363. *The Constitutions of Geodin and Erdin.*

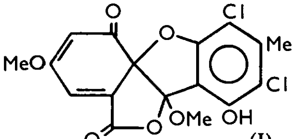
By D. H. R. Barton and A. I. Scott.

(+)-Geodin has been racemised and (±)-erdin resolved to give (+)-erdin. Degradation of dihydroerdin under mild alkaline conditions has been shown to furnish 2 : 6-dichloro-orcinol, 5-hydroxy-3-methoxyphthalic acid, and 2 : 4-dichloro-1 : 6-dihydroxy-3-methoxyxanthone-8-carboxylic acid. On the basis of these and other observations the formulæ proposed earlier for geodin and erdin are modified. The mechanism of the racemisation of (+)-geodin and (+)-erdin is discussed.

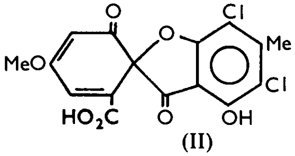
The fungal metabolites geodin and erdin were first isolated by Raistrick and Smith[1] from *Aspergillus terreus* Thom. Their chemistry was the subject of elegant and extensive experimentation by Raistrick and his collaborators[1,2,3] which culminated[4] in tentative structural proposals. Disregarding formulæ incompatible with Bredt's rule, they suggested that geodin should be represented as (I) and erdin as (II). The most interesting feature of the chemistry of geodin and erdin is that, whilst the former shows pronounced dextrorotation, the latter is optically inactive. Through the great kindness of Professor H. Raistrick, F.R.S., we have been able to investigate this phenomenon in more detail.

Geodin shows significant infrared bands at 1728, 1665, 1630, and 1610 cm.$^{-1}$. A ψ-ester structure such as (I), which should absorb at about 1780 cm.$^{-1}$, is therefore improbable. Additional chemical evidence cited below confirms that the ester grouping of geodin is normal (CO_2Me).

Erdin, in agreement with the earlier literature, was optically inactive in several solvents. On treatment with quinine methohydroxide[5] it gave a crystalline salt which with acid afforded optically active (+)-erdin with a rotation similar to that of naturally occurring geodin. The natural (racemic) erdin and (+)-erdin had identical infrared spectra in solution. Although (+)-erdin was optically stable in neutral solvents, it readily racemised at room temperature in dioxan containing 2% of hydrogen chloride to give back (±)-erdin. In a comparable experiment (+)-geodin furnished for the first time (±)-geodin. (+)- and (±)-Geodin had identical infrared spectra in solution.



(I)



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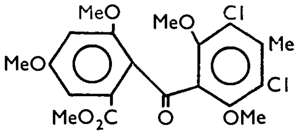

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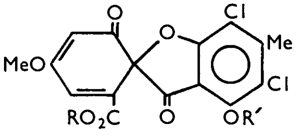

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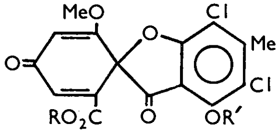

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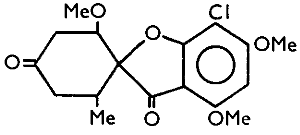

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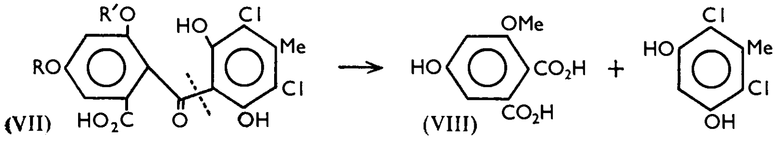

(VII) (VIII)

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[1] Raistrick and Smith, *Biochem. J.*, 1936, **30**, 1315.

[2] Clutterbuck, Koerber, and Raistrick, *ibid.*, 1937, **31**, 1089.

[3] Calam, Clutterbuck, Oxford, and Raistrick, *ibid.*, 1939, **33**, 579.

[4] *Idem, ibid.*, 1947, **41**, 458.

