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Indices of the Terpenes

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A REVIEW OF THE DENSITIES AND REFRACTIVE INDICES OF THE TERPENES

BY MAURICE D. SUTHERLAND

SUMMARY

Data from the literature of the density and refractive index of each of the naturally occurring terpenes is critically examined, and those values which are believed to be the most reliable are chosen. For five of the terpenes (allo-ocimene, limonene, α -phellandrene, α -pinene and β -pinene) the selected values are very satisfactory. The other terpenes have yet to be obtained in an apparently pure state, and the data concerning them is unsatisfactory. In the case of β -phellandrene, α -terpinene, myrcene and Δ^4 -carene, two sets of values are listed in order to emphasize the lack of reliable or concordant data.

In comparing the physical properties of the terpenes, use is made of a chart wherein the terpenes are plotted with density as ordinate and refractive index as abscissa. This type of diagram clearly indicates the physical properties of the terpenes and their relation to one another and is also of use in the analysis of terpene mixtures.

The most reliable values, corrected to d_4^{25} and n_D^{25} are given below:—

<i>Allo</i> -ocimene	{	A	.8020	1.5424	α -Phellandrene8284	1.4702
		B	.8078	1.5424			.8346	1.4804
Camphene8675	1.4695	β -Phellandrene	...	{ .8409	1.4778
Δ^3 -Carene8580	1.4709	α -Pinene8542	1.4631
Δ^4 -Carene	...	{	.8553	1.4752	β -Pinene8666	1.4768
			.8481	1.4739	Sabinene8358	1.4636
1 : 8 Cineole9210	1.4553	Santene8590	1.4644
1 : 4 Cineole8948	1.4438	α -Terpinene	...	{ .8300	1.4762
<i>p</i> -Cymene85341	1.48878			.8332	1.4746
Isolimonene8330	1.4682	β -Terpinene8356	1.4750
Limonene8387	1.4702	γ -Terpinene8450	1.4712
Myrcene	...	{	.7886	1.4628	Terpinolene8560	1.4864
			.7862	1.4681	α -Thujene8261	1.4493
Ocimene7946	1.4836				

Although steady progress is being made in terpene chemistry, some aspects of our present knowledge in this field are far from satisfactory. In particular, the reported physical constants of the terpenes are discordant and confusing, principally as a result of the low efficiency of the fractionating columns available to the early workers and the inapplicability of other methods of purification to mixtures of the terpene hydrocarbons. Much of the important chemical work in the terpene field was carried out on mixtures of terpenes, and, while the value of the results obtained was not thereby lessened in many cases, the physical constants of the pure substances could not be determined, owing to the presence of the impurities. According to the quantity and the nature of the impurities present, so the reported physical

properties of each of the terpenes have varied. Consequently the density and refractive index, and to a lesser extent the boiling point, have been of no great value in the identification of individual terpenes.

Recent developments in the technique of laboratory distillation have solved the problem of separating and purifying the terpenes. The high purity of the products obtainable from suitable stills has transformed the physical properties into significant characteristics of considerable diagnostic value. It is therefore appropriate that our present knowledge of the physical properties of the terpenes should be reviewed with the object of assessing the value of the data recorded in the literature, and of stimulating further measurements on the physical properties. In this review, the literature data on the density and refractive index of each of the natural terpenes has been analysed, and what are apparently the best values have been selected. Suggestions are offered in some cases as to the most promising methods of preparation of some of the terpenes in pure form. It is hoped that the list of selected values will be of use in suggesting the composition of terpene fractions, checking the purity of known terpenes and distinguishing the occurrence of new terpenes. For these purposes, neither the compilation of Egloff (1) nor that of Beilstein (2) is of immediate value, since both reliable and unreliable values are indiscriminately tabulated. Some selection of data has been made by Simonsen (3), but sufficiently critical attention has not been given to this aspect. No claim is made that this review represents a complete survey of the literature and some of the apparently less important papers have been examined in abstract form only.

TEMPERATURE CORRECTIONS

Before the density and refractive index values given in the literature can be compared, they must be corrected to the same temperature. Throughout this review all values quoted refer to 25°C., corrections having been applied where necessary by use of the factors .0008 per degree for specific gravity and .00045 per degree for refractive index. Thus all specific gravities are for the conditions d_{4}^{25} and all refractive indices for n_D^{25} .

Reference to Beilstein, the International Critical Tables and other sources reveals a serious lack of reliable data on the temperature variation of the physical properties of the terpenes. In Table I. is collected some of the information that is available. The correction factors given above are fairly satisfactory for each of terpenes listed in the Table and were also chosen by Auwers (4) to correct literature values for α -terpinene to 20°C.

It has been made clear by Ward and Kurtz (5) that the density correction factor depends both on the type of hydrocarbon (i.e., mono or di-cyclic, etc., olefinic or saturated, etc.), and also on the density of the particular hydrocarbon. Thus a small variation in the density correction factor for the different terpenes may be anticipated, yet the effect cannot be large. In the absence of pertinent information, the most satisfactory plan appears to be to apply the one correction factor to all terpenes alike. The resulting errors cannot be large compared with the discrepancies usual between the work of various authors in the terpene field. It would be an advantage if the density and refractive index of important samples were measured at both 25° and either 15° or 20° so that temperature corrections could be applied with confidence when necessary.

TABLE I.

Terpene	Refractive index factor	Density factor	Temperature range	Reference
Camphene	0.00080 .00084 .00082	.00046 — —	54° —63.4° 47.7°—58.9° 40° —60°	Bruhl (6). Riban (7). Perkin (11).
Limonene	.00088 .00080 .00079 .00078 .000795	.00045 — — — —	14.7°—19.6° 10.9°—23.1° 15° —25° 4° —25° 0° —20°	Auwers, Roth and Eisenlohr (8). Mitchel and Smith (9). Kay and Perkin (10). Perkin (11). Godlewski and Roshanowitsch (48).
α -Pinene	.00084 .00084 — .00081	.00038 — .00045 —	? 12.6°—23.8° 15° —35° 4° —25°	Padmanabhan and Jatkar (12). Mitchell and Smith (9). Fuguitt, Stallcup and Hawkins (13) Perkin (11).
β -Pinene	—	.00045	15° —35°	Fuguitt, Stallcup and Hawkins (13).

