

# LXI.—*The Constituents of Indian Turpentine from Pinus longifolia, Roxb. Part I.*

By JOHN LIONEL SIMONSEN.

THE manufacture of turpentine in India from the oleo-resin of *Pinus longifolia*, Roxb., is now an established industry, and large quantities of the oil are distilled in the Government factories at Jallo in the Punjab and Bareilly in the United Provinces. The oil, whilst quite suitable for the majority of technical purposes, is regarded as inferior to American turpentine, owing to the residue which it leaves on evaporation and to its proneness to oxidation.

The constituents of Indian turpentine have already formed the subject of several investigations (Rabak, *Pharm. Rev.*, 1905, **23**, 229; Schimmel's *Bericht*, April, 1906, 66; October, 1911, 93; *Bull. Imp. Inst.*, 1911, **9**, 8; Robinson, P., 1911, **27**, 247; Singh, *Ind. For. Rec.*, 1912, **4**, Pt. I), which have established the presence of *l*- $\alpha$ -pinene,  $\beta$ -pinene, a terpene yielding sylvestrene hydrochloride when treated with hydrogen chloride, and a sesquiterpene. Although in the literature it is definitely stated that sylvestrene is present (compare Parry, "Essential Oils," Vol. I, p. 18), yet Robinson (*loc. cit.*), to whom we owe the most careful investigation of the oil that has been made up to the present, drew the conclusion that the fraction previously assumed to contain sylvestrene in all probability contained some isomeric terpene, which on treatment with hydrogen chloride yielded sylvestrene hydrochloride. He also suggested that dipentene was probably present.

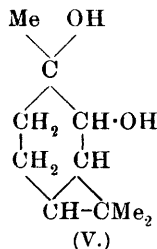
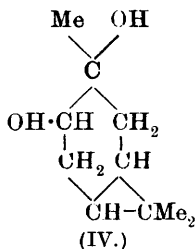
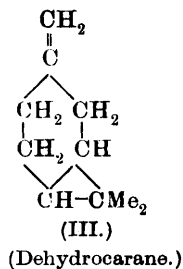
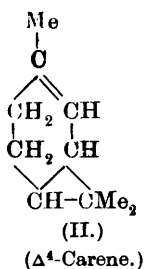
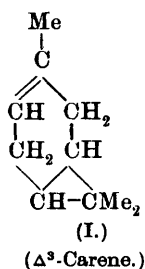
In view of the above results, it appeared to the author desirable that a careful re-examination of the constituents of Indian turpentine should be made, and the results so far obtained form the subject of this communication.

The oil used was distilled at the Government turpentine factory at Jallo, and was specially collected under the supervision of Mr. A. J. Gibson, Indian Forest Service, the officer in charge of the factory. It was carefully sealed up immediately after distillation in five-gallon drums, and prior to use it was dried for some days over anhydrous magnesium sulphate.

On careful fractional distillation, the presence of the following constituents was definitely proved: *l*- $\alpha$ -pinene,  $\beta$ -pinene, a new bicyclic terpene, for which the name *d-carene* is proposed, and a tricyclic sesquiterpene, *longifolene*.

The hydrocarbon, *d*-carene, which is without doubt identical with the hydrocarbon described by Robinson (*loc. cit.*), is an oil

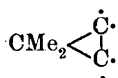
boiling at 168—169°/705 mm., and possessing a characteristic and curious, sweet odour. The constitution of this new terpene was determined by investigating its behaviour on treatment with hydrogen chloride and on oxidation with potassium permanganate. When treated in ethereal solution with hydrogen chloride, an oily hydrochloride was obtained, which partly solidified on cooling in a freezing mixture. The solid was found to be pure *d*-sylvestrene hydrochloride melting at 72°, whilst the terpene obtained from the liquid hydrochloride on removal of the hydrogen chloride in the usual manner (see p. 575) was found to be a mixture of sylvestrene and dipentene. The latter was identified by means of the tetrabromide after removing the greater part of the sylvestrene by treatment with potassium dichromate and sulphuric acid in the manner suggested by Baeyer (*Ber.*, 1894, **27**, 810, 3485). The formation of a mixture of sylvestrene and dipentene hydrochlorides is most simply explained if it is assumed that the new terpene is represented by one of the three following formulæ (I, II, or III),



since it is obvious that a bicyclic terpene possessing one of these structures would, on fission of the *cyclopropane* ring, yield a mixture of the hydrochlorides of the monocyclic terpenes.

