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59. **Michiko Kagawa**: Rearrangement of Cyclic Ethynylcarbinol. I. Meyer-Schuster Rearrangement of Ethynylborneol.*2

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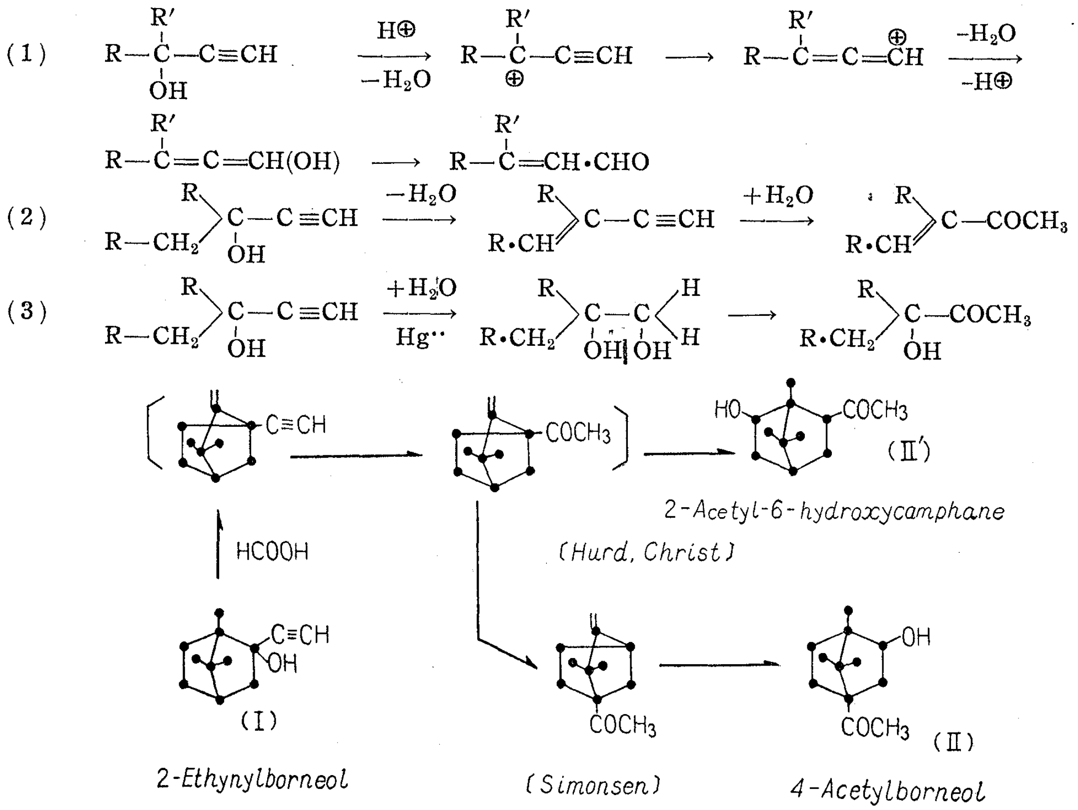
There are two forms of anionotropic rearrangement of derivatives of ethynylcarbinols, α,β-unsaturated aldehyde being obtained in one and α,β-unsaturated ketone in the other. The former is called Meyer-Schuster rearrangement (Chart 1,(1)) and occurs by the use of several mineral or organic acids, and the latter is called the Rupe reaction (Chart 1,(2)), chiefly by the use of formic acid.1)

By the rearrangement of ethynyl derivatives of menthone and several other ketonic terpenes, Rupe2) obtained α,β-unsaturated aldehydes by means of formic acid catalyst, these reactions belonging to the Meyer-Schuster rearrangement. Chanly3) and others reported several α,β-unsaturated ketones obtained by the rearrangement of cyclic ethynylcarbinols; for example, ethynylcyclohexanol gave acetylcyclohexene as a main product and a little quantity of cyclohexylideneacetaldehyde. These belong to Rupe reaction.



(1) $$R-\overset{R'}{\underset{OH}{C}}-C\equiv CH \xrightarrow[-H_2O]{H^{\oplus}} R-\overset{R'}{\underset{\oplus}{C}}-C\equiv CH \longrightarrow R-\overset{R'}{C}=C=\overset{\oplus}{C}H \xrightarrow[-H^{\oplus}]{-H_2O}$$

$$R-\overset{R'}{C}=C=CH(OH) \longrightarrow R-\overset{R'}{C}=CH\cdot CHO$$

(2) $$\begin{matrix}R\\R-CH_2\end{matrix}\!\!>\!\underset{OH}{C}-C\equiv CH \xrightarrow{-H_2O} \begin{matrix}R\\R\cdot CH\end{matrix}\!\!>\!C-C\equiv CH \xrightarrow{+H_2O} \begin{matrix}R\\R\cdot CH\end{matrix}\!\!>\!C-COCH_3$$

(3) $$\begin{matrix}R\\R-CH_2\end{matrix}\!\!>\!\underset{OH}{C}-C\equiv CH \xrightarrow[Hg^{\cdot\cdot}]{+H_2O} \begin{matrix}R\\R\cdot CH_2\end{matrix}\!\!>\!\underset{OH}{C}-\underset{OH}{C}\!<\!\begin{matrix}OH\\H\end{matrix} \longrightarrow \begin{matrix}R\\R\cdot CH_2\end{matrix}\!\!>\!\underset{OH}{C}-COCH_3$$

Chart 1.

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[*2] The nomenclature for camphor skeleton was used for ethynylcamphene and others as a matter of convenience.

1) G.F. Henion, R.B. Davis, D.E. Maloney: J. Am. Chem. Soc., **71**, 2813(1949); K. Meyer, K. Schuster: Ber., **55**, 619(1922).

2) H. Rupe: Helv. Chim. Acta, **9**, 672(1926); **11**, 449(1928); **12**, 193(1929); **14**, 708(1931).

3) J.D. Chanly: J. Am. Chem. Soc., **70**, 244(1948); C.D. Hurd, R.E. Christ: *Ibid.*, **59**, 118(1937); W.H. Linneu: J. Pharm. Pharmacol., **2**, 13(1950); H. Rupe, E. Kambli: Helv. Chim. Acta, **9**, 672(1926); T. Takeshima: Bull. Chem. Soc. Japan, **31**, 640(1958).

By heating in the presence of formic acid, ethynylborneol (I), derived from ethynylation of camphor, Hurd and Christ[4] obtained 2-acetyl-6-hydroxycamphane (II'), m.p. 77~78°(semicarbazone, m.p. 202°), proved it by preparing 6-hydroxycamphane-2-carboxylic acid by means of ozonolysis, and explained the reaction process as follows: In the first place, ethynylcamphene was produced by dehydration of ethynylborneol and then passing through 2-acetylcamphene, 2-acetyl-6-hydroxycamphane was formed by Wagner rearrangement of the latter. These reactions all proceeded completely by formic acid catalyst and no unsaturated ketone or aldehyde was obtained.

In 1949, Simonsen asserted in his book[5] that if 2-acetylcamphene is converted to camphane ring by Wagner rearrangement, it will always be accompanied by Nametkin rearrangement and probably 4-acetylborneol (II) would be formed. As will be described later, Simonsen's assertion was confirmed by comparison of the properties of Hurd-Christ's 2-acetyl-6-hydroxycamphane and 4-acetylborneol, the latter syhthesized by an indirect process.

