# ON UTILISATION OF INDIAN TURPENTINE OILS

## PART III

## (1) CATALYTIC ISOMERISATION OF $\alpha$-PINENE AND $\beta$-PINENE TO CAMPHENE (2) SYNTHESIS OF CAMPHOR FROM PINENE-CAMPHENE MIXTURE

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The method of direct conversion of both $\alpha$-pinene and $\beta$-pinene to bornyl ester with acetic acid in the presence of the catalyst boro-acetic-anhydride and with sulphuric acid as the promoter has been reported in part II The yield of borneols obtained was not satisfactory being about 36% of theory in the case of $\alpha$-pinene and 25% in the case of $\beta$-pinene It is well known that camphene is supposed to be the first intermediate product in the (catalytic) conversion of pinene to camphor It was considered desirable to study the effect of the presence of varying quantities of camphene in pinene and to study the effect of conversion of these mixtures into bornyl esters It has now been found that by using the above catalytic method to a mixture of $\alpha$-pinene and camphene, the yield of borneols could be considerably raised. It was found necessary, therefore, to study in detail first the catalytic liquid phase isomerisation of pinenes to camphene

In the presence of strong acids like sulphuric acid, phosphoric acid, etc, various products are formed with pinenes depending upon the concentration of the acid and the temperature of the reaction (Carter and Smith, *J Soc Chem Ind*, 1925, **44**, 543T, Charlton and Day, *Ind Eng Chem*, 1937, **29**, 92) Weak acids like acetic, benzoic, salicylic and oxalic have little action on pinenes at ordinary temperature, but when heated reaction takes place with the formation of terpenes with only a small quantity of borneols (Austerweil, *Bull Soc Chem*, 1926, **39**, 694) Certain salts like boron trifluoride, aluminium trichloride, etc, react vigorously with pinenes, yielding mono-terpenes and polymerised products Genveresse [*Annalen*, 1902, **26**, (7), 31] found that $\alpha$-pinene on heating with crystallised arsenic acid (25%) for half-an-hour, gives terpinene and terpineol With Florida earth (or 40% acid Japanese clay) Kuwata could obtain about 20% yield of camphene with 80% of monoterpenes consisting mostly of dipentene (*J Soc Chem Ind, Japan* (*suppl*), 1930, **33**, 372B) In recent patents by Hans, Meerwein and Fritz are described the isomerisation of α-pinene to camphene and β-pinene → α-pinene → camphene in the presence of certain active inorganic acids, complex acids, complex salts of inorganic acids and the neutral sulphates which retain one molecule of water of crystallisation upto the temperature of 220°C Among the inorganic acids, arsenic, antimonic, titanic, vanadic, silicic, tungstic and molybodic acids are claimed to be active (*Schering-Kahlbaum*, A-G, 597,258, May 19, 1934) Amongst the complex catalysts mention may be made of boro-acetic acid, boro-tungstic acid, zinc phosphoric acid (*Schering-Kahlbaum*, A-G, *French patent*, 739,770, 1932, *ibid*, 610, 402, 1935) The complex salts of inorganic acids like ammonium vanadate or tungstate, obtained by the incomplete removal of ammonia under certain conditions are described as quite active (*Sch-Kahl*, A-G, 405,306, February 5, 1934). The neutral sulphates, which retain one molecule of water of crystallisation upto 220° and found to be active are those of nickel, magnesium, cobalt, zinc, iron, etc, (*Sch-Kahl*, *British patent*, 391,073 April 20, 1933)

In the present investigation, the isomerisation of pure α-pinene and mixtures of α- and β- pinene (containing small amounts of carene, separated from the turpentine oil of *Pinus longifolia*) to camphene in the presence of a selected number of catalysts from each of the groups mentioned above has been studied Among the neutral sulphates, the action of $NiSO_4,H_2O$, and $MgSO_4,H_2O$ have been tried, the conversion of pinenes to camphene being only 8–10% The complex acid catalysts, boroacetic anhydride and boro-phosphoric acid, did not show any appreciable activity With the complex salts of ammonium vanadate and ammonium tungstate, yield of camphene was only about 12–15% in the case of α-pinene and slightly lower with mixtures of α- and β-pinenes Among the numerous inorganic acids, the catalytic effect of arsenic acid, antimonic acid and vanadium pentoxide have been tried