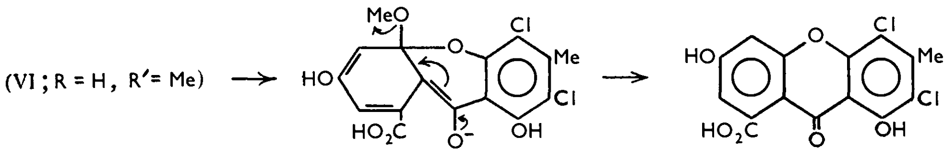
[5] Major and Finkelstein, *J. Amer. Chem. Soc.*, 1941, **63**, 1368.

On catalytic hydrogenation (+)-geodin and (±)-erdin readily afford dihydro-derivatives which give identical compounds on complete methylation with diazomethane.[2] The work of Calam, Clutterbuck, Oxford, and Raistrick[3] has shown both by degradation and by synthesis that the methylation product has structure (III). The behaviour on hydrogenation indicates, in agreement with Raistrick and his collaborators,[4] a *cyclo*hexadienone prevented from attaining phenolic aromaticity by one blocking (ethereal) group. One can therefore write formulæ (IV or V; R = Me, R′ = H) for geodin and (IV or V; R = R′ = H) for erdin.

Geodin and erdin show intense ultraviolet absorption at 284 mμ. A subtraction curve of the spectra of the model compound dihydrogriseofulvin[6] (VI) from that of erdin gave a curve showing $\lambda_{max.}$ 241 mμ (ε 14,000). This is fully consistent with a cross-conjugated dienone such as (V), but not with a linearly extended dienone such as (IV) which would be expected[7] to absorb beyond 300 mμ.

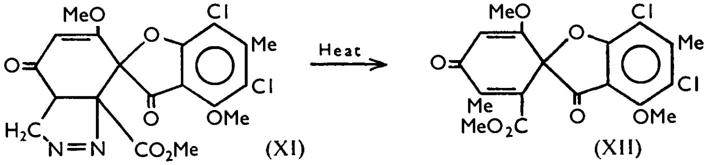
A decisive chemical differentiation between formulæ (IV) and (V) was achieved by degradation of dihydro-derivatives [as (III)]. It was reasoned that cleavage of the bond indicated would be observed in an alkaline degradation of (say) dihydroerdin (VII; R and R′ = Me and H) in which the orcinol ring should behave as a β-diketone system. In the event, treatment of dihydroerdin under mild alkaline conditions gave dichloro-orcinol and 5-hydroxy-3-methoxyphthalic acid (VIII). The structure of dihydroerdin is therefore (VII; R = H, R′ = Me), of erdin is (V; R = R′ = H), and of geodin (V; R = Me, R′ = H). These slight modifications of the formulæ of Calam, Clutterbuck, Oxford, and Raistrick[4] are in agreement with the infrared data. Thus (see above) in the geodin spectrum the band at 1728 cm.$^{-1}$ represents superimposed methoxycarbonyl and *cyclo*pentanone groups, that at 1665 cm.$^{-1}$ the doubly conjugated *cyclo*hexanone, and those at 1630 and 1610 cm.$^{-1}$ carbonyl-conjugated C=C stretching frequencies. In comparison, erdin showed bands at 1717 (broad; carboxyl and *cyclo*pentanone), 1667 (doubly conjugated *cyclo*hexanone), and 1639 and 1610 cm.$^{-1}$ (carbonyl-conjugated C=C).

From the alkaline cleavage of dihydroerdin (VII; R = H, R′ = Me) (see above) an interesting acidic by-product resulted. This gave analyses for $C_{15}H_8O_6Cl_2$ and contained no methoxyl group. Methylation with diazomethane gave a methyl ester dimethyl ether, suggesting the presence of two phenolic hydroxyl groups. The compound showed ultraviolet and infrared characteristics (see p. 1771) indicative of a xanthone. It must be formulated, therefore, as (IX), being produced as in (X). If this reaction mechanism is accepted, the fact that the xanthone has no methoxyl group confirms the orientation of the methoxyl group in erdin.



