PEG 20 M on Chromosorb W.

Analytical Chromatograms

Aliquots (3 μ l) of the two oils were analyzed on a 6-ft SE-30 column (at 65–180° C in 25 minutes in temperature-programmed runs; at 160° C in isothermal runs) to determine whether significant amounts of sesquiterpenes were present. In the commercial oil three peaks were recorded in trace amounts in the cedrene–cadinene range, but the oil from local plants had two minor and one fairly large component (approx. 4% of the oil) in this range. The latter was correlated with peak 26 of the PEG 20 M chromatogram (see Fig. 1(b)).

The oils were then systematically analyzed (isothermal runs) on all the analytical columns. The relative retention times (RRT) of monoterpene hydrocarbons (limonene = 1.00) on PEG 20 M (at 65° C; 64 ml helium/min); NGA polyester (18) (65° C; 160 ml); and ethylene glycol bis(propionitrile) (EGPN) (65° C;

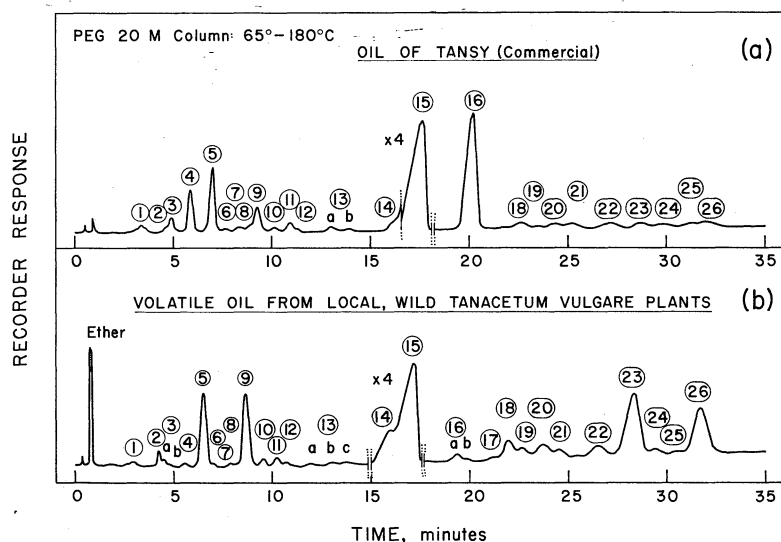


FIG. 1. Gas chromatograms of oil of tansy on a 6-ft polyethylene glycol column (temperature-programmed from 65° to 180° C). (a) Commercial oil; (b) oil from local tansy plants.

77 ml) and of the oxygenated monoterpenes (camphor = 1.00) on PEG 20 M (120° C; 92 ml); NGA (120° C; 109 ml); and QF-1 (19) (100° C; 115 ml) are shown in Table I. The relative retention times of *cis-trans*- and

TABLE I
Composition of the volatile oil of *Tanacetum vulgare* L.

Peak No.	Compound	Relative retention times*			Percent composition	
		A	B	C	I†	II‡
1	Unidentified	(3 unresolved peaks)			0.3	0.1
2	Unidentified	0.28	0.30	—	0.1	0.4
3a	<i>l</i> - α -Pinene	0.30	0.32	0.27	0.5	0.2
3b	(α -Thujene)	0.32	0.33	0.32	0.2	0.1
4	<i>l</i> -Camphene	0.42	0.41	0.45	2.3	0.2
5a	(β -Pinene)	0.59	0.57	0.54	Trace	Trace
5b	<i>d</i> -Sabinene	0.62	0.62	0.70	3.9	2.3
6	(? Car-4-ene)	0.71	0.76	—	Trace	0.1
7	(α -Terpinene)	0.94	0.90	0.98	0.2	0.1
8	<i>d</i> -Limonene	1.00	1.00	1.00	0.1	0.1
9	1:8-Cineole	1.07	1.15	1.68	1.5	2.3
10	γ -Terpinene	1.40	1.38	1.41	0.4	0.3
11	<i>p</i> -Cymene	1.63	1.38	2.38	0.6	0.4
12	(Terpinolene)	1.79	1.72	1.75	Trace	Trace
13	(? Alloocimene isomers)	(See experimental)			0.5	0.3
		D	E	F		
14	<i>l</i> -Thujone	0.61	0.70	0.68	1.0	19.4
15	<i>d</i> -Isothujone	0.67	0.75	0.70	68.5	58.0
16a	<i>l</i> -Camphor	1.00	1.00	1.00	13.9	0.8
16b	(? Carvomenthone)	1.15	1.33	1.06		0.2
17	Unidentified	1.30	—	—	Trace	Trace
18	<i>d</i> -Terpinen-4-ol	1.40	1.39	0.42	0.9	1.0
19	(Neoisothujyl alcohol)	1.68	1.34	0.34	0.2	0.7
	(Dihydrocarvone)	1.68	1.53	1.15		
20	(Isothujyl alcohol)	1.90	1.53	0.41	0.8	1.3
21	<i>l</i> -Carvotanacetone	2.06	2.00	1.24	0.5	0.7
22	<i>l</i> -Borneol	2.28	1.84	0.52	1.0	0.8
23	<i>l</i> -Carvone	2.66	2.32	1.53	0.8	5.8
24	Unidentified	2.98	—	—	0.5	0.5
25	(Crystalline alcohol and unidentified sesquiterpene)	3.30	2.46	0.68	0.5	0.3
26	Sesquiterpene	3.58	—	—	0.9	3.7

