370. *The Chemistry of Fungi. Part XXXII.*[1] *Rosololactone, a Metabolite of* Trichothecium roseum *Link.*

By Adelaide Harris, Alexander Robertson, and W. B. Whalley.

Rosololactone, $C_{20}H_{30}O_3$, from the mycelium of *T. roseum* Link, is a diterpenoid γ-lactone containing a secondary hydroxyl group and a vinyl residue and on dehydrogenation yields 1 : 7-dimethylphenanthrene. Dehydration of dihydrorosololactone readily gives a dienoic acid, dihydrorosenic acid, which on hydrogenation is converted into tetrahydrorosenic acid. Lactonisation of this acid yields a mixture of *allo*- and *neo*-hydroxyrosanoic γ-lactone identical with the two γ-lactones from *iso*(?)ros-11 : 12-en-16-oic acid (Part XXXI [1]), thereby establishing a close structural affinity between rosolo- and rosenono-lactone.

In addition to the major constituent, rosenonolactone, the mycelium of *Trichothecium roseum* Link contains a minor metabolite which in Part VI [2] was designated rosonolactone. The present communication details an investigation on the chemistry and structure of this compound which has the formula, $C_{20}H_{30}O_3$. Since the metabolite, which appears

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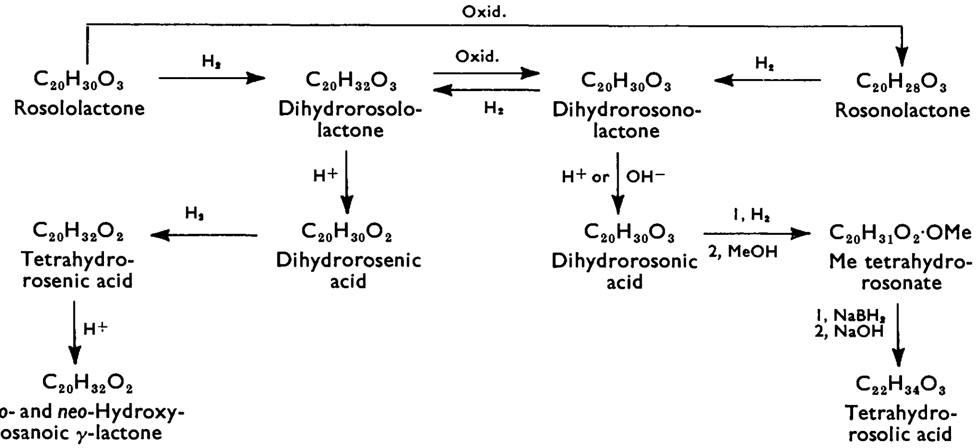
[1] Part XXXI, preceding paper.

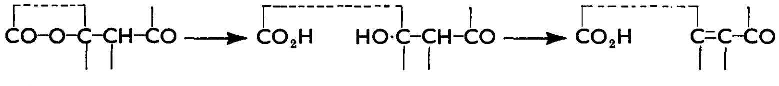
[2] Robertson, Smithies, and Tittensor, *J.*, 1949, 879.

to be a γ-lactone (infrared absorption at 1776 cm.$^{-1}$), has no ketonic or aldehydic group but contains an alcoholic hydroxyl group, which can be acetylated, the trivial name rosonolactone has been changed to rosololactone, and the term rosonolactone transferred to the ketone, $C_{20}H_{28}O_3$, formed by the chromic oxide oxidation of the parent hydroxy-lactone which is thus a secondary alcohol. Rosonolactone is isomeric with rosenonolactone. Like rosenonolactone,[1] rosololactone contains a vinyl residue since ozonolysis

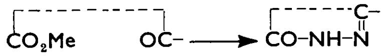


yields formaldehyde and carboxynor-rosololactone, $C_{19}H_{28}O_5$, and on hydrogenation gives the saturated dihydrorosololactone, $C_{20}H_{32}O_3$ (γ-lactone absorption at 1773 cm.$^{-1}$), which forms an acetate, $C_{22}H_{34}O_4$, and is oxidised to a keto-γ-lactone, dihydrorosonolactone, $C_{20}H_{30}O_3$ (infrared absorption at 1786 and 1730 cm.$^{-1}$), also obtained by hydrogenation of rosonolactone. Reduction of dihydrorosonolactone with potassium borohydride regenerates dihydrorosololactone (see chart). Dehydrogenation of rosololactone with selenium yields 1 : 7-dimethylphenanthrene, which, in conjunction with the fact that dihydrorosololactone is fully saturated, suggests that the lactone is a derivative of a tricyclic diterpene.