(X)

(IX)



(XI)

(XII)

The observation that fully methylated dihydroerdin and dihydrogeodin are identical (see above) speaks against a possible ψ-ester formula such as (I). Additional chemical

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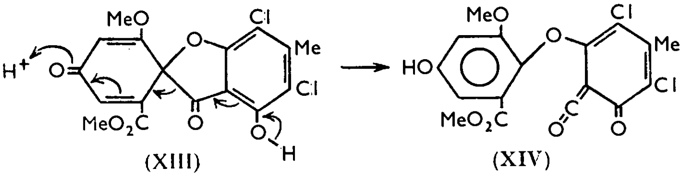
[6] Mulholland, *J.*, 1952, 3987.

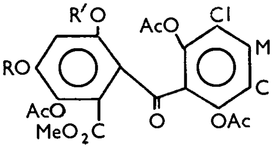
[7] *Inter al.*, Dauben and Richards, *J. Amer. Chem. Soc.*, 1956, **78**, 5329; Jeger, Ruegg, and Ruzicka, *Helv. Chim. Acta*, 1947, **30**, 1294; Meisels, Jeger, and Ruzicka, *ibid.*, 1950, **33**, 700.

evidence in favour of a normal ester formulation was secured as follows. Methylation of geodin with diazomethane affords[2] a pyrazoline in agreement with the presence of a reactive ene-1 : 4-dione system. The orientation of diazomethane addition is probably as in formula (XI) for the pyrazoline, since gentle pyrolysis gave a compound whose analysis indicates that it is homogeodin methyl ether (XII). The constitution of the latter was confirmed by its spectroscopic properties (see p. 1771). The pyrazoline from (+)-geodin had identical infrared absorption in solution to that of the pyrazoline from (±)-erdin. In Nujol, however, where differences in crystal lattice may be important, the infrared spectra were different. As expected, the pyrazolines from (+)-geodin and (+)-erdin were identical. Similarly the pyrazolines from (±)-geodin and (±)-erdin were the same compound.

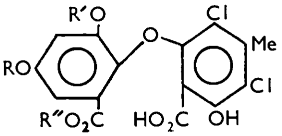
The ready racemisation of (+)-geodin and (+)-erdin, to which reference has been made above, is of theoretical interest since a mechanism must be devised for the inversion of a *quaternary* centre. A clue must be provided by the following observations. Mild acetylation of geodin with sodium acetate and acetic anhydride at room temperature gave a monoacetate (V; R = Me, R′ = Ac), whilst methylation with potassium carbonate and methyl iodide in acetone solution afforded a monomethyl ether (V; R = R′ = Me).



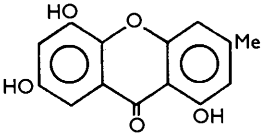
(XIII) (XIV)



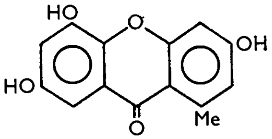
(XV)



(XVI)



(XVII)



(XVIII)

Both of these compounds were stable to hydrogen chloride in dioxan under conditions which led to the rapid racemisation of (+)-geodin and (+)-erdin (see above). Comparable experiments using acidic methanol are described in the Experimental section. The phenolic hydroxyl group of (+)-geodin and (+)-erdin is therefore involved in some way in the racemisation mechanism. This was confirmed by the fact that (+)-geodin reacted rapidly with pyridine to give an optically inactive adduct whereas the monomethyl ether was stable. A similar adduct was obtained from (±)-erdin. The nature of these adducts was not investigated further. The simplest racemisation mechanism for (+)-geodin would involve [see (XIII)] a keten-ketone (XIV) the reactivity of which might be such as to justify the hypothesis of recyclisation to (±)-geodin.

