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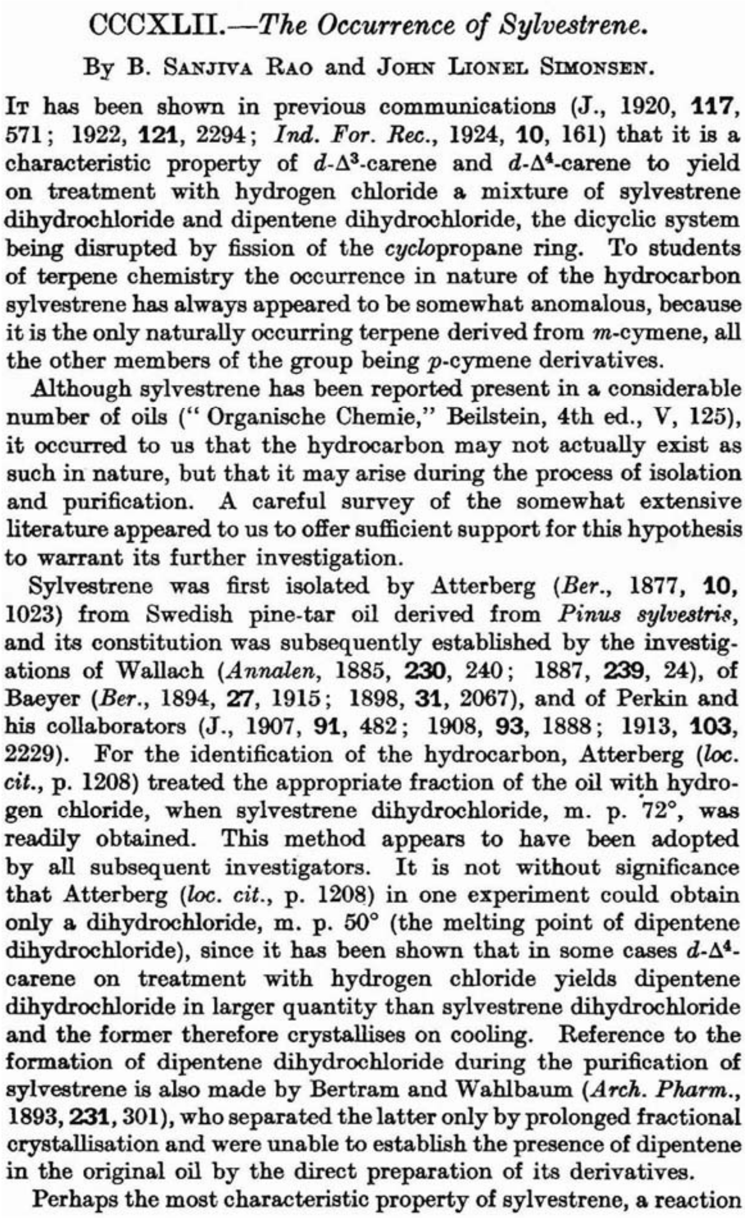
CCCXLII. - The occurrence of sylvestrene
B. S. Rao, and J. L. Simonsen



CCCXLII.—*The Occurrence of Sylvestrene.*

By B. Sanjiva Rao and John Lionel Simonsen.

It has been shown in previous communications (J., 1920, **117**, 571; 1922, **121**, 2294; *Ind. For. Rec.*, 1924, **10**, 161) 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 dicyclic system being disrupted by fission of the *cyclo*propane 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 (" Organische Chemie," Beilstein, 4th ed., V, 125), it occurred to us that the hydrocarbon may not actually exist as such in nature, but that it may arise during the process of isolation 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 Atterberg (*Ber.*, 1877, **10**, 1023) from Swedish pine-tar oil derived from *Pinus sylvestris*, and its constitution was subsequently established by the investigations of Wallach (*Annalen*, 1885, **230**, 240; 1887, **239**, 24), of Baeyer (*Ber.*, 1894, **27**, 1915; 1898, **31**, 2067), and of Perkin and his collaborators (J., 1907, **91**, 482; 1908, **93**, 1888; 1913, **103**, 2229). For the identification of the hydrocarbon, Atterberg (*loc. cit.*, p. 1208) 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 Atterberg (*loc. cit.*, p. 1208) 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^4-carene on treatment with hydrogen chloride yields dipentene dihydrochloride in larger quantity than 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 (*Arch. Pharm.*, 1893, **231**, 301), 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.

