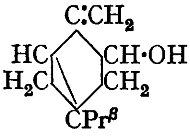
223. *Researches in the Thujone Series. Part II. The Catalytic Hydrogenation of* d-*Sabinol.*

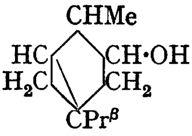
By Andrew G. Short and John Read.

In presence of Adams's platinum catalyst, *d*-sabinol (I) is hydrogenated to a mixture of thujyl alcohols (II) through addition of hydrogen to the double bond. A palladium sol effects a simultaneous fission of the *cyclo*propane ring, leading to the formation of a *cyclo*pentenol (III), in company with thujyl alcohols, hydrocarbons formed through dehydration, and other products. *d*-Sabinyl acetate, under similar conditions, is converted mainly into the acetate of the pentenol (III). A third stereochemically pure thujyl alcohol, namely, *l*-*neo*thujyl alcohol, derived from *l*-thujone, has been characterised (cf. J., 1938, 2017).

The catalytic hydrogenation of sabinol (I) has been investigated *inter alios* by Wallach (*Nach. Ges. Wiss. Göttingen*, 1919, **3**, 321) and Henderson and Robertson (J., 1923, **123**, 1715). In both instances, in presence of colloidal palladium, dihydrosabinol was reported as the chief product, together with related hydrocarbons; further, Wallach proved the chemical identity of dihydrosabinol with thujyl alcohol (II) by oxidising it to β-thujone. Stereochemically, the results were inconclusive, and even the chemical identity of Henderson and Robertson's dihydrosabinol seems to be doubtful, since it failed to react with *p*-nitrobenzoyl chloride.



(I.)



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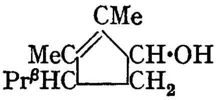

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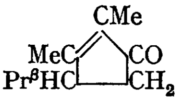

(IV.)

In experiments now recorded, *d*-sabinol when hydrogenated in presence of palladium sol yielded d-2 : 3-*dimethyl*-4-iso*propyl*-Δ^2-cyclo*pentenol* (III); the thujyl alcohols formed simultaneously furnished a third (J., 1938, 2017) stereoisomeride, l-neo*thujyl alcohol*, m. p. 22—23°, which was converted by oxidation into *l*-thujone. The hydrogenation was complex, and was accompanied by considerable dehydration leading to the formation of hydrocarbons.

d-Sabinyl acetate under similar conditions yielded a much more definite result, being converted mainly into the acetate of the above pentenol: thus, the *cyclo*propane ring appears to be less stable in *d*-sabinyl acetate than in *d*-sabinol. Upon oxidation, the free pentenol yielded the *l*-form of the so-called " Iso-Thujon " which Wallach (*Annalen*, **1895**, **286**, 102; " Terpene und Campher," Leipzig, 1914, 514) obtained in the *dl*-form by warming thujone with dilute sulphuric acid. In order to obviate confusion in the nomenclature (J., 1938, 2016), this substance should now be termed *l*-2 : 3-dimethyl-4-*iso*propyl-Δ^2-*cyclo*pentenone (IV). The corresponding pentanol (the " Thujamenthol " of Wallach, *op. cit.*, p. 516) was readily obtained by hydrogenating the pentenol (III) in presence of palladium sol. When oxidised, the pentanol yielded the pentanone (Wallach's " Thujamenthon "). Each of these last two products possibly consisted of a mixture of optically active stereoisomerides, since the respective molecules contain four and three dissimilar asymmetric carbon atoms.

In presence of Adams's platinum catalyst, *d*-sabinol underwent hydrogenation to a mixture of thujyl alcohols (II), consisting almost entirely of *l*-*neo*thujyl alcohol. In this case there was no evidence of the opening of the *cyclo*propane ring to form a pentenol. The platinum catalyst thus induces simple addition at the double bond, whereas the chief effect of the palladium catalyst is 1 : 4-addition to a system comprising a double bond conjugated with a three-membered ring. These results are in noteworthy agreement with the observations of Richter, Wolff, and Presting (*Ber.*, 1931, **64**, 871) on the hydrogenation of sabinene: here, in presence of palladium the formation of 1 : 2-dimethyl-3-*iso*propyl-Δ^1-*cyclo*pentene is followed by that of the corresponding *cyclo*pentane, whereas a platinum catalyst yields thujane.

