# 436.   *Autoxidation of α-Phellandrene.*

By A. BLUMANN and L. RYDER.

Autoxidation of α-phellandrene produces, besides the known *p*-menth-1-ene-3 : 6-diol, m. p. 164—165°, a mixture including an isomeric *diol*, m. p. 54°. These substances are shown to be *trans*- and *cis*-forms, respectively.

THE formation of a substance, $C_{10}H_{18}O_2$, m. p. 164—165°, from French bitter fennel oil was observed by Schimmel & Co. (Semi-annual Report, April 1901). Clover (*Philippine J. Sci.*, 1907, 1; *Amer. Chem. J.*, 1908, **39**, 640), who found the substance in oil of elemi, proved that it was derived from α-phellandrene (I). After further investigations (Schmidt, Thesis, Göttingen, 1925, pp. 39, 77; Faber, Thesis, Göttingen, 1927, p. 28; Mladenovic, *Monatsh.*, 1934, **64**, 177), Bodendorf (*Arch. Pharm.*, 1933, **271**, 9) suggested that it was a *p*-menth-1-ene-3 : 6-diol, a constitution which was proved by Dupont (*Bull. Ind. Chim. Belge*, 1940, 10) and is now confirmed by the action of acids on the diol.

(I.)   (II.)   (III.)
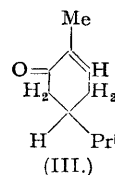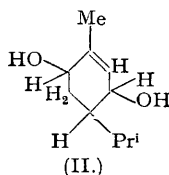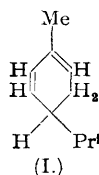
Concentrated acids convert the diol into carvotanacetone (III) which, at first sight, might be held to originate from an α-glycol (cf. Ralph, *Proc. Roy. Soc. N.S.W.*, 1947, **80**, 210; *Aust. J. Sci.*, 1948, Dec., 98). However, with very dilute sulphuric acid, the diol loses water to form an *oxide* (IV), which readily yields carvotanacetone (and *p*-cymene) in presence of concentrated acid. The same oxide is obtained from the oils remaining after removal of the diol, m. p. 164—165°, but then has a lower optical rotation.

Autoxidation of commercial (−)-α-phellandrene (from the oil of *Eucalyptus dives*) readily gives the same diol, m. p. 164—165°, but in small and variable yield, together with a much larger amount of a viscous mixture of isomers, whence an isomeric *diol*, m. p. 54°, can be isolated. Both compounds are also obtained by leaching the high-boiling (piperitone) fractions of *E. dives* oil with water.

The substances, m. p. 164—165° and 27°, are respectively *trans*- and *cis*-*p*-menth-1-ene-3 : 6-diol (cf. terpin hydrate and the glycol, m. p. 60°, from autoxidised limonene; Blumann and Zeitschel, *Ber.*, 1914, **47**, 2623; H. Schmidt, private communication; cf. von Baeyer, *Ber.*, 1896, **29**, 1198). The compound, m. p. 164—165°, has the higher b. p., is sparingly soluble in water, distils unchanged at atmospheric pressure (whereas the isomer decomposes), and gives, with acetic anhydride, a quantitative yield of a crystalline *diacetate* (the yield from the isomer is lower owing to decomposition). Thus, the diols behave relatively in the same way as do *neo*menthol and menthol (Zeitschel and Schmidt, *Ber.*, 1926, **59**, 2298).

(IV.)   (V.)   (VI.)
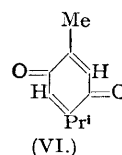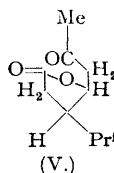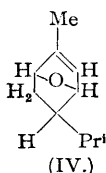
Both diols are readily hydrogenated in the presence of a nickel catalyst under mild conditions, but noble-metal catalysts are apparently unsuitable [cf. Bodendorf (*loc. cit.*) and Mladenovic (*loc. cit.*); cf. also the hydrogenation of α-terpineol (Zeitschel and Schmidt, *Ber.*, 1927, **60**, 1372)]. The saturated *cis*-form loses water readily when heated with 10% sulphuric acid, but the corresponding *trans*-form can be recrystallised unchanged from this medium.

The unsaturated diols and the saturated *cis*-diol have no odour or taste; the saturated *trans*-diol is also odourless, but produces on the palate and in the throat the same sensation as does pure menthol, although free from unpleasant taste.

With Beckmann's chromic acid mixture (cf. Henry and Paget, *J.*, 1928, 72) both diols yield the keto-lactone (V) and thymoquinone (VI).

