

THE OCCURRENCE OF SYLVESTRENE.¹

By B. Sanjiva Rao and John Lionel Simonsen.

It has been shown in previous communications² that it is a characteristic property of *d*- Δ^3 -carene and *d*- Δ^4 -carene to yield on treatment with hydrogen chloride a mixture of sylvestrene dihydrochloride and dipentene dihydrochloride, the bicyclic system being disrupted by fission of the *cyclopropane* ring. To students of terpene chemistry the occurrence in nature of the hydrocarbon sylvestrene has always appeared to be somewhat anomalous because it is the only naturally occurring terpene derived from *m*-cymene, all the other members of the group being *p*-cymene derivatives.

Although sylvestrene has been reported present in a considerable number of oils,³ it occurred to us that the hydrocarbon may not actually exist as such in nature, but that it arises during the process of identification and purification. A careful survey of the somewhat extensive literature appeared to us to offer sufficient support for this hypothesis to warrant its further investigation.

Sylvestrene was first isolated by Atterberg⁴ from Swedish pine-tar oil derived from *Pinus sylvestris*, and its constitution was subsequently established by the investigations of Wallach,⁵ Baeyer,⁶ and Perkin with his collaborators.⁷ For the identification of the hydrocarbon, Atterberg⁸ treated the appropriate fraction of the oil with hydrogen chloride when sylvestrene dihydrochloride, m.p. 72°, was readily obtained. This method appears to have been adopted by all subsequent investigators. It is not without significance that Atterberg⁹ in one experiment could obtain only a dihydrochloride, m.p. 50° (the melting point of dipentene dihydrochloride), since it has been shown that in some cases *d*- Δ^3 -carene on treatment with hydrogen chloride yields dipentene dihydrochloride in larger quantity than

¹ In abbreviated form, this paper was published in *The Journal of the Chemical Society*, 1925, 127, 2494.

² *J. Chem. Soc.*, 1920, 117, 571; 1922, 121, 2294; *Ind. For. Rec.*, 1924, X, 161.

³ *Beilstein* (Fourth edition), V, 125.

⁴ *Ber.*, 1877, 10, 1023.

⁵ *Annalen*, 1885, 230, 240; 1887, 289, 24.

⁶ *Ber.*, 1894, 27, 1915; 1898, 31, 2067.

⁷ *J. Chem. Soc.*, 1907, 91, 482; 1908, 93, 1888; 1913, 103, 1230, 2229.

⁸ *loc. cit.*, 1208.

⁹ *loc. cit.*, 1208.

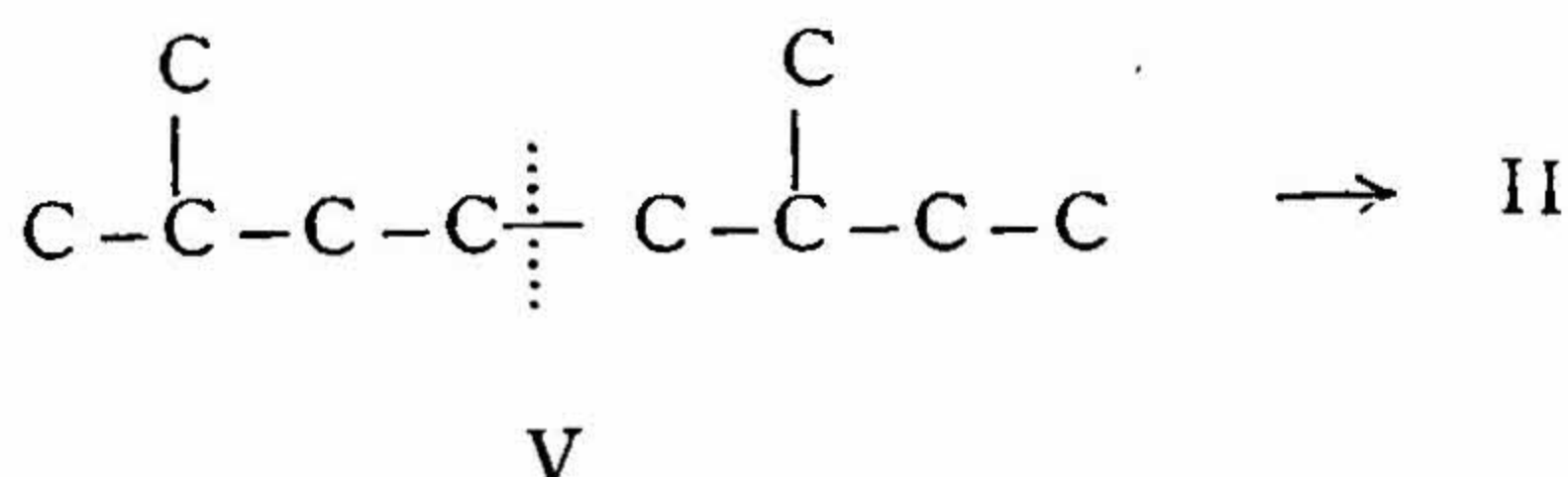
sylvestrene dihydrochloride and the former therefore crystallises on cooling. Reference to the formation of dipentene dihydrochloride during the purification of sylvestrene is also made by Bertram and Wahlbaum,¹ who separated the latter only by prolonged fractional crystallisation and were unable to establish the presence of dipentene in the original oil by the direct preparation of its derivatives.