Whilst dihydrorosololactone is stable to 4N-aqueous sodium hydroxide its oxidation product dihydrorosonolactone is unstable to warm N-acid or -alkali, giving an unsaturated keto-acid, $C_{20}H_{30}O_3$, named dihydrorosonic acid. The ultraviolet absorption spectrum of dihydrorosonic acid ($\lambda_{\text{max.}}$ 248 mμ, log ε 4·0; $\lambda_{\text{max.}}$ 314 mμ, log ε 1·8) indicates that the compound is an αβ-unsaturated ketone whilst the ready formation of this acid (contrast the behaviour of rosenono- and dihydrorosenono-lactone [1]) provides strong evidence that the hydroxyl group, which is liberated by the hydrolysis of the lactone system in the precursor, is in the β-position to the carbonyl residue according to the scheme:

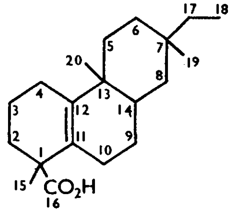

$$\mathrm{CO{-}O{-}C{-}CH{-}CO} \longrightarrow \mathrm{CO_2H \quad HO{\cdot}C{-}CH{-}CO} \longrightarrow \mathrm{CO_2H \quad C{=}C{-}CO}$$

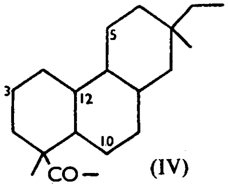
On dehydrogenation with sulphur or selenium, dihydrorosonic acid gave only 1 : 7-dimethylphenanthrene, indicating that skeletal changes do not occur in the transformations leading to this acid. Reduction of methyl dihydrorosonate with potassium borohydride furnished a γ-lactone (C) $C_{20}H_{30}O_2$ (infrared absorption at 1786 cm.$^{-1}$), derived from the precursor, methyl dihydrorosolate, by elimination of methanol. Hydrogenation of dihydrorosonic acid slowly gave the saturated keto-acid, tetrahydrorosonic acid, $C_{20}H_{32}O_3$ ($\lambda_{\text{max.}}$ 291 mμ, log ε 1·5), which yields an oxime, a 2 : 4-dinitrophenylhydrazone, a methyl ester, and a mercaptal with ethanedithiol. Attempts to form a hydrazone from methyl tetrahydrorosonate gave a non-acidic product, $C_{20}H_{32}ON_2$, devoid of a methoxyl group and having a molecule of methanol less than expected; the same compound was obtained by Wolff–Kishner reduction of tetrahydrorosonic acid; its formation indicates the presence of the system (I) which yields a five-, six-, or seven-membered ring (II) (cf., *e.g.*, marrubiin [3]).

(I)  (II)

Reduction with potassium borohydride of the keto-group in methyl tetrahydrorosonate gave the secondary alcohol, which, in contrast to the analogous product from methyl dihydrorosonate, did not readily lactonise.

When treated with naphthalene-2-sulphonic acid or boiling alcoholic hydrochloric acid, dihydrorosololactone gave a conjugated heteroannular dienoic acid, dihydrorosenic acid, $C_{20}H_{30}O_2$ ($\lambda_{max.}$ 238 mμ, log ε 4·15), which furnished 1 : 7-dimethylphenanthrene on dehydrogenation. Catalytic hydrogenation of this acid ceased after absorption of one mol., giving tetrahydrorosenic acid, $C_{20}H_{32}O_2$, which is probably a βγ-unsaturated acid since it readily undergoes decarboxylation at the melting point.