Antimonic acid gave good yield of camphene (45% with α-pinene and 30-35% with the mixture of α- and β- pinenes) and there being practically no side reaction except the formation of a small amount of borneol Arsenic acid also gave fairly good yield of camphene (25–30%), but large amounts of polymerised products and monoterpenes are formed with rise of the temperature of reaction The pinene-camphene mixture obtained by the above catalytic process was converted into bornyl esters by the acetic acid method (vide part II) The mixture containing α-pinene and camphene in the ratio of 60 40 gave 60 grams of borneol from 100 grams of the mixture corresponding to 53% of theory In the case of the isomerised mixture of α- and β-pinene containing about 30% of camphene, yield of borneols corresponding to 39% of theory, was obtained

Oxidation of borneols to camphor was found to proceed best with a mixture of nitric acid (50%) and sulphuric acid (50%) in the ratio of 15 1

## EXPERIMENTAL

### CATALYTIC ISOMERISATION OF PINENES TO CAMPHENE

In the following experiments are described the isomerisation of pure α-pinene (b p 150–52°/680 mm , $d^{26}_{26}=0\ 8559$ , $n^{28}_{D}=1\ 4626$, $(\alpha)^{26}_{D}+24\ 59$) obtained from the turpentine oil of *Pinus excelsa* and of the mixture of α- and β- pinenes containing small amounts of carenes, b p 153–58°/681 mm , $d^{27}_{27}=0\ 8575$ , $n^{27}_{D}=1\ 4671$ , $(\alpha)^{27}_{D}=-17\ 87$) separated from the turpentine oil of *Pinus longifolia*

### ISOMERISATION WITH NEUTRAL SULPHATE CATALYSTS

Pure nickel sulphate ($NiSO_4,7H_2O$) was finely powdered and dried at 110–120°C in an air oven for about 12 hours It was then heated at 160–170°C for 2 hours more by which 6 molecules of water of crystallisation were removed Magnesium sulphate ($MgSO_4$, $H_2O$) catalyst was similarly prepared In table I is given the results of the experiments in which pinene (200 g ) was heated under stirring and the catalyst (14–20 g ) was gradually added After the reaction period, the product was fractionally distilled and the camphene formed estimated *

TABLE I

| No | Pinenes | Catalyst | Temperature of reaction | Hours of reaction | Yield of camphene |
|---|---|---|---|---|---|
| 1 | α-Pinene | $NiSO_4,H_2O$ | 110–120 | 24 | 6–8% |
| 2 | α-Pinene | ,, | 130–140 | 30 | 8–10% |
| 3 | α- and β-Pinene | ,, | 130–140 | 24 | 8–10% |
| 4 | α-Pinene | $MgSO_4,H_2O$ | 130–140 | 24 | 8–10% |
| 5 | α- and β-Pinene | ,, | 130–140 | 24 | 7–8% |

## ISOMERISATION WITH INORGANIC ACID CATALYSTS

Of the numerous inorganic acid catalysts mentioned in the patent literature, we have studied the catalytic effect of (i) active arsenic acid, (ii) antimonic acid, and (iii) vanadium pentoxide

(i) *Arsenic acid catalyst*—White arsenic ($As_2O_3$, 100 g) was carefully oxidised by strong nitric acid (150 g) and

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* Accurate estimation of camphene in a mixture of pinene-camphene is very difficult Only a rough idea of the constituents can be obtained by fractional distillation The method of V I Lyuvomilov (*Org Chem Ind*, U S S R, 1939, **6**, 167 was, however, followed for this estimation