EXPERIMENTAL.

Oxidation of α-Phellandrene.—(a) Oxygen was bubbled through phellandrene, a_D −118°, at 35—40° until the density was >1. To 1 kg. of the product water was added, and the mixture (which was acid) was steam-distilled after addition of magnesium carbonate (148 g.). The residue was thoroughly washed with hot water, the aqueous extracts (X) were combined (see below), and the oily layer was distilled, yielding fractions (i) (29 g.) b. p. 138°/25 mm., n_D^{20} 1·4820, (ii) (74 g.) b. p. 130°/5·5 mm., n_D^{20} 1·4870, (iii) (28 g.) b. p. 145°/10 mm., n_D^{20} 1·4925, (iv) (130 g.) b. p. 180°/11·5 mm., (v) (16 g.) b. p. 186°/11·5 mm., and a residue (126 g.). Fractions (iv) and (v) partly crystallised, yielding 7·5 g. of *trans*-p-menth-1-ene-3 : 6-diol; the remainder of fractions (iv) and (v) was bulked with fraction (iii) and refractionated to yield (vi) (10 g.) b. p. 105°/7 mm., a_D −13·6°, (vii) (8 g.) b. p. 134°/7 mm., a_D −16·8°, (viii) (23 g.) b. p. 135°/8 mm., a_D −15·3°, (ix) (20·5 g.) b. p. 145°/8 mm., a_D −14·5°, (x) (21 g.) b. p. 155°/8 mm., a_D −7·0°, (xi) (20 g.) b. p. 157°/8 mm., a_D +11·0°, (xii) (18 g.) b.p. 175°/8 mm., (xiii) (2 g.) b. p. 178°/8 mm., and a residue (25 g.). Fractions (vi)—(x) were combined and washed with hot water, but only 2 g. were dissolved ; they were therefore washed with light petroleum, after which the bottom layer was fractionated, yielding fractions (xiv) (7·5 g.) b. p. 115°/4·5 mm., a_D −28°, (xv) (16·5 g.) b. p. 124°/3 mm., a_D −20°, (xvi) (5·5 g.) b. p. 130°/3·5 mm., a_D −18·1°, (xvii) (6·5 g.) b. p. 135°/3·5 mm., a_D +3·8°, (xviii) (2·5 g.) b. p. 142°/3·5 mm., and a residue (8 g.) ; fractions (xvii) and (xviii) crystallised.

The aqueous extracts (X) were concentrated *in vacuo* as far as possible and salted out. The top layer was dried at 80 mm. and extracted with 200 c.c. of benzene. The extract was filtered and, after removal of the benzene, distilled to give 10 g. of "*cis*-fraction," b. p. 125°/7 mm. to 170°/11 mm., a_D −35·8°, and a residue (19 g.).

(b) After 90 lb. of α-phellandrene had been exposed to air for several months, 1·3 g. of *trans*-diol and 14 g. of "*cis*-fraction," d^{23} 1·003, n_D^{23} 1·484, a_D −38·6°, were obtained.

Fractionation of E. dives Residues.—(a) Diols from last runnings of the piperitone distillation (71 lb. ; a_D 0; $d_D^{15·5}$ 0·970) were stirred with three lots each of 3·5 gallons of hot water. The combined aqueous layers, after being washed with a petroleum solvent, were concentrated as previously described, yielding fractions (i) (19·5 g.) b. p. 130°/4 mm., a_D −46·9°, $n_D^{18·5}$ 1·485, (ii) (28·5 g.) b. p. 133°/4 mm., a_D −49·2°, $n_D^{18·5}$ 1·4952, (iii) (8 g.), b. p. 135°/5 mm., a_D −51·3°, $n_D^{18·5}$ 1·486, (iv) (18 g.) b. p. 140°/5 mm., a_D −51·5°, $n_D^{18·5}$ 1·496, (v) (9 g.) b. p. 148°/5 mm., and a residue (6 g.).

(c) 1200 Lb. of residues from the distillation of *E. dives* oil were extracted as previously described. The corresponding "*cis*-fraction " had a_D −31·6°. 37 G. of *trans*-diol were also obtained.

Another extraction of 90 lb. of a similar fraction from the piperitone distillation gave a "*cis*-fraction," a_D −47·0°.

(trans)-p-*Menth*-1-ene-3 : 6-*diol*.—The specimens from phellandrene and *E. dives* oil had the same m. p. and a_D, in accord with those of Dupont (*loc. cit.*).