Further evidence in support of the above view was furnished by a study of the products formed on oxidation with potassium permanganate. When oxidised in the presence of alkali in ice-cold solution, the main product of the oxidation was found to be a *glycol*,  $\text{C}_{10}\text{H}_{18}\text{O}_2$ , melting at 69—70°. This glycol does not

appear to contain a primary alcohol group, since, in benzene solution, it does not react with phthalic anhydride, and it follows, therefore, that *d*-carene cannot be represented by formula III, and that the glycol must have either formula IV or V. All attempts to convert the glycol into a ketone by oxidation with chromic acid were unsuccessful, the reaction proceeding apparently abnormally with the formation of oils of high boiling point, from which nothing crystalline could be isolated. The alkaline liquid from which the glycol had been separated was acidified, and the acids formed during the oxidation carefully examined. The main product was a viscous oil, but two crystalline acids were obtained. Owing to the small yield, one of these, melting at 137°, could not be identified, but the second acid was found to be dimethylmalonic acid, thus proving definitely the presence of the grouping



in *d*-carene.

In the light of these observations, it appeared desirable to attempt to isolate caronic acid, and *d*-carene was therefore oxidised with potassium permanganate in the manner adopted by Baeyer and Ipatiev (*Ber.*, 1896, **29**, 2796) for the preparation of this acid from carone. The product of the oxidation was a viscous oil, from which nothing crystalline separated, and evidently did not contain any *cis*-caronic acid, but, on conversion into the ammonium salt, a small quantity of a crystalline salt was obtained, which was only sparingly soluble in cold water, and crystallised in glistening prisms. On acidification, an acid crystallising in prisms and melting at 212—213° was obtained, and there can be no doubt that this was *trans*-caronic acid, which is stated by Baeyer and Ipatiev to melt at this temperature (see p. 577).

So far as the author is aware, *d*-carene is the first naturally occurring terpene which has been found to contain the carane ring, and is therefore of more than usual interest. It has not been found possible to decide whether formula I or II correctly represents the structure of this terpene, and it does not appear unlikely that, as is assumed to be the case with sylvestrene, the hydrocarbon may be a mixture of the two isomerides. The molecular refraction was found to be 44.22, which agrees well with that calculated (44.19) for a compound containing a *cyclohexane* and a *cyclopropane* ring. The fact that the molecular refraction is practically normal points to the absence of conjugation of a double bond with the *cyclopropane* ring and renders it probable that *d*-carene is represented by formula I (*d*- $\Delta^3$ -carene). It is hoped to prepare

synthetically the hydrocarbon represented by formula II ( $\Delta^4$ -carene), and experiments in this direction are in progress.

The sesquiterpene for which the name *longifolene* is proposed has up to the present only been cursorily examined. It yields very beautiful derivatives with hydrogen chloride, hydrogen bromide, and hydrogen iodide, and from a consideration of its molecular refraction ( $M=64.15$ ) it is evidently tricyclic.

### EXPERIMENTAL.

The oil used for these experiments was reddish-brown, and, after drying over magnesium sulphate, had the following constants:  $D_{30}^{30}$  0.8717,  $n_D^{30}$  1.4725,  $\alpha_D -2.38^\circ$ , acid value 2.4.

A large quantity was submitted to a careful fractional distillation under diminished pressure, using a twelve-pear Young still-head, when it was readily separated into the following three fractions: up to  $118^\circ/200$  mm. (31 per cent.),  $118-130^\circ/200$  mm. (47.6 per cent.),  $149-155^\circ/36$  mm. (10.2 per cent.); loss and residue (by difference), 11.2 per cent.

The fractions boiling below  $130^\circ/200$  mm. were carefully refractionated under the ordinary pressure, and were divided into two main fractions, *A* distilling at  $155-167^\circ/706$  mm. (60.8 per cent.) and *B* at  $167-171^\circ/706$  mm. (14.8 per cent.). Fraction *A* consisted mainly of  $\alpha$ - and  $\beta$ -pinene, and a pure fraction of *l*- $\alpha$ -pinene was isolated boiling at  $153-154^\circ/700$  mm. and possessing the following constants:  $D_{27}^{27}$  0.8525,  $n_D^{28}$  1.4625,  $\alpha_D -34^\circ$ , which agree well with those usually found for this hydrocarbon. The identity was further confirmed by the formation of  $\alpha$ -pinonic acid on treatment with potassium permanganate in the usual manner. The presence in fraction *A* of  $\beta$ -pinene was proved by the isolation of nopinic acid (m. p.  $128^\circ$ ) from the products of the oxidation with potassium permanganate in the usual manner.