THE REFRACTIVE INDEX VERSUS DENSITY DIAGRAM

If appropriate values of the refractive index and the density as abscissa and ordinate respectively are marked out on graph paper, a diagram is obtained on which a substance can be represented by a point, the position of which is dependent on the value of its refractive index and density. The terpenes, plotted in this manner, form a group of points, in general conveniently dispersed. As is to be expected from considerations discussed in the following section, the dicyclic, monocyclic and the acyclic terpenes are each confined to separate areas of the diagram.

The comparison of the physical properties of various preparations of a particular terpene is facilitated by plotting the corresponding points in the n/d diagram, since the comparison involved is then one of the relative position of a number of points and the direction and magnitude of the displacement between points under comparison is related to the identity and quantity of impurity present.

The data of Fuguitt, Stallcup and Hawkins (13) shows that points representing mixtures of α -pinene and β -pinene lie very close to the straight line joining the points representing the two pure terpenes. The displacement along this line of the point for a given mixture is found to be proportional to the fraction (by volume) of the second hydrocarbon present. This is in agreement with the view that the density and refractive index of mixed hydrocarbons are additive on a volume basis (5). For mixtures of even the most dissimilar terpenes it would be unreasonable to expect significant variations from the ideal behaviour. This, however, does not necessarily apply to mixtures involving other chemical types,

e.g., mixtures of terpenes with the ether, cineole. Experimental exploration of such mixtures should be undertaken since the information on this point collected in the International Critical Tables does not include any mixtures involving terpenes or cineole (14). An example of non-ideal mixing is found in ethanol and water, and the line on the n/d diagram representing mixtures of these two substances is strongly curved.

From the above considerations it may be assumed that for mixtures of two or more terpenes, the observed point will be closely adjacent to the calculated position. Thus, if all the constituents of a binary or ternary mixture are known, the position of the point in relation to the points of the constituents will enable the composition of the mixture to be calculated. In addition, where one or more of the constituents of a mixture is not identified, the displacement of the point relative to the points of the known constituents will be a valuable indication of the physical properties and/or the quantity of the unidentified material.

It is appropriate here to indicate how full use may be made of the n/d diagram in essential oil analysis. The following technique is used in this laboratory. The terpenes are rectified in an efficient still, the distillate being collected in fractions of 2 to 10 ml., all of approximately equal quantity in any one distillation. Usually, 5 to 20 fractions are collected, depending on the quantity of material and the complexity of the mixture, and for each fraction the density and refractive index is determined. The data so obtained is plotted on a n/d diagram such as Fig. I., and by the course of the curve much valuable information on the nature of the constituents is revealed. This advantageous system of analysis is also applied to the oxygenated terpenes and to the sesquiterpenes. In Fig. I. is illustrated an example of a curve of this type traced out by the terpene fractions of an essential oil, a full report on which will be published elsewhere (15). The lowest boiling fraction is that of constants .8472 and 1.4518, and contains a proportion of an unidentified substance which cannot be one of the known terpenes. The identified constituents are α -pinene, β -pinene, limonene and γ -terpinene. A number of fractions, the points for which lie very close to the points for α -pinene and β -pinene are not represented in Fig. I. for the sake of clarity.

THE MOLECULAR REFRACTION OF THE TERPENES

An advantage resulting from the use of the n/d diagram is that the molecular refraction of a terpene sample is readily estimated from the position in the diagram of the point representing the sample. This is achieved by including three lines which represent permissible density-refractive index values for the calculated molecular refractions of the dicyclic, monocyclic and acyclic terpenes. Thus for each of the refractive index values listed in Table II. a density value was calculated from the formula:—

$$[R_L]_D = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{m}{d}$$

The calculated values for the molecular refractions of the various types of terpenes were obtained from the data of Auwers and Eisenhlohr for atomic and group refractions (16).

TABLE II.

n_D^{25} \ d_4^{25}	Dicyclic [R _L] _D = 43.51	Monocyclic [R _L] _D = 45.25	Acyclic [R _L] _D = 46.98
1.44	.8252	.7935	.7643
1.45	.8413	.8090	.7792
1.46	.8574	.8244	.7941
1.47	.8734	.8398	.8089
1.48	.8892	.8550	.8236
1.49	.9050	.8702	.8382
1.50	.9207	.8853	.8527

The three lines are almost straight, and converge slightly towards the lower left corner of the diagram. The separation between adjacent lines corresponds to about 1.74 units of molecular refraction so that the molecular refraction of a terpene may be estimated by the relation of its point to adjacent lines of known molecular refraction.

The obvious point of interest revealed in Fig. I. is that not one of the terpenes falls on any of the lines of calculated molecular refraction. This is perhaps not so unexpected since in addition to exaltations resulting from exocyclic double bonds and from conjugation effects for which more or less definite increments have been suggested, there are other minor effects due to the presence of small rings and to other factors more difficult to define. The problem involved is well illustrated by *n*/*d* diagrams given in a paper by Ward and Kurtz (5). Thus Fig. 3 of that paper shows the density refractive index relation of the isomeric octanes, and it is clear that a considerable variation of molecular refraction results from variation in the arrangement of the carbon skeleton. The introduction of a double bond as illustrated in Fig. 4 of the same paper brings about even greater variations of molecular refraction from the calculated value. It is therefore useless to anticipate that the difference between the observed and calculated values of the molecular refraction of a terpene can be simply explained in terms of exaltations due to conjugation, exocyclic double bonds and ring size only.

One regularity apparent from Fig. I. is that an increase in density, refractive index and molecular refraction (and boiling point also) results from the presence of an exocyclic double bond. Pairs illustrating this are α -pinene and β -pinene, α -thujene and sabinene, and γ -terpinene and terpinolene. If this regularity extends to other pairs, β -phellandrene may be expected in the region of Berry's sample (d) (see below). Similarly, β -carene should show a rather higher density and refractive index than β -pinene. The relative position of β -terpinene to γ -terpinene is not in accord with the other examples quoted, but it is possible that Wallach's β -terpinene was grossly impure.