Acetylation. Heating the diol (5 g.) and 15 g. of acetic anhydride (15 g.) under gentle reflux for 2 hours gave 7 g. of *diacetate*, needles, m. p. 28°, b. p. 148—149°/4 mm., a_D +69·15°, $n_D^{27·6}$ 1·4610 (Found : ester value, 438·5 ≡ 99·65%), whence hydrolysis with alcoholic sodium hydroxide regenerated the original diol.

Hydrogenation. A concentrated alcoholic solution of *trans*-p-menth-1-ene-3 : 6-diol was hydrogenated in a shaking vessel at atmospheric pressure, in presence of a neutral nickel catalyst, until no further absorption occurred (15 g. of diol absorbed 1800 c.c. of hydrogen). trans-p-*Menthane*-3 : 6-*diol* crystallised in shiny needles, m. p. 137°, a_D^{21} +32·8° (*c*, 0·0783 in ethanol), from ethanol in which it was more soluble than the original glycol ; it was also more soluble in water, but very sparingly soluble in benzene or light petroleum (Found : C, 69·4 ; H, 11·7. $C_{10}H_{20}O_2$ requires C, 69·7 ; H, 11·7%).

Oxide.—Steam was passed through a mixture of the *trans*-diol (20 g.) and 0·5% sulphuric acid (100 c.c.) while the volume was kept constant. 17 G. of the distillate were stirred with a saturated aqueous solution of sodium sulphite (28 g. of anhydrous) and sodium hydrogen carbonate (19 g.) for 6 hours. After filtration and separation, the product (14 g.) was recovered and distilled at 6 mm., giving fractions (a) (3·5 g.), a_D −33·4°, (b) (2·5 g.), a_D −58·6°, (c) (7·0 g.) a_D −88·6°, and a residue (1 g.). Fraction (c) when redistilled gave the pure *oxide* (IV), $[a]_D$ −95·68°, n_D^{20} 1·4775, and $d_{15·5}^{22}$ 0·926 (Found : C, 78·4 ; H, 10·6 ; $C_{10}H_{16}O$ requires C, 78·9 ; H, 10·6%).

When the oxide was kept in a sealed tube for several months, $[a]_D$ changed to −90°. Water was evolved when the oxide was distilled at atmospheric pressure ; bromination did not give a satisfactory product.

Fractions (a) and (b) were heated on a water-bath for 20 minutes with an equal weight of 90% formic acid and then washed until neutral. The residue (5 g.) was shaken with aqueous sodium sulphite–sodium hydrogen carbonate as described above. The solution was filtered, and extracted with light petroleum. The petroleum layer yielded an oil (2·5 g.), which, when distilled over sodium, had the odour, b. p., and n_D of *p*-cymene. When the aqueous solution was boiled for a short time with sodium carbonate and extracted with ether, it yielded carvotanacetone (1·3 g.), a_D −43·8° (semicarbazone, m. p. 174°).

cis-p-*Menth*-1-ene-3 : 6-*diol*.—The "*cis*-fractions" could not be induced to crystallise. When, however, those with the highest lævorotation (−51·5°) were kept in contact with water for many days at temperatures slightly above 0°, well-shaped crystals of a hydrate formed ; when spread on a porous tile, these rapidly became sticky. This hydrate could then be easily isolated from the autoxidation products of phellandrene, as well from "*cis*-fractions" of varying rotation, those having the greatest lævorotation giving the highest yield. Recrystallised from water, it melted at 27° and did not become sticky when kept at +8°. It is more soluble in cold than in hot water. The aqueous solution froths when shaken. Attempts to determine the water of crystallisation by keeping the hydrate in an evacuated desiccator over phosphoric oxide gave values corresponding to approximately 3 molecules, but were erratic because this substance loses water in air, even at 8°. The hydrate was readily dehydrated by heating at 100 mm. ; the anhydrous cis-*diol* thus obtained distilled mainly at 136—137°/4 mm. and then had $[a]_D$ (liquid) −51·5° and crystallised readily. Recrystallised from benzene, it had m. p. 53·5—54°,

$[\alpha]_D^{23\cdot5}$ $-33\cdot6°$ (c, $0\cdot1031$ in ethanol) (Found : C, $70\cdot05$; H, $10\cdot9$. $C_{10}H_{18}O_2$ requires C, $70\cdot55$; H, $10\cdot7\%$). When the *cis*-diol was distilled at atmospheric pressure, partial decomposition occurred ; the first distillate, which had an odour of cymene and of the oxide from the *trans*-diol, did not react with semi-carbazide but, after treatment with formic acid, gave a semicarbazone which did not depress the m. p. of that of carvotanacetone.