### *d*-Carene ( $d\text{-}\Delta^3$ - or $\text{-}\Delta^4$ -Carene).

The fraction *B* (see above) was found on repeated fractionation to yield an oil, which boiled quite constantly at  $168-169^\circ/705$  mm.,  $123-124^\circ/200$  mm. This hydrocarbon, for which the name *d*-carene is proposed, was found to have the following constants:  $D_{30}^{30}$  0.8586,  $n_{30}$  1.469,  $\alpha_D +7.69^\circ$ .  $M=44.23$ , calc. for  $C_{10}H_{16}^{\square}=43.5$ , which, with the increment for the presence of a cyclopropane ring (0.69), becomes 44.19 (compare Eisenlohr, "Spektrochemie der organischen Verbindungen," p. 131).

Another sample of *d*-carene from a different sample of turpen-

tine was found to have the following constants:  $D_{27}^{27}$  0.8594,  $n_D^{27}$  1.47,  $\alpha_D + 7.83^\circ$ .

Owing to the readiness with which *d*-carene is oxidised on exposure to the air, only approximate figures were obtained on analysis. A specimen distilled three times over sodium under diminished pressure and analysed immediately gave the following figures:

0.1019 gave 0.327  $\text{CO}_2$  and 0.107  $\text{H}_2\text{O}$ . C=87.5; H=11.7.

$\text{C}_{10}\text{H}_{16}$  requires C=88.2; H=11.8 per cent.

*d*-Carene is a colourless oil possessing a very characteristic, somewhat sweet odour. When dissolved in acetic anhydride and treated with a drop of concentrated sulphuric acid, a transient, green coloration was observed. Unlike sylvestrene and terpinene, it was found not to be acted on by a mixture of potassium dichromate and sulphuric acid. The ease with which it undergoes oxidation was shown by the fact that when 1 c.c. was placed in a closed vessel, it absorbed all the oxygen present in three days.

In chloroform solution, *d*-carene readily absorbed bromine, but after the addition of one molecular proportion, the absorption became very slow and hydrogen bromide commenced to be evolved. It was not found possible to obtain a solid bromo-derivative, whilst the nitrosochloride and the nitrosite could also only be obtained as oils; it yielded, however, a crystalline *nitrosate*. The terpene (5 grams) was mixed with acetic acid (2 c.c.) and amyl nitrite (4 grams), and nitric acid (D 1.4) (3.5 grams) was then added very slowly to the well-cooled mixture. A solid was slowly deposited, and, after an hour, alcohol was added and the solid collected. It was purified by crystallisation from a mixture of chloroform and light petroleum, when it was obtained in glistening prisms which decomposed at  $141.5^\circ$ :

\*0.089 gave 11 c.c.  $\text{N}_2$  at  $34^\circ$  and 741 mm. N=12.8.

$\text{C}_{10}\text{H}_{16}\text{O}_3\text{N}_2$  requires N=13.2 per cent.

*d*-Carene *nitrosate* is very sparingly soluble in methyl and ethyl alcohols or light petroleum, more readily so in acetone or chloroform.

*d*-Carene showed no tendency to undergo hydration when treated with dilute sulphuric acid. In one experiment, the terpene (20 grams) was heated at  $100^\circ$  for seven days with dilute sulphuric acid (5 per cent.) (100 c.c.) in a closed vessel from which the air had been displaced by carbon dioxide. The terpene distilled completely at  $123\text{--}124^\circ/200$  mm., and that it was quite unaffected

\* I wish to thank Prof. B. K. Singh for this analysis.

by the treatment is indicated by the following constants:  
 $D_{25}^{25}$  0.8595,  $n_D^{25}$  1.469.

*Action of Hydrogen Chloride on d-Carene.*

As has already been mentioned, *d*-carene on treatment with hydrogen chloride gives a mixture of *d*-sylvestrene and dipentene hydrochlorides. In one experiment, the terpene (30 grams) was dissolved in dry ether (60 c.c.), and dry hydrogen chloride passed into the well-cooled solution until it was saturated. After two days, the ether was removed in a vacuum, and the residual brown oil cooled in a freezing mixture, when it partly solidified. The crystals were rapidly collected, and, after draining on porous porcelain, were found to melt at 71° (yield, 6 grams). On recrystallisation from methyl alcohol, the hydrochloride separated in glistening needles melting at 72°, and evidently consisted of sylvestrene hydrochloride. In chloroform solution,  $[\alpha]_D$  had the value +20.31° (Found: Cl=33.7.  $C_{10}H_{18}Cl_2$  requires Cl=33.9 per cent.). A quantity of the hydrochloride was converted into the terpene, which was found to possess all the properties ascribed to *d*-sylvestrene.

