

For the fractions N_{41-44} the above data, the carbonyl absorption in the I.R. and the odour indicated *d*-bornylacetate. Saponification and back titration showed the presence of 45 % of the ester. *d*-Borneol was easily isolated by chromatography from the hydrolysate. M. p. and mixed m. p. 204—207° (sealed tube, uncorr.) $[\alpha]_D^{22} + 36.3^\circ$ (CHCl_3 , c 3.2). Fractions N_{45-48} showed carbon-carbon double bond absorptions in I.R. and the main part behaved chromatographically as a hydrocarbon while N_{49} was fairly pure cedrol. The hydrocarbon, boiling between bornylacetate and cedrol, may therefore possibly be a mixture of cedrenes.

Fractions N_6-7 and the crystalline material from N_6 were combined (19.9 g), recrystallized from aqueous methanol and sublimed *in vacuo*. M. p. and mixed m. p. with cedrol 87.5—88° $[\alpha]_D^{22} + 10.0^\circ$ (CHCl_3 , c 1.1).

Fraction N_9 (31.9 g) was distilled through the spinning band column. Pressure 14 mm.

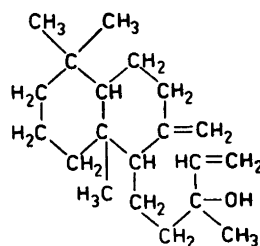
Fraction N_{91} , b. p. up to 110°, 0.45 g, $[\alpha]_D^{22} - 8.5^\circ$, n_D^{21} 1.5029; N_{92} , 184°, 3.61 g, -6.5° , 1.5136; N_{93} , 189°, 2.4 g, $+20^\circ$, 1.5178; N_{94} , 190°, 3.61 g, $+29^\circ$, 1.5160; N_{95} , 192°, 3.40 g, $+30^\circ$, 1.5148; N_{96} , 192°, 2.13 g, $+28^\circ$, 1.5147; N_{97} , 198°, 2.83 g, $+30^\circ$, 1.5139; N_{98} , 210°, 1.86 g, $+30^\circ$, 1.5167; N_{99} , 217°, 1.42 g, $+32^\circ$, 1.5273; N_{100} , 224°, 0.71 g, $+23^\circ$, 1.5344; N_{101} , 229°, 2.34 g, $+16^\circ$, 1.5348; N_{102} , 233°, 0.83 g, $+25^\circ$, 1.5412; Residue 6.3 g.

Fractions N_{94-97} (12 g or 0.3 %) distilled at fairly constant temperature. Molecular weight determinations (Rast, 289, 292), optical rotation, refractive index and I.R. absorption properties indicated manool. When the thick oily material was seeded with authentic manool it immediately started to crystallise. The solid was recrystallized from light petroleum, m. p. and mixed m. p. 53—53.5°. The infra red absorption spectra were identical.

The acid fraction *A* on standing deposited nootkatin (0.2 g). The remaining oil was distilled at low pressure yielding 13.9 g volatile material, which was subjected to a fractional distillation in the spinning band column. Pressure 27 mm.

Fraction A_1 , b. p. up to 129°, 1.44 g; A_2 , 129°, 1.33 g; A_3 , 156°, 0.86 g; A_4 , 175°, 0.94 g; A_5 , 175°, 0.43 g; A_6 , 216°, 2.46 g; tailings/13 mm, 1.03 g. Residue 5.7 g. The rotation of all fractions was close to zero.

Fractions A_1 and A_2 according to I. R. data and paper chromatography (in light petroleum, on dimethyl sulphoxide impregnated paper)³ contained carvacrol and etherification with chloroacetic acid gave carvacroxy acetic



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acid, m. p. and mixed m. p. 150—2°. Fractions A_3 and A_4 , according to paper chromatographic results⁴ contained β -thujaplicin (0.5 g), which crystallized when seeded with this compound. M. p. and mixed m. p. 51.5—52.0°. The solid fractions A_6 and A_7 were largely nootkatin, identified by paper chromatography⁴, m. p. and mixed m. p. 95—96°.

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Syntheses of Nonan-1,2-diol and Nonan-1,3-diol

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During the investigation of the structure of some natural products two diols hitherto not prepared *viz.* nonan-1,2-diol and nonan-1,3-diol have been synthesised. The two diols are, when solid, white, odorless and waxy products, soluble in all the common organic solvents. They react with 3,5-dinitrobenzoyl chloride and yield, under mild conditions, mono-dinitroben-

zoates and, under somewhat more rigorous conditions, di-dinitrobenzoates.