It is worth noting that the molecular refraction is not entirely independent of the temperature (17), and that the use of the density and refractive index correction factors given above, results in slightly lowering the molecular refraction as the temperature is raised. In addition, the molecular refraction of cymene and santene cannot be estimated by reference to the lines of known molecular refraction since they differ in molecular weight from the terpenes.

FIG. I.—Refractive index density diagram with selected values for the physical constants of the naturally occurring terpenes.

KEY TO FIG. I.

ALA	Allo-ocimene A	α P	α -Pinene
ALB	Allo-ocimene B	β P	β -Pinene
CAM	Camphene	α PH	α -Phellandrene
3 CAR	Δ^3 -Carene	β PH	β -Phellandrene
4 CAR	Δ^4 -Carene	SAB	Sabinene
4 CNL	1 : 4 Cineole	SA	Santene
8 CNL	1 : 8 Cineole	α TP	α -Terpinene
CYM	p-Cymene	β TP	β -Terpinene
ISLM	Isolimonene	γ TP	γ -Terpinene
LM	Limonene	TOL	Terpinolene
MYR	Myrcene	α TJ	α -Thujene
OCM	Ocimene		

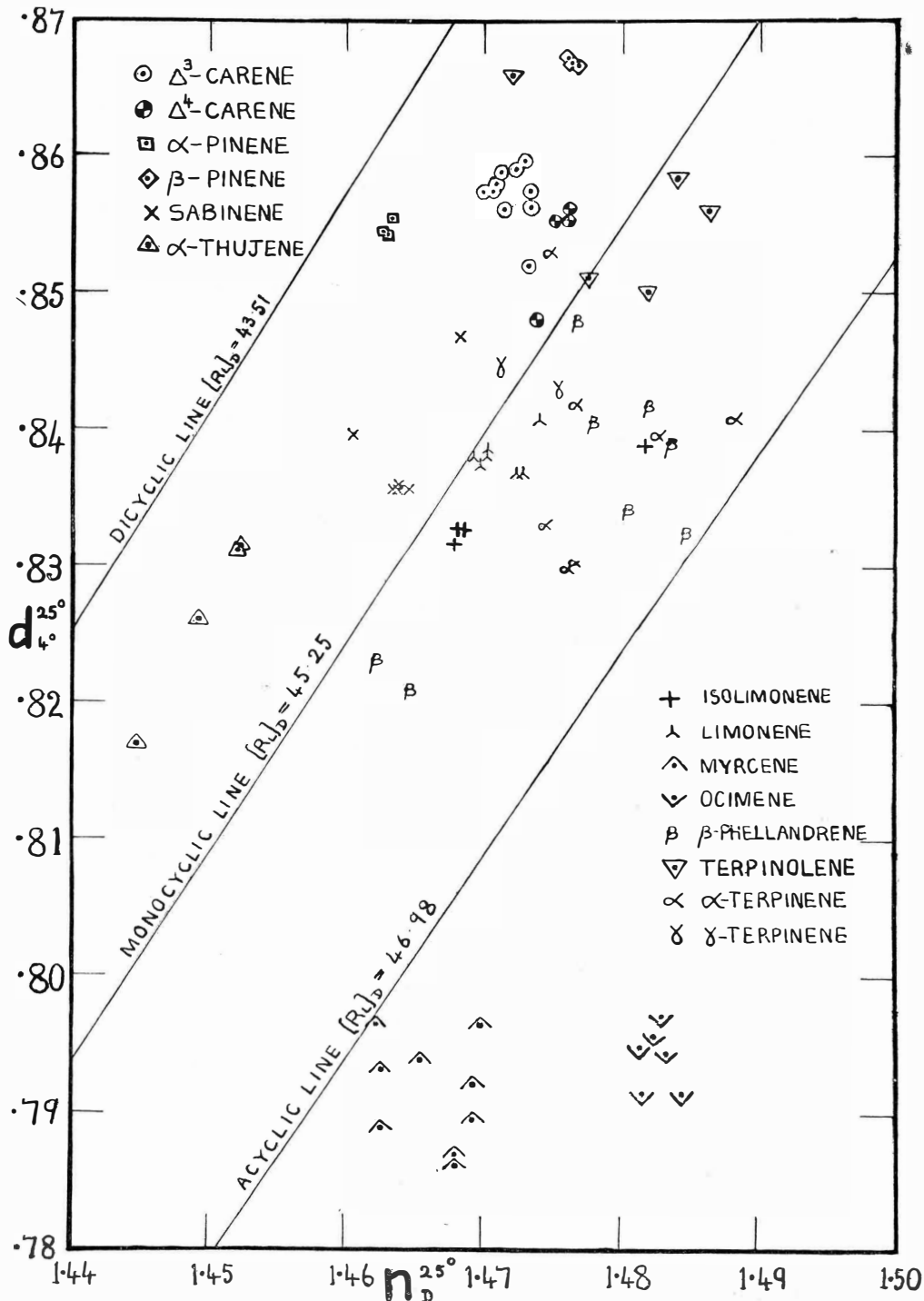


FIG. II.—Refractive index density diagram illustrating the wide variations found in the literature values of the physical constants of the terpenes.

INDIVIDUAL CONSIDERATION OF THE TERPENES

Below, sections are devoted to the literature data on each of the terpenes (in alphabetical order) and in Fig. II. are plotted points corresponding to the properties of the samples discussed. In Fig. I. will be found points for the values selected as the most reliable and a list of these values which is included in the Summary, will be found convenient for preparing n/d diagrams, etc. A few substances (p-cymene, cineole and santene) which are not terpenes have been included since they commonly occur in, and affect the physical properties of, terpene fractions.

From time to time announcements have been made of the isolation of new terpenes from essential oils, but in the absence of crystalline derivatives or other conclusive evidence, little reliance can be placed on such claims. For this reason such terpenes as chamene, orthodene and cryptotenene have been omitted from consideration.

Allo-ocimene.

Though *allo-ocimene* apparently does not occur naturally it may possibly be formed during extended fractionation of oils containing ocimene, and hence it is included here. Consideration of the accepted formula for *allo-ocimene* indicates the possible existence of four geometric isomers.