The liquid hydrochloride (40 grams) from which the *d*-sylvestrene hydrochloride had been separated was mixed with acetic acid (80 grams) and sodium acetate (40 grams) and heated for thirty minutes on the sand-bath. The hydrocarbon was distilled in a current of steam, separated, and, after boiling for a short time with potassium hydroxide solution, extracted with ether, the ether dried and evaporated, and the residual oil distilled at 200 mm., when 12 grams of an oil were obtained distilling between 120° and 140°. The hydrocarbon, which had a pleasant odour of lemons, gave, when dissolved in acetic acid, an intense sylvestrene coloration with sulphuric acid. In order to remove the greater portion of the sylvestrene, the mixture of terpenes was repeatedly shaken (twenty times) with small quantities of dilute potassium dichromate solution (compare Baeyer, *loc. cit.*). After drying over potassium carbonate, the remaining oil was distilled over sodium, when the greater portion passed over at about 130°/200 mm. (yield, 5 grams). The terpene, which still gave the sylvestrene reaction, although much less markedly than before, was dissolved in chloroform and treated with a chloroform solution of bromine until a permanent straw coloration was obtained, the chloroform removed in a vacuum, and the residual viscid oil cooled in a freezing mixture, when it rapidly crystallised. After draining on porous porcelain, the bromo-derivative was purified by crystallisation from ethyl acetate, when it was found to melt at

123—124°, and this melting point was not depressed on admixture with a specimen of dipentene tetrabromide from another source (Found: Br=70·6.  $C_{10}H_{16}Br_4$  requires Br=70·2 per cent.).

*Oxidation of d-Carene: I. d-Carene Glycol (IV or V).*

The terpene (50 grams) was mixed with sodium hydroxide solution (500 c.c.; 50 grams of NaOH), and, after the addition of ice, potassium permanganate solution (1·5 litres; 116 grams of  $KMnO_4$ ) was gradually added with constant shaking, the solution being kept at 0° during the addition. The oxidation, which proceeded rapidly at first, became very slow towards the end. When the colour of the potassium permanganate had disappeared, steam was passed into the solution to remove the unchanged terpene (20 grams), the solution filtered, and concentrated on the water-bath, carbon dioxide being passed into the liquid during evaporation. The alkaline solution was extracted ten times with ether to remove the neutral products formed during the oxidation, the ethereal extract dried over potassium carbonate, the ether evaporated, and the residual oil distilled under diminished pressure, when practically the whole passed over at 166—167°/42 mm. On keeping, the viscous oil rapidly crystallised in long needles melting at 69—70°:

0·1402 gave 0·361  $CO_2$  and 0·131  $H_2O$ . C=70·2; H=10·4.

$C_{10}H_{18}O_2$  requires C=70·6; H=10·6 per cent.

*d-Carene glycol* is readily soluble in all the ordinary organic solvents, and it was not found possible to recrystallise it. In chloroform solution it has  $[\alpha]_D +16·05$ . *d-Carene glycol* does not react with phthalic anhydride when heated in benzene solution on the water-bath, and it is therefore extremely unlikely that it contains a primary alcohol group. When mixed with sulphuric acid (D 1·25) it readily dissolved, and on keeping a viscid oil separated which could not, however, be obtained crystalline. It reacted readily with hydrogen bromide, but the product could not be obtained solid. In acetic acid solution it was oxidised by chromic acid with the formation apparently of a complex mixture, from which, owing to the small quantity of material at the author's disposal, nothing definite could be isolated.

The alkaline liquid from which the glycol had been separated was acidified with dilute sulphuric acid and repeatedly extracted with ether. On removal of the ether a viscid oil remained which had a strong odour of butyric acid. As the oil showed no tendency to crystallise it was esterified in the usual manner with alcohol and sulphuric acid, and the resulting mixture of esters carefully frac-

tionated under diminished pressure (44 mm.). A small quantity distilled below  $160^{\circ}$ , and three main fractions were collected: *A* at  $160-170^{\circ}$ , *B* at  $170-185^{\circ}$ , and *C* at  $180-200^{\circ}$ .

Fraction *A*, which was a pleasant-smelling oil, was hydrolysed with alcoholic potassium hydroxide solution in the usual manner, and after removal of the alcohol and acidification the aqueous solution was repeatedly extracted with washed ether, the ethereal extract dried and evaporated, when an oil was obtained which rapidly solidified. After draining on porous porcelain, the acid was recrystallised from water, when it separated in small plates which decomposed at  $186-187^{\circ}$  and evidently consisted of dimethylmalonic acid (Found,  $C=45.2$ ;  $H=5.8$ .  $C_5H_8O_4$  requires  $C=45.4$ ;  $H=6.1$  per cent.).