The modified formulæ for geodin and erdin afford explanations for all relevant prior knowledge. We may mention specifically the acetylation product[2] of (+)-geodin which has structure (XV; R = Ac, R′ = Me) rather than (XV; R = Me, R′ = Ac), and geodin and erdin hydrates[4] which are now formulated as (XVI; R = H, R′ = R″ = Me) and (XVI; R = R″ = H, R′ = Me) respectively. Norgeodin A and B, obtained by treating (+)-geodin with hydriodic acid, are probably to be formulated as (XVII) and (XVIII) respectively.

Recently the isolation of an antibiotic very similar in character to (+)-geodin was reported.[8] Professor H. Raistrick, F.R.S., very kindly forwarded to us a specimen of this substance obtained through the courtesy of Dr. Delmotte-Plaquée. By direct comparison (see p. 1770) we showed that, in spite of an opinion to the contrary,[8] this was simply (+)-geodin and not a new antibiotic.

[8] Delmotte-Plaquée, Delmotte-Plaquée, and Bastin, *J. Pharm. Belg.*, 1956, **11**, 200.

EXPERIMENTAL

M. p.s were taken on the Köfler block. Unless specified to the contrary, $[\alpha]_D$ are in $CHCl_3$, ultraviolet absorption spectra in EtOH (taken using the Unicam S.P. 500 Spectrophotometer), and infrared absorption spectra in $CHCl_3$. The latter spectra were kindly determined by Dr. G. Eglinton and his colleagues. Microanalyses were carried out by Mr. J. M. L. Cameron and his associates.

(+)- *and* (±)-*Geodin*.—(+)-Geodin had, after crystallisation from chloroform–ether, m. p. (prisms) 228—231°, $[\alpha]_D$ +140° (*c* 0·80), $\lambda_{max.}$ 284 mμ (ε 19,000). Geodin showed no m. p. depression on admixture with the compound isolated by Delmotte-Plaquée.[8] The latter had m. p. 227—231°, $[\alpha]_D$ +140° (*c* 1·00), and identical ultraviolet absorption at all wavelengths. The infrared spectra were also identical.

(+)-Geodin (50 mg.) was treated with 2% (w/w) hydrogen chloride in dry dioxan at 25° for 175 min. ($[\alpha]_D$ 0°). Addition of water (2 vols.) afforded a crystalline precipitate (45 mg.) which on further crystallisation from chloroform–ether gave (±)-*geodin* (40 mg.), m. p. (prisms) 225—227°, $[\alpha]_D$ 0° (*c* 2·00), $\lambda_{max.}$ 284 mμ (ε 19,000) (Found: C, 51·55; H, 3·5; OMe, 15·25. $C_{17}H_{12}O_7Cl_2$ requires C, 51·15; H, 3·05; 2OMe, 15·55%). The ultraviolet and infrared spectra of (+)- and (±)-geodin were identical.

(+)-*Geodin Acetate*.—(+)-Geodin (50 mg.) in acetic anhydride (5 ml.) containing fused sodium acetate (20 mg.) was kept at 25° for 16 hr. ($[\alpha]_D$ change from +100° to +128°.) Addition of water gave (+)-*geodin acetate* (50 mg.), needles (from methanol, m. p. 174—175°, $[\alpha]_D$ +180° (*c* 0·40 in dioxan) (Found: C, 51·6; H, 3·75; Ac, 9·5. $C_{19}H_{14}O_8Cl_2$ requires C, 51·75; H, 3·2; Ac, 9·75%). The infrared spectrum (in Nujol) showed bands at 1777 (phenolic acetate), 1735 (methoxycarbonyl and *cyclo*pentanone), 1665 (doubly conjugated *cyclo*hexanone), and 1610 cm.$^{-1}$ (C=C conjugated with carbonyl).

