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Alkaloids of *Darlingia ferruginea*

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Abstract

Darlingia ferruginea J. F. Bailey contains the new tropane alkaloids ferrugine (2) and 3α-benzoyloxy-2α-hydroxybenzyltropane (4) as well as darlingine (1) and ferruginine (3), which also occur in *D. darlingiana*.

Darlingia ferruginea J. F. Bailey is an arboreal species closely related to *D. darlingiana*,[1] the first proteaceous plant in which alkaloids were detected, and from which a range of bases have subsequently been isolated.[2,3] The *Darlingia* spp. are confined to north Queensland, but are closely related botanically[4] to the *Knightia*, two of which, occurring in New Caledonia some 1500 km to the east, also contain alkaloids.[5–8]

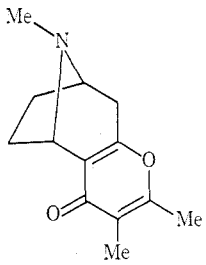
An extract of bark and leaves of *D. ferruginea* yielded about 0·08% of crude basic material from which the individual alkaloids were separated by column chromatography followed by p.t.l.c. on silica gel. The major alkaloid proved to be darlingine[2,3,9] (1),* identical with the principal base isolated from *D. darlingiana*. A second fraction contained (+)-ferrugine (2), whose structure and relative stereochemistry, deduced from spectroscopic evidence,[9] have now been confirmed by a synthesis in which diphenylcadmium was treated with hydroecgonidine acid chloride (Scheme 1). The latter substance was prepared from naturally occurring cocaine whose absolute stereochemistry is known,[10] and, since the synthetic product proved

* Traditional alkaloid nomenclature has been followed in this paper. The systematic name of tropane is 8-methyl-8-azabicyclo[3,2,1]octane and that of darlingine is 2,3,10-trimethyl-6,7,8,9-tetrahydrocyclohepta[*b*]pyran-5,8-imin-4(5*H*)-one.

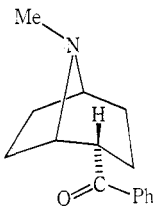
[1] Webb, L. J., 'An Australian Phytochemical Survey', Part II, CSIRO Bulletin No. 268, Melbourne, 1952.
[2] Anderson, B. F., Robertson, G. B., Bick, I. R. C., Gillard, J. W., and Leow, H.-M., *Chem. Ind. (London)*, 1977, 764.
[3] Bick, I. R. C., Gillard, J. W., and Leow, H.-M., *Aust. J. Chem.*, 1979, **32**, 2523.
[4] Johnson, L. A. S., and Briggs, B. G., *Aust. J. Bot.*, 1963, **11**, 21.
[5] Kan-Fan, C., and Lounasmaa, M., *Acta Chem. Scand.*, 1973, **27**, 1039.
[6] Lounasmaa, M., and Johansson, C.-J., *Tetrahedron Lett.*, 1974, 2509.
[7] Lounasmaa, M., Wovkulich, P. M., and Wenkert, E., *J. Org. Chem.*, 1975, **40**, 3694.
[8] Lounasmaa, M., *Planta Med.*, 1975, **27**, 83.
[9] Bick, I. R. C., Gillard, J. W., and Woodruff, M., *Chem. Ind. (London)*, 1975, 794.
[10] Hardegger, E., and Ott, H., *Helv. Chim. Acta*, 1955, **38**, 312.

to be the enantiomeric (−)-ferrugine, the absolute configuration of the natural base is thereby established as in (2).

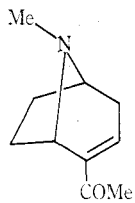
A minor component of the same fraction with the molecular formula $C_{22}H_{25}NO_3$ was provisionally designated alkaloid DF. The i.r. spectrum gave evidence of a hydroxy group, at least one monosubstituted benzene nucleus, and a conjugated ester carbonyl group; the presence of the last-named group was supported by the u.v. spectrum, which was consistent with a benzoyl chromophore. These deductions were in full accord with the ^{1}H n.m.r. spectrum: a two-proton multiplet at δ 7·78 corresponded to aromatic protons *ortho* to a carbonyl substituent, and there were a further eight aromatic protons in a multiplet at slightly higher field; this indicated the presence of two monosubstituted aromatic nuclei in all. A doublet at δ 4·71 suggested the presence of a proton on a benzylic carbon bearing a hydroxy group.



