A vast amount of work has been done, on the constitution of the camphor molecule. The earlier investigations on the ready formation of benzene derivatives by the breaking down of camphor led to the view that the molecule was a simple six-membered carbon ring. Subsequent research, however, showed that the formula proposed by J. Bredt *(Ber.,* 1893, 261 ρ.. 3047),.in which camphor is to be regarded as a McycZo-heptane derivative, is correct. This formula is based on the fact that camphoronic acid yields trimethylsuccinic, isobutyric, and carbonic acids, and carbon on dry distillation, and Bredt suggested that it was an *aaβ-* trimethylcarballylic acid,

HO2C∙CH2∙C(CH∣)(CO2H)∙C(CH,)2CO2H, a conclusion confirmed by its synthesis (see below). The Bredt .

formula is also supported by the synthesis of r-camphoric acid by G. Komppa *(Ber.,* 1901, 34, p. 2472 ; 1903, 36, p. 4332). In this syn­thesis ethyl oxalate is condensed with ⅛3-dimethyl glutaric ester, and the resulting diketoapocamphoric ester (1) is then methylated to diketocamphoric ester (2). The keto groups in (2) are converted in CH2 groups as follows:—Sodium amalgam converts this ester into dioxycamphoric ester (3), which with hydriodic acid and phosphorus yields r-dihydrocamphoric acid. At 125° C. this com­pound combines with hydrobromic acid to form ß-bromcamphoric acid, which on reduction with zinc and acetic acid yields r-camphoric acid (4):—

RO,C∙ςH∙C(CH1)2∙ςiΓCC⅛R-, ROîC·ÇH·CfCHA·ÇCCHO·COîR CO CO CO CO

(ο *ω*

H0ιC ■ ÇH · C(CH,⅛ · Ç(CIL·) · C0ιH<- RO2C · ÇH · C(CH1)1 - ÇtCH:) · COtR

CHι CHι HC(OH) -CH(OH)

(4) (3)

This series of reactions leads to a complete synthesis of camphor, since A. Haller *(Comptes rendus,* 1896, 122, p. 446) has shown that camphoric anhydride (1) on reduction yields campholid (2), which by the action of potassium cyanide and subsequent hydrolysis of the nitrile formed is converted into homocamphoric acid (3), the calcium salt of which yields camphor (4) on distillation:—

yCO. ×CHlχ zCIIι,COιH *.ÇH,*

CtHιt< >O-→C1HιZ >O→CsHk< -→C8HiZ∣

×COz ×COz ×CO2Π - ×CO.

(«) (») (3) (4)

Thus camphor and its oxidation products are to be represented as

Clh·ÇH C∏1(o) CHi·ÇH·CO2H COiH ÇOiH

I çtCHi¼ or) I I ς<c⅛)≈ I c(CH,h CH1C<C⅛) -CO(β), C⅛∙C(CH1)∙CO1Π, CHι ’ C(CH,)∙CO1H

Camphor, Camphoric acid, Camphoronic acid.

Camphor yields three classes of halogen substitution derivatives known respectively as *a, ß* and *τr* compounds, the positions being shown in the formula above. The *a* compounds result by direct substitution, the *ß* and χ derivatives being formed in an indirect manner. Cyancamphor, C10H∣sO∙CN, is formed by passing cyanogen gas into sodium camphor, or by digesting sodium oxymethylene camphor with hydroxylamine hydrochloride (L. Claisen, *Ann.,* 1894, 281, p. 351).

»■-Camphor sulphonic acid results from the action of fuming sulphuric acid on camphor (F. S. Kipping and W. J. Pope, *Jour. Chem. Soc.,* 1893, 63, p. 573). Camphoroxime, CioHi60:NOH, was first prepared by E. N⅛eli *(Ber.,* 1883, 16, p. 497).

/-Camphor is formed by the action of nitric acid on Z-bomeol (W. J. Pope and A. W. Harvey, *Jour. Chem. Soç.,* 1901, 79, ρ. 76). r-Camphor melts at 178-179° C. (for its preparation see A. Debiernc, *Comptes rendus,* 1899, 128, p. mo; W. A. Noyes, *Amer. Chem. Jour.;* 1905, 27, p. 430).

*Camphoric acid.* Four optically active and two inactive forms of this acid are known. The most important is the d-form, which is produced by the oxidation of (/-camphor with nitric acid. It crystallizes in plates or prjsms which melt at 187° C. Potassium permanganate oxidizes it to oxalic acid and Balbiano’s acid, CaH12Os, together with small quantities of camphanic, camphoronic and trimethyl succinic acids. It yields two series of acid esters, the αZZu-esters (1), formed by the partial saponification 'of the neutral esters, and the *ortho-esters* (2), formed by heating the anhydride with alcohols or sodium alcoholates.

CHi·ÇH·COiH CHi·ÇH·COîR

I Ç(CH.)i I Ç(CHi)>

CHι·C(CHι)·CO≈R CHι, C(tTL)^COιH

(I) (2)

/-Camphoric acid results on oxidizing Z-borneol or matricaria camphor. It melts at 1870 C. r-Camphoric acid is formed on mixing alcoholic solutions of equimolecular quantities of the *d-* and Z-acids, or by oxidizing í-camphor. It melts at 202—203° C.