It is clear that one kind of Rupe rearrangement occurred as the first process of Hurd-Christ reaction by boiling with formic acid. This rearrangement of ethynylborneol was attempted by heating at 40° in the presence of anionotropic catalyst, such as hydrochloric acid or formic acid, there seemed to be no Rupe reaction as Hurd and Christ reported but Meyer-Schuster rearrangement occurred to give α,β-unsaturated aldehyde.

The present report deals with these rearrangement reactions of ethynylborneol, describes the hydroxy-ketone, unsaturated ketone, and 4-acetylborneol as having some relation to the Hurd-Christ reaction.

Rearrangement of Ethynylborneol (I)

2-Ethynylborneol (I)(m.p. 55°, $[\alpha]_D$ +17.7°), prepared by passing acetylene through cold solution of sodiocamphor in benzene, formed a semisolid hydroxyketone ($b.p_{3.5}$ 125°,

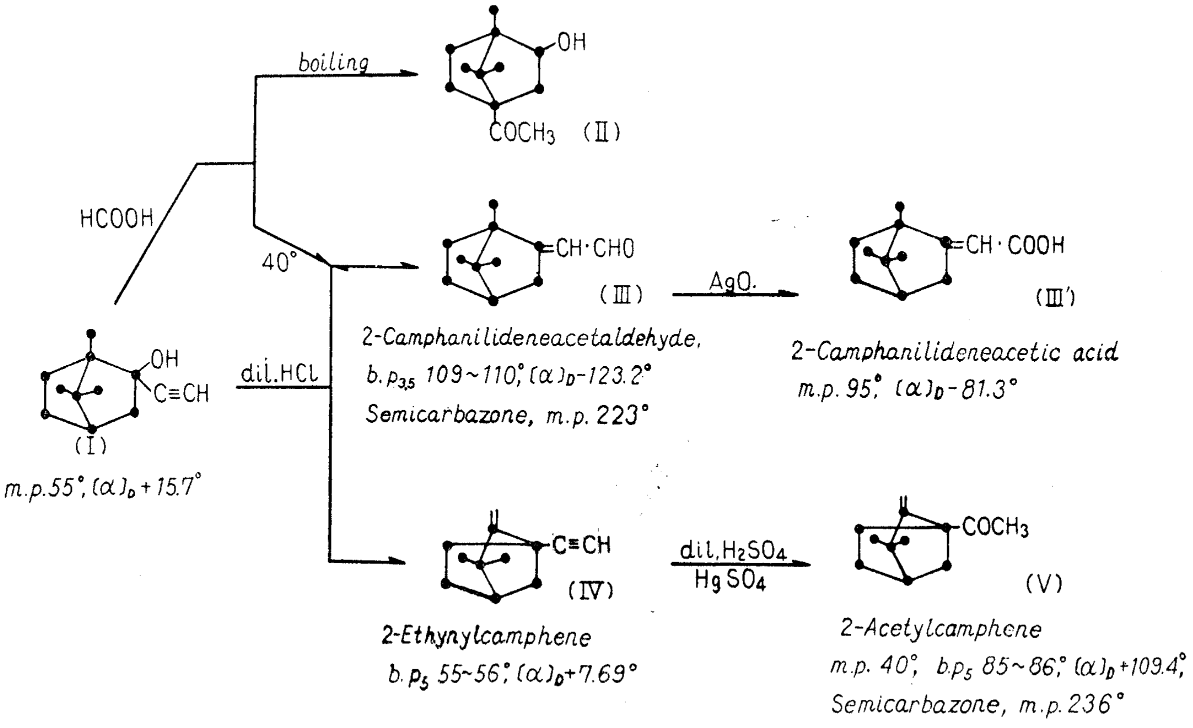

Chart 2.

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4) C. D. Hurd, R. E. Christ: J. Am. Chem. Soc., **59**, 118(1937).
5) J. Simonsen: "The Terpenes," **II**, 447(1947).

semicarbazone, m.p. 203°) by boiling with conc. formic acid as Hurd–Christ process. Its properties were identical with those of 2–acetyl–6–hydroxycamphene. It will later be explained that this hydroxyketone is 4–acetylbornel (II).

2–Ethynylborneol (I) converted to an only unsaturated aldehyde (III) (b.p$_{3.5}$ 109~110°, $[\alpha]_D$ −123.22°, n_D^{12} 1.5213, IR cm^{-1} : 790$\left(\begin{smallmatrix}C\\C\end{smallmatrix}>C{=}C<\begin{smallmatrix}C\\H\end{smallmatrix}\right)$, 1690 ($\alpha,\beta$–unsaturated aldehyde); semicarbazone, m.p. 223°) by heating with dil. hydrochloric acid in isopropanol, which was then purified from the reaction product by means of sodium hydrogen sulfite compound. Oxidation of this aldehyde with silver oxide produced the corresponding unsaturated acid (III′) (m.p. 95°, $[\alpha]_D$ −81.3°) and with chromium trioxide, camphor.

This fact shows that this unsaturated aldehyde is 2–camphylideneacetaldehyde (III), having a double bond outside the camphane ring. The other reaction product which did not combine with sodium hydrogen sulfite was a small quantity of oil (b.p$_5$ 55~56°; $[\alpha]_D$ +7.69°), the greater part being a resinous substance. This oil has an ethynyl group and no oxygen, so it was inferred to be 2–ethynylcamphene (IV). This hydrocarbon was hydrated with 6% sulfuric acid in the presence of mercuric sulfate giving a crystalline unsaturated ketone (b.p$_5$ 85~86°, m.p. 40°, $[\alpha]_D$ +109.4°; IR cm^{-1} : 890 $\left(\begin{smallmatrix}C\\C\end{smallmatrix}>C{=}CH_2\right)$, 1710 (CO); semicarbazone, m.p. 236°).

This ketone was changed to camphene–2–carboxylic acid by oxidation with sodium hypobromite and to 4–acetylborneol by Wagner–Nametkin rearrangement with trichloroacetic acid. It was thereby confirmed that this unsaturated ketone is 2–acetylcamphene (V) and the starting hydrocarbon is 2–ethynylcamphene (IV).

2–Camphylideneacetaldehyde (III) (b.p$_3$ 90~97°, $[\alpha]_D$ −120°; semicarbazone, m.p. 223°) and a small quantity of 2–ethynylcamphene were also obtained from 2–ethynylborneol by standing several days at 40°, with conc. formic acid.

These results show that 2–ethynylborneol underwent Meyer–Schuster rearrangement to produce α,β–unsaturated aldehyde by heating with dil. hydrochloric acid or standing at 40° with conc. formic acid. On treating with boiling formic acid Rupe reaction occurs to afford hydroxyketone.

4-Acetylborneol (II)

As described above, Hurd–Christ substance would probably be 4–acetylbornel as Simonsen asserted recently, so a comparison was made of the properties of 2–acetyl–6–hydroxycamphane and 4–acetylborneol, the latter being prepared now by an indirect method.