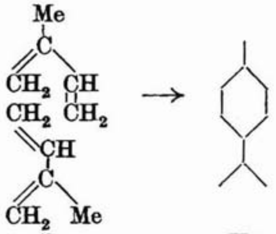
Perhaps the most characteristic property of sylvestrene, a reaction not shown by any other monocyclic terpene, is the deep blue colour developed by an acetic anhydride solution of the hydrocarbon when treated with a drop of concentrated sulphuric acid. The absence of this reaction in the case of the 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 Wahlbaum (*loc. cit.*, p. 299), working with Swedish pine-needle oil from *P. sylvestris*, obtained a faint violet coloration, and a similar observation was made by Umney (*Pharm. J.*, 1895, **55**, 167), working with Scotch pine-needle oil. Mörner (*Svensk Farm. Tids.*, 1909, 317), 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 communication (*ibid.*, p. 1913), 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.

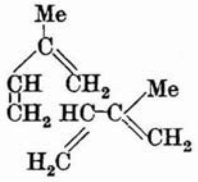
We have submitted the oil from *P. sylvestris* to a very careful examination. The oil used by us was obtained from A. Carlsson's Enkas Tallbarrolye Fabrik, Jönköping, Sweden, and was of undoubted authenticity. We have been quite unable to find any trace of sylvestrene in the oil, although we have found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

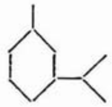
This hydrocarbon was identified by the preparation of the characteristic nitrosate (decomposing at 147·5°) and also by the formation of sylvestrene dihydrochloride, m. p. 72°. d-Δ^3-Carene was found to be present in all the fractions of the oil boiling below 180° (more than 70% of the total distillate), except in that distilling at 153—157°/684 mm. (see p. 2497). From the sesquiterpene fraction (b. p. 185—187°/100 mm.) l-cadinene was separated as the dihydrochloride, and this fraction of the oil gives the well-known colour reactions associated with this sesquiterpene. We consider ourselves justified in stating that the oil from *P. sylvestris* of Swedish origin contains d-Δ^3-carene and does not contain d-sylvestrene, the previous isolation of d-sylvestrene from the oil being due to the decomposition of the dicyclic terpene.

We have also examined a small sample of the oil from *P. pumilio*, of unknown origin, obtained by purchase from Messrs. Boake, Roberts and Co. The oil was considerably resinified and therefore had a high density; like the oil from *P. sylvestris*, it was found to be free from sylvestrene whilst containing Δ^3-carene. This terpene thus appears to occur somewhat frequently in nature, and in view of its ready identification by means of the sparingly soluble nitrosate, its detection presents little difficulty.*

The probable absence of sylvestrene from natural terpenes is not without theoretical importance. If, as is generally assumed, the terpenes and sesquiterpenes arise from polymerisation of two or more molecules of isoprene, the occurrence of sylvestrene would offer no difficulty (I, II, III, and IV).

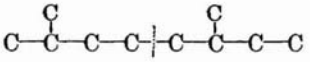






(I.) (II.) (III.) (IV.)

Recently, however, Ingold (*Annual Reports*, 1924, **21**, 102) has suggested that the geraniol chain (V) may more correctly be regarded as the first stage in the union of two isoprene molecules, with subsequent condensation to the dipentene (*p*-cymene) type (II).

(V.) 

$$\text{C}-\overset{\text{C}}{\overset{|}{\text{C}}}-\text{C}-\text{C}\,\vdots\,\text{C}-\overset{\text{C}}{\overset{|}{\text{C}}}-\text{C}-\text{C} \longrightarrow \text{(II.)}$$

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

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* Aschan (A., 1919, i, 336) has stated that during an investigation of Finnish turpentine he succeeded in isolating a new hydrocarbon, b. p. 163—165°, which, since it yielded pinene nitrosochloride, was closely related to α-pinene. We have been able to consult this paper in abstract only, but we venture to suggest that in all probability he was dealing with a mixture of α-pinene and Δ^3-carene, which are very difficult to separate.

which it would not have been possible for us to undertake this investigation.