(III) 

 (IV)

Reduction of methyl dihydrorosenate with lithium aluminium hydride gave the primary alcohol, dihydrorosenol, $C_{20}H_{32}O$, which on dehydration followed by dehydrogenation furnished a complex mixture from which there was isolated a small quantity of 1 : 7-dimethylphenanthrene together with the anthracene derivative obtained on dehydrogenation of the corresponding derivative of rosenonolactone.[1]

On lactonisation with sulphuric acid at −5° tetrahydrorosenic acid gave the isomeric saturated *allo*- and *neo*-hydroxyrosanoic γ-lactones, $C_{20}H_{32}O_2$, formed by the lactonisation [1] of *iso*(?)rosenoic acid [probably (III)] derived from rosenonolactone. The identity of the two pairs of lactones serves to establish that the carboxyl groups of rosenono- and rosololactone occupy corresponding positions; in rosenonolactone and thus also in rosololactone this group is probably such that its carbon atom is number 16 (cf. III).

Further, from the relationship of *neo*- to *allo*-hydroxyrosanoic lactone together with the partial structure of rosenonolactone (preceding paper [1]), it is clear that dihydrorosololactone contains both a methyl and an ethyl group in the 7-position (see III). Because there is no reason to suspect that the conversion of either rosenono- or rosolo-lactone into *neo*- and *allo*-hydroxyrosanoic lactone is accompanied by inversion or migration at the 1- and 7-positions, the stereochemistry at $C_{(1)}$ and $C_{(7)}$ is identical in dihydrorosenono- and in dihydrorosolo-lactone and consequently dihydrorosolo-lactone may be represented by the partial formula (IV).

Now formation of the lactone (C) involves the secondary hydroxyl group formed by the reduction of the keto-group of the precursor, methyl dihydrorosonate. This hydroxyl group may occupy the position of the parent keto-group or, if an allylic shift intervenes, a β-position to it. In either case the γ-lactone must terminate at $C_{(3)}$, $C_{(10)}$, or $C_{(12)}$. The γ-lactone group in rosonolactone terminates on one of the same carbon atoms. Consequently, on the reasonable assumption that the potential hydroxyl group of the γ-lactone system in rosonolactone is in the β-position to the isolated keto group, the ketonic group of rosonolactone is situated at $C_{(3)}$ or $C_{(10)}$ and hence rosonolactone contains the system (V) or (VI), which is in accord with the formation of a cyclic derivative from

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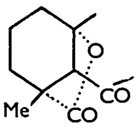
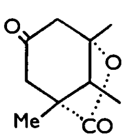
[3] Hardy, Rigby, and Moody, *J.*, 1957, 2955.

methyl tetrahydrorosonate and hydrazine. Further, the production of this derivative seems to exclude location of the ketonic residue at $C_{(5)}$.

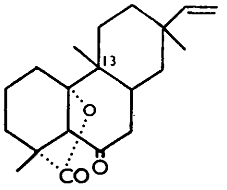
These considerations together with the transformations and degradations described may be rationalised in terms of the structure (VII) or (VIII) for rosonolactone, in which



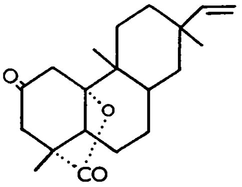
(V)



(VI)



(VII)



(VIII)

the *C*-methyl group is placed at $C_{(13)}$ by analogy with the associated rosenonolactone;[1] alternative equivalent structures cannot be excluded at present.

EXPERIMENTAL

Dehydrogenation of Rosololactone.—This lactone,[2] m. p. 186°, $[\alpha]_D^{18}$ +6·3° (*c* 2·3), log ε 2·25 at 210 mμ, from *Trichothecium roseum* Link [Found: C, 75·6, 75·5, 75·7, 75·2; H, 9·5, 9·4, 9·4, 9·4%; *M* (Rast), 324·6. Calc. for $C_{20}H_{30}O_3$: C, 75·4; H, 9·5%; *M*, 328], gave in boiling acetic anhydride–sodium acetate the *acetate* which separated from aqueous alcohol in needles, m. p. 167° (Found: C, 73·2; H, 8·9. $C_{22}H_{32}O_4$ requires C, 73·3; H, 9·0%).