2–Ethynylborneol was treated with dil. sulfuric aicd in the presence of mercuric sulfate (1/3 mole was required) in isopropanol and a hydroxyketone (m.p. 90°, $[\alpha]_D$ −32.1°, IR cm^{-1} : 3410 (OH), 1685 (CO); semicarbazone, m.p. 228°) was obtained. This hydroxyketone was derived to camphor or camphoric acid by oxidation with chromium trioxide or potassium permanganate, then both ketone and hydroxyl groups were in 2–position of camphane ring and this showed ketone to be 2–acetylborneol (VI).

2–Acetylborneol did not react with zinc chloride or phoshorus pentoxide in benzene solution, so it was treated by potassium hydrogen sulfate at 180° to yield a crystalline unsaturated ketone (V) (b.p$_3$ 76.5°, m.p. 35~40°, $[\alpha]_D$ +106.3°; IR cm^{-1} : 893$\left(\begin{smallmatrix}C\\C\end{smallmatrix}>C{=}CH_2\right)$, 1710 (CO); semicarbazone, m.p. 236°). These properties were identical with those of 2–acetylcamphene (V) prepared from 2–ethynylcamphene (IV), obtained as a by–product of 2–camphylideneacetaldehyde (III). This unsaturated ketone was oxidized with sodium hypobromite giving an oily bromo compound and crystalline carbon tetrabromide; the oily bromide was saponified and formed a crystalline unsaturated acid (m.p. 105°, $[\alpha]_D$ +7.4°). This acid was also obtained from the acid portion of the oxidation product and had strong resemblance to camphene-2-carboxylic acid (VII).

Houben and Pfankuch[6] reported that camphene-2-carboxylic acid (VII) (m.p. 109~110°; Asahina reported m.p. 85°, $[\alpha]_D$ +93.9°) isomerised to borneol-4-carboxylic acid (VIII) (m.p. 221~222°) by the action of trichloroacetic acid and the latter was oxidized with chromium trioxide to camphor-4-carboxylic acid (IX) (m.p. 234~240°, $[\alpha]_D$ −19.5°). This unsaturated acid was treated in the same way, changed to borneol-4-carboxylic acid (m.p. 220°, $[\alpha]_D$ +12°) and camphor-4-carboxylic acid (IX) (m.p. 240°, $[\alpha]_D$ −6°; oxime, m.p. 230°). All these were similar to Houben-Pfankuch's products. From these facts, it was clear that the starting unsaturated ketone is 2-acetylcamphene (V).

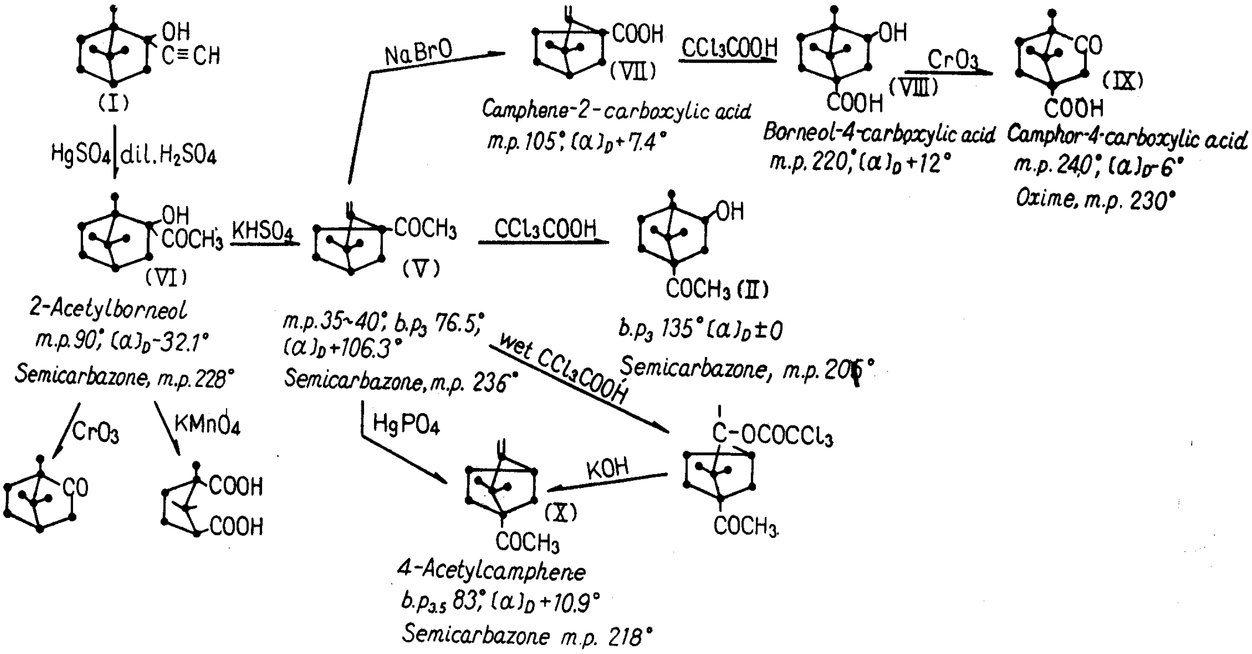

Chart 3.

2-Acetylcamphene (V) was heated with trichloroacetic acid, by which it underwent Wagner-Nametkin rearrangement, yielding 4-acetylborneol (II) (b.p$_3$ 135°, $[\alpha]_D$ ±0°; semicarbazone, m.p. 205°). These properties, excepting the melting point, are similar to those of 2-acetyl-6-hydroxycamphane (II′) as reported by Hurd and Christ; they said that it was difficult to crystallize 2-acetyl-6-hydroxycamphane and required long days and that 4-acetylborneol (II) also presented difficulty in determining the melting point. The melting point of the degradation product of Hurd-Christ substance, such as 6-hydroxycamphene-2-carboxylic acid, was identical with that of borneol-4-carboxylic acid (VIII) which is the corresponding product of 4-acetylborneol (II).

Simonsen's statement was therefore found to be correct. When 4-acetylborneol (II) was oxidized with chromium trioxide, camphor-4-carboxylic acid (IX) (m.p. 245°, $[\alpha]_D$ ±0°; oxime, m.p. 230°) was prepared.

By heating 2-acetylcamphene (V) with wet trichloroacetic acid, an addition product (b.p$_3$ 135°, $[\alpha]_D$ +1.4°) was obtained in which trichloroacetic acid should be bonded to the double bond of camphene ring. By the hydrolysis of this compound 4-acetylcamphene (X) (b.p$_3$ 72~73°, $[\alpha]_D$ +4.32°, $n_D^{32.5}$ 1.4859; semicarbazone, m.p. 218°) was formed by Nametkin rearrangement. The same ketone (X) (b.p$_{3.5}$ 83°, $[\alpha]_D$ +10.9°, n_D 1.4789; semicarbazone, m.p. 218°) was also obtained from 2-acetylcamphene (V) by the action of phosphoric acid in benzene solution.

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6) J. Houben, E. Pfankuch: Ann., **483**, 271(1930); **489**, 193(1931); **501**, 219(1953); Ber., **64**, 2719 (1939); Y. Asahina: Ber., **72**, 1540(1939).

4-Acetylcamphene (X)

There is one doubt about ethynylborneol, whether the endo- or exo-position of the hydroxyl has any influence on the rearrangement of this compound, as borneol and isoborneol behave differently to dehydrating agents or some other reagents.