*Hydrocarbons (at 65° C; limonene = 1.00): A: polyethylene glycol 20 M column (PEG 20 M); B: neopentyl glycol adipate polyester column (NGA); C: ethylene glycol bis(propionitrile) (EGPN).

Oxygenated monoterpenes and sesquiterpenes (camphor = 1.00): D: PEG 20 M (at 120° C); E: NGA (at 120° C); F: QF-1 polymer column (at 100° C).

†Commercial oil.

‡Oil from local tansy plants.

trans-trans-alloocimene were RRT 4.14, 4.85 and 3.32, 3.90 on PEG 20 M and EGPN respectively. The data of known monoterpenes as determined on the other analytical columns have been reported previously (11, 12, 13, 20). When the retention times of a particular peak agreed with that of a known compound on every column, the peak was considered as tentatively identified.

Some higher-boiling trace components which were recorded in temperature-programmed runs (PEG 20 M and NGA, 65–180° C; see Fig. 1(a and b)) were absent on the charts from isothermal runs. Only after pre-fractionation were the concentrations of these trace components high enough to be clearly recorded by the latter technique. For this reason the quantitative composition was calculated (triangulation method) from the areas under the peaks as recorded in the temperature-programmed runs. The calculated data was reproducible within the errors of the method (11, 12, 13, 21) in repeat runs on the same, as well as on different columns. Use of internal standards (known amounts of *n*-decane, limonene, 1:8-cineole, camphor, 4-terpineol, carvone, and/or *n*-decanol added to a known weight of oil) showed that 98±2% of the oils could be accounted for, provided the trace components were included. Since isothujone (peak 15) was present in such large

amounts, it could not be recorded at the same attenuation as the other peaks when the aliquot of oil was large enough (5 to 10 μ l) to permit recording of the trace components (see Fig. 1(a and b)). The use of a different attenuation and the skewing of the isothujone peak caused by the relatively large samples introduced fairly large errors (up to 5%) and it was found advantageous to calculate the quantitative data from runs with smaller aliquots (1-3 μ l) and to add to this the respective amounts of trace components as recorded in runs with 5- to 10- μ l samples.

Prefractionation

The commercial oil (100 ml) was fractionally distilled *in vacuo* (50 mm Hg) through a 1-mm \times 8-mm spinning band column (Podbielniak Inc., Chicago), using takeoff ratios from 1:60 to 1:100. Five fractions were collected and GLC analysis showed the following composition:

- I (5 ml, b.p. 50-75 $^{\circ}$ C) mainly monoterpene hydrocarbons;
- II (10 ml, b.p. 75-100 $^{\circ}$ C) hydrocarbons and isothujone;
- III (55 ml, b.p. 100-108 $^{\circ}$ C) mainly isothujone and some camphor;
- IV (15 ml, b.p. 108-112 $^{\circ}$ C) isothujone and midrange oxygenated monoterpenes;
- V (10 ml, b.p. 112-120 $^{\circ}$ C) mainly higher-boiling terpenes, including carvotanacetone and carvone, and sesquiterpenes.

The distillation residue showed extensive decomposition and polymerization and was not further investigated.

The oil from local plants was prefractionated in 0.2-ml aliquots on a 6-ft \times 3/8-in. SE-30 column at 90-180 $^{\circ}$ C (in 15 minutes). Cuts similar to those obtained in the fractional distillation were collected, the collecting mechanism of the Autoprep being operated by hand. Recovery of the hydrocarbons varied between 40 and 80%, losses due to aerosol formation being highest for the minor constituents. No decomposition peaks were recorded on reinjection of each fraction on analytical columns. Overlaps of compounds between adjacent fractions were not as marked as in the distillation.

