117. *A Total Synthesis of* (±)*-Ferruginol.*

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A total synthesis of (±)-ferruginol has been accomplished by Bogert–Cook ring-closure of a phenethyl*cyclo*hexanol derived from 2 : 2 : 6-trimethyl*cyclo*hexanone and *p*-methoxyphenylacetylene. The synthetic and the natural compound have been compared as crystalline benzoates, and the infrared spectra of the two derivatives found to be indistinguishable.

Ferruginol is a phenolic tricyclic diterpene first isolated from the exudate of the miro tree of New Zealand (*Podocarpus ferrugineus*) by Brandt and Neubauer.[1] It is a resin characterised by a crystalline formate, acetate, and benzoate. From the investigations of Brandt and Neubauer [1] and of Campbell and Todd [2] the constitution (I) emerged, and this was verified by partial syntheses of ferruginol from podocarpic acid and dehydroabietic acid.[3] The *trans*-configuration of the A/C ring junction in ferruginol was demonstrated by Barton and Schmeidler [4] and confirmed by Stork and Burgstahler.[5]

Although considerable attention has been given to the synthesis of the related resin acids,[6] there was no record, apart from a preliminary publication,[7] of such an investigation directed towards ferruginol before the inception of our experiments. The chosen route, which was outlined [8] in 1954, is similar to that devised in the attempted synthesis of dehydroabietic [6a] and podocarpic acid,[6b, c] and relies on the cyclisation of a suitable phenethyl*cyclo*hexanol (II). From the recent work of Barnes *et al.*[9] it was assumed that the methyl group at the potential quaternary position would suppress spiran formation, and the use of vigorous conditions should lead to a preponderance of the octahydrophenanthrene with the desired A/C *trans*-configuration.

In initial attempts to prepare the intermediate (II; R = H) from 2 : 2 : 6-trimethyl*cyclo*hexanone and a 4-methoxyphenethylmagnesium bromide the main products were 2 : 2 : 6-trimethyl*cyclo*hexanol and 4-methoxystyrene, the yield of crude adduct (II; R = H) not exceeding 10%. Similar behaviour of highly substituted ketones in the Grignard reaction has previously been noted,[10] although 2 : 6-dimethyl*cyclo*hexanone undergoes addition satisfactorily.[11] Condensation of phenethyl-lithium with 2 : 2 : 6-trimethyl*cyclo*hexanone was also unsatisfactory.

However, 2 : 2 : 6-trimethyl*cyclo*hexanone with sodium acetylide in liquid ammonia gives 1-ethynyl-2 : 2 : 6-trimethyl*cyclo*hexanol in high yield,[12] and with the Grignard

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[1] Brandt and Neubauer, *J.*, 1939, 1031.

[2] Campbell and Todd, *J. Amer. Chem. Soc.*, 1940, **62**, 1287.

[3] *Idem, ibid.*, 1942, **64**, 829.

[4] Barton and Schmeidler, *J.*, 1948, 1197.

[5] Stork and Burgstahler, *J. Amer. Chem. Soc.*, 1951, **73**, 3544.

[6] (*a*) Haworth and Barker, *J.*, 1939, 1299; (*b*) Haworth and Moore, *J.*, 1946, 633; (*c*) Bhattacharyya, *J. Indian Chem. Soc.*, 1945, **22**, 165; (*d*) Bachmann and Wick, *J. Amer. Chem. Soc.*, 1950, **72**, 2000; E. C. Horning, M. G. Horning, and Platt, *ibid.*, p. 2731; Saha, Bagchi, and Dutta, *Chem. and Ind.*, 1954, 1143; *J. Amer. Chem. Soc.*, 1955, **77**, 3408; Parham, Wheeler, and Dodson, *J. Amer. Chem. Soc.*, 1955, **77**, 1166; Raphael and Parker, *J.*, 1955, 1723.

[7] Gibson, *Experientia*, 1951, **7**, 177.

[8] F. E. King, T. J. King, and Topliss, *Chem. and Ind.*, 1954, 108.

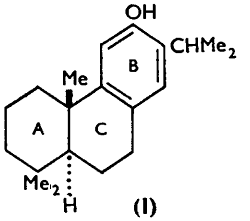
[9] Barnes *et al.*, *J. Amer. Chem. Soc.*, 1952, **74**, 35, 4091; 1953, **75**, 303, 3004.