For *allo-ocimene* from natural ocimene Enklarr (18) found .8053 and 1.5429. However, Hopfield, Hall and Goldblatt (19) have recently separated two of the geometric stereoisomers, A, m.p. -21.0° to -20.6° (.8020 and 1.5424) and B, m.p. -35.4° to -34° (.8078 and 1.5424) by fractional distillation followed by crystallization.

Owing to the very high refractive index of *allo-ocimene*, points for A and B cannot be conveniently included in Fig. I. and arrows at the edge of the diagram have been substituted.

Camphene.

Camphene is unique among the terpenes in being a solid at room temperature and although this simplifies purification, it also necessitates extrapolation to obtain the density and refractive index of liquid or dissolved camphene at 25°C . From the data in Beilstein and that collected by Egloff (1), graphical extrapolation suggests the constants .8675 and 1.4695, which have been used to place the point for camphene in Fig. I. These figures are in only fair agreement with those (.8660 and 1.4678) suggested by Gildemeister and Hoffman (20).

 Δ^3 -Carene.

This terpene was discovered in turpentine from *Pinus longifolia* by Simonsen, and is associated in that source with α -pinene and β -pinene. For two preparations Simonsen (21) gives .8588, 1.4712 and .8580, 1.4709. Padmanabhan and Jatkar (12) found .8575 and 1.4701 for carene from the same source. These three values are in reasonable agreement among themselves and to a lesser degree with carene from *P. sylvestris* (21). In this source also, α -pinene and β -pinene are present and the purest carene obtained, showed a slightly higher refractive index (.8575 and 1.4733) than for carene from *P. longifolia*. Simonsen and Rao (22) also investigated *P. pumilio* and obtained a similar fraction (.8563, 1.4733) "mainly Δ^3 -carene"

which gave an "excellent yield of nitrosate." From a recent investigation Rudakov and Antamanov (23) concluded that the carene (.8561 and 1.4714) obtained by them from *P. sylvestris* was not quite homogeneous owing to the presence of what was probably β -carene. This substance appears to be present in small quantities in the *P. longifolia* turpentine also (24, 25).

Other workers have reported constants for carene differing more or less from the above, these being due to Aschan (26) (.8521 and 1.4732), Schimmel and Co (27) (.8592 and 1.4723; .8597 and 1.4728) and Krestinski and Ssolodki (28) (.8576 and 1.4707). The results of Semmler and Schiller (29) are invalidated by the obvious ineffectiveness of their fractional distillations.

From the information available it is not possible to assess the purity of the various preparations and the arbitrary choice of Simonsen's second preparation has been made for inclusion in Fig. I. as the point for Δ^3 -carene. It would seem from Fig. II. that impurities other than α -pinene and β -pinene are present in the carene from both *P. sylvestris* and *P. longifolia* and as one of these impurities may well be β -carene, the results of the fractionation of these oils in modern stills will be of great interest.

Δ^4 -Carene.

There are few reports on Δ^4 -carene and owing to discrepancies between these, this hydrocarbon has been represented by two points in Fig. I. Simonsen first obtained Δ^4 -carene and found for two samples from the same source the constants (.8554 and 1.4762; .8563 and 1.4762) (30). These values were later closely supported by those of a synthetic sample (31) (.8553, 1.4752), and in addition Aschan (32) reported a density of .8530, a somewhat lower figure. Simonsen (33) later isolated Δ^4 -carene from another essential oil in which it was the only terpene found. Very different constants were given for this carene, and also for a sample supplied by Simonsen and further fractionated by Padmanabhan and Jatkar (12) (.8481 and 1.4739). In Fig. I. have been included points corresponding to the synthetic terpene and to that of Padmanabhan and Jatkar.

Cineole.

For specially purified 1 : 8-cineole, Berry and Swanson (34) found .9210 and 1.4553 (after correction from 15.5° and 20° respectively using the factors .0008 and .00045). For 1 : 4-cineole the constants .8948 and 1.4438 have been found in this laboratory (35). Any cineole present in terpene fractions must be removed before useful results can be obtained from the n/d curve.

Cymene.

p-Cymene is included in this discussion as it is an integral member of the cineole cymene terpinene complex which is common in essential oils. Cymene either prepared from pure thymol or purified from commercial cymene, was found by Le Fevre, Le Fevre and Robertson (36) to have density 0.85341 and refractive index 1.48878.

These preparations are probably very pure and a point based on them has been included in Fig. I.

Isolimonene.

In 1903 Tschugaev (37) gave the name isolimonene to a hydrocarbon which from the method of preparation was considered to be $\Delta^{2:8(9)}$ -p-menthadiene. Dihydrocarveol was converted to the methyl xanthate which was destructively distilled to yield two hydrocarbons, limonene and another of b.p. 172-172.5° which were separated by fractional distillation. Both the dextro and the laevo (.8330, 1.4682, $[\alpha]_D - 140.58^\circ$) isomers were prepared, the latter in a purer state but no crystalline tetrabromide or nitrosochloride could be obtained.

In 1921 Henry and Paget (38) obtained from oil of chenopodium a new terpene tetrabromide of m.p. 117° which was optically inactive and apparently derived from a new terpene. The terpene itself could not be separated by distillation from the associated α -terpinene and p-cymene, a difficulty which hindered the chemical investigation and obscured the physical properties. From the properties of a mixture of the terpene and p-cymene, obtained by removal of the α -terpinene by Beckmann's chromic acid mixture, the physical properties were estimated to be 0.839, 1.4818 and $[\alpha]_D - 57^\circ$. From degradation studies on the mixture of terpenes and the crystalline tetrabromide, the isolimonene structure was put forward for this hydrocarbon.

The tetrabromide was again prepared from the chenopodium oil terpenes by Berry (39) who claimed a slight optical activity, $[\alpha]_D + 2.2^\circ$. However, Berry's tetrabromide melted at 115° to 116° and may have been slightly impure since the crude tetrabromide was very impure ($[\alpha]_D = + 9.4^\circ$) and limited in quantity (1.5 g.).