The *l*-*neo*thujyl alcohol obtained in the present investigation had m. p. 22—23°, $[\alpha]_D$ − 7·54° (toluene), − 8·25° (alcohol), and thus resembled closely a thujyl alcohol, m. p. 28°, $[\alpha]_D$ − 9·12° (toluene), which Tschugaev and Fomin (*Ber.*, 1912, **45**, 1293) obtained in the reduction of β-thujone with sodium and alcohol, but did not oxidise to a thujone. By applying a modified method of separation, it proved possible to isolate both *l*-*neo*- and *d*-*iso*-thujyl alcohol (cf. J., 1938, 2017) in a state of stereochemical purity from this product. *l*-*neo*Thujyl alcohol is best prepared, however, by hydrogenating *d*-sabinol in presence of Adams's platinum catalyst, and *d*-*iso*thujyl alcohol by the method described in Part I (J., 1938, 2019).

An examination of the comparative reaction velocities of *l*-*neo*thujyl alcohol and *l*-thujyl alcohol with *p*-nitrobenzoyl chloride indicated the *cis*-H configuration for the *neo*-alcohol; in this respect, therefore, it corresponds to the *neo*menthols (J., 1934, 1781).

EXPERIMENTAL.

d-*Sabinol and Some* d-*Sabinyl Esters.*—When fractionally distilled, crude oil of savin, $\alpha_D^{13°}$ + 63·52° (*l* 1, homogeneous), $n_D^{14°}$ 1·4750, yielded two fractions consisting mainly of (i) *d*-sabinene (b. p. 67—80°/18 mm.; 38%), and (ii) *d*-sabinyl acetate with *d*-sabinol [b. p. 105—115°/18 mm., $n_D^{14°}$ 1·4756, $\alpha_D^{13°}$ + 67·41° (*l* 1); 51%]. The redistilled first fraction (27·5%) had b. p. 59—60°/10 mm., $n_D^{14°}$ 1·4718, $\alpha_D^{13°}$ + 68·48° (*l* 1).

The second fraction (100 g.) was boiled for 30 minutes with an excess (780 c.c.) of 5% methyl-alcoholic potassium hydroxide. The crude *d*-sabinol (53 g.), isolated by steam distillation and extraction with ether, had b. p. 95°/10 mm., $n_D^{14°}$ 1·4891, $\alpha_D^{14°}$ + 6·44° (*l* 1) (cf. Fromm, *Ber.*, 1898, **31**, 1200; Paolini and Rebora, *Atti R. Accad. Lincei*, 1916, [v], **25**, II, 377). The *p*-nitrobenzoate, obtained by esterifying crude *d*-sabinol (10 g.) in dry pyridine (50 c.c.) with *p*-nitrobenzoyl chloride (13·5 g.), crystallised from aqueous methyl alcohol in slender, yellowish prisms, m. p. 76°, $[\alpha]_D^{13°}$ + 10·0° (*c* 2·0, chloroform) (cf. Henderson and Robertson, J. 1923, **123**, 1715).

Pure *d*-sabinol, resulting from the hydrolysis of this ester with 5% methyl-alcoholic potassium hydroxide, had b. p. 90°/11 mm., $d_{4°}^{18·9°}$ 0·9488, $d_{4°}^{25°}$ 0·9461, $n_D^{25°}$ 1·4871, $\alpha_D^{18·9°}$ + 3·74° (*l* 1), $[\alpha]_D^{18·9°}$ + 3·94° (homogeneous), $[R_L]_D$ 46·23 (calc. for $C_{10}H_{16}O\,|\overline{1}$, 45·04; exaltation, 1·19).