Acetylation.   The anhydrous glycol (6 g.) and acetic anhydride (8 g.) were heated under gentle reflux for 2 hours and then fractionated, yielding fractions (i) b. p. up to $100°/110$ mm. (12 g.), (ii) b. p. $115°/6\cdot5$ mm. (3 g.), and (iii) b. p. $140°/6\cdot5$ mm. ($5\cdot5$ g.).   Fractions (ii) and (iii) were combined, washed until neutral, and dried.   The resultant diacetate had α_D $-128\cdot8°$, the ester value ($337\cdot7$) corresponding to $85\cdot6\%$ purity.

Hydrogenation.   This was carried out as for the *trans*-diol.   The distilled saturated product did not at once crystallise but, when shaken with water, gave a crystalline *trihydrate* (Found : loss over sulphuric acid in a vacuum, $23\cdot7\%$. $C_{10}H_{20}O_2,3H_2O$ requires H_2O, $23\cdot9\%$), which, when recrystallised from water, formed shiny plates, m. p. $58—59°$.   At room temperature these soon changed into an amorphous powder which was recrystallised from benzene, giving anhydrous cis-p-*menthane*-3 : 6-*diol* as prisms, m. p. $88—89°$, $[\alpha]_D^{21}$ $+32\cdot7°$ in ethanol (Found : C, $69\cdot4$; H, $11\cdot95$. $C_{10}H_{20}O_2$ requires C, $69\cdot7$; H, $11\cdot7\%$).

Oxidation.   The anhydrous *cis*-diol ($2\cdot55$ g.) was shaken with water (15 c.c.).   While this mixture was cooled, a mixture of potassium dichromate (9 g.), sulphuric acid (12 g.), and water (40 c.c.) was slowly added.   Reaction ended in $1\frac{1}{2}$ hours.   The green solution was twice extracted with benzene and the extract steam-distilled.   Treatment of the yellow distillate with semicarbazide gave thymoquinone monosemicarbazone, m. p. $202°$ (decomp.), whereas the residue from the distillation gave the semi-carbazone, m. p. $185—186°$, of the C_9 lactone of Henry and Paget (*loc. cit.*).   M. p.s were undepressed on admixture with the semicarbazones of the corresponding oxidation products of the *trans*-diol.

ADDENDUM by REX T. PRIDER.

Crystallography and Optical Constants of trans-p-*Menth*-1-*ene*-3 : 6-*diol.*—The optical and goniometrical examination of crystals of the *trans*-diol indicate that this compound belongs to

FIG. 1.

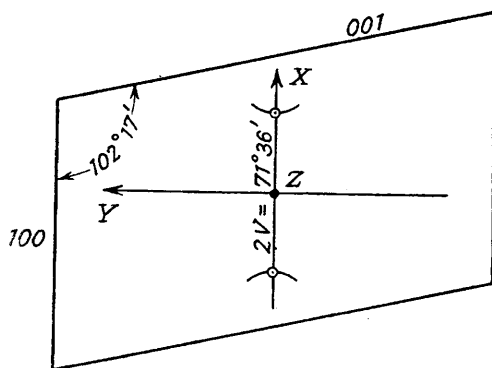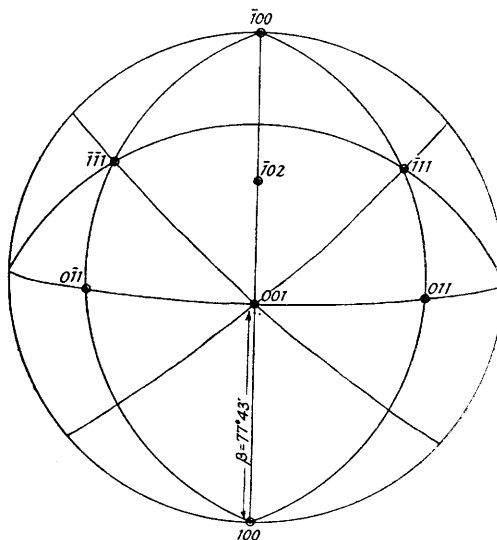*Optic orientation of* trans-p-*menth*-1-*ene*-3 : 6-*diol.*

FIG. 2.

Stereogram of forms developed :
trans-p-*menth*-1-*ene*-3 : 6-*diol.*

the normal class of the monoclinic system.   The optical properties (all constants determined for sodium light) are : colourless, biaxial, positive optical character ; n (by immersion in oils), $\gamma = 1\cdot591 \pm 0\cdot001$, $\beta = 1\cdot540 \pm 0\cdot001$, $\alpha = 1\cdot516 \pm 0\cdot001$, $\gamma - \alpha = 0\cdot075$; optic axial angle (by Fuess axial-angle apparatus) $(+)2V = 71° 36'$; dispersion of the optic axes is noticeable $r > v$, but there is no noticeable dispersion of the bisectrices ; optic elongation of acicular crystals and cleavage fragments is positive.