Perhaps the most characteristic reaction of sylvestrene, a reaction not shown by any other monocyclic terpene, is the deep blue colour developed by an acetic anhydride solution of the hydrocarbon when treated with a drop of concentrated sulphuric acid. The absence of this reaction in the case of the crude terpene separated from the oil of *P. sylvestris* was observed by Wallach, but in spite of this he was inclined to regard the presence of the terpene in the original oil as being established. Bertram and Wahlbaum² working with Swedish pine-needle oil from *P. sylvestris* obtained a faint violet coloration and a similar observation was made by Umney³ working with Scotch pine-needle oil. Morner,⁴ in a paper which does not appear to have been abstracted, has made a full and careful investigation of the colour reactions of the various fractions of the oil from *P. sylvestris*. He found that all fractions of the oil boiling below 185° gave a transient violet coloration, and that an indigo-blue colour was given only by the sesquiterpene fraction which is known to contain cadinene. He specifically mentions that the blue colour shown by certain samples of the *whole* oil from *P. sylvestris* needles cannot be due to the presence of sylvestrene. In a later communication⁵ he established the same facts in the case of the oils derived from *P. sylvestris*, *P. Pumilio* and *P. Abies* of varying origins. The evidence, therefore, appeared to be against the existence of sylvestrene in these oils, and it is significant that a transient purple or violet coloration is characteristic of carene.

We have submitted the oil from *P. sylvestris* to a very careful examination. The oil used by us was obtained from A. Carlsson's Enkas Tallbarrsolye Fabrik, Jönköping, Sweden, and was of undoubted authenticity. We have been quite unable to find any trace of sylvestrene in the oil although we have found it to contain d - Δ^3 -carene in considerable quantity.

This hydrocarbon was identified by the preparation of the characteristic nitrosate (decomposing at 147.5°) and also by the formation of sylvestrene dihydrochloride, m.p. 72°. d - Δ^3 -carene was

union of two isoprene molecules, with subsequent condensation to the dipentene (*p*-cymene) type (II).



This proposal, owing to its simplification of sesquiterpene chemistry, has obviously much to recommend it; but it would clearly be inapplicable if sylvestrene occurred in nature. The proof offered in this note of the absence of sylvestrene in the oils from *P. sylvestris* and *P. Pumilio* makes it improbable that this terpene occurs in other oils and thus lends support to Ingold's suggestion.

We wish to take this opportunity of expressing our thanks to Professor V. Henriques of the University of Copenhagen for obtaining for us the sample of the oil from *P. sylvestris*, without which it would not have been possible for us to have undertaken this investigation.

EXPERIMENTAL.