The view that this acid was dimethylmalonic acid was confirmed by the fact that when mixed with a specimen of dimethylmalonic acid from another source no depression of the decomposition point was observed.

Fraction *B*, which was a somewhat viscous, unpleasant-smelling oil, was hydrolysed with alcoholic potassium hydroxide solution, and the acid obtained in this way was isolated by extraction with ether in the usual manner. The acid was a very viscous, unpleasant-smelling oil, which on trituration with a little water partly solidified. The solid was separated, drained on porous porcelain, and purified by crystallisation from dilute methyl alcohol, when it crystallised in long, prismatic needles melting at  $136-137^{\circ}$ . On analysis it gave the following figures:

0.1349 gave 0.3537  $CO_2$  and 0.1008  $H_2O$ .  $C=71.5$ ;  $H=8.3$ .

This result agrees best with the formula  $C_{10}H_{14}O_2$  ( $C=72.3$ ;  $H=8.4$  per cent.), but owing to the very poor yield of this acid it was not found possible to determine its constitution.

Fraction *C* on hydrolysis gave a viscous oil smelling strongly of fatty acids. It could not be obtained crystalline, and was not further investigated.

## II. *trans*-Caronic Acid.

The method adopted for the preparation of *trans*-caronic acid from *d*-carene was identical with that used by Baeyer and Ipatiev (*loc. cit.*) for the preparation of this acid from carone. The oily mixture of acids obtained from the oxidation (no trace of the *cis*-acid could be detected) was converted into the ammonium salt when after concentration the ammonium hydrogen salt of *trans*-caronic acid separated. This was recrystallised from a little water, in which it was only sparingly soluble when it was obtained in small

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prisms. The free acid was purified by crystallisation from hot water, when it separated in prisms melting at  $212-213^{\circ}$ . This acid possessed all the properties ascribed to *trans*-caronic acid, and the melting point was not depressed on admixture with a specimen of *trans*-caronic acid specially prepared for comparison.

The silver salt was obtained as a crystalline precipitate (Found,  $\text{Ag}=57.7$ .  $\text{C}_7\text{H}_8\text{O}_4\text{Ag}_2$  requires  $\text{Ag}=58.1$  per cent.).

*d*-Longifolene.

The fraction of the original oil boiling at  $149-151^{\circ}/36$  mm. was repeatedly distilled over sodium, when the sesquiterpene *d*-longifolene was obtained as a colourless, somewhat viscous oil with a faint and not unpleasant odour. It distilled at  $254-256^{\circ}/706$  mm.,  $150-151^{\circ}/36$  mm., and had the following constants:  $D_{30}^{20}$  0.9284,  $n_D^{20}$  1.495,  $M=64.15$ ,  $\alpha_D + 42.73^{\circ}$ .

*d*-Longifolene does not yield a solid nitrosochloride, nitrosate, or nitrosite.

The *hydrochloride* was best prepared by saturating an ethereal solution of the hydrocarbon with hydrogen chloride and allowing it to remain overnight. On removing the ether under diminished pressure, the hydrochloride separated as a crystalline solid which crystallised from methyl alcohol in long prisms or prismatic needles melting at  $59-60^{\circ}$  and having, in chloroform solution,  $[\alpha]_D + 7.1^{\circ}$ :

0.1866 gave 0.1109  $\text{AgCl}$ .  $\text{Cl}=14.7$ .

$\text{C}_{15}\text{H}_{25}\text{Cl}$  requires  $\text{Cl}=14.7$  per cent.

The *hydrobromide* was best prepared by dissolving the terpene in an acetic acid solution of hydrogen bromide (saturated at  $0^{\circ}$ ) when, on keeping, the hydrobromide separated in prisms which after crystallisation from alcohol melted at  $69-70^{\circ}$ :

0.1672 gave 0.111  $\text{AgBr}$ .  $\text{Br}=28.2$ .

$\text{C}_{15}\text{H}_{25}\text{Br}$  requires  $\text{Br}=28.0$  per cent.

The *hydriodide* which was prepared in a similar manner to the hydrobromide crystallised from alcohol in magnificent prismatic needles which melted at  $71^{\circ}$ :

0.119 gave 0.0838  $\text{AgI}$ .  $\text{I}=38.2$ .

$\text{C}_{15}\text{H}_{25}\text{I}$  requires  $\text{I}=38.0$  per cent.

In conclusion, the author wishes to thank his assistant, Mr. T. P. Ghose, for help in the experimental work, and Mr. M. Gopal Rau for many of the analyses and for kindly undertaking the preparation of the dimethylmalonic acid and *trans*-caronic acid required for the purpose of comparison.

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