(+)-*Geodin Methyl Ether*.—(+)-Geodin (50 mg.) in "AnalaR" acetone (7 ml.) was treated with methyl iodide (100 mg.) at 60—70° in the presence of anhydrous "AnalaR" potassium carbonate (150 mg.) until an aliquot part gave no colour with alcoholic ferric chloride. Crystallisation of the neutral product from chloroform–ether afforded (+)-geodin methyl ether, plates, m. p. 173°, $[\alpha]_D$ +170° (*c* 0·54 or 0·85), $\lambda_{max.}$ 280 mμ (ε 16,600), infrared bands at 1735 and 1720 (*cyclo*pentanone and methoxycarbonyl), 1660 (doubly conjugated *cyclo*hexanone), and 1605 cm.$^{-1}$ (C=C conjugated with carbonyl) (Found: C, 52·6; H, 3·1; OMe, 22·25. $C_{18}H_{14}O_7Cl_2$ requires C, 52·3; H, 3·4; 3OMe, 22·55%).

(+)- *and* (±)-*Erdin*.—(±)-Erdin, crystallised from chloroform–methanol, had m. p. (needles) 210—212°, $[\alpha]_D$ 0° (*c* 1·00 or 2·00 in $CHCl_3$; or *c* 1·20 in dioxan), $\lambda_{max.}$ 284 mμ (ε 21,000).

(±)-Erdin (1·08 g.) in ethanol (15 ml.) was treated with 0·35N-aqueous quinine methohydroxide [5] (7·65 ml., 1 equiv.). The solvents were removed *in vacuo* and the residual bright yellow oil taken up in ethanol (15 ml.) with addition of dioxan (120 ml.). The crystalline salt (deposited during 16 hr.) was recrystallised five times from ether–ethanol, to give (+)-erdin quinine metho-salt (1·18 g.), yellow prisms, m. p. 193°, $[\alpha]_D$ −94° (*c* 0·70 in EtOH). This was acidified with 10% w/w sulphuric acid (40 ml.) with shaking in the presence of ether. Recovery from the ether gave (+)-*erdin* (400 mg.). Recrystallised from chloroform–light petroleum this (250 mg.) had m. p. (prisms) 210—212°, $[\alpha]_D$ +149° (*c* 0·41 in dioxan) (Found: C, 49·3; H, 2·8; Cl, 18·35; OMe, 8·55. $C_{16}H_{10}O_7Cl_2$ requires C, 49·9; H, 2·6; Cl, 18·4; OMe, 8·05%). (+)-Erdin showed absorption identical with that of (±)-erdin in both the ultraviolet and the infrared region. Treatment of (+)-erdin (5 mg.) with 2% hydrogen chloride in dioxan as for (+)-geodin gave back (±)-erdin, identified by m. p., mixed m. p., and rotation {$[\alpha]_D$ 0° (*c* 0·50)}.

Treatment of (±)-erdin with aqueous sulphuric acid as previously described [4] gave the known erdin hydrate, m. p. (from aqueous methanol) 218—219°, $\lambda_{max.}$ 217 and 317 mμ (ε 45,000 and 8000 respectively). The spectrum is comparable with that [$\lambda_{max.}$ 316 mμ (ε 6000)] recorded by Ungnade [9] for 2-carboxy-3-hydroxydiphenyl ether.

Action of Diazomethane on Geodin and Erdin.—(a) (+)-*Geodin*. Treatment with ethereal diazomethane [2] gave the known pyrazoline, m. p. 149—151° (decomp.), $[\alpha]_D$ −49° (*c* 1·00 in C_6H_6), −69° (*c* 0·65 in $CHCl_3$).

(b) (±)-*Geodin*. Similar treatment afforded the racemic pyrazoline, identical in m. p., mixed m. p., and infrared spectrum (in Nujol) with the derivative of (±)-erdin (see below).

(c) (±)-*Erdin*. Similar treatment furnished the known [2] racemic pyrazoline, m. p. 152—153° (decomp.), $[\alpha]_D$ 0° (*c* 1·10 in C_6H_6). The infrared spectra of the racemic and optically

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[9] Ungnade, *J. Org. Chem.*, 1951, **16**, 1318.

active pyrazolines were identical in $CHCl_3$ but differed significantly, especially in the "fingerprint" region, in Nujol. The ultraviolet absorption spectra were identical, showing $\lambda_{max.}$ 270 mμ (ε 18,000).

