*Terpinene,* ∆l : 4(8) terpadiene (?), is found in cardamom oil and in oil of marjoram. It is formed by the action of alcoholic sul­phuric acid on dipentene, terpin hydrate, cineol phellandrene or terpineol; or by the action of formic acid on linalool.

*Phellandrene* is a mixture of Δ1:5 terpadiene and Δ2:1(7) terpadiene (pseudo-phellandrene) (F. W. Semmler, *Ber.,* 1903, 36, p. 1749). It is found as *d*-phellandrene in oil of water-fennel and oil of elemi, and as /-phellandrene in Australian eucalyptus oil and oil of bay. It is an exceedingly unstable compound, and must be extracted from the oils by distillation *in vacuo.* The hydrocarbons obtained from elemi oil and eucalyptus oil correspond to Δ1∙5 terpadiene. A similar hydrocarbon was obtained by C. Harries and Μ. Johnson *(Ber.,* 1905, 38, p. 1832) by converting carvone hydro­bromide into Δ6 terpenone-2, then, by phosphorus pentachloride, into chlor-2-phellandrene, which is finally reduced.

*Sylvestrene,* ∆1. 8(9) meta-terpadiene, is found in Swedish and Russian oil of turpentine and in various pine oils. It boils at 175-176° C. and is dextro-rotatory. It is one of the most stable of the terpenes and gives a characteristic deep blue colour on the addition of a drop of sulphuric acid to its solution in acetic an­hydride. On treating the hydrobromide with bromine in the presence of iodine, a product is obtained which on reduction yields meta-cymene (A. v. Baeyer and V. Villiger, *Ber.,* 1898, 31, p. 2067).

*Carvestrerie* is obtained by the distillation of carylamine or vestry- lamine hydrochloride (A. v Baeyer, *Ber.,* 1894, 27>, pp. 3485 seq.). It is regarded by Baeyer as *i*-sylvestrene. it was synthesized by W. H. Perkin and G. Tattersall *(Proc. Chem. Soc.,* 1907, 22. p. 268) by the application of the Grignard reaction to the ethyl ester of γ-ketohexahydrobenzoic acid (1). By the action of magnesium methyl iodide this ester yields the lactone of γ-hydroxy-hexahydro- meta-to1uic acid, which is transformed by hydrobromic acid into the corresponding γ-bromo-hexahydro-meta-toluic acid. This latter substance by the action of pyridine yields tetrahydro-meta- toluic acid, the ester of which by magnesium methyl iodide is con­verted into ∆·l-meta menthenol-8 (2). The meta-menthenol on dehydration by potassium bisulphate yields carvestrene (3) of boiling-point 179-180° C.

of the double linking in the molecule is shown by the use of the symbol Δ followed by the number of the carbon atom immediately preceding it.