Pure *d*-sabinyl 3 : 5-dinitrobenzoate formed soft, yellowish needles, m. p. 109°, $[\alpha]_D^{13°}$ + 22·5° (*c* 1·0, chloroform). The acetate, prepared in quantitative yield by heating pure *d*-sabinol with acetic anhydride (1·5 mols.) under reflux, was more mobile than *d*-sabinol, which it resembled in odour; b. p. 101—102°/11·5 mm., $n_D^{20°}$ 1·4699, $\alpha_D^{20°}$ + 86·18° (*l* 1, homogeneous), $[\alpha]_D^{20°}$ + 79·9° (*c* 2·1, chloroform). A specimen prepared similarly from the above crude *d*-sabinol had $\alpha_D^{15°}$ + 77·4° (*l* 1). Natural *d*-sabinyl acetate, isolated by Elze (*Chem. Ztg.*, 1910, **34**, 767), had

$\alpha_D^{10°}$ + 68°. The hydrogen phthalate crystallised from light petroleum in small, hard needles, m. p. 101—102°, $[\alpha]_D^{17.5°}$ — 17·5° (*c* 1·0, methyl alcohol) and + 10·0° (*c* 1·0, chloroform) (Found: C, 72·0; H, 6·6. Calc.: C, 72·0; H, 6·7%). Paolini and Rebora (*loc. cit.*) found m. p. 94—95°, $[\alpha]_D$ — 14° 13′ (methyl alcohol) for this derivative, which gave *d*-sabinol, b. p. 208°, $d^{15°}$ 0·9518, $n_D^{18°}$ 1·4895, $[\alpha]_D$ + 7·56°: these specimens were evidently impure.

Of the following esters, also prepared from the above crude *d*-sabinol, the first three were mobile liquids and the last two were viscid syrups: propionate, $\alpha_D^{18°}$ + 68·54° (*l* 1, homogeneous), $[\alpha]_D^{18°}$ + 61·8° (*c* 2·0, chloroform); *n*-butyrate, $\alpha_D^{18°}$ + 53·72° (*l* 1), $[\alpha]_D^{18°}$ + 48·3° (chloroform); benzoate, $[\alpha]_D^{19°}$ + 20·0° (chloroform); cinnamate, $[\alpha]_D^{19°}$ ± 0·0° (chloroform), + 9·8° (*c* 0·2, methyl alcohol). The high rotatory power of *d*-sabinyl acetate is remarkable.

l-neo*Thujyl Alcohol and* l-*Thujone from* d-*Sabinol*.—1. A solution of *d*-sabinol (50 g., $\alpha_D^{14°}$ + 6·44°) in ether (100 c.c.) was hydrogenated in presence of Adams's platinum catalyst (0·6 g.) ("Organic Syntheses," Coll. Vol. I, 1932, 452) under an over-pressure of 7 atms. The theoretical quantity of hydrogen (1 mol.) was taken up in 30 minutes, and absorption was then complete. The spent catalyst became spontaneously inflammable when dry. The crude product (45 g.) was a viscid liquid with a sweet smell, b. p. 98·5—99·5°/13·5 mm., $n_D^{14°}$ 1·4690, $\alpha_D^{14°}$ — 0·65° (*l* 1, homogeneous).

This mixture of thujyl alcohols (83 g. from 100 g. sabinol) was mixed in dry pyridine (415 c.c.) with *p*-nitrobenzoyl chloride (110 g.; 1·1 mols.) and left overnight. The crude ester, after being washed in ethereal solution with dilute acid, dilute alkali, and water, was obtained as a pale yellow syrup which crystallised when cooled and stirred. Two recrystallisations from methyl alcohol furnished pure l-neo*thujyl* p-*nitrobenzoate*, separating in long, hard, faintly yellow needles (100 g.), m. p. 90°, $[\alpha]_D^{18°}$ — 12·50° (*c* 1·0, chloroform) (Found: C, 67·4; H, 6·8. $C_{17}H_{21}O_4N$ requires C, 67·3; H, 6·9%). Hydrolysis with boiling methyl-alcoholic potassium hydroxide (1·2 mols., 5%, 30 mins.), followed by steam distillation and distillation under diminished pressure, yielded pure *l*-*neo*thujyl alcohol as a viscid liquid which crystallised in colourless leaflets, m. p. 22—23°, b. p. 96°/13 mm., $[\alpha]_D^{18.5°}$ — 7·54° (*c* 1·2, toluene), $[\alpha]_D^{20°}$ — 8·84° (*c* 1·3, alcohol), $n_D^{25°}$ 1·4624, $d_{4°}^{25°}$ 0·9223, $[R_L]_D$ 45·92 (calc. for $C_{10}H_{18}O$, 45·51; exaltation, 0·41).