(+)-*Erdin.* Similar treatment gave the optically active pyrazoline, identical in m. p., mixed m. p., rotation {$[\alpha]_D$ −45° (*c* 0·70 in C_6H_6), −68° (*c* 0·51 in $CHCl_3$)}, and infrared spectrum (in Nujol) with the pyrazoline from (+)-geodin.

Pyrolysis of the Pyrazoline from (±)-*Erdin.*—The pyrazoline (50 mg.) was heated at 155—160° for 2 min. (copious gas evolution). Crystallization from ether afforded (±)-*homogeodin methyl ether*, prisms, m. p. 178—180°, $\lambda_{max.}$ 278 mμ (ε 19,200) (Found: C, 53·6; H, 4·1; *C*-Me, 4·05. $C_{18}H_{14}O_7Cl_2$ requires C, 53·4; H, 3·8; 1*C*-Me, 3·5%).

Dihydrogeodin and Dihydroerdin.—Dihydrogeodin, prepared according to Raistrick and Smith,[1] had m. p. 216—218°, $[\alpha]_D$ 0° (*c* 2·00), $\lambda_{max.}$ 279 mμ (ε 20,000), 320 mμ (ε 22,000 in 0·01N-NaOH), 295 mμ (ε 21,000 in 0·01N-potassium carbonate). Dihydroerdin, prepared similarly, had m. p. 230—232°, $\lambda_{max.}$ 285 mμ (ε 16,000), 320 mμ (ε 22,200 in 0·01N-NaOH).

Action of Alkali on Dihydroerdin.—Dihydroerdin (420 mg.) in N-sodium hydroxide (40 ml.) was heated on the steam-bath for 2 hr. under nitrogen. The solution was then saturated with carbon dioxide at 5° and the phenolic fraction removed by ether-extraction. Sublimation of the latter at 80°/1 mm. afforded 2 : 6-dichloro-orcinol (60—80 mg.), identified by m. p. and mixed m. p.

The acid fraction was separated into ether-soluble and water-soluble acids. After removal, by fractional crystallisation from ethanol, of some dihydroerdin, the former fraction gave 2 : 4-*dichloro*-1 : 6-*dihydroxy*-3-*methylxanthone*-8-*carboxylic acid*, bright yellow needles (from ethanol), m. p. 330—335°, $\lambda_{max.}$ 240, 274, 314, and 360 mμ (ε 38,000, 11,000, 17,000, and 6000 respectively) (Found: C, 50·35; H, 3·05; Cl, 19·4; OMe, 0. $C_{15}H_8O_6Cl_2$ requires C, 50·7; H, 2·3; Cl, 19·95, 0%). The infrared spectrum showed bands at 1690 (carbonyl), 1605 (hydrogen-bonded xanthone-carbonyl) and 1580 cm.$^{-1}$ (aromatic C=C). Treatment in methylene dichloride with diazomethane for 2 days gave the *methyl ester dimethyl ether.* From chloroform–methanol this formed yellow prisms, m. p. 230—232°, $\lambda_{max.}$ 243, 280 (shoulder), 305, and 340 mμ (ε 37,600, 11,400, 11,400, and 6300 respectively) (Found: C, 54·9; H, 3·75; OMe, 23·0. $C_{18}H_{14}O_6Cl_2$ requires C, 54·5; H, 3·35; 3OMe, 23·4%). The infrared spectrum showed bands at 1730 (methoxycarbonyl), 1660 (xanthone-carbonyl), and 1610 and 1585 cm.$^{-1}$ (aromatic C=C). The spectra of xanthone, measured at the same time, showed $\lambda_{max.}$ 243, 263, 288, and 333 mμ (ε 37,600, 18,000, 5000, and 6100) as well as infrared bands at 1660, 1610, and 1585 cm.$^{-1}$ (see above).