Hydrocarbons

Fractions I and II from distilled commercial oil were injected repeatedly (30- to 50- μ l aliquots) onto a 6-ft \times 3/8-in. PEG 20 M column, which was temperature-programmed from 65 $^{\circ}$ to 90 $^{\circ}$ C during 12 minutes. The components which were isolated in sufficient amount and purity to permit recording of infrared spectra and physical data were identified by comparison with the corresponding data of authentic monoterpene hydrocarbons as: peak 3a, *l*- α -pinene (n_D^{24} 1.4606, $[\alpha]_D -21.6^{\circ}$) contaminated with a compound which had the same retention time as α -thujene (peak 3b, see Table I); peak 4, *l*-camphene (m.p. 30-42 $^{\circ}$ C, $[\alpha]_D -111.1^{\circ}$); peak 5b, *d*-sabinene (n_D^{24} 1.4678, $[\alpha]_D +43.4^{\circ}$); peak 8, impure *d*-limonene (positive rotation); peak 9, 1:8-cineole (n_D^{23} 1.4584, $[\alpha]_D \pm 0$); peak 10, γ -terpinene (n_D^{23} 1.4712, $[\alpha]_D \pm 0$); peak 11, *p*-cymene (n_D^{24} 1.4800, $[\alpha]_D \pm 0$). *p*-Cymene was further identified by its ultraviolet spectrum. The data of these components as isolated from fractions I and II of the oil from the local plants were in good agreement with those reported above.

Peaks 1 (mixture of at least 3 components) and 2 could not be identified, whereas peaks 3b, 5a, 6, and 7 were tentatively identified by relative retention times (cf. Table I). Peaks 13a, b, and c had retention times in the alloocimene range (see above) but none could be isolated pure as some decomposition was encountered.

Thujones

Fraction III from distilled commercial oil was fractionated on the same GLC column using a temperature range of 90-140 $^{\circ}$ C. Essentially pure *d*-isothujone (peak 15) was obtained; n_D^{24} 1.4503, $[\alpha]_D +65.9^{\circ}$ (*c*, 2.3, CHCl₃). The derived semicarbazone had m.p. 174-175 $^{\circ}$ C, $[\alpha]_D +216.8^{\circ}$ (*c*, 2.0, EtOH) after recrystallization from aqueous ethanol. Found: C, 63.38; H, 9.18; N, 20.22%. Calculated for C₁₁H₁₉N₃O: C, 63.12; H, 9.15; N, 20.08%.

Just ahead of the isothujone peak (peak 15), a shoulder (peak 14) was also recorded in preparative runs. This material was collected in small amounts. The infrared spectrum was similar to that of thujone and the optical rotation was negative; n_D^{24} 1.4500. GLC analysis showed contamination with about 10% isothujone.

In the oil from local plants peak 14 was a major constituent which was partially resolved from isothujone. By collecting the early portions of peak 14 and late ones of peak 15, both components were isolated fairly pure; n_D^{24} 1.4498 and 1.4501 and $[\alpha]_D -10^{\circ}$ and $+67^{\circ}$ respectively. These data, as well as the infrared spectra, were in good agreement with those of *l*-thujone and *d*-isothujone respectively.

l-Camphor

Fraction III of the commercial oil also contained fairly large amounts of peak 16, which was isolated chromatographically pure in the above runs. The collected material had m.p. 150-170 $^{\circ}$ C, $[\alpha]_D -39.8^{\circ}$ (*c*, 2.2, CHCl₃). Further purification by recrystallization proved difficult and the material was converted to the oxime, m.p. 115.5-116.5 $^{\circ}$ C, $[\alpha]_D +50.4^{\circ}$ (*c*, 2.2, EtOH), after recrystallization from aqueous ethanol. Found: C, 72.08; H, 10.25; N, 8.57%. Calculated for C₁₀H₁₇NO: C, 71.81; H, 10.25; N, 8.38%.

In the oil from local plants peak 16 was only a trace component and analytical chromatograms showed an overlap with a second component (peak 16b). In the preparative runs these components were collected as one fraction. The infrared spectrum showed as characteristic absorption only a strong carbonyl band (1735-1715 cm⁻¹), indicating that both components are ketones.

Higher-Boiling Minor Components

The individual components from fraction IV could not be obtained pure by preparative GLC. All fractions collected, except peak 18, were subsequently shown to be mixtures of two or more components. Peak 18, as collected from the 6-ft \times 3/8-in. PEG column (120–190° C), had n_D^{24} 1.4754, $[\alpha]_D +17.0^\circ$ (*c*, 1.3, CHCl_3) and its infrared spectrum was similar in all respects with that of terpinen-4-ol.