l-neo*Thujyl* 3 : 5-*dinitrobenzoate* crystallised from methyl alcohol in colourless leaflets, m. p. 103°, $[\alpha]_D^{15°}$ — 10·00° (*c* 2·0, chloroform) (Found: C, 59·0; H, 5·6. $C_{17}H_{20}O_6N_2$ requires C, 58·6; H, 5·8%). When oxidised with chromic acid, *l*-*neo*thujyl alcohol gave *l*-thujone, b. p. 83°/15 mm., $n_D^{15°}$ 1·4512, $\alpha_D^{15°}$ — 18·32° (*l* 1, homogeneous); semicarbazone, m. p. 186—188° (J., 1938, 2018).

2. A solution of palladium chloride (0·3 g.) in hot water (25 c.c.) containing a little hydrochloric acid (2 drops, dilute) was washed into a hydrogenating bottle with hot water (25 c.c.) and mixed with a solution of gum arabic (0·5 g., powdered) in boiling water (200 c.c.). *d*-Sabinol (50 g.) was added to the cold solution, and hydrogen was admitted in the usual way after evacuation with the water-pump. Absorption of hydrogen (1 mol.) ceased after 15 minutes' stirring. The crude product, obtained by extracting the filtered liquid with ether, had a slight positive or negative optical rotation in different experiments. When distilled, it yielded a large terpene fraction.

Esterification of the crude product with *p*-nitrobenzoyl chloride in dry pyridine, followed by extraction with chloroform and washing as described above, yielded a crude ester from which terpene was removed by steam distillation. The residual reddish-brown syrup slowly deposited a small amount of crystalline material, which was separated by treatment with cold methyl alcohol. Fractional crystallisation from aqueous methyl alcohol then yielded a less soluble lævorotatory ester and a more soluble dextrorotatory ester, m. p. 46° (*vide infra*). The lævorotatory ester consisted of long needles of somewhat impure *l*-*neo*thujyl *p*-nitrobenzoate, m. p. 90°, $[\alpha]_D^{18°}$ — 8·25° (*c* 2·0, chloroform) (Found: C, 67·0; H, 6·8. Calc.: C, 67·3; H, 6·9%). The derived *l*-*neo*thujyl alcohol had b. p. 94°/8 mm., m. p. 20°, $[\alpha]_D^{18°}$ — 5·52° (*c* 1·3, methyl alcohol). When oxidised with Beckmann's chromic acid mixture, this gave *l*-thujone, b. p. 82°/11·5 mm., $n_D^{18.5°}$ 1·4470, $\alpha_D^{18°}$ — 15·9° (*l* 1, homogeneous), identified by means of the semicarbazone and 2 : 4-dinitrophenylhydrazone (J., 1938, 2018). The lævorotatory ester, alcohol, and ketone were all slightly impure. The yield of *l*-*neo*thujyl alcohol in this hydrogenation was very small, several other substances being formed simultaneously (*vide infra*).

Derivatives of cyclo*Pentene and* cyclo*Pentane from* d-*Sabinol*.—1. The above-mentioned fraction of oil of savin, b. p. 105—115°/18 mm., $\alpha_D^{13°}$ + 67·41° (*l* 1), consisting mainly of *d*-sabinyl acetate, was hydrogenated (5 lots of 50 g.) without a solvent in presence of colloidal palladium, as described above for *d*-sabinol. The first rapid absorption of hydrogen (1 mol.) was complete in about 10 minutes. The product was extracted with ether and hydrolysed with 4% methyl-alcoholic potassium hydroxide (1·2 mols.; reflux; 30 minutes). In the ensuing steam distillation the first distillate, containing methyl alcohol and terpene, was neglected; the oil distilling later was extracted with ether and esterified in dry pyridine (5 c.c. per g.) with 3 : 5-dinitrobenzoyl chloride (1·1 mols.). The crude ester was a reddish-brown syrup (131 g.) which slowly crystallised, yielding a material, m. p. 60—65°, $[\alpha]_{\mathrm{D}}^{17\cdot5^\circ}$ + 64·0° (*c* 2·0, chloroform). Three recrystallisations from methyl alcohol gave an apparently homogeneous ester (80 g.), separating in rectangular leaflets, m. p. 63—64°, $[\alpha]_{\mathrm{D}}^{20^\circ}$ + 64·75° (*c* 2·0, chloroform). This substance proved to be d-2 : 3-*dimethyl*-4-iso*propyl*-Δ²-cyclo*pentenyl* 3 : 5-*dinitrobenzoate* (Found: C, 59·2; H, 5·7. $C_{17}H_{20}O_6N_2$ requires C, 58·6; H, 5·8%).