The lactone (14 g.) was heated with powdered selenium (26 g.) at 320—330° for 36 hr., cooled, and extracted with ether. The extract was washed with 2N-aqueous sodium hydroxide, dried, and evaporated, leaving a residue which, on chromatography from light petroleum (b. p. 60—80°) on aluminium oxide followed by crystallisation from methanol, gave 1 : 7-dimethylphenanthrene in plates (5·8 g.), m. p. and mixed m. p. 85° (Found: C, 93·2; H, 7·1; *C*-Me, 9·3. Calc. for $C_{16}H_{14}$: C, 93·2; H, 6·8; 2*C*-Me, 14·6%). The picrate had m. p. and mixed m. p. 132° (Found: C, 60·8; H, 3·9; N, 9·7. Calc. for $C_{22}H_{17}O_7N_3$: C, 60·7; H, 3·9; N, 9·7%), and the trinitrobenzene complex had m. p. and mixed m. p. 160° (Found: C, 62·9; H, 4·3; N, 10·0. Calc. for $C_{22}H_{17}O_6N_3$: C, 63·0; H, 4·1; N, 10·0%). The alkaline extract of the crude product did not yield phenolic material.

Ozonolysis of Rosololactone.—The lactone (1 g.), in chloroform (100 ml.) at 0°, was oxidised with ozone and oxygen for 40 min. and after the removal of the solvent in a vacuum the residual syrup was decomposed with water (150 ml.). Decanted from the solid product next day, the aqueous liquors were distilled into aqueous 2 : 4-dinitrophenylhydrazine sulphate, and the resulting formaldehyde 2 : 4-dinitrophenylhydrazone (0·25 g.) purified from alcohol, forming yellow needles, m. p. and mixed m. p. 161° (Found: N, 26·4. Calc. for $C_7H_6O_4N_4$: N, 26·7%). A solution of the solid in ether was extracted with N-aqueous sodium hydrogen carbonate and evaporated, leaving an intractable neutral fraction (0·3 g.). Acidification of the bicarbonate extracts furnished *carboxynor-rosololactone* which separated from alcohol in needles (0·4 g.), m. p. 286° (decomp.) (Found: C, 67·7; H, 8·4%; equiv., 316. $C_{19}H_{28}O_5$ requires C, 67·8; H, 8·4%; equiv., 336).

Rosonolactone.—A solution of chromic oxide (0·8 g.) in acetic acid (20 ml.) was added dropwise to rosololactone (2 g.) in acetic acid (40 ml.) at 45—50° in 30 min. and the cooled mixture neutralised with 2N-aqueous sodium carbonate. The resulting gummy precipitate was purified from alcohol and then benzene–light petroleum (b. p. 60—80°), giving *rosonolactone* in prisms (1 g.), m. p. 126°, $\lambda_{max.}$ 291 mμ (log ε 1·5) in 2N-aqueous sodium carbonate or 2N-aqueous sodium hydroxide (Found: C, 75·7, 75·8; H, 8·8, 8·8. $C_{20}H_{28}O_3$ requires C, 75·9; H, 8·9%). When this compound (0·1 g.) was warmed with 5% aqueous sodium hydroxide (40 ml.) at 100° for 20 min., the resulting clear yellow solution did not deposit a solid on cooling and dilution with water, but on subsequent acidification gave a precipitate of *rosonic acid* which separated from alcohol or ethyl acetate–light petroleum (b. p. 60—80°) in needles (0·04 g.), m. p. 161°, readily soluble in 2N-aqueous sodium hydrogen carbonate, $[\alpha]_D^{18}$ −118° (*c* 0·3) (Found: C, 75·8; H, 8·9%; equiv., 318. $C_{20}H_{28}O_3$ requires C, 75·9; H, 8·9%; equiv., 316).

On ozonolysis in chloroform, rosonolactone (1 g.) gave formaldehyde (isolated as the 2 : 4-dinitrophenylhydrazone) and *carboxynor-rosonolactone* which separated from aqueous alcohol in needles (0·1 g.), m. p. 271° (decomp.) (Found: C, 68·2; H, 8·0. $C_{19}H_{26}O_5$ requires C, 68·2; H, 7·8%).