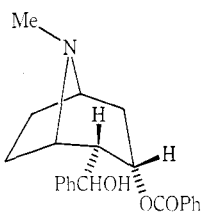
(1) darlingine



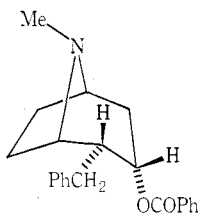
(2) (+)-ferrugine



(3) (+)-ferruginine



(4) alkaloid DF
(3α-benzoyloxy-2α-hydroxytropane)

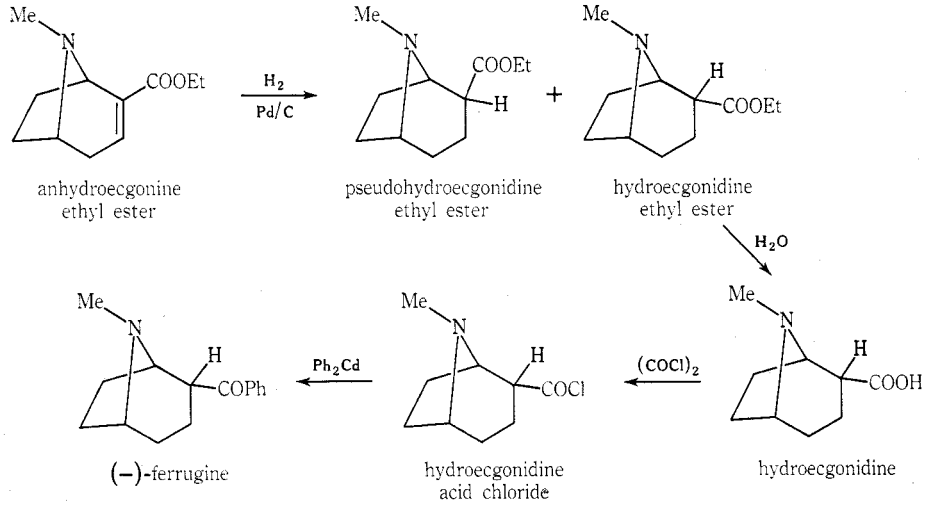


(5) alkaloid A

The mass spectrum supported the presence of benzoate ester and hydroxybenzyl groups in the structure of DF: an intense peak at *m/z* 230, and a prominent ion at *m/z* 244 suggested the loss of these two groups respectively, and furthermore, the presence of a benzoyl group was in agreement with the appearance of a strong ion at *m/z* 105, while another prominent ion at *m/z* 124 could be attributed to the loss of both benzoyloxy and hydroxybenzyl groups with hydrogen transfer. The two base peaks in the spectrum, of about equal intensity, occurred at *m/z* 82 and 96, and showed that the alkaloid had a tropane nucleus.[11,12] The ^{1}H n.m.r. spectrum was consistent with this finding, with a three-proton singlet indicating the presence of an *N*-methyl group and two one-proton multiplets at slightly lower field corresponding in chemical shift with recorded values for methine protons on the

[11] Blossey, E. C., Budzikiewicz, H., Ohashi, M., Fodor, G., and Djerassi, C., *Tetrahedron*, 1964, **20**, 585.
[12] Parello, J., Longevialle, P., Vetter, W., and McCloskey, J. A., *Bull. Soc. Chim. Fr.*, 1963, 2787.