d-2 : 3-*Dimethyl*-4-iso*propyl*-Δ²-cyclo*pentenol*, obtained by hydrolysing the above ester with methyl-alcoholic potassium hydroxide, was a colourless, viscid liquid, b. p. 90—91°/10 mm., $\alpha_{\mathrm{D}}^{19^\circ}$ + 28·22° (*l* 1, homogeneous), $n_{\mathrm{D}}^{20\cdot5^\circ}$ 1·4670 (Found: C, 77·9; H, 11·9. $C_{10}H_{18}O$ requires C, 77·9; H, 11·7%). It rapidly decolorised cold dilute aqueous permanganate and a solution of bromine in chloroform, and also absorbed hydrogen (1 mol.) in presence of colloidal palladium. The *p*-nitrobenzoate crystallised from methyl alcohol in fine, pale yellow needles, m. p. 46·5°, $[\alpha]_{\mathrm{D}}^{16^\circ}$ + 93·5° (*c* 1·0, chloroform).

When oxidised with Beckmann's chromic acid mixture, the above pentenol yielded *l*-2 : 3-dimethyl-4-*iso*propyl-Δ²-*cyclo*pentenone as a pale green, mobile liquid with a characteristic odour somewhat like that of the thujones; it had b. p. 89°/13 mm., $\alpha_{\mathrm{D}}^{18^\circ}$ − 12·72° (*l* 1, homogeneous), $n_{\mathrm{D}}^{19^\circ}$ 1·4641. The optical rotation changed to $\alpha_{\mathrm{D}}^{16^\circ}$ − 17·68° when the ketone was kept for 24 hours in an alcoholic solution of sodium ethoxide. The *semicarbazone* was deposited from aqueous methyl alcohol as a white amorphous solid, m. p. 155—156°, $[\alpha]_{\mathrm{D}}^{16^\circ}$ + 55·0° (*c* 1·0, methyl alcohol) (Found: C, 63·4; H, 9·2. $C_{11}H_{19}ON_3$ requires C, 63·2; H, 9·1%). The 2 : 4-*dinitrophenylhydrazone* crystallised from methyl alcohol–chloroform in long, dark red needles, m. p. 137·5°, $[\alpha]_{\mathrm{D}}^{15^\circ}$ + 31·0° (*c* 1·0, chloroform) (Found: C, 57·7; H, 5·9. $C_{16}H_{20}O_4N_4$ requires C, 57·6; H, 6·1%). The oxime was a viscid syrup, $n_{\mathrm{D}}^{21^\circ}$ 1·4958, $[\alpha]_{\mathrm{D}}^{19^\circ}$ + 10·97° (*c* 1·0, methyl alcohol).

The alcohol obtained by hydrolysing crude *d*-2 : 3-dimethyl-4-*iso*propyl-Δ²-*cyclo*pentenyl acetate, prepared as described above, readily absorbed hydrogen (1 mol.) in presence of colloidal palladium. The 3 : 5-dinitrobenzoate derived from the hydrogenated product crystallised partly when kept overnight, and three recrystallisations from methyl alcohol furnished brownish leaflets of a 2 : 3-*dimethyl*-4-iso*propyl*cyclo*pentyl* 3 : 5-*dinitrobenzoate*, m. p. 82—83°, $[\alpha]_{\mathrm{D}}^{15^\circ}$ − 2·0° (*c* 1·0, chloroform) (Found: C, 58·8; H, 5·9. $C_{17}H_{22}O_6N_2$ requires C, 58·6; H, 5·8%). Hydrolysis with 5% methyl-alcoholic potassium hydroxide gave a 2 : 3-dimethyl-4-*iso*propyl-*cyclo*pentanol as a colourless, viscid liquid with a faint sweet smell, b. p. 94°/12 mm., $\alpha_{\mathrm{D}}^{15^\circ}$ − 1·56° (*l* 1, homogeneous), $n_{\mathrm{D}}^{15\cdot5^\circ}$ 1·4649.