The optic orientation (Fig. 1) is : $Z = b$, $X = c$ (approximately), opt. ax. pl. $\perp 010$.

The following three distinct crystallographic habits were noted in the material examined.

(i) Single crystals, up to $4 \times 4 \times 2\frac{1}{2}$ mm., completely bounded by rather dull-lustred faces, tabular parallel to the base (001).   These crystals show the development of the base (001), clinodome (011), orthopinacoid (100), and hemipyramid ($\bar{1}$11), and have cleavage parallel to

(001), (100), and (011). The dull-lustred faces did not permit of accurate determination of the interfacial angles on the two-circle goniometer, but the following table gives the average angles when the crystal was set with the base (001) normal to the vertical circle axis :

Face.*	ρ.	φ.	Face.*	ρ.	φ.
001	0° 00′	—	Ī11	80° 35′	48° 30′
Ī00	102° 00′	0° 00′	0Ī1	67° 48′	270° 00′
100	78° 00′	180° 00′	011	67° 48′	90° 00′
Ī̄11	80° 35′	311° 30′			

* Indices on assumption that the hemipyramid is the unit form (Ī11).

Thus β = 78° 00′, and the axial ratio $b : c = 1·000 : 2·503$.

(ii) Cleavage plates, measuring on the average $5 \times 5 \times \frac{1}{2}$ mm., with highly perfect basal (001) cleavage giving the substance a micaceous habit. In addition this form has very good (100) cleavage and fair (010) or (011) cleavage. As a result, when crushed for optical examination in oils, it cleaves into extremely thin prisms elongated parallel to b, which have straight extinction and positive optical elongation. On this material the refractive indices γ and β′ were measured by immersion in oils but, because of the highly perfect basal cleavage, α cannot be conveniently determined. The optic axial angle quoted above was determined on this material. Measurement of the angles between the cleavages on the single-circle goniometer gave (001)∧(100) = 77° 51′.

(iii) Acicular crystals, up to 10 mm. long and 0·15 mm. in diameter, with brilliantly reflecting faces parallel to the axis of the needle and terminated by two extremely small faces. These needles are elongated parallel to the ortho-axis (b) and all have straight extinction and positive optical elongation. When immersed in oils, some lie on the orthopinacoid (100) and some on the base (001). As a result the refractive index α is best determined in this crop of crystals (i.e., in those crystals lying on 100). The interfacial angles of these acicular crystals were measured on the two-circle goniometer with the following results (the crystal was mounted with the long axis (b) parallel to the vertical circle axis) :

Face.	ρ.	φ.	Face.	ρ.	φ.
001	0° 00′	0° 00′	Ī00	0° 00′	102° 17′
100	0° 00′	282° 17′	Ī02	0° 00′	54° 50′
10Ī̄	0° 00′	234° 50′	011	67° 42′	0° 00′
00Ī	0° 00′	180° 00′	01Ī	67° 42′	180° 00′

Thus the significant interfacial angles are : 001 ∧ 100 = 77° 43′; 001 ∧ Ī02 = 54° 50′; 001 ∧ 011 = 67° 42. Thence the following axial elements were calculated : $a : b : c = 1·124 : 1·000 : 2·496$; β = 77° 43′. These values are in fair agreement with the figures obtained from the larger crystal with duller faces. In view of the more brilliant facets on the acicular crystals the crystallographic data from them are the more accurate.

The crystallographic data for this compound may be summarised thus. Monoclinic, normal class. Axial elements, $a : b : c = 1·124 : 1·000 : 2·496$; β = 77°43′. Interfacial angles : 001 ∧ 100 = 77° 43′; 001 ∧ Ī02 = 54° 50′; 001 ∧ 011 = 67° 42′; 001 ∧ Ī11 = 80° 35′; Ī11 ∧ Ī̄11 = 97° 00′. Cleavage : 001 highly perfect; 100 very good; 010 (or 011) fair. Habit either tabular ∥001 (showing development of 001, 100, 011, Ī11) or acicular elongated parallel to the ortho-axis (showing development of 001, 100, Ī02 and minor development of 011).

A stereogram of the forms developed on this compound is shown in Fig. 2.

2, PARKWAY, NEDLANDS, W. AUSTRALIA.