SECTION I.—THE OIL FROM 'PINUS SYLVESTRIS.'

The oil used in these experiments was pale yellow, and after drying over anhydrous magnesium sulphate had the following constants:— d_{30}^{30} 0.8661, n_D^{30} 1.4729, $[\alpha]_D^{30}$ + 13.2°, acid value 0.28, saponification value 6.7, saponification value after acetylation 15.0.

A quantity of the oil was distilled under diminished pressure (100 mm.) using a four-pear Young still-head, when the following fractions were obtained:—

TABLE I.

No.	B.P. (100 mm.)	d_{30}^{30}	n_D^{30}	$[\alpha]_D^{30}$	Yield per cent.
1	up to 105°	0.8546	1.4661	+ 16.0°	45.3
2	105-115°	0.8556	1.4690	+ 11.8°	31.0
3	115-140°	0.8724	1.4766	+ 4.9°	6.6
4	above 140°	15.3

The first two fractions were repeatedly refractionated at the ordinary pressure (684 mm.) a fractionating column being employed when ultimately the following fractions resulted:—

TABLE II.

No.	B.P. (684 mm.)	d_{30}^{30}	n_D^{30}	$[\alpha]_D^{30}$	Yield per cent. of original oil
I	153-157°	0.8553	1.4637	+ 20.0°	17.4
II	157-161°	0.8553	1.4656	+ 16.7°	18.7
III	161-167°	0.8556	1.4676	+ 11.7°	30.0
IV	167-176°	0.8573	1.4711	+ 8.0°	8.1

Fraction I.—This fraction consisted of nearly pure α -pinene the presence of this hydrocarbon being established by the preparation of the nitrosochloride decomposing at 107° and the nitrolpiperide, m.p. 118-119°.

Fraction II.—This fraction was found to consist of a mixture of α -pinene, β -pinene and d - Δ^3 -carene. The presence of α -pinene was proved by the preparation of the derivatives mentioned above and by oxidation to pinonic acid (semicarbazone decomposing at 207°).

β -pinene was shown to be present in very small amount by oxidation to nopinic acid identified by the method of mixed melting point. The presence of d - Δ^3 -carene was established by the preparation of the nitrosate, which after recrystallisation decomposed at 147.5° and was found to be identical in every way with a specimen of the nitrosate from another source. On treatment of a portion of the oil with hydrogen chloride, d -sylvestrene dihydrochloride was obtained which melted at 72°, and this melting point was unaltered on admixture with a specimen of the d -dihydrochloride from another source.

Fraction III.—This fraction consisted essentially of d - Δ^3 -carene (nitrosate decomposed 147.5°; d -sylvestrene dihydrochloride, m.p. 72°). When oxidised in acetone solution with potassium permanganate, only a very small trace of a keto-acid was formed and this was identified as pinonic acid. No indication was obtained of the presence of either Δ^4 -carene or β -pinene. When dissolved in chloroform and treated with a chloroform solution of bromine, one molecule of bromine was absorbed, the fairly sharp end-point indicating the probable absence of any but bicyclic terpenes in this fraction of the oil. When dissolved in acetic anhydride and treated with a drop of concentrated sulphuric acid a transient purple coloration was observed.

Fraction IV.—This fraction consisted of nearly pure *d*- Δ^3 -carene.

Fractions 3 and 4 (Table I).—These two fractions were combined and after treatment with an alcoholic solution of potassium hydroxide to hydrolyse any esters present the residual oil was carefully fractionated, when two main fractions were obtained:—(a) b.p. 167–173°/683 mm. which was identified as *d*- Δ^3 -carene (d_{30}^{30} 0.8573, n_D^{30} 1.471, nitrosate, decomposed 147.5°); and (b) a viscid yellow oil b.p. 185–187°/100 mm. This after distillation over sodium had the constants d_{30}^{30} 0.9082, n_D^{30} 1.499, $[\alpha]_D^{30}$ 24.0°. When dissolved in acetic anhydride and treated with a drop of concentrated sulphuric acid, an emerald green colour was obtained which changed into a deep indigo-blue. This colour reaction was due to *l*-cadinene, the presence of which was established by the preparation of the dihydrochloride m.p. 118°, this melting point not being depressed on admixture with an authentic specimen. In chloroform solution (5 per cent.) $[\alpha]_D^{30}$ —38.1° was observed, which is in good agreement with the value found by Wallach¹— $[\alpha]_D$ (36.8°) for this substance.