carbons linked to nitrogen, while a broad triplet at δ 5·35 indicated a proton located at C3, to which an α-acyloxy group is attached.[12] The evidence is in accord with structure (4) for alkaloid DF, which thus appears to be a close analogue of alkaloid A (5) isolated from *Knightia deplanchei*;[5–7] other alkaloids from this source have a hydroxybenzyl group as in DF. The orientation of the latter group in DF is unknown, but it is tentatively allocated an α-configuration similar to that of the benzoyl group in ferrugine (2), as well as the benzyl groups in alkaloids A, B, C and D and the hydroxybenzyl group of alkaloid F from the above-mentioned New Caledonian plant.[5–7]

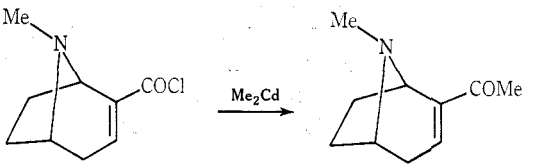


Scheme 1

The major component of the third fraction, ferruginine (3), also occurs in *D. darlingiana*.[3] Its mass spectrum suggested a tropane structure: an intense ion at *m/z* 82 characteristic of this nucleus was present,[11,12] but the base peak corresponded to the loss of C_2H_5, and another strong peak at *m/z* 94 could be attributed to the *N*-methylpyridinium ion; these observations were consistent with a tropene residue. The mass spectrum also showed strong ions corresponding to the loss of 15 and 43 mass units from the molecular ion; this suggests the presence of an acetyl group. Other spectroscopic data supported these deductions: the u.v. and i.r. spectra were in accord with the presence of an α,β-unsaturated carbonyl group, and in the ^{1}H n.m.r. spectrum two three-proton singlets which could be ascribed to acetyl and methylimino groups were present, as well as an olefinic proton signal; the remainder of the spectrum included two peaks corresponding to protons attached to carbons adjacent to nitrogen. In sum the spectroscopic data pointed to structure (3), which has been confirmed synthetically (Scheme 2): anhydroecgonine acid chloride prepared from (−)-cocaine was treated with dimethylcadmium to give (−)-ferruginine, the enantiomer of the naturally occurring base. The synthesis at the same time established the absolute configuration of (+)-ferruginine as shown in (3). Soon after it had been completed, the preparation of the same enantiomer by a somewhat different method was reported as a stage in the synthesis of the algal toxin anatoxin-a.[13]

[13] Campbell, H. F., Edwards, O. E., and Kolt, R., *Can. J. Chem.*, 1977, **55**, 1372.

Several minor alkaloidal constituents of the plant were present in amounts too small for adequate purification and structural investigation.



anhydroecgonine acid chloride

(−)-ferruginine

Scheme 2

Experimental

General

Experimental details are those given in the preceding paper.[3] In addition, column chromatography was carried out with Merck silica gel 60.

Extraction and Separation Procedure

Air-dried leaves, stems and roots of *Darlingia ferruginea* collected from Davies Creek, north Queensland, were ground to a fine powder in a Wiley mill. The powdered material (20 kg) was continuously extracted by percolation with methanol at room temperature until a sample of the extract gave a negative Mayer test for alkaloids. The extract was concentrated in vacuum at a temperature below 35° to give a tarry mass, which was dissolved in warm glacial acetic acid (2 l.). The solution was poured in a thin stream into water (20 l.) which was rapidly agitated by a vibro-mixer. The non-alkaloidal material which precipitated on standing overnight was removed by filtration through a bed of Celite. A further non-alkaloidal precipitate which formed upon neutralization was similarly removed. The filtrate was basified with ammonia (*d* 0·880) and thoroughly extracted with chloroform (20 × 1 l.). The chloroform extract was concentrated in vacuum to half its volume, then thoroughly extracted with 5% sulfuric acid (12 × 500 ml). The aqueous acid solution was extracted with ether (6 × 250 ml), basified with ammonia, and the liberated alkaloids were extracted into chloroform (15 × 250 ml). The chloroform extract was dried (Na_2SO_4) and evaporated in vacuum to give a strong-smelling thick brown oil (16 g, 0·08%). The crude bases were dissolved in chloroform and introduced into a column containing silica gel (800 g). Elutions were made with chloroform containing increasing proportions of methanol. The course of elution was monitored by analytical t.l.c., and fractions were grouped accordingly. Three major fractions were obtained, and each was further purified by p.t.l.c.