Dihydrorosololactone.—In alcohol (150 ml.) containing a catalyst (from 0·1 g. of palladium chloride and 0·35 g. of charcoal) rosololactone (1·4 g.) absorbed 97 ml. (*ca.* 1 mol.) of hydrogen in 20 min. Reaction then ceased and the resulting *dihydrorosololactone* was isolated and purified from methanol, forming needles (1·2 g.), m. p. 183°, $[\alpha]_D^{18}$ +20° (*c* 3), which sublime unchanged at 212°/0·15 mm. and give a negative tetranitromethane or perbenzoic acid reaction (Found: C, 74·8; H, 10·0; *C*-Me, 8·3. $C_{20}H_{32}O_3$ requires C, 75·0: H, 10·1%). The solution formed by boiling dihydrorosololactone (0·5 g.) with aqueous-alcoholic (50% v/v) 4N-sodium hydroxide for 3 hr. remained clear on dilution with water, and acidification gave only the unchanged lactone (0·4 g.), m. p. and mixed m. p. 183° after purification. Boiling acetic anhydride–sodium acetate (2 hr.) gave the *lactone acetate*, needles (from alcohol), m. p. 160° (Found: C, 72·9; H, 9·4. $C_{22}H_{34}O_4$ requires C, 72·9; H, 9·5%); deacetylation regenerated the parent compound.

Dihydrorosonolactone.—(*a*) Hydrogenation of rosonolactone (0·5 g.) in alcohol (75 ml.) with palladium–charcoal (1 mol. of hydrogen rapidly absorbed in 15 min.) gave *dihydrorosonolactone* which separated from methanol and then benzene–light petroleum (b. p. 60—80°) in needles (0·4 g.), m. p. 138° (Found: C, 75·3; H, 9·4. $C_{20}H_{30}O_3$ requires C, 75·4; H, 9·5%). The *oxime* formed needles, m. p. 222° (decomp.), from methanol (Found: C, 71·7; H, 9·3; N, 4·1. $C_{20}H_{31}O_3N$ requires C, 72·0; H, 9·4; N, 4·2%).

(*b*) Oxidation of dihydrorosololactone (1 g.) in acetic acid (20 ml.) with chromic oxide (0·4 g.) in acetic acid (10 ml.) at 40° gave dihydrorosonolactone (0·7 g.), forming needles, m. p. and mixed m. p. 138°, $\lambda_{max.}$ 295 mμ (log ε 1·4) (Found: C, 75·5; H, 9·5%). Reduction of dihydrorosonolactone (0·6 g.), dissolved in methanol (10 ml.), with a solution of potassium borohydride (0·3 g.) in water (2 ml. containing 1 drop of 2N-aqueous sodium hydroxide) added dropwise in 1 hr. regenerated dihydrorosololactone in needles (0·4 g.) which on purification from aqueous methanol had m. p. and mixed m. p. 183° and the requisite infrared absorption spectrum.

Dehydrogenation of dihydrorosonolactone (4 g.) with powdered selenium (8 g.) at 320—330° for 36 hr. gave 1 : 7-dimethylphenanthrene (1·6 g.), m. p. and mixed m. p. 85° after purification by chromatography and crystallisation from methanol; the picrate had m. p. and mixed m. p. 132°.

Dihydrorosonic Acid.—Formed by warming a mixture of dihydrorosonolactone (0·5 g.) and N-aqueous sodium hydroxide (15 ml.) on the steam-bath for 20 min., a yellow solution remained clear on dilution with water and on acidification gave a precipitate of *dihydrorosonic acid* which was purified from ethyl acetate–light petroleum (b. p. 60—80°) and then methanol, forming prisms (0·3 g.), m. p. 173°, $\lambda_{max.}$ 248 mμ (log ε 4·05), $\lambda_{max.}$ 314 mμ (log ε 1·83), $[\alpha]_D^{18}$ −148° (*c* 2), insoluble in water and readily soluble in cold N-aqueous sodium hydrogen carbonate (Found: C, 75·7; H, 9·47%; equiv., 316, 318. $C_{20}H_{30}O_3$ requires C, 75·4; H, 9·5%; equiv., 318). This acid is inert to the usual carbonyl reagents.