Pigoulevski and Gorbounova (40) have repeated and confirmed Tschugaev's preparation of isolimonene. They considered that the Raman spectrum of the hydrocarbon indicated the presence of an olefine bond linking two secondary carbon atoms. While the value of the Raman spectrum in terpene chemistry has been questioned (41), the structure of Tschugaev's isolimonene can hardly be doubted. However, the purity of the preparation of Pigoulevski and Gorbounova leaves something to be desired since after two fractionations, the hydrocarbon (.8320, 1.4680, $[\alpha]_D - 140.06^\circ$) yielded 1.8% of limonene tetrabromide. A third rectification changed these constants to .8329, 1.4687 and $[\alpha]_D - 140.51^\circ$, the yield of tetrabromide being reduced to a trace. Considering the probable solvent effect of the isolimonene tetrabromide one must conclude that a substantial proportion of limonene was still present. The possibility that the optically active isolimonene tetrabromide is very soluble and was prevented from separating in crystalline form by the solvent effect of the limonene tetrabromide cannot be disregarded. As Tschugaev's isolimonene was very similar in physical constants to that of Pigoulevski and Gorbounova it is probable that it contained only slightly less limonene.

Henry and Paget's tetrabromide, being inactive, must be a derivative of the inactive hydrocarbon and from the estimated rotation of -57° for the chenopodium terpene, about 59% of the dl mixture would have been present. Assuming that, as in the case of limonene, the inactive tetrabromide is less soluble than the active forms, the observations of Henry and Paget on one hand and Tschugaev on the other are not in conflict. The nitrosochlorides of α -pinene show a similar behaviour.

Comparing the physical constants of the various preparations by means of Fig. II., it is seen that Henry and Paget's isolimonene is somewhat higher in density and very considerably higher in refractive index than the samples of the Russian

workers. The very considerable exaltation of Henry and Paget's sample is not in accord with the isolimonene structure, being probably a consequence of the chromic acid treatment, used to remove the α -terpinene. Tschugaev's values have been used to place a point for isolimonene in Fig. I., although, owing to the probable presence of some limonene, the point may be slightly displaced from its true position towards the point for limonene.

Both the natural and the synthetic isolimonene would repay fractionation in an efficient still by results of considerable interest. It is apparent from the data reported by Henry and Paget in the experimental section of their second paper (42) that isolimonene will be comparatively readily separated from the less volatile α -terpinene and p-cymene by use of a suitable still and technique. Acid treatment being avoided, the natural hydrocarbon may show an approximate coincidence with the point for Tschugaev's isolimonene. The preparation of pure inactive isolimonene by Tschugaev's method and the nature of the tetrabromide obtained therefrom could also provide decisive evidence for or against the proposed isolimonene structure of the chenopodium terpene. However, the possibility of cis and trans isomers complicates the problem.

Limonene.

The constants given in the literature for limonene may be distinguished as three groups. Firstly, the limonenes prepared by Goldblatt and Palkin (43) (.8375 and 1.4698), by Fuguitt and Hawkins (44) (.8387 and 1.4702), by Auwers, Roth and Eisenlohr (8) (.8381 and 1.4703), and by Richter and Wolff (45) (.8381 and 1.4694) are all in good agreement. The second group contains the values obtained by Bruhl (46) (.8371 and 1.4727); .8370 and 1.4725) for l- and d-limonenes from natural sources. These samples are in agreement with the first group as regards density, but show a higher refractive index and a marked exaltation in molecular refraction. The third group includes limonene prepared from limonene dihydrochloride by Wallach (47) (.8410 and 1.4742) and a sample prepared from α -terpineol by Kay and Perkin (10) (.8461) the high density in both cases being due probably to the presence of terpinolene (45).

The limonene described by the first named authors was obtained by the thermal isomerisation of α -pinene and was separated from other products (pyronenes, *allo*-ocimene, etc.) by distillation through a thirty-five (theoretical) plate column. The distillation curves indicate a not perfectly pure product, whereas that prepared by the same method by Fuguitt and Hawkins (44) contained "little impurity," having been redistilled through very efficient column. This would appear to be the most reliable sample of limonene yet described and to be of very high purity for a terpene hydrocarbon. The point for limonene in Fig. I. has been based on the figures of these authors.

Godlewski and Roshanowitsch (48) prepared limonene (.8385) by the debromination of the tetrabromide, using zinc in alcohol. Braun and Lemke (49), using magnesium in ether, obtained similar figures (.8371 and .8382) for the d and l forms, but unfortunately in neither case were refractive indices reported. These densities agree satisfactorily with the best figures for the density of limonene, but in the absence of refractive index values no conclusion can be drawn as to the reliability of the debromination procedure (c.f. β -phellandrene and terpinolene).

Myrcene.

The myrcene (.7862 and 1.4681) separated (thirty-five theoretical plate still) by Goldblatt and Palkin (50) from the products of the thermal isomerisation of

β -pinene is undoubtedly one of the purest samples of myrcene yet described and a point in Fig. I. for myrcene has been based on this material. Another sample of myrcene with very similar constants has been described. Dupont and Desreux (51) gave the values .7870 and 1.4682, but the source or method of purification is not given in Beilstein, Chemical Abstracts, etc.

The difficulties in purifying myrcene are shown by consideration of a sample (.7890, 1.4628 and $\alpha + 2.5^\circ$) of myrcene separated from oil of bay by Palkin and Wells (53) in 1933. Using a still containing thirty-two gauze plates, they were not able to obtain myrcene free from optical activity which they attributed to the presence of α -phellandrene. Consideration of the physical properties of this fraction (see Fig. II.) as compared with Goldblatt and Palkin's myrcene suggests contamination by a substance of somewhat similar density but considerably lower refractive index. Some phellandrene could be present in addition, but phellandrene alone could not cause the observed displacement of the myrcene point. It seems probable that another acyclic hydrocarbon was also present. Power and Kleber (54) also isolated myrcene (.7935 and 1.4628[?]) from oil of bay, being the first to do so. Their figures tend to confirm the report of Palkin and Wells, whereas Booker, Evans and Gillam (55) recently found .7922 and 1.4692, that is, a product of the higher refractive index type. It is likely that the higher densities recorded by Power and Kleber and by Booker, Evans and Gillam result from the incomplete removal of monocyclic terpenes which would, however, leave the refractive index virtually unaffected.

A similar but not so clearcut discrepancy exists in the properties of myrcene obtained from oil of hops as reported by Semmler and Meyer (52) (.7897 and 1.4694) and by Chapman (56) (.7966 and 1.4623).