When the unsaturated aldehyde was prepared by Meyer-Schuster rearrangement with dilute acid, the properties of 2-ethynylborneol (I) that remained in the reaction mixture, its melting point and rotatory power, were identical with those of the starting material, there being no special difference in the endo- or exo-form.

Ethynylborneol (I) was dehydrated by heating with phosphoric acid in benzene solution, producing a hydrocarbon surmised as ethynylcamphene (XI) (b.p$_5$ 52°, $[\alpha]_D$ $-35.4°$, n_D 1.4819; IR cm^{-1}: 3300 (-C≡C-), 880 $\left(\begin{smallmatrix}C\\C\end{smallmatrix}{>}C{=}CH_2\right)$). In this case, also the properties of the residual unchanged ethynylborneol were identical with those of the starting substance. Accordingly there should be one type of endo- or exo-from in this ethynylborneol which was prepared by ethynylation of sodiocamphor by cooling.

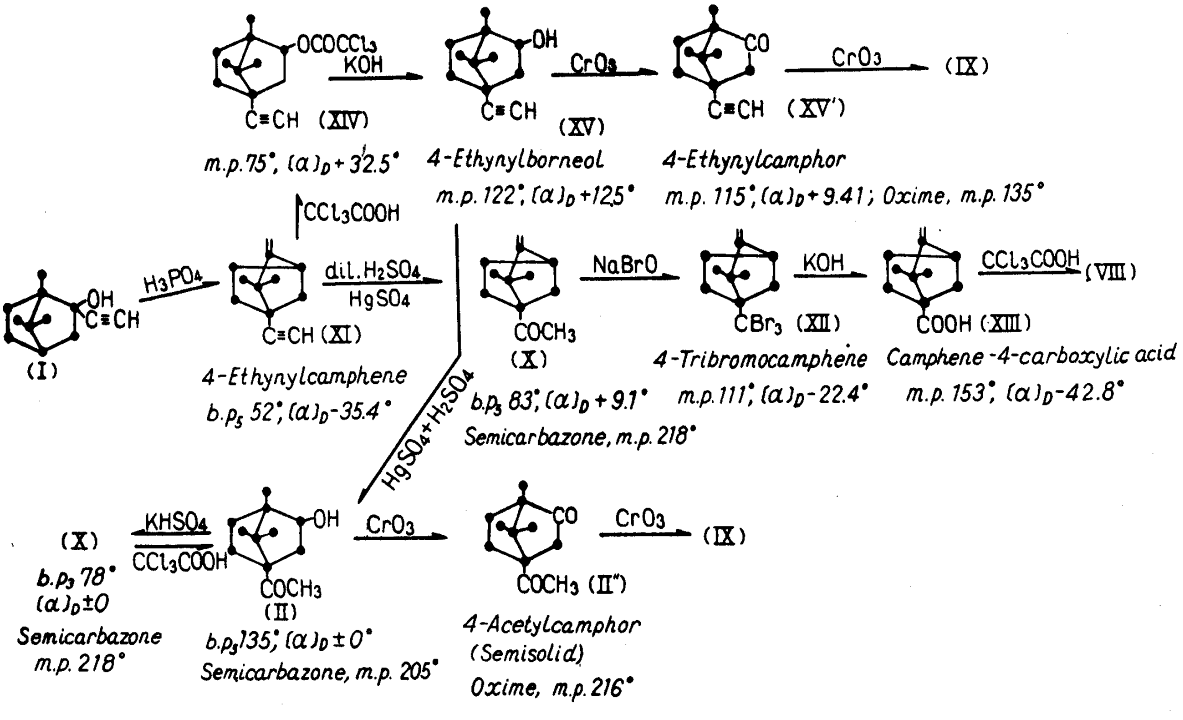

Chart 4.

Ethynylcamphene was hydrated by treating with dil. sulfuric acid in the presence of mercuric sulfate in isopropanol, producing an oily acetylcamphene (X) (b.p$_5$ 83°, $[\alpha]_D$ $+9.1°$, n_D 1.4790; IR cm^{-1}: 890$\left(\begin{smallmatrix}C\\C\end{smallmatrix}{>}C{=}CH_2\right)$, 1700 (CO); semicarbazone, m.p. 218°.). This oily acetylcamphene differed from the crystalline 2-acetylcamphene (V) which was prepared by the hydration of 2-ethynylcamphene (IV), obtained as a by-product of Meyer-Schuster rearrangement of 2-ethynylborneol (I). These should be isomers, although the absorption bands of infrared spectrum were identical. When this oily acetylcamphene was oxidized with sodium hypobromite, a bromo compound (m.p. 116°, $[\alpha]_D$ $-22.4°$) was obtained and an unsaturated acid (XIII) (m.p. 153°, $[\alpha]_D$ $-42.8°$) was produced on hydrolysis of the latter, and was identical with camphene-4-carboxylic acid (XIII) (m.p. 147~148°; Asahina reported m.p. 158~159°, $[\alpha]_D$ $-56.6°$). So the starting hydrocarbon was 4-ethynylcamphene and this had been hydrated to 4-acetylcamphene (X). Camphene-4-

carboxylic acid (XIII) also changed to borneol-4-carboxylic acid (VIII) (m.p. 215°, $[\alpha]_D$ +6.1°) and camphor-4-carboxylic acid (IX) (m.p. 240°, $[\alpha]_D$ −4°; oxime, m.p. 230°) by the same treatment as described for degradation products of 2-acetylcamphene (V).

4-Acetylcamphene (X) was changed to 4-acetylbornel (II) (b.p$_3$ 135°, $[\alpha]_D$ ±0°; semicarbazone, m.p. 205°) and the latter was oxidized to camphor-4-carboxylic acid (VIII) (m.p. 245°, $[\alpha]_D$ ±0°; oxime, m.p. 230°) through 4-acetylcamphor (II″) (semisolid; oxime, m.p. 216°), these indicating the normal degradation course.

4-Ethynylborneol (XV)

The properties of 2-ethynylcamphene (IV), obtained as a by-product of Meyer-Schuster rearrangement, resembled greatly those of 4-ethynylcamphene (XI), prepared by dehydration of 2-ethynylborneol with phosphoric acid, both ethynylcamphenes changing alike to ethynylborneol trichloroacetate (m.p. 75°, $[\alpha]_D$ +32.5°) by heating with trichloroacetic acid, and 4-ethynylborneol (XV) (m.p. 122°, $[\alpha]_D$ +12.45°) was obtained by the hydrolysis of the latter ester.

4-Ethynylborneol was oxidized with chromium trioxide to camphor-4-carboxylic acid and hydrated to 4-acetylborneol (II) (b.p$_{8.5}$ 125°, $[\alpha]_D$ −6.7°; semicarbazone, m.p. 203°) by the action of mercuric sulfate and dil. sulfuric acid. 4-Acetylborneol (II) was again dehydrated with potassium hydrogen sulfate giving 4-acetylcamphene (X) (b.p$_8$ 78°, $[\alpha]_D$ ±0°; semicarbazone, m.p. 218°), the latter formed again 4-acetylborneol (b.p$_4$ 135°, $[\alpha]_D$ ±0°; semicarbazone, m.p. 203) with trichloroacetic acid, but these were completely racemized.