[10] Conant and Blatt, *ibid.*, 1929, **51**, 1227.

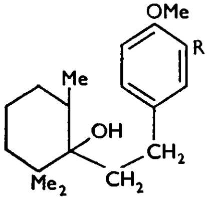
[11] Sterling and Bogert, *J. Org. Chem.*, 1939, **4**, 20; F. E. King and T. J. King, *J.*, 1954, 1373.

[12] Milas, Macdonald, and Black, *J. Amer. Chem. Soc.*, 1948, **70**, 1829.

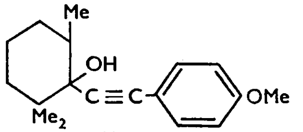
reagent from 6-methylocta-3 : 5-dien-7-yn-2-ol affords 8-(1-hydroxy-2 : 2 : 6-trimethyl-*cyclo*hexyl)-6-methylocta-3 : 5-dien-7-yn-2-ol.[13] The reaction of 2 : 2 : 6-trimethyl*cyclo*hexanone with sodio-*p*-methoxyphenylacetylene in liquid ammonia was accordingly investigated: a 74—75% yield of 1-*p*-methoxyphenylethynyl-2 : 2 : 6-trimethyl*cyclo*hexanol (III) was obtained.



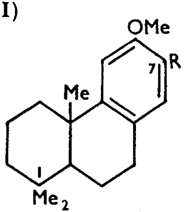
(I)
Ferruginol



(II)



(III)



(IV)

The triple bond was conveniently and almost quantitatively reduced at a palladium catalyst, giving the required intermediate (II; R = H), which was cyclised by phosphoric oxide at 150° to a liquid product (70%), shown to be 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydro-6-methoxy-1 : 1 : 12-trimethylphenanthrene (IV; R = H) by analysis, perphthalic acid titration, and selenium dehydrogenation to 6-methoxy-1-methylphenanthrene. Demethylation of the cyclisation product (IV; R = H) gave the corresponding phenol, but neither this nor its benzoate could be obtained crystalline, an indication that the intermediate (IV; R = H) consisted of both *cis*- and *trans*-isomers.

The next stage, introduction of an acetyl group into the 7-position of the octahydrophenanthrene, was carried out with the mixed isomers in the hope of separating the products by means of ketonic derivatives. Entry of the acetyl group at the 7-position was assumed from the close analogy afforded by the preparation of methyl 7-acetyl-*O*-methylpodocarpate from methyl *O*-methylpodocarpate.[2] 7-Acetyl-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydro-6-methoxy-1 : 1 : 12-trimethylphenanthrene (IV; R = Ac) was, in fact, obtained as a mixture of stereoisomers in 90% yield by using acetyl chloride–aluminium chloride in nitrobenzene. The 2 : 4-dinitrophenylhydrazones were inseparable, but fractional crystallisation gave the semicarbazone (23%, based on the ketone mixture) of a single stereoisomer (IV; R = Ac). Regeneration of the ketones from the residues followed by chromatography on alumina and reconversion into semicarbazones afforded a further 2% of the homogeneous semicarbazone. No other pure derivative was isolated. The fractionally crystallised product was hydrolysed in 90% yield with aqueous-alcoholic hydrochloric acid to a single stereoisomer (IV; R = Ac), the over-all yield from (IV; R = H) being 20%.

Reaction of the pure isomer (IV; R = Ac) with methylmagnesium iodide gave the tertiary alcohol (IV; R = $CMe_2{\cdot}OH$), which was dehydrated by acetic anhydride to the *iso*propenyl derivative (IV; R = $CMe{:}CH_2$) (yield from the 7-acetyl compound, 75—80%). This was hydrogenated to 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydro-6-methoxy-1 : 1 : 12-trimethyl-7-*iso*propylphenanthrene (IV; R = Pr^i) in 90% yield with Adams catalyst in ethanol, then demethylated by prolonged boiling with hydrobromic acid in acetic acid, the resulting product (I) (90% yield) being a resin closely resembling natural ferruginol in physical properties and ferric reaction. It gave a solid benzoate which was purified by chromatography and repeated crystallisation. The solubilities of the synthetic benzoate

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[13] Attenburrow, Cameron, Chapman, Evans, Hems, Jansen, and Walker, *J.*, 1952, 1094.

and (+)-ferruginyl benzoate were very similar and certain resemblances in the crystalline forms of the two benzoates were observed. The synthetic (±)-benzoate melted 23° below the (+)-benzoate, and a 1 : 1-mixture melted between the individual melting points. That the synthetic benzoate was, in fact, racemic ferruginyl benzoate and not the diastereoisomer having *cis*-fusion of rings A and C was proved by identity of the infrared spectra (measured in CCl_4 solution on a single-beam instrument). The pure diastereoisomeric semicarbazone from (IV; R = Ac) is therefore the *trans*-isomer, as also are the ensuing intermediates.