The acid was also formed when a solution of dihydrorosonolactone (1 g.) in alcohol (10 ml.) and 2N-sulphuric acid (10 ml.) was boiled for ½ hr.; the cooled mixture deposited the acid (0·6 g.), m. p. and mixed m. p. 173° (from methanol). On esterification with methyl sulphate–potassium carbonate in boiling acetone (20 ml.) for 6 hr. the acid (0·5 g.) furnished *methyl dihydrorosonate*, b. p. 166°/0·3 mm. (Found: C, 75·8; H, 9·6. $C_{21}H_{32}O_3$ requires C, 75·9; H, 9·7%). Reduction of the ester (1 g.), in methanol (20 ml.), with potassium borohydride (0·45 g.) in water (3 ml., containing 2 drops of N-aqueous sodium hydroxide), added dropwise in 2 hr., gave *γ-lactone* (C) which separated from aqueous methanol in needles (0·4 g.), m. p. 130°, infrared spectrum band at 1786 cm.$^{-1}$ (in CCl_4) (Found: C, 79·4; H, 9·9; OMe, 0. $C_{20}H_{30}O_2$ requires C, 79·4; H, 10·0%). This lactone was insoluble in cold 2N-aqueous sodium hydroxide but dissolved when heated under reflux for 1 hr. with N-alcoholic sodium hydroxide. The solution remained clear on dilution with water but addition of excess of 2N-hydrochloric acid precipitated the parent lactone.

Dehydrogenation of dihydrorosonic acid (3·0 g.) with selenium (6·0 g.) by the method employed for dihydrorosololactone gave 1 : 7-dimethylphenanthrene (1·4 g.), m. p. and mixed m. p. 85°, forming the picrate m. p. and mixed m. p. 132°; a phenolic fraction was not obtained.

Tetrahydrorosonic Acid.—On hydrogenation in methanol (80 ml.) with a catalyst (from 0·08 g. of palladium chloride and 0·3 g. of charcoal) dihydrorosonic acid (0·5 g.) slowly absorbed hydrogen (40 ml.) for 6 hr. Purification of the product from methanol gave *tetrahydrorosonic acid* in needles (0·4 g.), m. p. 217°, $[\alpha]_D^{18}$ −11·5 (*c* 1·5) (Found: C, 74·8; H, 10·0%; equiv., 315. $C_{20}H_{32}O_3$ requires C, 75·0; H, 10·1%; equiv., 320). This compound, which is insoluble in water, readily dissolves in N-aqueous sodium hydrogen carbonate and has a negative tetranitromethane reaction in chloroform. The 2 : 4-*dinitrophenylhydrazone* separated from benzene–light petroleum (b. p. 60—80°) in yellow needles, m. p. 259° (Found: C, 62·3; H, 7·5; N, 11·2. $C_{26}H_{36}O_6N_4$ requires C, 62·4; H, 7·2; N, 11·2%), and the *oxime* from aqueous methanol in needles, m. p. 208° (decomp.) (Found: C, 71·5; H, 9·9; N, 4·1. $C_{20}H_{33}O_3N$ requires C, 71·6; H, 9·9; N, 4·2%). Formed quantitatively by the methyl sulphate–potassium carbonate method in 6 hr., *methyl tetrahydrorosonate* separated from light petroleum (b. p. 40—60°) in prisms, m. p. 86° (Found: C, 75·5; H, 10·4; OMe, 9·6. $C_{20}H_{31}O_2{\cdot}OMe$ requires C, 75·4; H, 10·3; OMe, 9·3%), and gave an *oxime* which crystallised from aqueous methanol in needles, m. p. 148° (Found: C, 72·1; H, 10·0; N, 4·0. $C_{21}H_{35}O_3N$ requires C, 72·2; H, 10·1; N, 4·0%).

A mixture of methyl tetrahydrorosonate (0·5 g.), alcohol (5 ml.), and 95% hydrazine hydrate (1·5 ml.) was heated under reflux for 4 hr., cooled, and diluted with water. Purified from aqueous methanol, the precipitate furnished a *substance* in plates (0·25 g.), m. p. 174° (Found: C, 76·2; H, 10·4; N, 9·2; OMe, 0. $C_{20}H_{32}ON_2$ requires C, 75·9; H, 10·2; N, 8·9%). The same product (0·1 g.), m. p. and mixed m. p. 174°, was obtained when a mixture of tetrahydrorosonic acid (1 g.), diethylene glycol (20 ml.), sodium (0·6 g.), and 100% hydrazine hydrate (4 ml.) was heated under reflux at 100° for 1 hr. and then at 200° for 6 hr.