*Camphoronic acid,* C>HuOβ. From a study of its distillation products J. Bredt *(Ber.,* 1893, 26, p. 3049) concluded that this acid

was an ααβ-trimethylcarballylic acid, a conclusion which was confirmed by its synthesis by W. H. Perkin, junr., and J. F. Thorpe *(Jour. Chem. Soc.,* 1897, 71, 1169):—Aceto-acetic ester is con­densed with α-bromisobutyπc ester, the ιesulting hydroxytrimethyl glutarate (1) converted into the chlor- and then into the corre­sponding cyan-trimethyl glutarate (2), which on hydrolysis with hydrochloric acid yields camphoronic acid (3) and some trinιethyl glutaconic acid :—

(CH1⅛CBr · CO1R-f-CH1COCH.· COιR →(CH1)1C(COιR)· C(OH)(CΠ1)· C∏i∙ CO∣R

(I)

(CH,)1C(CO1H) · C(COiH)(CH>) ■ CH1∙COtH\*- (CH,hC(CC⅛R) · C(CN)(CH>) · CH1,COlR ω *ω*

*Fenchone,* CtoHlβO, is trimethyl - (2 · 7 · 7) - *bicyclo-*(1 · 2 · 2)· ħepta- n0ne-3. It occurs in *d∙* and Z-forms, the former in oil of fennel and the latter in oil of thuja. It may be obtained from these oils, by treating the fraction boiling between 190-195° C. with nitric acid and distilling the product in a current of steam. The fenchones are pleasant-smelling oils which boil at 192-193° C., and on solidification melt at 5⅞° C. They do not combine with sodium bisulphite. They dissolve unchanged in cold concentrated hydrochloric and sulphuric acids, and are very stable; thus the monobromfenchone is only formed by heating the ketone with bromine to 100° C. under pressure (H. Czerny, *Ber.,* 1900, 33, p. 2287). On oxidation with potassium permanganate it yields acetic and oxalic acids together with dimethylmalonic acid. By the action of hot concentrated sulphuric acid it yields acetyl-ortho- xylene,

CH,CO(4)C,H,(CH,)f(l∙2)

(J. E. Marsh, *Jour. Chem. Soc.,* 1899, 75, p. 1058). When heated with phosphorus pentoxide to 115-1300 C. it forms metacymene. Since it does not yield any oxymetnylene compounds, it cannot contain the grouping—CH2∙CO—in the molecule.

Hydrocarbons, C10Hu, of the Terpene Series

*Menthene,* CiHs (C H t) (CjH7) , is methyl-1 -isopropyl-4-cycZ0hexcne-3. It is obtained by the action of anhydrous zinc chloride or copper sulphate on menthol (J. W. Brühl, *Ber.,* 1892, 25, p. 142), by boiling menthyl chloride with aniline (G. Wagner, *Ber.,* 1894, 27, p. 1636), by heating menthyl chloride with potassium phenolate (L. Masson, *Ber.,* 1896, 20, p. 1843), and by the dry distillation of the methyl ester of menthyl xanthate (L. Tschugaeff, *Ber.,* 1899, 32, p. 3333)∙ It is a colourless liquid which boils at 167-168° C. When strongly heated with copper sulphate it yields cymene. According to Tschugaeff, the xanthate method alone gives a pure menthene of the above constitution, the menthene obtained from the dehydration of menthol being a cycZ0hexene-4 ; and the one obtained by O. Wallach *(Ann.,* 1898, 300, p. 278) from Z-menthyl- amine being a *cyclohe×ene-2.*

*Carvomenthene,* CtHj(CHa)(CsH7), is probably methyl-i-isopropyl- 4-cycZ0hexcne-ι. It is prepared by heating carvomcnthyl bromide with quinoline, or by heating carvomenthol with potassium bisul­phate to 200o C. It is a liquid which boils at 175-176° C.

*Camphane,* C7H9(CHs)2 is ι∙7∙7-trimethyl-WcycZ0-(ι∙2∙2)-heptane. It is prepared by the action of sodium and alcohol on pinene hydrio- dide, or by reducing the hydriodide with zinc in acetic acid solution. It is *a* crystalline solid which melts at 153° C. and boils at 160° C.

Olefine Terpenes

*Myrcene,* Cι0Hu, was first isolated by F. B. Power and C. Kleber from oil of bay (Schimmel & Co., *Bulletin,* April 1895, p. 11); it is also found in oil of sassafras leaves. It is obtained from bay oil by shaking the oil with a 5 per cent, solution of caustic soda, followed by fractionation *in vacuo.* It boils at 67-68° C. (20 mm.), and polymerizes when heated for some time. When oxidized by potassium permanganate it yields succinic acid. By the action of glacial acetic acid in the presence of dilute sulphuric acid, a liquid is produced, which on hydrolysis yields myrcenol, C10HuO, an alcohol which is probably an isomer of linalool (P. Barbier, *Comptes rendus,* 1901, 132, p. 1048). The hydrocarbon is probably to be considered as being (CHs)2C : CH · (CH2)2 · C( : CH,) · CH : CHs (Enk)aar, *Bul­letin 0$ Rouse-Bertrand fils,* Nov., 1906, p. 92). Ocymene is an isomer which can be extracted from the leaves of the basil. Enklaar *(loc. cit.)* represents it as (CHi)2Ct CH · CH2 · CH : C(CHs) · CH : CH2. Anhydro-geraniol, CιoHιi, the first olefine terpene isolated, was pre­pared in 1891 by F. W. Semmlcr; it is formed when geraniol is heated with potassium bisulphate to 170° C.

Alcohols, Aldehydes and Ketones d-Ci∕roMcZZoZ,CιoHnOHorCHi∙C(ιCH2)∙(CH2)j∙CH(CHj)∙(CHj)2OH, or 2∙6 dimethyl-octene-ι-ol-8 occurs in Réunion geranium oil and was first prepared by F. D. Dodge *(Amer. Chem. Jour.,* 1889, ll,-p. 463) by reducing, the corresponding aldehyde (<Z-citronellal). It is an odorous oil which boils at 117-118°. C. (17 mm.). Oxida­tion by chromic acid mixture converts it into cιtronellal, whilst