Pinene-camphene (5 c c or 2 c c with more than 20% camphene), formic acid (10 g of 98% strength) and concentrated sulphuric acid (1 0 g ) was shaken at room temperature for 3 minutes Saturated sodium chloride solution (100 c c ) was added to prevent saponification and the excess of the acid was titrated with 0 5N NaOH solution saturated with sodium chloride Blank titration was also made under identical conditions By following the above method first a standard table of the amount of alkali (in c c ) required with known mixtures of pinene-camphene was made With the help of the above table the camphene content in the unknown mixture was determined evaporated on the water bath to a syrupy consistency This was then heated over a free flame and nitric acid completely removed The product was again dissolved in water and carefully heated so as to obtain a partially dried catalyst composed of the acid and its oxides

A mixture of pinene (200 g ) and the catalyst (15–20 g ) contained in a three-necked flask was heated for 20–24 hours under stirring The results of the experiments are given in table II

TABLE II

| No | Pinenes | Temperature of reaction °C | Hours of reaction | Products |
|---|---|---|---|---|
| 1 | α-Pinene | 70–75 | 24 | Camphene (12–15%) , slight polymerisation |
| 2 | α-Pinene | 85–90 | 24 | Camphene (20–25%), polymerised product (15%) , small amounts of monoterpenes and borneols |
| 3 | α-Pinene | 95–100 | 20 | Camphene (25–27%), polymerised product (20%) , small amounts of terpenes and borneol |
| 4 | α- and β-Pinene | 85–90 | 24 | Camphene (15–20%), polymerised product (15–18%) |

In the experiments (2), (3) and (4), the reaction products were first steam distilled to separate the polymerised product and then fractionated Small amount of borneol (m p 195–97°) and other terpenes were also formed

(ii) *Antimonic acid catalyst* —To an intimate mixture of antimony trioxide ($Sb_2O_3$ , 40 g ) and water (80 c c ), hydrogen peroxide (60 g , 30%) was added gradually under constant stirring and after the initial reaction had subsided, the mixture was warmed for 10 minutes, and then evaporated to dryness on the water-bath The product was finely powdered and further dried at 120–130° for 4–5 hours and finally at 168–70°, whereby an active form of partially dehydrated antimonic acid was obtained

Pinene (200 g) was heated with the catalyst (10–15 g) for 20–25 hours The product was filtered and fractionated, and the amount of camphene formed estimated The results of the experiments are given in table III

TABLE III

| No | Pinenes | Temperature of reaction °C | Hours of reaction | Products |
|---|---|---|---|---|
| 1 | α-Pinene | 90–100 | 8 | Camphene (12–14%) |
| 2 | α-Pinene | 90–100 | 24 | Camphene (30–35%) |
| 3 | α-Pinene | 100–110 | 24 | Camphene (40–45%) |
| 4 | α-Pinene | 110–120 | 24 | Camphene (15%), small amounts of borneol and polymerised products |
| 5 | α-Pinene | 120–130 | 20 | Camphene (40–45%), more polymerisation |
| 6 | α- and β-pinenes | 100–110 | 24 | Camphene (25–30%) |
| 7 | α- and β-pinenes | 110–120 | 24 | Camphene (30%), slight polymerisation |

In all the above experiments, very small amounts of polymerised product were formed. In the experiments (3), (4) and (5), small amounts of solid borneol (m p 196–98°C ) could be obtained

(iii) *Vanadium pentoxide catalyst*—Ammonium vanadate (25 0 g ) was heated in a crucible over a free flame until no more ammonia evolved, and the residue fused with sodium hydroxide (30 g ) and sodium nitrate (5 g ) The fused mass was cooled, extracted with water and precipitated with dilute hydrochloric acid The precipitate was washed free of chloride and transferred to a porcelain dish and heated with fuming nitric acid (5 c c ) on water-bath to dryness, and finally ignited to remove nitric acid

α-Pinene (200 g ) was heated at 110–120° with vanadium pentoxide (10 g ) for 24 hours under stirring The product after filtration was distilled, yielding about 12–15% camphene. Under similar conditions, α- and β- pinene mixture gives only 8–10% yield of camphene