Isolation, Purification and Characterization of the Alkaloids

Fraction 1

This was eluted from the column with 2% $MeOH/CHCl_3$. Analytical t.l.c. with different solvent systems revealed the presence of one major component, which was subjected to p.t.l.c.; development with 12% $MeOH/CHCl_3$ gave one major band of R_F 0·55. Material eluted from this band (420 mg) was twice recrystallized from ether to give white needles, m.p. 166–167°, identical (m.m.p., R_F, u.v., i.r., n.m.r. and m.s. data) with darlingine.[3]

The minor components were present in amounts too small for further studies.

Fraction 2

This was eluted from the column with 4% $MeOH/CHCl_3$. Analytical t.l.c. with different solvent systems revealed the presence of two components running very close together. P.t.l.c. on silica gel impregnated with 0·5 N KOH enabled the best resolution of the two bases, which were finally separated after several multiple developments with 13% $MeOH/CHCl_3$.

The major component, contained in the upper band, was further repurified by p.t.l.c., then recrystallized twice from ethanol to give white rosettes (301 mg) of *ferrugine* (2α-benzoyltropane), m.p. 101–102°, $[\alpha]_D^{19}$ +55° ($CHCl_3$); R_F 0·37 (12% MeOH/$CHCl_3$), 0·52 (10% Et_3N/$CHCl_3$) and 0·56 (MeOH/NH_3 100:1·5) (Found: C, 78·7; H, 8·3; N, 6·1. $C_{15}H_{19}NO$ requires C, 78·6; H, 8·3; N, 6·1%). λ_{max} (EtOH): 242 nm (log ε 4·11). ν_{max} ($CHCl_3$): 1711w, 1678s (carbonyl), 1598m, 1580w, 1475m, 1449s, 1373m, 1275m, 1255s, 1229m, 1170m, 1105m, 1055m, 1015m, 938m, 750s, 695s cm^{-1}. ^1H n.m.r. δ: 7·96, m, 2H, ArH; 7·48, m, 3H, ArH; 3·90, m, 1H, H2; 3·41, m, 1H, H1; 3·25, m, 1H, H5; 2·39, s, 3H, NCH_3; 2·20–1·20, m, 8H, aliphatic. ^{13}C n.m.r. δ: 136·2, s, C1; 133·0, d, C4′; 128·8, d, C2′ and C6′; 128·4, d, C3′ and C5′; 63·9, d, C1; 61·6, d, C5; 47·3, d, C2; 40·2, q, NCH_3; 29·6, t, C4; 25·9, t, C6; 22·7, t, C7; 18·6, t, C3. Mass spectrum: *m/z* 229 (24%, M, $C_{15}H_{19}NO$), 201 (5, $C_{13}H_{15}NO$), 124 (24, $C_8H_{14}N$), 107 (43), 105 (45, C_7H_5O), 97 (50), 96 (98, $C_6H_{10}N$), 94 (45), 83 (51), 82 (100, C_5H_8N), 77 (64), 68 (23), 56 (36), 42 (90, C_2H_4N). The base formed a *picrate*, prepared in and recrystallized from ethanol, m.p. 192–194° (Found: C, 55·3; H, 4·7. $C_{15}H_{19}NO$,$C_6H_3N_3O_7$ requires C, 55·0; H, 4·8%).