The synthesis of (±)-ferruginol represents the first established synthesis of the racemic form of a naturally occurring tricyclic diterpene.

EXPERIMENTAL

1-p-*Methoxyphenylethynyl*-2 : 2 : 6-*trimethyl*cyclo*hexanol* (III).—To liquid ammonia (250 c.c.) and ferric nitrate (0·04 g.), cooled in carbon dioxide–methanol, sodium (2·05 g., 1 mol.) was added, in portions with stirring, during 10 min. After 40 min. the blue colour had been discharged and *p*-methoxyphenylacetylene [14] (11·6 g., 1 mol.) in ether (10 c.c.) was added during 20 min. Stirring was continued for another ½ hr. and then 2 : 2 : 6-trimethyl*cyclo*hexanone [15] (12·3 g., 1 mol.) in ether (10 c.c.) was added in ½ hr. After 2 hr. the ammonia was allowed to evaporate. The sodio-compound was decomposed with saturated ammonium chloride solution (300 c.c.), the product extracted with ether (2 × 100 c.c.), and the ethereal solution washed with water, dried (K_2CO_3), and evaporated. The residue was distilled, giving a colourless distillate (17·8 g.), b. p. 149°/0·2 mm., which readily solidified (m. p. 62—63°; 74·5%). Recrystallisation from light petroleum (b. p. 60—80°) gave 1-p-*methoxyphenylethynyl*-2 : 2 : 6-*trimethyl*cyclo*hexanol* as prisms, m. p. 71—72° (Found : C, 79·3; H, 8·75. $C_{18}H_{24}O_2$ requires C, 79·4; H, 8·9%).

1-4′-*Methoxyphenethyl*-2 : 2 : 6-*trimethyl*cyclo*hexanol* (II; R = H).—1-*p*-Methoxyphenylethynyl-2 : 2 : 6-trimethyl*cyclo*hexanol, m. p. 62—63° (17·3 g.), in ethanol (150 c.c.) was hydrogenated at 1—3 atm. and room temperature with 5% palladium hydroxide–calcium carbonate (1·5 g.). Reduction was complete in ½ hr. After removal of the catalyst and solvent the residue was distilled, 1-4′-*methoxyphenethyl*-2 : 2 : 6-*trimethyl*cyclo*hexanol* (17·0 g., 97%) condensing as a viscous oil, b. p. 148°/0·2 mm., n_D^{23} 1·5294 (Found : C, 78·1; H, 10·0. $C_{18}H_{28}O_2$ requires C, 78·2; H, 10·2%).

1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*Octahydro*-6-*methoxy*-1 : 1 : 12-*trimethylphenanthrene* (IV; R = H).—1-4′-Methoxyphenethyl-2 : 2 : 6-trimethyl*cyclo*hexanol (5·6 g.) mixed with phosphoric oxide (11 g.) was heated under water-pump vacuum, the temperature being raised from 20° to 150° during ½ hr. with subsequent heating at 130—150° for 1 hr. The reaction mixtures from three such experiments were cautiously decomposed with dilute sodium hydroxide solution, and the combined products extracted with ether (3 × 100 c.c.), washed with water, and dried (K_2CO_3). Distillation gave 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydro-6-methoxy-1 : 1 : 12-trimethylphenanthrene (11·0 g., 70%), b. p. 122—124°/0·2 mm.; a portion distilled from phosphoric oxide was obtained as a colourless, viscous oil, n_D^{20} 1·5478, showing a violet fluorescence (Found : C, 83·6; H, 9·6. $C_{18}H_{26}O$ requires C, 83·7; H, 10·1%). Titration with perphthalic acid indicated the presence of 1% of olefinic material.