Myrcene has also been obtained by the dehydration of linalool. Enklaar (57) found .7940 and 1.4656 for myrcene obtained by this method, using either phenyl isocyanate or heated activated copper as dehydrating agents. Arbusov and Abramov (58) effected the dehydration by heating with a trace of iodine and obtained myrcene (.7967 and 1.4700) which they considered might contain a small proportion of the isomeric limonene-type terpene, i.e., 2 : 6 dimethylene— Δ^7 -octene. The rather high density of this preparation may have resulted from the presence of some monocyclic terpene formed during the dehydration as observed by Brooks and Humphrey (59). In refractive index, Enklaar's preparation lies between the two groups, but the preparation of Arbusov and Abramov is definitely in the higher refractive index class. It is possible that the myrcene of low refractive index contain a substantial proportion of the limonene-type isomer or some other acyclic hydrocarbon. To focus attention on this interesting point, Palkin and Wells' sample has also been included in Fig. I., although it is known to be not homogeneous.

Ocimene.

There is a remarkable measure of agreement by various workers on the physical properties of ocimene in spite of the ease of autoxidation and of isomerisation.

Van Romburgh (60) was the first to isolate ocimene, the source being *Ocimum basilicum*. The density (.7916) was reported at two temperatures, but no temperature was specified for the refractive index. Assuming either of the temperatures used for the density measurements, the values 1.4848 and 1.4818 are obtained. Points corresponding to both values have been included in Fig. II. This ocimene

had a lower density than subsequent preparations by other workers, but its value is limited by the uncertainty in the refractive index. Moreover, Enklaar (61), who carried out extended investigations on ocimene and *allo*-ocimene, found rather different figures (.7958 and 1.4826) for ocimene which was most probably obtained from the same source.

Three subsequent isolations of ocimene are of interest here. Asahina (62) found .7949 and 1.4817 for material from *Evodia rutaecarpa*. Penfold (63) found .7946 and 1.4836 for ocimene from *Homoranthus flavescens*. Apart from van Romburgh's sample, this ocimene has the lowest density of those considered here, and has been chosen on that ground as the purest, although Penfold stated that the associated pinene was found difficult to remove. Another source of ocimene was found by Jones and Smith (64) in *Tagetes glandulifera*. The refractive index (1.4832) agrees well with the other samples, but the density (.7974) is slightly higher, probably owing to the presence of some limonene which was found to boil at the same temperature as ocimene at 30 mm. pressure and only slightly above ocimene at 3-4 mm.

The point for ocimene in Fig. I. is based on Penfold's values, but confirmation by the fractionation of ocimene in an efficient still is desirable. In attempting the purification of ocimene an important factor to be considered is the probable existence of *cis* and *trans* isomers. Two disadvantages inherent in the use of the high reflux ratios which are desirable when using high efficiency stills are accentuated in the distillation of ocimene. The lengthy period of distillation increases the opportunity for oxidative attack by air from adventitious leaks and also for the thermal isomerisation to *allo*-ocimene.

α-Phellandrene.

The sample of *α*-phellandrene $[\alpha]_D -177.4^\circ$ prepared by Hancox and Jones (65) is undoubtedly the purest described in the literature, since analysis showed the presence of 99.7 to 100% of conjugated dienes. This sample (0.8284 and 1.4702) has therefore been included in Fig. I. as the point for *α*-phellandrene. Samples of *α*-phellandrene considered to be pure by previous workers have had much higher densities and probably contained much cymene. For example, Richter (66) for *α*-phellandrene from *Eucalyptus dives* gave figures 0.8360, 1.4707 and $[\alpha]_D -115^\circ$.

β-Phellandrene.

Owing to the obvious impurity of the various samples of *β*-phellandrene which have been described in the literature it is not possible to fix the properties of this hydrocarbon with any certainty.

In 1904 Wallach and Beschke (67) separated a *β*-phellandrene concentrate from water fennel oil, but the constants (.8480 and 1.4766) did not show the marked exaltation of molecular refraction expected as a consequence of the conjugated double bonds, one of which is in the exocyclic position. Macbeth, Smith and West (68) described *β*-phellandrene (.8409 and 1.4778) from Canada balsam oil, and stated that it "may be assumed to be very pure." This showed a marked exaltation as expected, but the hydrogen absorption on catalytic hydrogenation of a very similar sample (69) from the same source, was only about 76% of the theoretical value. Either the sample contained impurities such as *β*-pinene (also present in Canada balsam oil), or cymene, or possibly some disproportionation of phellandrene to cymene and menthane took place under the influence of the catalyst.

Attempts have been made to prepare the phellandrenes by the removal of the hydrogen bromide from 1 : 2 dibromomenthane. Kondakov and Schindelmeiser (70), by this method obtained a mixture of hydrocarbons, including a fraction b.p. 175-180° (.8210 and 1.4647) from which they prepared two nitrosites similar to the β -phellandrene nitrosites, and they concluded that their product contained β -phellandrene. From a very similar experiment, Henderson and Schotz (71) obtained an oil, b.p. 172-174° of similar constants (.8232 and 1.4621) which, however, did not form a nitrosite or tetrabromide, and they concluded that their product was not a phellandrene, some rearrangement having taken place.

Berry (72) has recently described samples of β -phellandrene obtained by regeneration from the crystalline tetrabromide (73, 74), but it appears from consideration of the experimental details that the debromination product is not pure phellandrene, but a mixture of three or more substances. Two debromination experiments using magnesium in ether, are described, the first of which resulted in two fractions (a) (.8326 and 1.4843) and (b) (.8346 and 1.4804). Two fractions from other experiments are (c) (.8420 and 1.4819) and (d) (.8393 and 1.4836). These values are plotted in Fig. II., and from an examination of their relative positions it seems clear that at least three substances are involved. It appears that the debromination procedure is unsatisfactory for the preparation of β -phellandrene, possibly owing to the conjugated position of the double bonds to be introduced (c.f. limonene and terpinolene).