A diol with the molecular formula $C_9H_{20}O_2$ was obtained by Anchel¹ on catalytic reduction of the polyacetylene biformin. Later Bohlmann² and Bu'Lock³ mention that biformin is probably nonan-4,6,8-triyn-1,2-diol, as its hydrogenation product on oxidation with chromic acid gave octanic acid. Consequently the glycol obtained from biformin ought to be nonan-1,2-diol. According to the figures published there is, however, a small discrepancy as to its melting point compared to that of the glycol now synthesised. Anchel¹ reports that the glycol from biformin, after purification in a sublimation vessel, melted at 40–43°, whereas the synthetic glycol, purified by several sublimations at reduced pressure, melted at 33.5–34°. The derivatives of the glycol from biformin, *viz.* mono-3,5-dinitrobenzoate and the α -naphthylamine addition compound of the di-3,5-dinitrobenzoate melt 6–9° lower than the corresponding derivatives of the nonan-1,2-diol, but these low melting points may depend on the difficulties to purify small amounts of natural products. If the hydrogenation product of biformin really is nonan-1,2-diol the different melting points of the two glycols can either be due to the fact that nonan-1,2-diol can exist in two different modifications as for instance nonan-4,5-diol⁴, or that the glycol from biformin is an optical antipode whereas the synthetic one is a racemic compound.

Experimental. Nonan-1,2-diol was prepared by hydroxylation of 1-nonen with performic acid according to the method used by Swern *et al.*⁵ for the preparation of octan-1,2-diol.

To a well stirred mixture of 1-nonen⁶ in formic acid 25.6 % hydrogen peroxide (in 2.5 % excess) was added in one portion. The mixture was heated and stirred at 40° for about 15 h at which time the solution was homogeneous. The formic acid was removed by distillation at reduced pressure and the residue was refluxed for about one hour with excess of 3 N alcoholic potassium hydroxide. After the alcohol had been evaporated, the residue was treated with ether and water. The ether was removed and the residue distilled. The glycol boiled at 155°/17 mm and solidified at once to a crystalline product which after several sublimations in vacuum melted at 33.5–34° (Found: C 67.90; H 12.43. Calc. for $C_9H_{20}O_2$: C 67.45; H 12.58).

Nonan-1,3-diol was prepared by a Grignard reaction. To an ether solution of *n*-hexyl-

magnesium bromide β -hydroxypropionaldehyde⁷ was added dropwise. The solution was refluxed for half an hour and then worked up in the usual way. The diol boiled at 144–146°/12 mm and after cooling in an ice mixture solidified to a waxy product melting at 14–16°. Purification in a sublimation vessel did not raise the melting point (Found: C 67.13; H 12.42).

The mono-3,5-dinitrobenzoates of the diols were prepared by treating their benzene solutions with an equimolecular amount of 3,5-dinitrobenzoyl chloride and a few drops of pyridine. The solutions were heated to boiling, cooled and worked up as usual. The benzoates were recrystallised from benzene-petroleum ether and that of the 1,2-diol melted at 60–61° (Found: C 54.30; H 6.21. Calc. for $C_{16}H_{22}O_7N_2$: C 54.23; H 6.26). The corresponding derivative from biformin is reported¹ to melt at 50–55°. The benzoate of the 1,3-diol melted at 66.5–67° (Found: C 54.03; H 6.03).

In order to obtain the di-3,5-dinitrobenzoates the benzene solutions of the diols were treated as before but with the reagent in excess and by refluxing the solutions for half an hour before they were worked up. As the di-ester of the 1,2-diol was obtained as an oil its ethereal solution was treated with α -naphthylamine in excess. After recrystallisation from absolute ethanol, the addition compound with two moles of α -naphthylamine was obtained as rosettes of orange needles melting at 120–121° (Found: C 61.90; H 4.88. Calc. for $C_{43}H_{42}O_{12}N_6$: C 61.86; H 5.07). The corresponding addition compound obtained by Anchel¹ melted at 111–112°.

The di-ester of the 1,3-diol, after recrystallisation from aqueous acetone, melted at 113.5–114° (Found: C 50.21; H 4.34. Calc. for $C_{23}H_{24}O_{12}N_4$: C 50.37; H 4.41).

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