The water-soluble acid fraction was obtained from the aqueous phase (see above) by saturation with ammonium sulphate followed by continuous ether-extraction. Purification by sublimation (twice) at 160°/10^{-2} mm. gave 5-*hydroxy*-3-*methoxyphthalic anhydride* (50 mg.), m. p. 230° (Found: C, 56·1; H, 3·7; OMe, 15·5. $C_9H_6O_5$ requires C, 55·7; H, 3·1; OMe, 15·9%). The compound gave no colour with ferric chloride. Treatment with ethereal diazomethane followed by refluxing for 2 hr. in N-sodium hydroxide and sublimation of the resultant acid furnished 3 : 5-dimethoxyphthalic anhydride, m. p. and mixed m. p. 148—149° (sublimes at 130°) (with an authentic specimen of the same m. p. prepared according to Birkinshaw and Bracken's directions [10]).

3-*Hydroxy*-5-*methoxyphthalic Anhydride.*—5-Hydroxy-3-methoxybenzoic acid [11] was converted into the oily methyl ester by dissolution in methanol containing a trace of sulphuric acid. This oil (5·5 g.) in ether (50 ml.) was aded to a stirred suspension of zinc cyanide (7·5 g.) in ether (100 ml.) at 0—5° and the mixture saturated with dry hydrogen chloride. Decantation and dissolution of the residual aldimine hydrochloride in hot water (10 ml.) gave on ether-extraction the crude aldehyde. This was dried and treated with potassium hydroxide (5 g.) and water (1·0 ml.) at 190° for 30 min. (nickel crucible). Dissolution in water, acidification with dilute sulphuric acid, saturation with ammonium sulphate, and extraction into ether afforded 3-hydroxy-5-methoxyphthalic acid, m. p. (from ethyl acetate–light petroleum) 185—190° (decomp.), giving a red colour with ferric chloride. For this compound Nikuni [12] recorded m. p. 177—179°.

The acid was heated at 180—190° for 15 min. and the product then sublimed at

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[10] Birkinshaw and Bracken, *J.*, 1942, 308.

[11] Mauthner, *J. prakt. Chem.*, 1927, **116**, 315.

[12] Nikuni, *Bull. Agric. Chem. Soc. Japan*, 1942, **18**, 41; *Chem. Abs.*, 1951, **45**, 5140.

180°/10^{-4} mm., to furnish 3-*hydroxy*-5-*methoxyphthalic anhydride* as prisms, m. p. 232—234° (sublimes at 180° and upwards) (Found: C, 55·15; H, 3·5. $C_9H_6O_5$ requires C, 55·7; H, 3·1%). The compound gave no immediate colour with ferric chloride; it was depressed in m. p. by 15° on admixture with 5-hydroxy-3-methoxyphthalic anhydride (see above). Treatment with ethereal diazomethane followed by alkaline hydrolysis, etc., as in the cognate preparation above, gave 3 : 5-dimethoxyphthalic anhydride (m. p. and mixed m. p.).