It is clearly not yet possible to fix even approximately the constants of β -phellandrene. On one hand, the high density samples of Wallach and Bieske and of Macbeth, Smith and West are known to be impure, and on the other hand the low density preparations from dibromomenthane do not appear to have been proved to contain β -phellandrene. Of Berry's samples (a), (b) and (d), it may be said that they show the very considerable exaltation expected for the β -phellandrene structure, but are undoubtedly heterogeneous. The regularity pointed out in the section entitled "Molecular Refraction of the Terpenes" would suggest that the point for β -phellandrene will lie close to that of Berry's sample (d).

In Fig. I. two points rather than one, have been included to represent β -phellandrene with the object of emphasising the unsatisfactory state of our knowledge. These are the Canada balsam phellandrene and Berry's sample (b), for which is recorded the highest rotation yet found for β -phellandrene.

For the preparation of pure β -phellandrene the most promising possibility would appear to be the fractionation in an efficient still of either *Pinus coulteri* (75) or *Pinus contorta* (76) turpentine, which are respectively 35-45% and "almost entirely" β -phellandrene. However, these are not produced commercially and there is perhaps a doubt in both cases as to which phellandrene is present (77).

α -Pinene.

Probably the purest α -pinene described to date is the sample prepared by Fuguitt, Stallcup and Hawkins (13), using a seventy-five (theoretical) plate still. The constants of this sample (.8542 and 1.4631) are in good agreement with those obtained by Savich and Goldblatt (78) for material purified in a forty (theoretical) plate still (.8553 and 1.4634). A sample of α -pinene of very similar constants (.8543 and 1.4628) was separated from the essential oil of *Calythrix tetragona* (15) in this laboratory by the use of a one metre Bower and Cooke type still (79) of

maximum efficiency of fifty-five (theoretical) plates. An examination of previous work on α -pinene reveals very considerable variation in the reported properties even for samples obtained by regeneration from the crystalline nitroschloride. Some of the earlier values, however, agree satisfactorily with those of Fuguitt, et al, which have been used to locate the point for α -pinene in Fig. I.

β -Pinene.

β -pinene also was purified very carefully by Fuguitt, Stallcup and Hawkins (13) and the reported constants (.8666 and 1.4763) have been used to locate the point for β -pinene in Fig. I. This terpene when purified by Goldblatt and Palkin (80), was found to have much the same values (.8672 and 1.4760) as did also a sample (.8668 and 1.4765) obtained in this laboratory from the oil of *Calythrix tetragona* (15). The good agreement between these three samples, each prepared from a different source, indicates a high degree of purity. Many of the values reported by earlier workers are greatly in error apparently owing to the presence of α -pinene and camphene due to insufficient rectification.

Sabinene.

Semmler (81) first separated sabinene from oil of savin and considered that no other terpenes were present. The constants of Semmler's sabinene (.8360 and 1.4638) were closely duplicated by another sample (.8358 and 1.4638) prepared from the same source by Auwers, Roth and Eisenlohr (8). In 1931 Richter, Wolff and Presting (82) fractionated the savin oil terpenes and obtained two principal sabinene fractions, No. 7 (.8358 and 1.4636) and No. 8 (.8358 and 1.4646). It is interesting to note that judging from the displacement of Richter's fraction No. 2 (.8398 and 1.4606) relative to fraction No. 7, it is likely that both α -thujene and α -pinene are also present in oil of savin.

The excellent agreement by various workers on the properties of sabinene from oil of savin, is not extended to sabinene isolated from other essential oils, which are more complex mixtures. Thus Padmanabhan and Jatkar (12) give .8470 and 1.4682 for sabinene from *Cupressus torulosa* oil which contains α -pinene, limonene and terpinene also. Closer agreement is shown by a sabinene fraction (.8380 and 1.4656) separated from Ceylon cardamon oil by Wallach (83).

Probably the most pure of these samples is Richter's fraction No. 7, and a point has been placed in Fig. I. corresponding to this. However, the examination of oil of savin in an efficient still to obtain a more accurate placing of this point is highly desirable.

Santene.

The point for santene in Fig. I. is based on santene (.8590 and 1.4644) obtained from sandalwood oil by Semmler (84). The constants of santene as reported by various workers (2) show fairly wide discrepancies, however.

α -Terpinene.

The case of α -terpinene illustrates clearly the state of confusion which may develop concerning the density and refractive index of a simple terpene hydrocarbon. Points representing a variety of the preparations of α -terpinene which are described in the literature have been included in Fig. II., and of these, two have been chosen for inclusion in Fig. I. also.

Wallach's method for the preparation of α -terpinene involves the action of concentrated sulphuric acid on turpentine and yields a product for which the properties .8530 and 1.4748 have been recorded (85). This terpinene is, however, contaminated with γ -terpinene, terpinolene, limonene, etc., and probably also the cineoles to which the high density and low refractive index may be attributed. A similar mixture containing a not particularly high proportion of α -terpinene is obtained by the action of acids on α -terpineol (86, 87, 88).

α -Terpinene (.8410 and 1.4883) prepared by Semmler's method (89) (the reduction of 2-chloro- $\Delta^1:3$ -p-menthadiene with sodium and alcohol) although described as "fairly homogeneous" has been shown to be a mixture of hydrocarbons (90).

The α -terpinene (.8397 and 1.4827) of Harries and Majima (91) obtained by the destructive distillation of the phosphate of 2-amino- Δ^3 -p-menthene has been described as "essentially" α -terpinene but nevertheless contained some γ -terpinene.

Auwers and Heyden (92) prepared α -terpinene b.p. 174.8°-175.4° (.8300 and 1.4762) by a synthetic method, the last stage of which involved decarboxylation of $\Delta^1:3$ -p-menthadiene-3-carboxylic acid. The density of this product is the lowest of the various α -terpinenes here mentioned and on this ground it may be regarded as more free from γ -terpinene, terpinolene and other dense impurities. Closely similar constants (.8304 and 1.4767) were later reported by Roth and Auwers (93) for another preparation by this method.