Upon oxidation the pentanol yielded a 2 : 3-dimethyl-4-*iso*propyl*cyclo*pentanone as a mobile, faintly green liquid, with a strong odour of the thujone type; it had b. p. 80°/11 mm., $\alpha_{\mathrm{D}}^{18^\circ}$ + 9·94° (*l* 1, homogeneous), $n_{\mathrm{D}}^{17^\circ}$ 1·4542. Treatment with cold alcoholic sodium ethoxide changed the optical rotation to $\alpha_{\mathrm{D}}^{15^\circ}$ + 17·54° (*l* 1). The 2 : 4-*dinitrophenylhydrazone* crystallised from methyl alcohol–chloroform in fine orange needles, m. p. 101·5°, $[\alpha]_{\mathrm{D}}^{15^\circ}$ + 60·0° (*c* 1·0, chloroform) (Found: C, 57·6; H, 5·8. $C_{16}H_{22}O_4N_4$ requires C, 57·5; H, 6·6%). The semicarbazone was an amorphous solid, m. p. 135—137°, $[\alpha]_{\mathrm{D}}^{15^\circ}$ + 122·0° (*c* 1·0, methyl alcohol).

2. The dextrorotatory *p*-nitrobenzoate obtained by hydrogenating *d*-sabinol in presence of colloidal palladium (*vide supra*) formed soft, colourless needles, m. p. 46°, $[\alpha]_{\mathrm{D}}^{13^\circ}$ + 84·5° (*c* 2·0, chloroform), these constants being unaltered after recrystallisation. It appeared to consist of mixed crystals, since another specimen, obtained by hydrogenating *d*-sabinyl *p*-nitrobenzoate in presence of colloidal palladium, had m. p. 46°, $[\alpha]_{\mathrm{D}}^{16^\circ}$ + 67·5° (*c* 2·0, chloroform). The product was identified as impure *d*-2 : 3-dimethyl-4-*iso*propyl-Δ²-*cyclo*pentenyl *p*-nitrobenzoate.

The bulk of the *p*-nitrobenzoate obtained from the product of hydrogenation of *d*-sabinol in presence of colloidal palladium remained as a reddish-yellow, mobile syrup. A specimen having $[\alpha]_{\mathrm{D}}^{15^\circ}$ + 13·9° (*c* 1·1, chloroform), upon hydrolysis with methyl-alcoholic potassium hydroxide, yielded a viscid, sweet-smelling liquid, b. p. 95—96°/12 mm., $n_{\mathrm{D}}^{18\cdot5^\circ}$ 1·4662, $\alpha_{\mathrm{D}}^{15^\circ}$ − 4·66° (*l* 1, homogeneous). This crude alcohol gave a syrupy 3 : 5-dinitrobenzoate, and, unlike the thujyl alcohols, readily decolorised dilute acid permanganate and bromine dissolved in chloroform. Oxidation with Beckmann's chromic acid mixture yielded a mobile, sweet-smelling liquid with ketonic properties, b. p. 88—90°/12·5 mm., $\alpha_{\mathrm{D}}^{15^\circ}$ − 28·00° (*l* 1, homogeneous), $n_{\mathrm{D}}^{17^\circ}$ 1·4620. The derived 2 : 4-*dinitrophenylhydrazone*, after four recrystallisations from methyl alcohol–chloroform, separated in flat, orange-red needles, m. p. 131°, $[\alpha]_{\mathrm{D}}^{15^\circ}$ + 14·0° (*c* 1·0, chloroform) (Found: C, 57·7; H, 6·1. $C_{16}H_{20}O_4N_4$ requires C, 57·6; H, 6·0%); this appeared to be a pure specimen of the 2 : 4-dinitrophenylhydrazone of an isomeride of *l*-2 : 3-dimethyl-4-*iso*propyl-Δ^2-*cyclo*pentenone (m. p. 137·5°, $[\alpha]_{\mathrm{D}}$ + 31·0°, *vide supra*). These observations show that the hydrogenation of *d*-sabinol in presence of colloidal palladium leads to the formation of *l*-*neo*thujyl alcohol, *d*-2 : 3-dimethyl-4-*iso*propyl-Δ^2-*cyclo*pentenol, and other substances, possibly including stereoisomerides of these two alcohols, as well as the corresponding pentanol, thujane, etc. The high optical rotation, $\alpha_{\mathrm{D}}^{15°}$ − 28·00°, of the above mixture of ketones suggests also an alternative fission of the *cyclo*propane ring; but treatment with 2 : 4-dinitrophenylhydrazine failed to disclose the presence of carvotanacetone.*