Compound	Solvent system	Time after dissolution (in min.) with (in parentheses) $[\alpha]_D$°
(+)-Erdin	2% (w/w) HCl in dioxan	2 (+130), 25 (+82), 55 (+38), 175 (±0)
(+)-Geodin	2% (w/w) HCl in dioxan	2 (+103), 25 (+60), 55 (+28), 175 (±0)
	2% (w/w) HCl in dry MeOH	2 (±0)
	0·2% (w/w) HCl in dry MeOH	2 (+70), 10 (+50), 30 (+22), 105 (+1)
	0·2% (w/w) $CH_2Cl{\cdot}CO_2H$ in dry MeOH	2 (+119), 30 (+115), 24 × 60 (+100), 168 × 60 (+50), 240 × 60 (+25)
	Pyridine	2 (+120), 100 (+20), 190 (±0)
(+)-Geodin methyl ether	2% (w/w) HCl in dioxan	2 (+137), 140 (+137)
	2% (w/w) HCl in dry MeOH	2 (+80), 20 (+40), 40 (+10)
	0·2% (w/w) HCl in dry MeOH	2 (+100), 15 (+95), 35 (+80), 185 (+30)
	0·2% (w/w) $CH_2Cl{\cdot}CO_2H$ in dry MeOH	2 (+146), 60 (+146), 19 × 60 (+146), 67 × 60 (+146)
	Pyridine	2 (+173), 170 (+173), 960 (+173)
(+)-Geodin acetate	2% (w/w) HCl in dioxan	2 (+180), 55 (+177), 205 (+177)
(+)-Geodin pyrazoline derivative	Pyridine	2 (−55·5), 25 (−55·5), 180 (−55·5)

Racemisation Experiments.—The Table shows rates of loss of optical activity in the solvent systems indicated in all cases at 25° at a concentration of approximately 0·5 w/v %.

The products from the action of hydrogen chloride in dioxan on (+)-erdin and (+)-geodin have been described above. That (+)-geodin acetate and methyl ether were unaffected under these conditions was confirmed by recovery of the starting materials. The action of pyridine on (+)-geodin afforded, on dilution with water, an *adduct*. Recrystallised from chloroform–methanol this had m. p. (orange-yellow needles) 320°, $[\alpha]_D$ ±0°, $\lambda_{max.}$ 245 and 370 mμ (ε 40,000 and 21,400), infrared max. at 1726, 1625, 1612, 1585, and 1535 cm.$^{-1}$ (Found: C, 55·4; H, 4·4; N, 3·1; OMe, 12·6. $C_{22}H_{17}O_7Cl_2N$ requires C, 55·25; H, 3·6; N, 2·95; 2OMe, 13·0%). Treated under the same conditions (±)-erdin gave a comparable *adduct*, m. p. (yellow needles from pyridine) >330° (Found: C, 53·6; H, 3·2; N, 3·15. $C_{21}H_{15}O_7Cl_2N$ requires C, 54·3; H, 3·3; N, 3·0%). (+)-Geodin methyl ether and (+)-geodin pyrazoline were recovered unchanged from dissolution in pyridine.

The experiments in methanol were followed spectrophotometrically with the appropriate controls. In all experiments in this solvent where racemisation occurred, the initial $\lambda_{max.}$ at 284 mμ (ε *ca.* 19,000) was replaced by a peak of lower intensity at 317—319 mμ (ε 6000 to 9000 depending on the degree of completion of the reaction). The latter band corresponds to the diphenyl ether chromophore of erdin hydrate (see above). Treatment of (±)-erdin (25 mg.) with 2% methanolic hydrogen chloride as above afforded *erdin hydrate dimethyl ester methyl ether* (15 mg.) as prisms (from aqueous ethanol or methanol), m. p. 140—142°, $\lambda_{max.}$ 317 mμ (ε 9000), infrared max. (in Nujol) at 1708 and 1660 cm.$^{-1}$ (unbonded and hydrogen-bonded CO_2Me), insoluble in aqueous sodium hydrogen carbonate, soluble in aqueous sodium hydroxide, and giving a violet ferric colour very similar to that of methyl salicylate (Found: C, 51·25, 51·3; H, 3·90, 3·75; OMe, 27·9. $C_{19}H_{18}O_8Cl_2$ requires C, 51·25; H, 4·1; 4OMe, 27·9%). The same compound was obtained on treatment of (+)-geodin in the same way. This ester (6 mg.) with ethereal diazomethane, when worked up in the usual way, gave erdin hydrate dimethyl ester[4] dimethyl ether (3 mg.). From the ferric reaction mentioned above and the infrared indication of a hydrogen-bonded methoxycarbonyl group, this dimethyl ester dimethyl ether must have the phenolic hydroxyl in the dichloro-orcinol ring.

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