## ISOMERISATION WITH COMPLEX ACID CATALYSTS

*Boro-Phosphoric Acid*—Phosphoric acid (10 g , sp gr 1 75) was thoroughly mixed with freshly fused powdered boric anhydride (10 g ) and the mixture heated at 110° until the whole mass solidified This solid mass was finely powdered, and heated at 120–125° for 3 hours more and cooled in a desiccator

α-Pinene (200 g ) was heated at 85–90° with 10 grams of the catalyst for 20 hours. The product was filtered, and fractionated, most of the pinene was recovered back as only a small amount of camphene (5–6%) was formed.

*Boro-Acetic Anhydride*—Freshly fused boric anhydride (6 g ) was dissolved in acetic anhydride (60 c.c ) by heating at 110° and the catalyst thus formed was heated with α-pinene (200 g ) for 20 hours under stirring, the temperature of the reaction being maintained at 110–115° Only 6–8% of camphene was formed in this reaction, whereas, with α- and β- pinene mixture only traces of camphene is formed

## ISOMERISATION WITH COMPLEX SALTS OF INORGANIC ACIDS

*Ammonium Tungstate Catalyst*—Tungstic acid ($WO_3$, 50 g ) was allowed to stand over a 25% solution of ammonia in a closed vessel, till the absorption of ammonia was complete. The ammonium tungstate so formed was dried at 60° and finely powdered and heated slowly to 150° for 10 minutes for partial removal of ammonia This was then heated in an autoclave with water at 290° for 3–4 hours and finally dried at 60°.

α-Pinene (200 g) was heated at 95–100° with 10 grams of the catalyst for 24 hours under stirring The product on analysis was found to contain 12–15% of camphene, there being practically no other product of side reaction α- and β- Pinene mixture under similar conditions yielded about 8–10% of camphene

*Ammonium Vandate Catalyst* was prepared similarly as i the case of ammonium tungstate α-Pinene (200 g) was heated a 100–110° for 24 hours with 10 grams of the catalyst under stirring yielding 15% of camphene

## DIRECT CONVERSION OF CAMPHENE-PINENE MIXTURE TO THE BORNYL ESTER

After conducting a number of experiments with differen proportions of pinene and camphene obtained from the catalyti reactions, it was found that a yield of 53% (theory) borneols can b obtained from a mixture of pinene-camphene in the ratio of 60 40 by the acetic acid method

Pinene-camphene mixture (200 g) was heated at 105–110 with acetic acid (160 g), acetic anhydride (60 g) and boric anhydrid (4 g) under slow stirring for 12–14 hours Sulphuric acid (80% 15 g) was slowly added to the cold reaction mixture with constan shaking and then heated at 50–55° for 4–5 hours Anhydrous sodiu acetate was then added to remove free sulphuric acid The produc was carefully fractionated and the ester fractions collected betwee 105–120°/25 mm was hydrolysed with methyl alcoholic soda Yiel of crude borneol-isoborneol separating out as solid was 120–125 g

α- and β- Pinene mixture (b p 153–57°) treated with antimoni acid catalyst at 110–120° yielded a mixture containing about 30% o camphene This mixture (200 g) under the above experimental con ditions gave 85–90 grams of borneols This lower yield may b possibly due to the presence of small quantities of carenes in t original α- and β- pinene mixture, and perhaps to the ease with whic β-pinene gets polymerised in presence of sulphuric acid

## OXIDATION OF BORNEOL-ISOBORNEOL TO CAMPHOR

The borneol-isoborneol mixture (1 part) was dissolved in a mixture of 50% nitric acid (5 parts) and 50% sulphuric acid (1/3rd part) The solution was heated on the water bath at 85–90° for 8–10 hours with constant shaking

The reaction mixture separated in two layers, the upper layer consisting mostly of camphor was poured into water, whereby camphor was precipitated and was further purified by sublimation at 110°, m p 169–171°.

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