The minor component, eluted from the lower band, was further repurified by p.t.l.c., then recrystallized twice from light petroleum to give white needles (30 mg), m.p. 136–138°. This base, *alkaloid DF* (3α-benzoyloxy-2α-hydroxybenzyltropane), had $[\alpha]_D^{19}$ +28° ($CHCl_3$); R_F 0·29 (12% MeOH/$CHCl_3$) and 0·45 (10% Et_3N/$CHCl_3$) (Found: C, 75·6; H, 6·8; N, 3·7. $C_{22}H_{25}NO_3$ requires C, 75·2; H, 7·1; N, 4·0%). λ_{max} (EtOH): 210, 232, 280 nm (log ε 4·02, 4·01, 3·0). ν_{max} ($CHCl_3$): 3320m (hydroxy), 1709s (ester carbonyl), 1595m, 1578w, 1445m, 1273s, 1110s, 1060m, 733s, 690s cm^{-1}. ^1H n.m.r. δ: 7·78, m, 2H, ArH; 7·65–7·0, m, 8H, ArH; 5·35, br t, 1H, H3; 4·71, d, *J* 8 Hz, 1H, CHOH; 3·47, m, 1H, H1; 3·25, m, 1H, H5; 2·25, s, 3H, NCH_3; 2·6–1·5, m, 6H, aliphatic. Mass spectrum: *m/z* 351 (18%, M, $C_{22}H_{25}NO_3$), 332 (6), 244 (18), 230 (50), 229 (36), 124 (28), 105 (33), 97 (75), 96 (99), 83 (61), 82 (100), 77 (37), 68 (36), 58 (44), 57 (36), 55 (31), 43 (54), 42 (77).

Fraction 3

This was eluted from the column with 6% MeOH/$CHCl_3$. Analytical t.l.c. with a number of different solvent systems revealed the presence of one major component, which was separated by p.t.l.c. on silica gel impregnated with 0·5 N KOH. Development with 15% MeOH/$CHCl_3$ and elution of the main band yielded a base which was further repurified by p.t.l.c. A clear oil (42 mg) was finally isolated, which appeared homogeneous on t.l.c., with R_F 0·22 (12% MeOH/$CHCl_3$), 0·70 (silica gel–0·5 N KOH: 10% Et_3N/$CHCl_3$) and 0·48 (silica gel–0·5 N KOH: 15% MeOH/$CHCl_3$), but could not be induced to crystallize. This base, *ferruginine*, had $[\alpha]_D^{19}$ +37° ($CHCl_3$). λ_{max} (EtOH): 233 nm (log ε 4·00). ν_{max} ($CHCl_3$): 1655 (α,β-unsaturated carbonyl), 1620 cm^{-1} (olefinic). ^1H n.m.r. δ: 6·70, t, $J_{3,4ax}$ 5, $J_{3,4eq}$ 5 Hz, 1H, H3; 3·92, d, *J* 7 Hz, 1H, H1; 3·28, br m, 1H, H5; 2·70, d, $J_{4eq,4ax}$ 17 Hz, 1H, H4*eq*; 2·30, s, 3H, NCH_3; 2·25, s, 3H, $COCH_3$; 2·10, dd, $J_{4ax,3}$ 5, $J_{4ax,4eq}$ 17 Hz, 1H, H4*ax*. Mass spectrum: *m/z* 165 (33%, M, $C_{10}H_{15}NO$), 150 (22), 136 (100), 122 (41), 121 (29), 94 (35), 82 (47), 81 (32), 44 (49), 43 (66), 42 (73). The base formed a *picrate*, m.p. 161–163° (Found: C, 49·1; H, 4·3. $C_{10}H_{15}NO$,$C_6H_3N_3O_7$ requires C, 48·7; H, 4·6%).

The minor components were isolated in amounts too small for further studies.