In analytical runs it was found that QF-1 polymer retained ketones and esters strongly with respect to alcohols and hydrocarbons (see Table I). A 6-ft \times 3/8-in. preparative column was made up and fraction IV was fractionated on a 0.03-g scale into alcohols and ketones. GLC analysis on the PEG 20 M column of the alcohol fractions showed the presence of six components with RRT 1.40, 1.68, 1.89, 2.28, 3.26, and 3.58 (peaks 18, 19, 20, 22, 25, and 26 respectively). Of these, peak 18 (RRT 1.40) was readily identified as *d*-terpinen-4-ol. Peaks 19 and 20 had RRT values corresponding with those of neoisothujyl and isothujyl alcohols respectively. However, neither component could be obtained pure in sufficient amount to confirm their identities. Peak 22 (RRT 2.28) was obtained crystalline (m.p. 120–180° C, $[\alpha]_D -23^\circ$) and its infrared spectrum agreed in all respects with that of borneol. α -Terpineol (RRT 2.24) could be a contaminant, but this was not confirmed by the infrared spectrum. Peak 25 (RRT 3.26) was also obtained crystalline (m.p. 45–60° C, $[\alpha]_D -43^\circ$). The infrared spectrum had strong bands at 3300, 2960–2860, 1655, 1465–1455, 1360, 1332, 1150, 1050, 975, and 882–877 cm^{-1} and well-defined weak bands at 3070, 850, and 765 cm^{-1} .

Of the ketonic components only carvotanacetone (peak 21, RRT 2.06) and carvone (peak 23, RRT 2.66) were positively identified (see below). A component of RRT 1.68, i.e. the same peak as 19, was isolated fairly pure and its infrared spectrum corresponded with that of dihydrocarvone. Because of paucity of material no crystalline derivative was obtained.

Carvotanacetone and Carvone

Fraction V of the commercial oil was composed of about 85% of peak 21 and smaller amounts of peaks 22, 23, 24, and 26. Peak 25 was not recorded and may have been lost in the distillation. Preparative GLC (using the QF-1 column first and then the PEG 20 M column) gave peak 21 practically pure; n_D^{24} 1.4808, $[\alpha]_D \pm 0$. The infrared spectrum was similar to that of carvotanacetone. The oxime, m.p. 92.5–93.5° C, $[\alpha]_D +0.5^\circ$, after recrystallization from aqueous ethanol was obtained directly from fraction V. Found: C, 72.22; H, 10.32; N, 8.46%. Calculated for $\text{C}_{10}\text{H}_{17}\text{NO}$: C, 71.81; H, 10.25; N, 8.38%.

Peak 23 was isolated fairly pure in small amounts; n_D^{24} 1.4855, $[\alpha]_D -10.8^\circ$. The infrared spectrum was similar to that of *l*-carvone. During attempts to isolate peaks 24, 25, and 26 decomposition was encountered and these fractions from the commercial oil were not further investigated.

Peaks 21 and 23 were obtained fairly pure in small amounts from fraction IV of the oil from local plants. The infrared spectra agreed with those of carvotanacetone and carvone respectively and the optical rotations were negative (-45° and -11°).

Sesquiterpenes

In the oil from local plants peak 26 was recorded in fairly high amounts (about 3.7%). By using the SE-30 preparative column small amounts of this material were isolated fairly pure. The infrared spectrum resembled that of cadinene (strong infrared bands in the 2940–2860 cm^{-1} range, weak bands at 1645–1605 cm^{-1} , medium bands at 875 and 825 cm^{-1}), but the retention time on the PEG 20 M (41.5 min) and NGA column (71.0 min) at 120° C differed from that of cadinene (38.7 and 60.3 min respectively).

RESULTS AND DISCUSSION

Typical temperature-programmed chromatograms (as obtained on the PEG 20 M column) of the commercial oil of tansy and that obtained from local wild tansy plants are shown in Fig. 1(a and b). Nearly 30 different peaks were recorded and on comparison with chromatograms obtained in isothermal GLC runs the better detection of the higher-boiling minor components (peaks 18 to 26) in the temperature-programmed runs was evident. Therefore, it is likely that the values reported earlier for corresponding components in the volatile oils of the leaves of *Thuja occidentalis* L. (11), *Thuja plicata* D. Don (12), and black, white, and Colorado spruce (13) as determined by isothermal GLC require an upward correction. That the calculated values for oxygenated higher-boiling monoterpenes tended to be low in comparison with those of the lower-boiling hydrocarbons was already pointed out (20), but the error was thought to be mainly due to tailing. The use of internal standards in this study showed that $98 \pm 2\%$ of the components of each oil were accounted for provided that all peaks were recorded at the same attenuation and trace components were included. The presence of a single component in excess of 50% caused inaccuracies in calculating quantitative data since fairly large aliquots (5–10 μl) of the oil had to be injected to record the trace components adequately. This

required a change of attenuation and resulted in considerable skewing of the large peaks (cf. Fig. 1). Both factors increased the error in quantitative calculations.

