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Part I.—MYRCENE

BY

MAURICE D. SUTHERLAND and Miss S. J. WILSON

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The Physical Properties of Pure Terpenes

PART I.—MYRCENE.

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SUMMARY.

Myrcene was purified to 99.5-100% purity and was found to have the properties d_4^{25} 0.7847, n_D^{25} 1.4679 and $\epsilon_{\max} = 1.84 \times 10^4$ at $\lambda = 224.5 \text{ m}\mu$ in alcohol.

The full development of the n/d diagram method (1, 2, 3) for the analysis of essential oils demands a more precise knowledge of the density and refractive index of most of the terpenes than is at present contained in the literature, and this paper describes the preparation and properties of a sample of myrcene of 99.5-100% purity as a contribution to this end.

The essential oil of *Medicosa cunninghamii* (4) was chosen as a suitable source of myrcene for purification since no substance other than myrcene had been detected in the fractions boiling between α -pinene and limonene. In addition these substances are well separated from myrcene in boiling point, have much higher densities than the latter and were strongly optically active in this essential oil.

The properties of the fractions from the final fractional distillation are set out in Table I. Fractions 6, 7, and 8 are the purest judged by the criterion of density which in this case was the property most sensitive to impurity.

TABLE I.

Fraction No.	Volume (ml)	α_D	n_D^{25}	d_4^{25}	Ultra-violet absorption maximum		Purity by diene analysis (av.)	α -pinene (by rotation)*	α -pinene (by density)†
					ϵ_{\max}	$\lambda_{\max} \text{ m}\mu$			
1	5.0	+0.68°	1.4678 ₄	0.7856 ₅	—	—	—	1.6%	1.3%
2	5.0	+0.20°	1.4679 ₂	0.7856 ₂	—	—	—	0.5%	1.3%
3	10.0	$\pm 0^\circ$	1.4678 ₇	0.7849 ₀	—	—	—	0.0%	0.2%
4	1.0	—	—	—	—	—	—	—	—
5	10.0	$\pm 0^\circ$	1.4679 ₀	0.7849 ₀	—	—	99.8%	0.0%	0.2%
6	5.0	$\pm 0^\circ$	1.4678 ₇	0.7847 ₄	$1.83_8 \times 10^4$	224.5	100.3%	0.0%	0.0%
7	0.5	—	—	—	—	—	—	—	—
8	10.0	$\pm 0^\circ$	1.4678 ₇	0.7847 ₅	$1.83_5 \times 10^4$	224.5	—	0.0%	0.0%
9	4.5	$\pm 0^\circ$	1.4679	0.7852 ₂	—	—	—	—	—

* Assuming α -pinene ($\alpha_D^{25} = +42.94^\circ$) to be the only source of optical rotation in the fraction.

† Assuming α -pinene ($d_4^{25} = 0.8542$) to be the only impurity and fraction No. 6 to be pure myrcene.

Calculation of the proportion of α -pinene in the early fractions from the optical rotation shows the elimination of α -pinene to be complete by the third fraction. The difference in pinene content as calculated from rotation and from density is attributed to the rapid autoxidation of part of the distillate which was in the receiver of the still overnight. The rise in density of fraction 9 without the appearance of a corresponding rotation suggests the presence of a trace of a previously unsuspected optically inactive constituent of lower boiling point than limonene.

Conjugated diene analysis gave useful results in indicating the fractions 5 and 6 to be virtually wholly composed of conjugated terpenes, but it was not sufficiently precise under the conditions used to form a satisfactory basis for the estimation of impurity, differences between duplicates ranging up to 0.6%. The refractive index threw little light on the variation in composition of the fractions.

Redistillation of the best fractions to reveal a possible further lowering of the density was discouraged by the very ready polymerisation of the myrcene and was not attempted as the object of this work—to place closely and reliably the point for myrcene on the n/d diagram—had been achieved. The gross uncertainty in the properties of other terpenes demands prior attention, though the preparation of a larger sample of pure myrcene will be attempted when fresh supplies of myrcene become available.