The catalytic hydrogenation of *d*-sabinol according to Henderson and Robertson (J., 1923, **123**, 1715) led to similar results. With a palladium–calcium carbonate catalyst, very little hydrogen was absorbed, even at an overpressure of 7 atms.

d-iso*Thujyl Alcohol*, d-iso*Thujone*, l-neo*Thujyl Alcohol, and* l-*Thujone from* β-*Thujone*.—β-Thujone (50 g.) from tansy oil (J., 1938, 2018), with $n_{\mathrm{D}}^{18°}$ 1·4582, $\alpha_{\mathrm{D}}^{14°}$ + 36·42° (*l* 1), was dissolved in ethyl alcohol (375 c.c.; dried for a fortnight over quicklime) and reduced under reflux with sodium (37·5 g.), added in coarse pieces. The resulting mixture of thujyl alcohols (35 g.) had $n_{\mathrm{D}}^{17°}$ 1·4687, $\alpha_{\mathrm{D}}^{14°}$ + 36·84° (*l* 1) (cf. J., 1938, 2019). An attempted conversion of this product into the hydrogen phthalate by the method of Pickard and Littlebury (J., 1912, **101**, 109) led to dehydration and charring, but a modification of the method of Duveen and Kenyon (J., 1936, 622) proved successful.

A mixture of the thujyl alcohols (50 g.), phthalic anhydride (48 g.), and dry pyridine (27 c.c.) was kept at 115—120° for 4 hours. The warm liquid was then treated with 5% sodium carbonate solution (700 c.c.). After an hour, the product was extracted twice with ether. When the aqueous solution was acidified with hydrochloric acid, the hydrogen phthalate was precipitated as an oil which soon solidified. By extraction with chloroform it was obtained as a hard, crystalline mass (91 g.), which began to melt at about 79° and had $[\alpha]_{\mathrm{D}}^{16°}$ + 28·65° (*c* 2·0, chloroform), + 28·87° (*c* 1·6, alcohol).

The crude thujyl hydrogen phthalate (265 g.) was dissolved in the minimum quantity of hot alcohol and treated with cinchonine (258 g.). A small amount of undissolved cinchonine was removed by filtration, and the solution crystallised when kept overnight. The first fraction of the cinchonine salt had $[\alpha]_{\mathrm{D}}^{14°}$ + 120·0° (*c* 1·0, chloroform); and two further recrystallisations from alcohol yielded large needles (72 g.), m. p. 171—172°, $[\alpha]_{\mathrm{D}}^{17°}$ + 143·0°.

Steam distillation of the powdered cinchonine salt (72 g.) at this stage with 5% aqueous potassium hydroxide (350 c.c.; 2·5 mols.) yielded slightly impure *d*-*iso*thujyl alcohol (17·2 g.), b. p. 93°/8·5 mm., $\alpha_{\mathrm{D}}^{14·5°}$ + 105·88° (*l* 1), $n_{\mathrm{D}}^{17·5°}$ 1·4621. This was readily purified by means of the *p*-nitrobenzoate (J., 1938, 2019), yielding *d*-*iso*thujyl alcohol (11·5 g.), b. p. 91°/9·5 mm., $\alpha_{\mathrm{D}}^{19°}$ + 108·1° (*l* 1), $d_{4}^{19°}$ 0·9221, $[\alpha]_{\mathrm{D}}^{19°}$ + 117·2° (homogeneous), $[\alpha]_{\mathrm{D}}^{19°}$ + 111·0° (*c* 1·1, alcohol), $n_{\mathrm{D}}^{25°}$ 1·4600, $d_{4°}^{25°}$ 0·9189, $[R_L]_{\mathrm{D}}$ 45·92 (calc. for $C_{10}H_{18}O$, 45·51; exaltation, 0·41).