Experimental

Ethynylborneol (I) **from Camphor**—A solution of 1 kg. camphor in 1 L. dehyd. benzene was added to a boiling mixture of 350 g. $NaNH_2$ and 3 L. dehyd. benzene, and the mixture was refluxed for 15 hr. with stirring. When the generation of NH_3 became inactive, the reaction mixture was cooled to 0°, and acetylene was passed through for 15 hr. with stirring. After standing overnight, the solution was poured into ice water and benzene layer was separated, washed with 5% H_2SO_4, dried over anhyd. Na_2SO_4, and the solvent was evaporated. The crystalline residue weighed 1200 g. and melted at 118°. The crystals were dissolved in MeOH and treated with ammoniacal $AgNO_3$, whereupon an abundant white amorphous precipitate was formed. This was collected, washed with MeOH, and dried. The silver salt was extracted with Et_2O to separate it from camphor and resinous matter. The purified silver salt (900 g.) was added to a solution of 500 g. of NH_4Cl in 700 cc. of H_2O and heated for 3 hr. The precipitated AgCl was filtered off and the filtrate was extracted with Et_2O. The ethereal solution was dried over anhyd. Na_2SO_4 and evaporated. 500 g. of 2-ethynylborneol was obtained, m.p. 55°, $[\alpha]_D^{20}$ +17.7°(in EtOH, l=10 cm, c=20). *Anal.* Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.13; H, 10.26.

4-Acetylborneol (II) **from 2-Ethynylborneol**—A mixture of 10 g. of 2-ethynylborneol and 60 cc. of 90% HCOOH was refluxed for 2 hr. The solution turned to a deep brown color and oily layer separated. The reaction mixture was diluted with H_2O and extracted with Et_2O, the extract was washed with Na_2CO_3 solution, dried over anhyd. Na_2SO_4, and Et_2O was evaporated. The residue was distilled under a reduced pressure. Fraction (1) : b.p$_{8.5}$ 100~101° was saponified with ethanolic KOH and 4-ethynylborneol (m.p. 120°, $[\alpha]_D^{20}$ +20°(in EtOH, l=10 cm., c=20); yield 10%) was obtained.

Fraction (2) : b.p$_{8.5}$ 110~113° was saponified with 10% ethanolic KOH and 4-acetylborneol (b.p$_{8.5}$ 130~135°, semisolid, $[\alpha]_D$ ±0°; semicarbazone, m.p. 205°, 67% yield) was obtained.

2-Camphylideneacetaldehyde (III) **from 2-Ethynylborneol**—To a mixture of 250 cc. of HCl and 560 cc. of H_2O addition was made of 100 g. of 2-ethynylborneol in 450 cc. of *iso*-PrOH and the mixture was refluxed for 1 hr. with stirring. The reaction mixture was diluted with H_2O, extracted with Et_2O, the organic layer was washed with H_2O, dried, and the solvent distilled off. To the residue was added a saturated solution of $NaHSO_3$ and shaken until the addition product crystallized. After standing overnight the crystals were collected by filtration and washed with MeOH. The crystals were decomposed with saturated solution of Na_2CO_3 and the oily layer was extracted with Et_2O. The organic layer was washed with H_2O, dried, and the solvent distilled off. The residual oil weighed 70 g., b.p$_{8.5}$ 109~110°, $[\alpha]_D^{15}$ −123.22°(in EtOH, l=10 cm., c=20), n_D^{15} 1.523.
Semicarbazone : m.p. 223°. *Anal.* Calcd. for $C_{13}H_{21}ON_3$: C, 66.35; H, 9.0; N, 17.9. Found : C, 66.29; H, 8.9; N, 17.58.

In this rearrangement, 2-ethynylborneol, m.p. 54°, $[\alpha]_D^{20}$ +17°(in EtOH, l=10 cm, c=20), was obtained by fractional distillation from the substance which was not combined with $NaHSO_3$, identical with the starting material.

2-Camphylideneacetic Acid (III′)—20 g. of camphylideneacetaldehyde was added to an ice-cooled mixture of 340 cc. MeOH, 46 g. of $AgNO_3$ in 460 cc. of NH_4OH, and 46 g. of NaOH in 50 cc. H_2O, and the mixture was left to stand overnight. The reaction mixture was filtered, diluted with H_2O and the neutral substance was extracted with Et_2O. The alkaline layer was acidified with dil. H_2SO_4 and extracted with Et_2O. The organic layer was washed with H_2O, dried, and concentrated. The crystalline residue was recrystallized from petr. ether, m.p. 95°; $[\alpha]_D^{20}$ −81.3°(in EtOH, $l=10$ cm., c=20). *Anal.* Calcd. for $C_{12}H_{18}O_2$: C, 74.2; H, 9.3. Found : C, 73.66; H, 9.20.

Oxidation of 2-Camphylideneacetic Acid (III′)—i) With CrO_3 : A solution of 1 g. 2-camphylideneacetic acid in 5 cc. glacial AcOH was added to a mixture of 2 g. CrO_3 in 5 cc. glacial AcOH, and warmed on a water bath for 2 hr. The reaction mixture was diluted with H_2O and extracted with Et_2O. The organic layer was washed with H_2O and dil. Na_2CO_3, dried over anhyd. Na_2SO_4, and evaporated. The crystalline residue melted at 170°(semicardazone, m.p. 238°) indicating this to be camphor.

ii) With alkaline $KMnO_4$: 1 g. of the acid was added to a solution of 2.7 g. $KMnO_4$, 1.13 g. KOH, and 100 cc. H_2O at room temperature. After shaking until the disappearance of reddish violet color, the reaction mixture was filtered and the filtrate was extracted with Et_2O. The organic layer was separated, washed with H_2O, dried, and the solvent distilled off. The reaction product, camphor, was obtained, m.p. 170°(semicarbazone, m.p. 239°).

The alkaline layer was acidified with dil. H_2SO_4. The acid product was recrystallized from H_2O and camphoric acid, m.p. 182°, was obtained.

2-Ethynylcamphene (IV), as the By-product of the Aldehyde—About 40 g. of oily product was collected from the filtrate of the crystalline addition compound of the aldehyde and $NaHSO_3$, and fractionated as follows :

b.p$_{3.5}$	(1)	65～85°	oil	10 g.	hydrocarbon
	(2)	85～110°	solid	4 g.	camphor+ethynylborneol
	(3)	110～130°	oil	6 g.	aldehyde+high molecular substance
	(4)	residue			

By rectification of fraction (1), 8.5 g. of a distillate was obtained; b.p$_{3.5}$ 54.5～54.6°, $[\alpha]_D^{20}$ +7.69°, n_D^{20} 1.4859, and treated with ammoniacal $AgNO_3$, forming a white amorphous Ag salt. This was decomposed as usual.