Fractions 6 and 8 are regarded as being myrcene of 99.5-100% purity and the properties of myrcene are determined as d_4^{25} 0.7847; n_D^{25} 1.4679; and $\epsilon_{\max} = 1.84 \times 10^4$ at $\lambda = 224.5 \text{ m}\mu$.

Comparison with previously described samples of myrcene (1) suggest that the material separated by Goldblatt and Palkin (5) of d_4^{25} 0.7862 (corrected from 20° C.) contained only about one to two per cent. of β -pinene and/or limonene as impurity. Most other samples described in the literature are grossly impure. It would appear from the literature that two substances are described under the name myrcene and these may be distinguished by the considerable difference in refractive index (1). If it is assumed that the low refractive index of some samples of myrcene (1, 6, 7, 8) results from the presence of an α -form of myrcene then it is clear that only the β -form is present in the essential oil of *M. cunninghamii* unless the two forms have exactly the same boiling points, a rather remote possibility, considering the properties of simpler hydrocarbons showing the same difference in structure.

The ultraviolet absorption spectrum of the present sample of myrcene, in alcohol, shows a maximum at the same wavelength (224.5 $\text{m}\mu$) as that found for a sample (d_4^{25} 0.7922 (corrected from 15° C.) $\epsilon_{\max} = 1.46 \times 10^4$) prepared by Dr. T. F. West and described by Booker, Evans and Gillam (9), but it has a very much stronger absorption, $\epsilon_{\max} = 1.84 \times 10^4$, in agreement with its greater purity. Woodward (10) has put forward a rule for the position of absorption maxima of conjugated dienes, which leads to a calculated value of 222 $\text{m}\mu$ for the myrcene molecule but the measurements recorded here substantiate the difference of 2.5 $\text{m}\mu$ between the observed and calculated values and confirm the existence of "subtle constitutional factors which shift the maximum slightly towards that characteristic of one or other of the two component systems."

EXPERIMENTAL.

A volume of 164 ml. of myrcene-rich material obtained by fractionation of *M. cunninghamii* oil was rectified in a twenty plate still previously described (2) at a pressure of 20 mm. The distillate was collected in 10 ml. fractions, 143 ml. being taken off in all, the loss being partly due to the formation of polymer. The refractive index showed comparatively little change throughout the distillation but the density of the early fractions and the last showed some variation. Fractions 4 to 14 all had densities of d_4^{25} 0.7854 or lower and 92 ml. were bulked for redistillation in another still containing a one metre length of the packing described by Bower and Cooke (11). This column has been tested to a maximum

efficiency of fifty-five plates when operated at total reflux under atmospheric pressure and has a hold up of approximately 2 ml. The rectification was carried out at 50 mm. pressure and with a reflux ratio of approximately thirty-five. Owing to the necessity of starting the still each day and allowing time for the establishment of equilibrium, the distillation extended over several days. Fractions 4 and 7 were fractions obtained at the start of the third and fourth days and were rejected as possibly containing autoxidised myrcene which may have formed in the receiver overnight despite the carbon dioxide atmosphere introduced on closing down the apparatus. Loss of myrcene through polymerisation in the pot was excessive and resulted in the premature appearance of material of high density in the distillate as shown by the higher density of fraction 9.

The various fractions showed no difference in boiling point (about 83° to 84°) which could be attributed to changes in composition rather than to pressure changes. The refractive indices were measured with a Pulfrich refractometer and the densities in a pycnometer holding a little over three grams of myrcene. The temperature of the pycnometer bath was held at 25° C. to within a few hundredths of a degree using a checked thermometer.

The diene estimations were carried out by a method similar to that of Kaufmann, Batles and Josephs (12) and Jones and Hancox (13). It was found that the time (1½ hours) suggested by Kaufmann *et al* for complete reaction of the myrcene with maleic anhydride in benzene solution was insufficient and that three hours in toluene on the water bath, was necessary for satisfactory results.

The ultraviolet absorption of myrcene was measured in rectified spirits solution using a Beckmann DU spectrophotometer, the density and wavelength scales of which have been checked.

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