The derived *d*-*iso*thujone (cf. J., 1938, 2018) had b. p. 73°/10 mm., $\alpha_{\mathrm{D}}^{21°}$ + 73·94° (*l* 1), $d_{4°}^{21°}$ 0·9147, $[\alpha]_{\mathrm{D}}^{21°}$ + 80·83° (homogeneous), $n_{\mathrm{D}}^{25°}$ 1·4500. The ketone had a distinct greenish-yellow colour, which deepened with the passage of time.

When acidified with hydrochloric acid, the first two mother-liquors from the fractional crystallisation of the above cinchonine salt yielded a crude thujyl hydrogen phthalate (66 g.), which was readily obtained crystalline by extraction with chloroform, $[\alpha]_{\mathrm{D}}^{15°}$ + 17·57° (*c* 1·1, alcohol). The salt with strychnine (71 g.) was produced by mixing the constituents in chloroform, which was then removed. After two recrystallisations from *iso*butyl alcohol this salt was obtained in fine needles (33 g.), m. p. 217—218° (decomp.), $[\alpha]_{\mathrm{D}}^{15°}$ − 20·0° (*c* 1·0, chloroform).

Material of this kind (63·5 g.), when powdered and steam distilled with 5% aqueous potassium hydroxide (300 c.c.; 2·5 mols.), gave impure *l*-*neo*thujyl alcohol (11·8 g.), b. p. 94·5°/10·5 mm., $[\alpha]_{\mathrm{D}}^{16°}$ − 5·45° (*c* 1·6, alcohol). The derived *p*-nitrobenzoate after two recrystallisations had m. p. 90°, $[\alpha]_{\mathrm{D}}^{18·5°}$ − 13·0° (*c* 1·0, chloroform), and yielded *l*-*neo*thujyl alcohol (6 g.), b. p. 95°/13·5 mm., m. p. 22—23°, $[\alpha]_{\mathrm{D}}^{19°}$ − 8·25° (*c* 1·8, alcohol). Oxidation with Beckmann's reagent gave *l*-thujone (4·25 g.), $\alpha_{\mathrm{D}}^{17·5°}$ − 18·46° (*l* 1), $d_{4°}^{17·5°}$ 0·9116, $[\alpha]_{\mathrm{D}}^{17·5°}$ − 20·25° (homogeneous), $[\alpha]_{\mathrm{D}}^{17·5°}$ − 17·52° (*c* 1·1, alcohol). This ketone was only faintly coloured.

Comparative Reaction Velocities of l-neo*Thujyl Alcohol and* l-*Thujyl Alcohol*.—To a solution of equal weights (2·6 g.) of each of the alcohols in dry pyridine (25 c.c.), maintained at 25° (J., 1934, 1782), was added gradually an insufficient quantity (0·67 mol.) of *p*-nitrobenzoyl chloride for complete esterification. The well-washed crude ester (4·12 g.) had $[\alpha]_{\mathrm{D}}^{19°}$ − 24·0° (*c* 2·0,

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* *d*-Carvotanacetone 2 : 4-dinitrophenylhydrazone separates readily from methyl alcohol–chloroform in red-gold leaflets, m. p. 191—192°, $[\alpha]_{\mathrm{D}}^{19°}$ +110·0° (*c* 0·5, chloroform).

chloroform), and thus consisted of 58·2% of *l*-thujyl *p*-nitrobenzoate, $[\alpha]_D^{15°}$ − 32·25° (J., 1938, 2019), and 41·8% of *l*-*neo*thujyl *p*-nitrobenzoate, $[\alpha]_D^{18°}$ − 12·50° (*vide supra*). It follows that *l*-thujyl alcohol reacts more rapidly than *l*-*neo*thujyl alcohol with *p*-nitrobenzoyl chloride.

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