The preliminary runs on the SE-30 column showed that the commercial oil contained only traces of sesquiterpenes in the cedrene-cadinene range, and no oxygenated sesquiterpenes were recorded. The oil from the local plants, however, contained appreciable amounts of sesquiterpenes (peaks 24 to 26). Of these one (peak 26) was isolated fairly pure. The infrared spectrum showed it to be similar to cadinene but it was more strongly retained on GLC columns.

The average quantitative composition of the two oils as determined on a variety of columns in temperature-programmed runs is shown in Table I. All the major and several of the minor components were identified after isolation by preparative GLC. The results obtained confirm that *d*-isothujone (peak 15) is the major component in both oils. In the commercial oil the second largest component was *l*-camphor (peak 16), but this was only present in trace amounts in the oil from local tansy plants. Instead, *l*-thujone (peak 14) was a major constituent. The latter oil also contained fairly large amounts of *d*-sabinene (peak 5*b*), 1:8-cineole (peak 9), *l*-carvone (peak 23), and the unsaturated sesquiterpene (peak 26). In the commercial oil, the latter two components were only minor constituents and somewhat more *l*- α -pinene (peak 3*a*) and *l*-camphene (peak 4) were recorded. The presence of minor amounts of *l*-borneol (peak 21) was confirmed but no camphor having an oxime of m.p. 141° C, as reported by Ionescu *et al.* (3), was isolated. Of the other minor peaks *d*-limonene (peak 8), γ -terpinene (peak 10), *p*-cymene (peak 11), *d*-terpinen-4-ol (peak 18), and *l*-carvotanacetone (peak 21) were identified positively. Peaks 3*b*, 5*b*, 6, 7, 12, 19*a*, 19*b*, and 20 were identified tentatively by retention data (and to some extent by infrared spectra) as α -thujene, β -pinene, car-4-ene, α -terpinene, terpinolene, neoisothujyl alcohol, dihydrocarvone, and isothujyl alcohol respectively. Peaks 13*a* to *c* were recorded in the alloocimene range and the retention times of peaks 13*b* and *c* agreed fairly well with those of *trans-cis*- and *trans-trans*-alloocimene (see also ref. 22). By analogy, peak 13*a* could be *cis-cis*-alloocimene. Peak 25 appears to be a mixture of a sesquiterpene (trace amounts) and the unidentified crystalline alcohol of melting point 45–60° C, $[\alpha]_D -43^\circ$. The infrared spectrum of the latter indicated the presence of a terminal methylene group (sharp, medium strong bands at 1655 and 880 cm^{-1}). No reports of a crystalline monoterpene alcohol with such characteristics could be found in the literature.

Examination of the amount of carvotanacetone in the commercial oil as recorded by GLC and that present in fractions IV and V from the fractional distillation showed a considerable increase of this compound during distillation. Since the thujones have been isomerized to carvotanacetone at 280° C (23) it is likely that this rearrangement has occurred during distillation even though the pot temperature did not exceed 160° C. Disproportionation of carvone to carvacrol and more saturated ketones, including carvotanacetone (24, 25), may also have taken place. The fact that the compound isolated from the distilled fraction was optically inactive lends strong support that rearrangement from isothujone to carvotanacetone has occurred preferentially. When this compound was isolated by GLC from the oil of local plants a negative rotation was recorded. Also, when pure thujone, isothujone, and carvone were injected onto analytical GLC columns the relative amounts recorded were the same as those injected (within $\pm 2\%$) and no sign of decomposition could be detected. Thus, the use of preparative GLC for the pre-fractionation of essential oils is to be preferred over fractional distillation. However, the poor recovery of some components (due to aerosol formation) is as yet a disadvantage.

Most of the oxygenated compounds found in the oil of tansy are substituted at C-2. This suggests a biogenetic relationship and it may be that a sequence in the formation of these compounds similar to the one described by Reitsema (26) for mint oils is operative. This aspect, as well as the effect of environmental changes on the composition of the oil, is being studied in this laboratory.

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