1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-Octahydro-6-methoxy-1 : 1 : 12-trimethylphenanthrene (1 g.) was heated with selenium powder at 280—340° for 48 hr. The product, isolated with ether and distilled *in vacuo*, gave a distillate (0·53 g.) from which 6-methoxy-1-methylphenanthrene was obtained by crystallisation from methanol, in rods, m. p. 79—80°. Passage in benzene through a short alumina column, followed by crystallisation from methanol, raised the m. p. to 84—85°, unchanged by further recrystallisation (Sherwood and Short [16] give m. p. 87—87·5°). The picrate, prepared from methanolic solutions, crystallised from methanol in orange needles, m. p. 136—137° (Sherwood and Short [16] give m. p. 140—141·5°). The mother-liquors from the first crystallisation of the phenanthrene also gave some crude picrate (0·10 g.). The total quantity of phenanthrene isolated from the reaction was thus *ca.* 0·25 g. (29%). The yield based on the weight of distillate was 47%.

1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-Octahydro-6-methoxy-1 : 1 : 12-trimethylphenanthrene (0·30 g.)

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[14] Manchot, *Annalen*, 1911, **387**, 283.
[15] F. E. King, T. J. King, and Topliss, *J.*, 1957, in the press.
[16] Sherwood and Short, *J.*, 1938, 1006.

was refluxed for 7½ hr. with 48% hydrobromic acid (1·5 c.c.) in acetic acid (5 c.c.). The mixture was made alkaline with 2N-sodium carbonate and extracted with ether (2 × 50 c.c.). The ethereal solutions were washed with water, dried (K_2CO_3), and chromatographed on alumina (30 g.). Elution with ether removed neutral material and the phenol (0·20 g.) was obtained by elution with acetone. The phenol, which did not solidify, was treated with benzoyl chloride (0·35 c.c.) in pyridine (1 c.c.), then kept at room temperature for 12 hr., heated on a water-bath for 2 hr., and poured into 2N-hydrochloric acid (50 c.c.). Extraction with ether, repeated washing, chromatography in light petroleum on alumina, and elution with light petroleum–benzene failed to give a crystalline product.

trans-7-*Acetyl*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydro*-6-*methoxy*-1 : 1 : 12-*trimethylphenanthrene* (IV; R = COMe).—To 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydro-6-methoxy-1 : 1 : 12-trimethylphenanthrene (IV; R = H) (11 g., 1 mol.) and acetyl chloride (6·1 c.c., 2 mols.) in nitrobenzene (110 c.c.) at 5°, powdered aluminium chloride (11·6 g., 2 mols.) was added in portions during ¼ hr. The mixture was kept at 5° for 95 hr., then hydrolysed with 2N-hydrochloric acid (400 c.c.). The nitrobenzene was removed by steam, and the product taken up in ether (3 × 100 c.c.) which was washed with water and dried (K_2CO_3). The ketone (IV; R = COMe) remaining after evaporation of the ether was distilled, being obtained as a stiff, yellow gum (11·5 g., 90%), b. p. 192—196°/0·6 mm.

Treatment of the product with alcoholic 2 : 4-dinitrophenylhydrazine sulphate gave a mixed 2 : 4-dinitrophenylhydrazone which crystallised from ethanol or propan-2-ol as prisms, m. p. 102—108° (decomp.), inseparable by crystallisation or partition chromatography (Found : C, 65·2; H, 6·7; N, 11·3. Calc. for $C_{26}H_{32}O_5N_4$: C, 65·0; H, 6·7; N, 11·7%).