2-Acetylcamphene (V) from 2-Ethynylcamphene—A solution of 8 g. of 2-ethynylcamphene in 20 cc. of *iso*-PrOH was added to a warmed mixture of 1 g. $HgSO_4$, 27 cc. H_2O, and 2 cc. conc. H_2SO_4, and the mixture was maintained at 60～70° for 2 hr. with stirring. The reaction mixture was filtered and the filtrate was extracted with Et_2O. The ethereal solution was washed with 10% NaOH, dried, and evaporated. The residue was distilled *in vacuo*. b.p$_5$ 85～86°, m.p. 40°, $[\alpha]_D^{20}$ +109.4°. *Anal.* Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found : C, 80.74; H, 10.15.
Semicarbazone : m.p. 236°. *Anal.* Calcd. for $C_{13}H_{21}ON_3$: C, 66.35; H, 9.0; N, 17.86. Found : C, 66.58; H, 8.72; N, 17.92.

2-Camphylideneacetaldehyde (III) from 2-Ethynylborneol with HCOOH—7 g. of 2-ethynylborneol was added to 42 cc. of HCOOH and the mixture was left standing at 40° for 3 days. The reaction mixture was treated as in the case of rearrangement with dil. HCl. Finally, 3 g. of the aldehyde was obtained, b.p$_8$ 90～97°, $[\alpha]_D^{15}$ −120°. Semicarbazone : m.p. 223°.

2-Acetylborneol (VI) from 2-Ethynylborneol—A solution of 100 g. of 2-ethynylborneol in 300 cc. *iso*-PrOH was added to a warm mixture of 50 g. $HgSO_4$, 720 cc. H_2O, and 30 cc. conc. H_2SO_4, and the mixture was maintained at 60～70° for 3 hr. with stirring. A white precipitate turned yellow and at last gray. The precipitate was separated and the filtrate was treated as usual. Finally, 52 g. of crystals were obtained, which was recrystallized from petr. ether to m.p. 90°; $[\alpha]_D^{10}$ −32.1°(in EtOH, $l=10$ cm., c=20). *Anal.* Calcd. for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found : C, 73.20; H, 10.23. Semicarbazone : m.p. 228°. *Anal.* Calcd. for $C_{13}H_{23}O_2N_3$: C, 61.66; H, 9.15; N, 16.59. Found : C, 61.63; H, 9.5; N, 16.62.

Oxidation of 2-Acetylborneol—i) With $K_2Cr_2O_7$ and H_2SO_4 : A solution of 1 g. of 2-acetylborneol in 6 cc. of Et_2O was added to a mixture of 3.39 g. of $K_2Cr_2O_7$ in 100 cc. of 4.5% H_2SO_4 at room temperature and shaken for 24 hr. The reaction mixture was treated as usual and 0.5 g. of camphor was obtained, m.p. 170°; $[\alpha]_D^{10}$ +37°. Semicarbazone : m.p. 238°

ii) With $KMnO_4$ and NaOH : Oxidation of 2-acetylborneol produced camphor, m.p. 180°, as the neutral fraction and camphoric acid, m.p. 180°, as the acidic fraction.

2-Acetylcamphene (V) from 2-Acetylborneol—A mixture of 11 g. of acetylborneol and 17 g. of anhyd. $KHSO_4$ was treated at 180° for 0.5 hr. until water evaporated. The reaction mixture was diluted with H_2O and extracted with Et_2O. The organic layer was washed with water and dil. Na_2CO_3, dried, and evaporated. The residual oil weighed 10 g. b.p$_8$ 76.5°, m.p. 35～40°, $[\alpha]_D^{15}$ +106.3°. *Anal.* Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.2. Found : C, 80.6; H, 9.8.

Semicarbazone: m.p. 236°. *Anal.* Calcd. for $C_{13}H_{21}ON_3$: C, 66.4; H, 9.0; N, 17.8. Found: C, 66.3; H, 8.72; N, 17.46.

Camphene-2-carboxylic Acid (VII) from 2-Acetylcamphene—NaBrO solution was prepared by adding 78.4 g. of Br_2 to 58.9 g. of NaOH in 1176 cc. of H_2O at −5° with stirring. After 1 hr. 10 g. of 2-acetylcamphene was added and the mixture was shaken for 2 days at 0°. The reaction mixture was filtered, 8 g. of crystals of crude bromo compound was obtained, and it was recrystallized from MeOH to CBr_4 of m.p. 85°. The filtrate, after removal of CBr_4, was extracted with Et_2O, the organic layer was washed with Na_2CO_3 solution, dried, the solvent was evaporated, and oily bromo compound (6 g.) was obtained. The latter was saponified and 2 g. of acid was obtained. The residual alkaline solution of extraction was acidified with H_2SO_4, extracted with Et_2O, the organic layer was washed with H_2O, dried, the solvent distilled off, and an oily substance (4 g.) was obtained. All these acid products were collected and purified by steam distillation. From the distillate, 5 g. of crystals were obtained; these were recrystallized from petr. ether to m.p. 105°, $[\alpha]_D^{5}$ +7.4°(in EtOH, l=10 cm., c=20). *Anal.* Calcd. for $C_{11}H_{16}O_2$: C, 73.3; H, 8.9. Found: C, 73.31; H, 8.97.

Borneol-4-carboxylic Acid (VIII) from Camphene-2-carboxylic Acid—A mixture of 7 g. camphene-2-carboxylic acid and 10.5 g. CCl_3COOH was warmed at 60~70° for 3 hr. After diluting with H_2O and basification with Na_2CO_3, neutral product was extracted with Et_2O. The ethereal solution was washed with H_2O, dried, and evaporated to give 13 g. of an ester. The ester was saponified with 100 cc. of 10% ethanolic KOH by warming on a water bath for 3 hr. EtOH was distilled off, the residue was diluted with H_2O, and was filtered after addition of carbon for purification. The filtrate was acidified with H_2SO_4, extracted with Et_2O, and treated as usual. The crude crystals (5 g.) were recrystallized from petr. ether, m.p. 220°, $[\alpha]_D^{18}$ +12°(in EtOH, l=10 cm., c=20). *Anal.* Calcd. for $C_{11}H_{18}O_3$: C, 66.6; H, 9.1. Found: C, 66.62; H, 9.20.

Camphor-4-carboxylic Acid (IX) from Borneol-4-carboxylic Acid—To a solution of 3 g. borneol-4-carboxylic acid dissolved in 10 cc. of glacial AcOH, 3 g. of CrO_3 was added with cooling at 5~10°. After standing overnight, the reaction mixture was warmed for 1 hr. and AcOH was removed by distillation under a reduced pressure. The residual product was diluted with H_2O, extracted with Et_2O, the ethereal layer was washed with Na_2CO_3 solution, dried, and the solvent removed. The crystalline residue was recrystallized from a mixture of AcOH and petr. ether, m.p. 240°, $[\alpha]_D^{20}$ −6°(in EtOH, l=10 cm., c=25). *Anal.* Calcd. for $C_{11}H_{16}O_3$: C, 67.3; H, 8.1. Found: C, 62.42; H, 8.04.
Oxime: m.p. 230°. *Anal.* Calcd. for $C_{11}H_{17}O_3N$: C, 62.54; H, 8.11; N, 6.63. Found: C, 62.42; H, 8.04; N, 6.58.