The preparation of α -terpinene by the removal of hydrogen chloride from terpinene dihydrochloride has been described a number of times. Of interest is the preparation of Wallach (94), who obtained an α -terpinene fraction (.8420 and 1.4768) of b.p. 179-181°. Auwers (92) for a fraction of similar boiling point found very similar properties. It is now clear, however, that α -terpinene boils at about 174° rather than 180°. Richter and Wolff (95) obtained by the action of aniline on terpinene dihydrochloride a mixture of hydrocarbons and by rectification probably more efficient than that used by earlier workers, separated an α -terpinene fraction (.8332 and 1.4746) of b.p. 173.5-174.8°. This gave a rich yield of terpinene nitrosite and is probably the purest α -terpinene yet described in the literature. Accepting this view, the preparations of Wallach and Auwers are then intermediate fractions containing a mixture of α - and γ -terpinene and possibly terpinolene. In agreement with this view is the fact that Gascoigne (96) found the lowest boiling fraction from the product of the treatment of terpinene dihydrochloride with aniline to contain the highest percentage (94%) of conjugated dienes. It is significant that the agreement in molecular refraction between Richters and Wolff's α -terpinene and pure α -phellandrene is very satisfactory.

In Fig. I., points representing Auwers' terpinene b.p. 174.8°-175.4° and also Richter and Wolff's α -terpinene have been included. It is clear, however, that neither sample is entirely pure and the inclusion of both points in Fig. I. emphasises the unsatisfactory nature of our knowledge of this hydrocarbon. In view of the importance of α -terpinene as a constituent of essential oils and as a product of a wide variety of reactions involving terpenes, efforts are being made in this laboratory to determine the true density and refractive index.

β -Terpinene.

β -Terpinene has not been found in essential oils, but it seems likely that it may be present in the complex mixtures boiling between 170° and 180° which are

found in some essential oils. In favour of this view is the occurrence in β -terpinene of the $\Delta^{1:7}$ double bond as in β -pinene, β -phellandrene, etc. Wallach (97) prepared β -terpinene and recorded the constants .8356 and 1.4741.

γ -Terpinene.

The physical constants of γ -terpinene have been settled with some degree of satisfaction. Richter and Wolff (98) separated from Ajowan oil by fractionation a γ -terpinene fraction which they regarded as pure and which had the properties .8450 and 1.4712. From oil of samphire the same authors (99) obtained a γ -terpinene of rather different constants (.8434 and 1.4754) but with a slight optical activity. By referring to Fig. II. it will be seen that the first of these preparations has an observed molecular refraction less than that calculated for a monocyclic terpene free from conjugation effects. On the other hand, the sample from oil of samphire must contain some optically active impurity. Limonene and β -phellandrene are the highest boiling of the optically active terpenes, but it is obvious that the presence of limonene in the γ -terpinene from samphire oil could not account for the relative position of the two points in Fig. II. Assuming that β -phellandrene is truly represented by Berry's sample (d), then the presence of a proportion of β -phellandrene (a constituent of samphire oil) in the γ -terpinene would account for its position and optical activity. Results from the dehydration of terpinen-4-ol as yet unpublished (35) closely confirm Richter and Wolff's values (for the Ajowan oil sample) and a corresponding point has been included in Fig. I. Other preparations of γ -terpinene have been described, but owing to the meagre details available or obvious impurities they do not warrant consideration.

Terpinolene.

It would appear that the purest terpinolene yet described in the literature is that prepared by Henry and Paget (100) by the debromination of pure terpinolene tetrabromide by the use of zinc dust in an alcohol ether mixture. The relatively high purity of this sample (.8560 and 1.4864) was proved by reconversion to crystalline tetrabromide in 88% yield. Henry and Paget's constants have been used to place the point for terpinolene in Fig. I.

In Fig. II. points have been plotted for a number of other preparations of interest. Semmler and Schossberger (101) also prepared terpinolene by the action of zinc dust on the tetrabromide in alcohol ether mixture but with very different results, the resulting hydrocarbon having the constants .8500 and 1.4818. A product of somewhat similar constants (.8510 and 1.4773) was obtained by Richter (102) by the action of sulphuric acid on pinene and, judging from the method of preparation and the constants, it was probably contaminated with γ -terpinene at least. Haworth and Perkin and Wallach (103) carried out the debromination by the action of zinc in acetic acid, but in this case the constants (.8658 and 1.4720) suggest the presence of a more dense impurity, possibly an oxygenated substance such as cineole. In contrast to these preparations, terpinolene isolated from *Pinus sylvestris* (104) turpentine had properties (.8583 and 1.4839) in fair agreement with Henry and Paget's preparation. Terpinolene should be readily separated in a pure state from the products of the dehydration of α -terpineol by some method which does not also give rise to γ -terpinene, since other possible products boil at a much lower temperature than does terpinolene.

α -Thujene.

The constants of α -thujene are subject to considerable uncertainty owing to the probability that even the purest samples yet described have been contaminated with either α -pinene or β -thujene. For a natural α -thujene contaminated with some α -pinene the constants (.8316 and 1.4524) have been recorded by Simonsen (105). For α -thujene prepared by the thermal decomposition of the methyl xanthate of thujyl alcohol Tschugaev and Fomin found .8261 and 1.4493 (106). β -Thujene is also produced in this decomposition, and as the α -thujene was purified by fractionation only, it is possible that the whole of the β -thujene was not removed. A point for β -thujene (106) (.8168 and 1.4449) has been included in Fig. II. The points for natural and "synthetic" α -thujene both lie close to a line joining the points for α -pinene and β -thujene, and consequently the point for pure α -thujene must also lie on or close to this line. Simonsen's α -thujene was known to contain a denser impurity, i.e., α -pinene, and consequently the constants of the preparation of Tschugaev and Fomin, though it may also have been impure, have been used to place tentatively the point for α -thujene in Fig. I. Other samples of α -thujene obtained from thujyl alcohol have been described, but have all been less dense than the one considered above and probably contained more β -thujene.

Birch and Earl (107) have shown that the "origanene" fraction of *Eucalyptus dives* oil contains some α -thujene and α -pinene. The purest sample (.8314 and 1.4522) of α -thujene which was obtained from this source closely resembled Simonsen's sample and likewise contained some α -pinene. Preliminary experiments in this laboratory have shown that α -pinene and α -thujene may be separated by the use of a high efficiency still and the preparation of pure α -thujene will be attempted shortly.

The author would appreciate from those interested, communications or copies of published papers relating to the physical properties of the terpenes (and other constituents of essential oils) with the object of extending the list of selected density and refractive index values and of incorporating new information as advances are made.

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