The ketone (11·5 g.) in ethanol (200 c.c.) was treated with semicarbazide hydrochloride (13 g., 3 mols.) and sodium acetate trihydrate (26 g.) in water (50 c.c.) and kept at 0° for 36 hr. The resulting solid was collected, washed with water, and dried (yield 5·1 g.). The filtrate was then concentrated at 5—10° under reduced pressure and the new solid (4·0 g.) also collected. Further concentration gave a gum which was dissolved in ethanol, combined with the residue, and treated with semicarbazide hydrochloride (6·5 g.) and sodium acetate trihydrate (13 g.) in aqueous-ethanolic solution, which after 40 hr. at 0° gave an additional 4·5 g. of crude semicarbazone, the total yield being quantitative. The semicarbazone crystallised from ethanol or methanol in prisms and was recrystallised until the product (3 g.) had m. p. 210°, repeated recrystallisation giving a maximum m. p. of 215—216°. Final purification was achieved by the following procedure. Semicarbazone (1·15 g.), m. p. 207—209°, was digested with boiling methanol (*ca.* 150 c.c.), and the residual solid was then dissolved in a large volume of methanol. Concentration and cooling gave a product (0·12 g.) of m. p. 221—222°, which by further recrystallisation from methanol yielded trans-7-*acetyl*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydro*-6-*methoxy*-1 : 1 : 12-*trimethylphenanthrene semicarbazone* (0·10 g.) as prisms, m. p. 222—223° (Found: C, 70·3; H, 8·8; N, 11·7. $C_{21}H_{31}O_2N_3$ requires C, 70·6; H, 8·7; N, 11·75%). A mixture of specimens of m. p. 222—223° and 215—216° had m. p. 215—216°, the figures in every case being for slow heating. The combined semicarbazone mother-liqours were concentrated to 200 c.c. and refluxed with 5N-hydrochloric acid (100 c.c.) for 3 hr. After dilution with water (1 l.) the ketone was extracted with ether (2 × 250 c.c.), and the ethereal solution washed with aqueous sodium carbonate and water, dried (K_2CO_3), and evaporated. The residual gum was chromatographed in benzene (50 c.c.) on alumina (250 g.), and the column eluted with benzene followed by benzene–ether. The resulting fractions were treated with semicarbazide hydrochloride (1½ parts, 4 mols.) and sodium acetate trihydrate (3 parts) in aqueous ethanol. After 2 days at 0° and 2 days at room temperature the solids were collected and recrystallised from methanol. The semicarbazones isolated from the various fractions (total 0·315 g. from 4·48 g. of ketone) were identical with the semicarbazone previously isolated (mixed m. p.). In all, 3·415 g. of *trans*-7-acetyl-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydro-6-methoxy-1 : 1 : 12-trimethylphenanthrene semicarbazone, m. p. 210°, were obtained, *i.e.*, 25% based on the compound (IV; R = COMe) or 22·5% on (IV; R = H).

Semicarbazone, m. p. *ca.* 210° (1·49 g.), was refluxed with 2N-hydrochloric acid (25 c.c.) and ethanol (25 c.c.) for 1½ hr. After dilution with water, the ketone was collected in ether (2 × 75 c.c.), and the ethereal solution washed with water, dried (K_2CO_3), and evaporated. Distillation of the residue gave the ketone (1·12 g., 90%) as a colourless gum, b. p. *ca.* 160—170° (air-bath)/0·1 mm.; regeneration from a sample of semicarbazone, m. p. 222—223°, gave pure trans-7-*acetyl*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydro*-6-*methoxy*-1 : 1 : 12-*trimethylphenanthrene*

(Found: C, 80·0; H, 9·4. $C_{20}H_{28}O_2$ requires C, 80·0; H, 9·4%). The over-all yield of moderately pure *trans*-ketone from (IV; R = H) was 20%.

trans-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*Octahydro-6-methoxy-*1 : 1 : 12-*trimethyl-*7-iso*propenylphenanthrene* (IV; R = $CMe{:}CH_2$).—*trans*-7-Acetyl-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydro-6-methoxy-1 : 1 : 12-trimethylphenanthrene (1·12 g.) (regenerated from semicarbazone, m. p. *ca.* 210°), in dry ether (40 c.c.), was added in portions during 25 min. to a stirred solution prepared from methyl iodide (2 c.c.), magnesium turnings (0·77 g.), and dry ether (50 c.c.). The mixture was refluxed for 1 hr. and the complex then decomposed with 2N-hydrochloric acid (100 c.c.). The aqueous layer was separated and extracted with ether (75 c.c.), and the combined ethereal solutions were washed with aqueous sodium thiosulphate and water, dried (K_2CO_3), and evaporated. The residue was refluxed in acetic anhydride (12 c.c.) for 1 hr., and the excess of anhydride destroyed with 2N-sodium hydroxide. The product was isolated with ether and on distillation gave colourless trans-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydro-6-methoxy-*1 : 1 : 12-*trimethyl-*7-iso*propenylphenanthrene* (0·84 g., 76%), b. p. 120—130° (air-bath)/0·05 mm. (Found: C, 83·9; H, 10·3. $C_{21}H_{30}O$ requires C, 84·5; H, 10·1%).