4-Acetylborneol (II) from 2-Acetylcamphene—A mixture of 4 g. of 2-acetylcamphene and 14 g. CCl_3COOH was warmed at 70° for 10 hr. The reaction mixture was treated as usual to give 7 g. of trichloroacetate, b.p$_5$ 145~150°. The ester was boiled with 50 cc. of 20% ethanolic KOH on a water bath for 3 hr., the reaction mixture was diluted with H_2O, and extracted with Et_2O. The organic layer was washed with water, dried over anhyd. Na_2SO_4, and the solvent was removed to give 3 g. of semisolid, b.p$_4$ 135°, $[\alpha]_D$ ±0°.
Semicarbazone: m.p. 205°. *Anal.* Calcd. for $C_{13}H_{23}O_2N_3$: C, 61.63; H, 9.15; N, 16.59. Found: C, 60.49; H, 9.02; N, 16.62.

Camphor-4-carboxylic Acid (IX) from 4-Acetylborneol—A mixture of 1.2 g. of CrO_3 in 10 cc. of glacial AcOH was added to a solution of 1 g. of 4-acetylborneol in 2 cc. of glacial AcOH with cooling. After standing overnight, the reaction mixture was treated by the usual method and 0.6 g. of crystalline acid obtained was recrystallized from a mixture of AcOEt and petr. ether. m.p. 240°, $[\alpha]_D$ ±0°.
Oxime: m.p. 230°.

4-Acetylcamphene (X) from 2-Acetylcamphene—i) With wet CCl_3COOH: A mixture of 12 g. of 2-acetylcamphene and 13.5 g. CCl_3COOH (containing 5% H_2O) was heated at 130° for 3 hr., the reaction mixture was diluted with H_2O, and extracted with Et_2O. The organic layer was washed with Na_2CO_3 solution, dried, and evaporated. The addition product was distilled at 135° under 3 mm. Hg; $[\alpha]_D^{20}$ +1.4°(in EtOH, l=10 cm., c=20).
Semicarbazone: m.p. 175°. *Anal.* Calcd. for $C_{15}H_{21}O_3N_3Cl_3$: C, 45.98; H, 5.45; N, 10.45; Cl, 25.65.

7 g. of the addition product was saponified with 20 cc. of 20% ethanolic KOH for 3 hr. on a water bath and the reaction mixture was treated as usual. An oil was obtained, b.p$_8$ 72~73°, $n_D^{12.5}$ 1.4859, $[\alpha]_D^{20}$ +4.32°.
Semicarbazone: m.p. 218°. *Anal.* Calcd. for $C_{13}H_{21}ON_3$: C, 66.38; H, 8.93; N, 17.87. Found: C, 66.2; H, 8.81; N, 17.65.

ii) With H_3PO_4: A mixture of 2 g. 2-acetylcamphene dissolved in 20 cc. dehyd. benzene and 1 g. H_3PO_4 was refluxed for 2 hr. After benzene was removed, the residue was diluted with H_2O, extracted with Et_2O, the organic layer was washed with Na_2CO_3 solution, dried, and the solvent evaporated. Fractional distillation of the residue gave a colorless liquid, b.p$_5$ 83°, $[\alpha]_D^{20}$ +10.9°, n_D^{20} 1.4789.
Semicarbazone: m.p. 218°.

4-Ethynylcamphene (XI) from 2-Ethynylborneol—To a solution of 9 g. of 2-ethynylborneol in 60 cc. of dehyd. benzene, 3 g. of H_3PO_4 was added and after boiling on a water bath for 2.5 hr., the reaction mixture was diluted with H_2O, the benzene layer was washed with Na_2CO_3 solution, dried, and evaporated. The residue was fractionally distilled to give 4.5 g. of b.p$_5$ 52°, $[\alpha]^{20}_{D}$ −35.4°, n^{20}_{D} 1.4819.
Ag Salt : *Anal.* Calcd. for $C_{12}H_{15}Ag$: C, 53.96; H, 5.62; Ag, 40.42. Found : C, 53.85; H, 5.65; Ag, 40.66.

4-Acetylcamphene (X) from 4-Ethynylcamphene—A solution of 10 g. of 4-ethynylcamphene in 30 cc. *iso*-PrOH was added to a mixture of 4.5 g. $HgSO_4$, 70 cc. H_2O, and 3 cc. conc. H_2SO_4, and warmed for 3 hr. at 60~70° with stirring. The reaction mixture was filtered and the filtrate was extracted with Et_2O. The ethereal solution was washed with 10% NaOH and H_2O, dried, and evaporated to yield 5.5 g. of 4-acetylcamphene, b.p$_5$ 83°, $[\alpha]^{20}_{D}$ +9.1°, n^{20}_{D} 1.4790.
Semicarbazone : m.p. 218°. *Anal.* Calcd. for $C_{13}H_{21}ON_3$: C, 66.35; H, 9.0; N, 17.8· Found : C, 66.20; H, 8.81; N, 17.65.

Camphene-4-carboxylic Acid (XIII) from 4-Acetylcamphene—5 g. of 4-acetylcamphene was oxidized with NaBrO at 5° for 2 days and treated by the usual method. The bromo compound was recrystallized from petr. ether to 2 g., m.p. 116°, $[\alpha]^{16}_{D}$ −22.41°(in Me_2CO, l=10 cm., c=20). *Anal.* Calcd. for $C_{11}H_{15}Br_3$: C, 36.1; H, 3.79; Br, 60.06. Found : C, 35.34; H, 3.80; Br, 59.52.

The bromo compound was saponified with 20 cc. of 20% ethanolic KOH on a water bath for 3 hr., followed by the removal of EtOH by distillation. The residue was diluted with H_2O and neutral product was removed with Et_2O. The solution was acidified with H_2SO_4 and extracted with Et_2O. The organic layer was washed with H_2O, dried, and evaporated. 0.5 g. of acidic substance was obtained, m.p. 153° (from petr. ether), $[\alpha]^{16}_{D}$ −42.8°(in EtOH, l=10 cm., c=20). *Anal.* Calcd. for $C_{11}H_{16}O_2$: C : 73.3; H, 8.95. Found : C, 72.69; H, 8.65.

Borneol-4-carboxylic Acid (VIII) from Camphene-4-carboxylic Acid—A mixture of 5 g. of camphene-4-carboxylic acid and 15 g. of CCl_3COOH was warmed at 60~70° for 3 hr. and the reaction mixture was treated as usual, m.p. 215°, $[\alpha]^{18}_{D}$ +6.1°(in EtOH, l=10 cm., c=20). *Anal.* Calcd. for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found : C, 66.51; H, 8.97.

Camphor-4-carboxylic Acid (IX) from Borneol-4-carboxylic Acid—A solution of 1 g. of borneol-4-carboxylic acid in 2 cc. glacial AcOH was added to the solution of 1.2 g. of CrO_3 in 10 cc. of glacial AcOH with ice-water cooling. After standing overnight the reaction mixture was warmed at 80° for 1 hr. and treated as above. The acid product melted at 240°, $[\alpha]^{18}_{D}$ −4°(in EtOH, l=10 cm., c=20). Oxime : m.p. 230°.

4-Acetylborneol (II) from 4-Acetylcamphene—A mixture of 3 g. of 4-acetylcamphene and 10 g. of CCl_3COOH was warmed at 70~80° for 3 hr. The reaction mixture was diluted with H_2O, extracted with Et_2O, and treated as usual. Ester, b.p$_5$ 147°, was obtained. The ester was saponified with 20% ethanolic KOH on a water bath for 3 hr. and EtOH was distilled off. The residue was diluted with H_2O, extracted with Et_2O. The ethereal layer was washed with H_2O, dried, evaporated, and an oil was obtained, b.p$_4$ 135°, $[\alpha]_D$ ±0°.
Semicarbazone : m.p. 205°. *Anal.* Calcd. for $C_{13}H_{23}O_2N_3$: C, 61.63; H, 9.15; N, 16.59. Found : C, 60.49; H, 8.84; N, 16.71.