Monocyclic Terpene Group

Lfníonene, Δi:8(9) terpadiene, C10H16, is known in three forms, namely d-limonene, *l*-limonene, and *i*-limonene or dipentene. *d*-Limonene is the chief constituent of oil of orange-rind, and is also found in oil of lemon and oil of bergamot.' /-Limonene is found in oil of fir-cones and in Russian peppermint oil. Both are pleasant-smelling liquids, which boil at 175-176° C. They differ from each other only in rotatory power. Dry hydrochloric acid gas converts them into optically active limonene hydrochloride, while in the moist condition it gives dipentene dihydrochloride. When heated to a sufficiently high temperature they are con­verted into dipentene. Four optically active nitrosochlorides are known, two corresponding to each of the active limonenes, and these on heating with alcoholic potash are converted into *d-* and ∕-carvoxime. Dipentene (ι-limonene) is found widely distributed in many essential oils, e.g. of camphor, Russian turpentine, cubebs, bergamot, cardamom, &c., and is also a product of the dry dis­tillation of many vegetable resins. It may be produced by heating many terpenes (pinene, camphene, sylvestrene. limonene) for several hours at 250-270° C. ; or by the polymerization of isoprene at 300° C. To obtain pure dipentene it is best to heat dipentene hydrochloride with anhydrous sodium acetate and glacial acetic acid (O. Wallach, *Ann. Chem. Pharm.,* 1887, 239, p. 3). It is a pleasant-smelling liquid, which boils at 175-176° C., and poly­merizes on heating to high ' temperatures. When warmed with alcoholic sulphuric acid it yields terpinene, whilst concentrated sulphuric acid or phosphorus pentasulphide convert it into para­cymene. Dipentene dinydrochloride, C10Hl6∙2HCl, best prepared by passing a current of hydrochloric acid gas over the surface of a glacial acetic acid solution of dipentene, crystallizes in rhombic tables which melt at 50° C. and boil at 118-120° C. (10 mm.). It is apparently a *trans*-compound, for A. v. Baeyer *(Ber.,* 1893, 26, p. 2863) has obtained a *cis*-dihydrochloride of melting-point 25° (*circa),* by the action of hydrochloric acid on cineol. *Terpinolene,* Δ1:4(8) terpadiene, has not as yet been observed in essential oils. It is formed by the action of hot dilute sulphuric acid on terpineol, terpin hydrate and cineol. It is an inactive liquid boiling at 183-185° C., and is readily converted into terpinene by acids.

zCO∙CHsv zC(CH>)ιCHκ *zC(CHj)∙.CHκ* zCH1

H1C< >CH COOΠ →⅛C( )UI∙C'⅛OH ÷Π-C( >CH∙C<

×CH3∙CH∕ xCHi —C∏∕ xCH3—CH>z xCH3.

(1) · . ^ (2) (3)

(A synthetical monocyclic terpene, viz. 1-methyl-4-isopropyl dihydrocymene was prepared by A. v. Baeyer *(Ber.,* 1893, 26, p. 232). Succino-succinic ester is converted into the methyl iso­propyl derivative, which on hydrolysis and elimination of carbon

dioxide yields l-methyl-4-isopropyldiketohexamethylene. This ketone is then reduced to the secondary alcohol, the hydroxyl groups replaced by bromine, and hydrobromic acid is then removed from the bromo-compound by boiling it with quinoline, leaving the ter­pene. It is a liquid which boils at 174° C. and shows a complete terpene character.

Alcohol and Ketone Derivatives

*Menthol* (terpan-0l-3), C10H20O. The *laevo* variety is the chief portion of oil of peppermint; it may be prepared by reducing the menthone obtained by E. Beckmann and Μ. Pleissner *(Ann.,* 1891, 262, p. 21) from pulegone hydrobromide with sodium and alcohol. It crystallizes in prisms which melt at 43° C. and boil at 212° C. It is readily oxidized by chromic acid to the corresponding ketone menthone. By the action of phosphorus pentoxide, or zinc chloride, it is converted into menthene, C10H18s, and when heated with anhydrous copper sulphate to 250° C. it yields para-cymene. It is reduced by hydriodic acid and phosphorus to hexahydrocymene. The phosphorus haloids yield haloid esters of composition C10H19Cl, which, according to I. L. Kondakow *(Jour. prakt. Chem.,* 1899 [2], 60, p. 257) are to be regarded as tertiary esters ; a similar type of reaction is found in the case of carvomenthol. A (/-menthol has been prepared from the *i*-mixture obtained by reducing menthone with sodium. The mixture is benzoylated, and the liquid (/-menthol benzoate separated and hydrolysed.