Synthesis of (−)-Ferruginine (2-Acetyltrop-2-ene)

A Grignard reagent was prepared from magnesium (2·1 g), anhydrous ether (200 ml) and methyl iodide (15 g), in an atmosphere of nitrogen. The solution was cooled in an ice bath and anhydrous cadmium chloride powder (8 g), which had been dried to constant weight at 110° and stored in a desiccator over calcium chloride, was added. The mixture was stirred and gently refluxed for 1 h. Ether was then distilled from the stirred mixture and the solvent was gradually replaced by benzene. Anhydroecgonine acid chloride hydrochloride (2·05 g), prepared according to the procedure of Einhorn,[14] was poured into the stirred mixture in an atmosphere of nitrogen. Stirring was continued for 1 h at room temperature. The mixture was gently refluxed for 3 h with continuous vigorous stirring, then poured into ice and 10% hydrochloric acid. The aqueous layer

[14] Einhorn, A., *Ber. Dtsch. Chem. Ges.*, 1887, **20**, 1221.

was separated, basified with ammonia (*d* 0·880), and thoroughly extracted with chloroform. The chloroform extract was washed with water, dried (Na_2SO_4) and evaporated to dryness in vacuum to give a yellow oil. This was subjected to p.t.l.c. ($MeOH/CHCl_3/NH_3$ 20 : 80 : 1·5) and the band of R_F 0·67 was extracted to give a clear oil (0·30 g, 20% yield), $[\alpha]_D^{19}$ −37° ($CHCl_3$). The product, which could not be crystallized, had R_F, u.v., i.r., n.m.r. and m.s. data identical to those of natural (+)-ferruginine, and its specific optical rotation was equal but opposite in sign.

Synthesis of (−)-Ferrugine (2α-Benzoyltropane)

Preparation of Anhydroecgonine Ethyl Ester

Anhydroecgonine hydrochloride[14] (2·3 g) was gently refluxed with absolute ethanol (75 ml), which had been saturated with dry hydrogen chloride, for 1 h. The solution was cooled and ethanol was removed in vacuum. Water (75 ml) was added, and the aqueous solution was basified with 5% sodium hydroxide and then extracted with chloroform (5 × 50 ml). The chloroform extract was washed with water, dried (Na_2SO_4) and evaporated to dryness to give anhydroecgonine ethyl ester as a semicrystalline almost colourless oil (2·09 g, 95%), R_F 0·75 ($MeOH/CHCl_3/NH_3$ 20 : 80 : 1), $[\alpha]_D^{19}$ −50° ($CHCl_3$) (lit.[15] −51·6°). The base formed a picrate, m.p. 168–169° (lit.[15] 168°).

Catalytic Hydrogenation of Anhydroecgonine Ethyl Ester

A solution of anhydroecgonine ethyl ester (1 g) in ethanol (50 ml) was shaken with 10% Pd/C (0·25 g) in a hydrogen atmosphere at room temperature and atmospheric pressure for 3 h. The catalyst-free solution was then evaporated to dryness in vacuum to give a clear colourless oil (0·97 g). T.l.c. ($MeOH/CHCl_3/NH_3$ 20 : 80 : 1) showed the presence of two components; neither absorbed u.v. light, but both were stained with potassium iodoplatinate, one (R_F 0·68) purplish-black and the other (R_F 0·60) purplish-brown. The two products were separated by p.t.l.c.

The product of higher R_F was isolated as a semicrystalline colourless oil (0·27 g). ^1H n.m.r. δ: 4·23, q, *J* 7 Hz, 2H, CH_2CH_3; 3·42, m, 1H, H1; 3·17, m, 1H, H5; 2·75, m, 1H, H2; 2·20, s, 3H, NCH_3; 1·30, t, *J* 7 Hz, 3H, CH_2CH_3. Mass spectrum: *m/z* 197 (M). ν_{max}: 1708 cm^{-1} (ester carbonyl). It did not form a crystalline picrate and thus appears to correspond to the pseudo-hydroecgonidine ethyl ester described by Findlay.[16]