4-Acetylcamphor (II″) and Camphor-4-carboxylic Acid (IX) from 4-Acetylborneol—5 g. of 4-acetylborneol in 7 cc. of glacial AcOH was oxidized with 12 g. of CrO_3 dissolved in 30 cc. of glacial AcOH with cooling. After standing overnight, the reaction mixture was warmed at 30~40° for 2 hr., diluted with H_2O, and extracted with Et_2O. The organic laper was washed with Na_2CO_3 solution, dried, and evaporated. 0.5 g. of 4-acetylcamphor (semisolid) was obtained.
Oxime : m.p. 216°. *Anal.* Calcd. for $C_{12}H_{19}O_2N$: C, 68.86; H, 9.15; N, 6.69. Found : C, 68.6; H, 8.92; N, 6.71.

The Na_2CO_3 solution obtained by washing of organic layer was concentrated by distillation under a reduced pressure, the residue was acidified with H_2SO_4, and extracted with Et_2O. The ethereal solution was washed with H_2O, dried, and evaporated. The acid substance melted at 245°, $[\alpha]_D$ ±0°.
Oxime : m.p. 230°.

4-Ethynylbornyl Trichloroacetate (XIV) from 4-Ethynylcamphene—A mixture of 5 g. of 4-ethynylcamphene and 7 g. of CCl_3COOH was warmed on a water bath for 3 hr. The reaction mixture was diluted with H_2O and extracted with Et_2O. The ethereal solution was washed with H_2O and dil. Na_2CO_3 solution, dried, and the solvent evaporated. The residue was fractionated by distillation. b.p$_3$ 135~137°, m.p. 75°, $[\alpha]^{6}_{D}$ +32.5°(in Me_2CO, l=10 cc., c=20). *Anal.* Calcd for $C_{14}H_{17}O_2Cl_3$: C, 52.17; H, 5.27; Cl, 32.29. Found : C, 51.81; H, 5.25; Cl, 32.3.

4-Ethynylborneol (XV) from the Ester—5 g. of the ester was saponified with 50 cc. of 20% ethanolic KOH by refluxing for 2 hr. and EtOH was removed by distillation. The residue was diluted with Et_2O and treated as usual. The crude crystals were recrystallized from petr. ether, m.p. 122°, $[\alpha]^{16}_{D}$ +12.45°(in EtOH, l=10 cm., c=20). *Anal.* Calcd. for $C_{12}H_{18}O$: C, 80.9; H, 10.2. Found : C, 80.87; H, 10.47.

4-Ethynylcamphor (XV′) and Camphor-4-carboxylic Acid (IX) from 4-Ethynylborneol—A solution of 5 g. of 4-ethynylborneol in 10 cc. glacial AcOH was added to a mixture of 15 g. of CrO_3 in 50 cc. of glacial AcOH, cooled with ice water. After standing overnight, the reaction mixture was warmed at 60~70° for 2.5 hr. and AcOH was removed by distillation. The residue was diluted with H_2O, neutralized with Na_2CO_3, and the neutral substance extracted with Et_2O. 1 g. of 4-ethynylcamphor was obtained, m.p. 115°, $[\alpha]^{20}_{D}$ +9.41°.
Oxime: m.p. 135°. *Anal.* Calcd. for $C_{12}H_{17}ON$: C, 75.3; H, 8.9; N, 7.3. Found: C, 74.4; H, 9.29; N, 7.25.

The alkaline solution was acidified with H_2SO_4, extracted with Et_2O, and treated as usual. 2 g. of acid substance, melting at 240°, was obtained and recrystallized from petr. ether, $[\alpha]^{7}_{D}$ −10.28° (in EtOH, $l=10$ cm., c=20). *Anal.* Calcd. for $C_{11}H_{16}O_3$: C, 63.3; H, 8.1. Found: C, 67.08; H, 8.23.
Oxime: m.p. 230°. *Anal.* Calcd. for $C_{11}H_{17}O_3N$: C, 62.5; H, 8.1; N, 6.6. Found: C, 62.16; H, 79.8; N, 6.42.

4-Acetylborneol (II) from 4-Ethynylborneol—A solution of 8 g. of 4-ethynylborneol in 30 cc. of *iso*-PrOH was added to a warmed mixture of 5 g. of $HgSO_4$ in 72 cc. H_2O and 3 cc. conc. H_2SO_4, and the mixture was maintained at 60~70° for 3 hr. with stirring. The reaction mixture was filtered and the filtrate was extracted with Et_2O. The organic layer was washed with 10% NaOH and H_2O, dried over anhyd. Na_2SO_4 and the solvent was distilled off. The residue was fractionated by distillation, b.p$_{3.5}$ 125°, $[\alpha]^{19}_{D}$ −6.7°(in EtOH, $l=10$ cm., c=20). Semicarbazone: m.p. 203°.

4-Acetylcamphene (X) from 4-Acetylborneol—A mixture of 4 g. of 4-acetylborneol and 5 g. $KHSO_4$ was treated at 130~160° for 0.5 hr., the reaction mixture was diluted with H_2O and extracted with Et_2O. The organic layer was washed with Na_2CO_3 solution, evaporated, and the residue fractionated by distillation. b.p$_3$ 78°, $[\alpha]_D$ ±0°. Semicarbazone: m.p. 218°.

4-Acetylborneol (II) from 4-Acetylcamphene—A mixture of 2 g. of 4-acetylcamphene obtained as above and 6 g. of CCl_3COOH was warmed at 60~70° for 3 hr. The reaction mixture was diluted with H_2O, neutralized with Na_2CO_3, and extracted with Et_2O. The ethereal layer was washed with H_2O, dried, and the solvent evaporated. The residual substance was distilled at 135°/4 mm. $[\alpha]_D$ ±0°. Semicarbazone: m.p. 203°.

Summary

1. 4-Acetylborneol was synthesized by an indirect process and it was cofirmed that the Hurd-Christ's 2-acetyl-6-hydroxycamphane is 4-acetylborneol and one kind of Rupe reaction occurs in this case.

2. By heating 2-ethynylborneol with dilute hydrochloric acid, 2-camphanylideneacetaldehyde was obtained, no unsaturated ketone having been found, which is a product of Rupe reaction. Therefore the Meyer-Schuster rearrangement occurs in this case.

3. 2-Camphanylideneacetaldehyde was obtained by standing 2-ethynylborneol with conc. formic acid at 40°, showing that it undergoes Meyer-Schuster rearrangement at 40° and Rupe reaction at high temperature.

4. 4-Acetylborneol, 2-ethynylcamphene, 2-acetylcamphene, 2-acetylborneol, 4-ethynylcamphene, 4-acetylcamphene, 4-acetylcamphor, 4-ethynylborneol, and 4-ethynylcamphor, presumed to be related with anionotropic rearrangement of 2-ethynylborneol, were synthesized and their properties were studied.

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