*Tertiary menthol* (terpan-ol-4), a liquid boiling at 97-101° C. (20 mm.), has been obtained by the hydrolysis of the ester prepared by heating menthene with trichloracetic acid (A. Reychler and L. Masson, *Ber.,* 1896, 29, p. 1844). It possesses a faint pepper­mint odour. W. H. Perkin, junr. *(Proc. Chem. Soc.,* 1905, 21, p. 255) synthesized it from 1∙4 methylcyclohexanone: sodium carbonate converts α-bromhexahydro-para-toluic acid (1) into ∆∙1-tetrahydro-para-toluic acid and a-oxyhexahydro-para-toluic acid, and the latter on treatment with dilute sulphuric acid yields 1∙4-methylcyclohexanone (2), which by the action of magnesium isopropyl iodide and subsequent hydrolysis is converted into tertiary menthol (3).

zCH1∙CIk zCHs∙CHκ zCH3∙CHικ zOH

Ca>∙CΠ< >C Br∙C0sH →CHj∙CM< )CO→CHι∙CH( >C<

**×CHi∙CHsz** xCH2∙CHZ ×CIL∙CHiz ×C1Hj.

(«) ri) (3)

the action of acetic acid on linalool. The racemic variety has been prepared by the action of formic acid on geraniol, and was synthesized by the following method (W. H. Perkin, junr., *Jour. Chem. Soc.,* 1904, 85, P∙ 654). y-Cyanpentane tricarboxylic ester (1) (prepared by the

*Terpin* (terpan-diol 1∙8), CιoHιβ(OH)2, is known in two stereo­isomeric forms, *cis*-terpin and *trans*-terpin. The *trans-* form is obtained by adding silver acetate to a glacial acetic acid solution of dipentene dihydrochloride, filtering and neutralizing the filtrate by caustic soda. It is then extracted with ether, and the acetyl derivative so obtained is hydrolysed by alcoholic potash. It crystallizes in prisms, which melt at 156-158° C., and boil at 263-265° C. It is converted into terpineol by dilute sulphuric acid. The *cis*-compound melts at 104-105° C. and may be pre­pared by heating its hydrate. Terpin hydrate, C10H18(OH)2∙H2O, crystallizes in prisms which melt at 116° C. It is prepared by acting with dilute mineral acids on limonene or dipentene. When boiled with glacial acetic acid it is converted Into terpineol, while concentrated hydriodic acid at 210° C. reduces it to hexahydro­cymene. When heated with dilute sulphuric acid it gives a number of compounds, which may be considered as arising from the loss of one or two molecules of water from one molecule of terpin.

*Cineol,* C10H18O, is an inner oxide of terpin. It is found in the oils of wormseed, cajaput, eucalyptus, laurel, galanga, camphor and of lavender. It may be prepared by passing a current of dry hydrochloric acid gas into wormseed oil, the precipitated hydro­chloride being then distilled in a current of steam (O. Wallach and W. Brass, *Ann.,* 1884, 225, p. 297). It is an inactive liquid, which boils at 176° C. The oxygen atom in the molecule does not appear to possess either an alcoholic, ketonic, aldehydic or acid function.

*Terpineol* (Δ1-terpen-ol-8), C10H17(OH). The term “terpineol” has been used to denote what is now known to be a mixture of various isomeric alcohols. Liquid terpineols have been isolated from the oils of *Erigeron canadense,* of marjoram and of camphor. Liquid terpineol is generally prepared by the action of dilute sul­phuric acid on terpin hydrate. It consists of a mixture of various isomers, from which a solid terpineol melting at 35° C. and an isomeric Δ∙8(9) terpen-ol-l, melting at 32° C., have been isolated (K. Stephan and J. Halle, *Ber.,* 1902, 35, p. 2147. See also G. Bouchardat, *Comptes rendus,* 1887, 104, p. 996; 1895, 121, p. 141; Schimmel & Co., *Semi-annual Reports,* Oct. 1897, p. 11; J. Godlewsky, *Chem. Centralblatt,* 1899 (I.), p. 1241). Solid ter­pineol exists in active and racemic forms. The active form was obtained by F. W. Semmler *(Ber.,* 1895, 28, p. 2190) by replacing the halogen atoms in the active monohydrobromide of limonene by the hydroxyl group; it has also been obtained by