trans-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*Octahydro-6-methoxy-*1 : 1 : 12-*trimethyl-*7-iso*propylphenanthrene* [(±)-*Ferruginyl Methyl Ether*] (IV; R = $CHMe_2$).—*trans*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-Octahydro-6-methoxy-1 : 1 : 12-trimethyl-7-*iso*propenylphenanthrene (0·74 g.) in ethanol (15 c.c.) was hydrogenated in the presence of Adams catalyst (0·30 g.) at room temperature; the calculated uptake was complete in ½ hr. The filtered solution was evaporated and the residue distilled, (±)-*ferruginyl methyl ether* (0·65 g., 88%) collecting as a colourless gum, b. p. 120—130° (air-bath)/0·05 mm. (Found: C, 83·6; H, 10·5. $C_{21}H_{32}O$ requires C, 83·9; H, 10·7%). The *iso*propenyl compound in ethanol was unaffected by hydrogen and 5% palladium hydroxide–calcium carbonate.

trans-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*Octahydro-6-hydroxy-*1 : 1 : 12-*trimethyl-*7-iso*propylphenanthrene* [(±)-*Ferruginol*] (I).—(±)-Ferruginyl methyl ether (0·55 g.) was refluxed with 48% hydrobromic acid (2 c.c.) in glacial acetic acid (8 c.c.) for 9 hr. The spent acids were removed under reduced pressure and the residue was refluxed with fresh 48% hydrobromic acid (1 c.c.) and glacial acetic acid (8 c.c.) for a further 5 hr. and then poured into excess of 2N-sodium carbonate. The product, extracted with ether (2 × 75 c.c.) and washed in the usual way, was a greenish-black resin. The pale yellow (±)-ferruginol (0·47 g., 90%) obtained by distillation, b. p. 130—140° (air-bath)/0·07 mm., gave a yellowish-green colour with alcoholic ferric chloride; even by redistillation it could not be obtained analytically pure. The pure *product* was obtained by hydrolysis of the benzoate (Found, in a distilled specimen: C, 83·8; H, 10·7. $C_{20}H_{30}O$ requires C, 83·8; H, 10·6%).

trans-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*Octahydro-6-hydroxy-*1 : 1 : 12-*trimethyl-*7-iso*propylphenanthrene Benzoate* [(±)-*Ferruginyl Benzoate*].—(±)-Ferruginol (0·37 g.) was dissolved in pyridine (2 c.c.), and benzoyl chloride (0·25 c.c.) added with cooling. The mixture was left at room temperature for 12 hr. and then heated for 2 hr. on a steam-bath. 2N-Hydrochloric acid (50 c.c.) was added and the benzoate extracted with ether (2 × 75 c.c.). The washed (hydrochloric acid, aqueous sodium carbonate, and water) and dried (Na_2SO_4) ethereal solution was evaporated, and the residual gum was chromatographed in light petroleum (25 c.c.) on alumina (50 g.). The column was eluted with 25 c.c. portions of light petroleum–benzene (1 : 1), giving the following fractions: (*a*) 0·065 g., (*b*) 0·190 g., and (*c*) 0·080 g. Each was a nearly colourless resin which solidified on trituration with light petroleum or on long standing. Crystallisation of the combined fractions from methanol gave (±)-*ferruginyl benzoate* (0·20 g., 40%) as colourless prisms, m. p. 114—117°; recrystallisation from methanol followed by repeated crystallisation from ethanol raised the m. p. to 130—130·5° (Found: C, 83·3; H, 8·7. $C_{27}H_{34}O_2$ requires C, 83·1; H, 8·8%). This benzoate (1 part), m. p. 130—130·5, mixed with (+)-ferruginyl benzoate (1 part), m. p. 153—154·4°, had m. p. 137—140° softening at 130—137°.

The infrared spectra were determined, through the kindness of Dr. M. A. T. Rogers, by Mr. M. St.C. Flett, Imperial Chemical Industries Limited, to whom we are indebted for this assistance. We thank Dr. B. A. Hems, Glaxo Laboratories Ltd., for a generous gift of 2 : 2 : 6-trimethyl*cyclo*hexanone, Dr. L. G. Neubauer, Wellington, New Zealand, for a sample of (+)-ferruginyl benzoate, and the Department of Scientific and Industrial Research for the award (to J. G. T.) of a Maintenance Grant.

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