EXPERIMENTAL.

Section I. The Oil from Pinus sylvestris.

The oil used in these experiments was pale yellow in colour and after drying over anhydrous magnesium sulphate had the following constants: $d_{30^\circ}^{30^\circ}$ 0·8661, $n_D^{30^\circ}$ 1·4729, $[\alpha]_D^{30^\circ}$ + 13·2°, acid value 0·28, saponification value 6·7, saponification value after acetylation 15·0.

A quantity of the oil was subjected to a prolonged systematic fractionation using a four-pear Young still-head, the distillation being carried out at first under diminished pressure and finally at the ordinary pressure, when the following fractions were obtained:

TABLE I.

No.	B.p. (684 mm.).	$d_{30^\circ}^{30^\circ}$.	$n_D^{30^\circ}$.	$[\alpha]_D^{30^\circ}$.	Yield % 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 consisted 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 points. 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 m. p. 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, decomp. 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 dicyclic 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.

During the distillation of the oil a considerable fraction was obtained which distilled above 115°/100 mm.; after treatment with alcoholic potassium hydroxide solution 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 ($d_{30^\circ}^{30^\circ}$ 0·8573, $n_{\mathrm{D}}^{30^\circ}$ 1·471; nitrosate, decomp. 147·5°), and (*b*) a viscid, yellow oil, b. p. 185—187°/100 mm. This after distillation over sodium had the constants $d_{30^\circ}^{30^\circ}$ 0·9082, n_{D}^{30} 1·499, $[\alpha]_{\mathrm{D}}^{30^\circ} + 24{\cdot}0^\circ$. When it was dissolved in acetic anhydride and treated with a drop of concentrated sulphuric acid, an emerald-green colour was obtained which changed to deep indigo-blue. This colour reaction was due to the presence of *l*-cadinene, the presence of which was established by the preparation of the dihydrochloride, m. p. 118°; and this m. p. was not depressed on admixture with an authentic specimen. In chloroform solution (5%), $[\alpha]_{\mathrm{D}}^{30^\circ} = - 38{\cdot}1^\circ$, which is in good agreement with the value found by Wallach ($[\alpha]_{\mathrm{D}} - 36{\cdot}8^\circ$) (*Annalen*, 1899, **252**, 150) for this substance.

Section II. The Oil from Pinus pumilio.

The oil, of which only slightly more than 100 g. were available for examination, was dried over anhydrous magnesium sulphate and the constants were determined: $d_{30^\circ}^{30^\circ}$ 0·9221, $n_{\mathrm{D}}^{30^\circ}$ 1·4831, $[\alpha]_{\mathrm{D}}^{30^\circ}$ $- 9{\cdot}3^\circ$, acid value 7·5, saponification value 31·5, saponification value after acetylation 89·6. The density of the oil was considerably higher than had been previously observed for samples of this oil, a fact probably due to the oil containing a large quantity of resinous material, which remained behind in the distilling flask on fractionation.

After the separation of the portion distilling above 140°/100 mm., the oil * was fractionated at the ordinary pressure, when the following fractions were obtained :—

TABLE II.

No.	B.p. (685 mm.).	$d_{30^\circ}^{30^\circ}$.	$n_{\mathrm{D}}^{30^\circ}$.	$[a]_{\mathrm{D}}^{30^\circ}$.	Yield % of 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	0·853	1·4691	−15·7	7·0
iv	166—175	0·8561	1·4711	−21·3	8·0

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* Prior to distillation, the oil was treated with an alcoholic solution of potassium hydroxide to remove the free acids and to hydrolyse any esters.

An examination of these fractions has shown *fraction* (*i*) to consist essentially of α-pinene (nitrosochloride, decomp. 107°; nitrolpiperide, m. p. 118—119°); Δ^3-carene was absent, since no crystalline nitrosate was obtained. *Fractions* (*ii*) and (*iii*) contained α-pinene and Δ^3-carene,* since both fractions gave a nitrosochloride (decomp. 107°) and a nitrosate (decomp. 147·5°). 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 it was dissolved in acetic anhydride and treated with a drop of concentrated sulphuric acid, a transient purple coloration was observed, but the blue coloration characteristic of sylvestrene could not be obtained.

The higher-boiling fractions of the oil were not examined.

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