Acids.—The alkaline solution obtained by the hydrolysis of the esters present in Fractions 3 and 4 (see above) was concentrated until free from alcohol, acidified with dilute sulphuric acid and distilled in steam, the acids which passed over being collected in two fractions and converted into the silver salts.

Fraction I.—

0.045 gave 0.0166 Ag.	Ag = 35.5 per cent.
$C_{12}H_{23}O_2Ag$ requires	Ag = 35.2 ,,

Fraction II.—

0.039 gave 0.012 Ag.	Ag = 30.7 per cent.
$C_{14}H_{27}O_2Ag$ requires	Ag = 29.8 ,,
$C_{16}H_{31}O_2Ag$,,	Ag = 32.3 ,,

These results would appear to indicate the presence in the oil of lauric acid and a mixture of myristic and palmitic acids.

SECTION II.—THE OIL FROM 'PINUS PUMILIO.'

The oil, of which only slightly over one hundred grams was available for examination, was dried over anhydrous magnesium sulphate and the constants determined. d_{30}^{30} 0.9221, n_D^{30} 1.4831,

¹ *Annalen*, 1899, 252, 150.

$[\alpha]_D^{30} -9.3^\circ$, acid value 7.5, saponification value 31.5, saponification value after acetylation 89.6. The density of the oil was considerably higher than has been previously observed for samples of the oil, a fact probably due to the oil containing a large quantity of resinous material which remained in the distilling flask on fractionation.

Before fractionation, the oil was treated with an alcoholic solution of potassium hydroxide to remove the free acids and to hydrolyse any esters present. It was then distilled under diminished pressure (100 mm.) and the following fractions taken:—

TABLE III.

No.	B.P. (100 mm.)	Yield per cent.
I	95-105°	51.6
II	105-115°	3.7
III	115-140°	2.5
IV	140-170°	7.9
V	above 170°	9.0

The first three fractions were repeatedly redistilled at the ordinary pressure (685 mm.) when the following fractions finally resulted:—

TABLE IV.

No.	B.P. (685 mm.)	d_{30}^{30}	n_D^{30}	$[\alpha]_D^{30}$	Yield per cent. (calculated on the original oil)
I	155-160°	0.8512	1.4648	-12.6°	16.5
II	160-163°	0.8529	1.4675	-14.7°	14.3
III	163-166°	0.8530	1.4691	-15.7°	7.0
IV	166-175°	0.8561	1.4711	-21.3°	8.0

An examination of these fractions has shown Fraction I to consist essentially of α -pinene (nitrosochloride, decomposed 107° ; nitrolpiperide, m.p. $118-119^\circ$); Δ^3 -carene was absent since no crystalline nitrosate was obtained. Fractions II and III were found to contain α -pinene and Δ^3 -carene since both fractions gave a nitrosochloride (decomposed 107°) and a nitrosate (decomposed 147.5°). It was not determined whether Δ^3 -carene was present in the dextro or laevorotatory form.

Owing to the small quantity of material available, no attempt was made to examine these fractions for β -pinene, the presence of this hydrocarbon in the oil from *P. Pumilio* having been established by previous workers.

Fraction IV consisted mainly of Δ^3 -carene, an excellent yield of the nitrosate being obtained. When dissolved in acetic anhydride and treated with a drop of strong sulphuric acid a transient purple coloration was observed, but the blue coloration characteristic of sylvestrene could not be obtained.

Fractions IV and V (Table III) which contained esters and sesquiterpene derivatives were not investigated.

*Department of Organic Chemistry,
Indian Institute of Science,
Bangalore.*

[Accepted, 10-11-25.]