The product of lower R_F was isolated as a semicrystalline clear colourless oil (0·52 g). ^1H n.m.r. δ: 4·13, q, *J* 7 Hz, 2H, CH_2CH_3; 3·43, m, 1H, H1; 3·15, m, 1H, H5; 2·76, m, 1H, H2; 2·35, s, 3H, NCH_3; 1·25, t, *J* 7 Hz, 3H, CH_2CH_3. Mass spectrum: *m/z* 197 (M). ν_{max}: 1721 cm^{-1} (ester carbonyl). It formed a crystalline picrate, prepared in and recrystallized from absolute ethanol, m.p. 112–114° (lit.[16] 113–114·5°). This major product thus appears to correspond to the hydroecgonidine ethyl ester described by Findlay.[16]

In another experiment, anhydroecgonine ethyl ester was hydrogenated at a pressure above atmospheric, whereupon only one product was formed. A solution of anhydroecgonine ethyl ester (1 g) in ethanol (50 ml) was shaken with 10% Pd/C (0·25 g) at room temperature in a hydrogen atmosphere at 8 p.s.i. above atmospheric pressure for 4 h. The catalyst-free solution was then evaporated to dryness in vacuum to give a semicrystalline clear colourless oil (0·98 g), which was shown by t.l.c. to contain a single pure component of R_F 0·60. This product gave a purplish brown colour with potassium iodoplatinate and formed a crystalline picrate, and was identical to the major component isolated earlier. It is henceforth referred to as hydroecgonidine ethyl ester.

Hydroecgonidine Acid Chloride

Hydroecgonidine ethyl ester (1·3 g) was gently refluxed in water (30 ml) for 8 h, after which only one spot appeared on the baseline on t.l.c. The solution was then evaporated to dryness in vacuum to a colourless oil, which when kept in vacuum over KOH formed a white crystalline mass (1·11 g) of hydroecgonidine, m.p. 196–197°, after recrystallization from methanol. Mass spectrum: *m/z* 169 (M). Hydroecgonidine (1 g) was suspended in dry benzene (12 ml) and to the stirred suspension, cooled in an ice bath, was added a drop of pyridine and then, dropwise, a solution of oxalyl chloride (2·5 ml) in dry benzene (10 ml). The whole assembly was protected from moisture and

[15] Liebermann, C., *Ber. Dtsch. Chem. Ges.*, 1907, **40**, 3602.
[16] Findlay, S. P., *J. Am. Chem. Soc.*, 1953, **75**, 1033.

left overnight at room temperature. The clear solution was then concentrated in vacuum at room temperature, diluted with fresh dry benzene, and reconcentrated; the procedure was repeated twice more. The benzene solution of the acid chloride was arylated without further purification.

Arylation with Diphenylcadmium

The experiment was conducted in an atmosphere of nitrogen. A Grignard reagent was prepared from magnesium (0·57 g), anhydrous ether (60 ml) and bromobenzene (3·82 g). The solution was cooled in an ice bath and stirred slowly while finely powdered anhydrous cadmium chloride (2·22 g), dried to constant weight at 110° and stored over calcium chloride, was added in portions during 2 min. After stirring for 1 h, the suspension of liquid diphenylcadmium in ether was treated with the benzene solution of the acid chloride. Stirring was continued at room temperature for 10 h. Ice and 10% hydrochloric acid (60 ml) were then added; the solution was stirred for 5 min, then shaken in a separating funnel. The aqueous layer was separated, basified with ammonia (*d* 0·880) and thoroughly extracted with chloroform. The chloroform extract was washed with water, dried (Na_2SO_4) and evaporated to dryness in vacuum to give a yellow oil. P.t.l.c. purification of this afforded a clear oil which yielded white crystals on standing (0·32 g, 23·6% yield based on acid). After recrystallization from ethanol the product had m.p. 100–102°, $[\alpha]_D^{19}$ −55° ($CHCl_3$), and gave R_F, u.v., i.r., n.m.r. and m.s. data identical to those of natural (+)-ferrugine. Its specific optical rotation, however, was equal but opposite in sign (Found: C, 78·3; H, 8·2; N, 6·0. Calc. for $C_{15}H_{19}NO$: C, 78·6; H, 8·3; N, 6·1%).

Acknowledgments

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