Condensation of methyl tetrahydrorosonate (1 g.) with ethanedithiol (1·5 ml.) was effected by hydrogen chloride at 0° in 1 hr.; 6 hr. later the product was precipitated with methanol and purified from benzene, giving the *mercaptal* in plates (0·93 g.), m. p. 191° (Found: C, 67·3; H, 9·1; OMe, 8·1. $C_{23}H_{38}O_2S_2$ requires C, 67·3; H, 9·3; OMe, 7·6%).

Methyl Tetrahydrorosolate.—Reduction of methyl tetrahydrorosonate (0·5 g.) in methanol (5 ml.) was effected with potassium borohydride (0·25 g.) in water (2 ml., containing 2 drops of N-aqueous sodium hydroxide) in 2 hr., and from aqueous methanol the resulting *methyl tetrahydrorosolate* formed needles (0·23 g.), m. p. 157° (Found: C, 74·8; H, 10·8; OMe, 9·4. $C_{20}H_{33}O_2{\cdot}OMe$ requires C, 75·0; H, 10·8; OMe, 9·2%). Prepared with boiling acetic anhydride for 2 hr., the *acetate* formed needles (from aqueous methanol), m. p. 144° (Found: C, 73·1; H, 10·1; OMe, 8·2. $C_{22}H_{35}O_3{\cdot}OMe$ requires C, 73·0; H, 10·1; OMe, 8·2%).

Dihydrorosenic Acid.—(*a*) A mixture of dihydrorosololactone (1 g.) and naphthalene-2-sulphonic acid (0·03 g.) (dried over concentrated sulphuric acid) was heated at 3 mm., first with a small flame to initiate effervescence and then on the steam-bath until the mixture became solid (*ca.* 45 min.). An ethereal solution of the product was washed with N-aqueous sodium hydrogen carbonate, and the washings were acidified, giving *dihydrorosenic acid* which separated from light petroleum (b. p. 60—80°) in needles (0·68 g.), m. p. 147°, $[\alpha]_D^{22}$ +205° (*c* 0·1), having an intense orange tetranitromethane reaction in chloroform (Found: C, 79·6; H, 9·7%; equiv., 30·4. $C_{20}H_{30}O_2$ requires C, 79·4; H, 10·0%; equiv., 302).

(*b*) A solution of dihydrorosololactone (0·75 g.) in N-alcoholic hydrochloric acid (75 ml.) was boiled for 2 hr., cooled, diluted with water (50 ml.), basified, and extracted with ether. This extract gave only a small amount of an intractable gum. The residual aqueous liquor was then acidified and extracted with ether, and on evaporation the dried extract left a residue (0·5 g.) which on purification from methanol followed by light petroleum (b. p. 60—80°) furnished dihydrorosenic acid in needles (0·12 g.), m. p. and mixed m. p. 147°. Prepared with diazomethane, *methyl dihydrorosenate* separated from methanol in prisms, m. p. 70° (Found: C, 79·5; H, 9·8; OMe, 9·6. $C_{20}H_{29}O{\cdot}OMe$ requires C, 79·7; H, 10·2; OMe, 9·8%).

Dehydrogenation of dihydrorosenic acid (3 g.) with selenium (6 g.) as previously described gave 1 : 7-dimethylphenanthrene (1·06 g.), m. p. and mixed m. p. 85° (picrate, m. p. and mixed m. p. 135°); a phenolic fraction was not obtained.

Tetrahydrorosenic Acid.—Hydrogenation of dihydrorosenic acid (1 g.) in methanol (40 ml.) with a catalyst (from 0·25 g. of palladium chloride and 0·25 g. of charcoal) was complete in 1 hr. (1 mol. absorbed). The resulting *tetrahydrorosenic acid* separated from aqueous methanol in needles, m. p. 151°, $[\alpha]_D^{26}$ −15° (*c* 0·8), having a yellow tetranitromethane reaction in chloroform (Found: C, 79·0; H, 10·4. $C_{20}H_{32}O_2$ requires C, 78·9; H, 10·6%).

Tetrahydrorosenic acid (25 mg.) was heated in a sealed tube at 250° for 1½ hr., the product isolated with ether, and the extract washed with N-aqueous sodium hydrogen carbonate, and distilled, to yield a *product* (15 mg.) as a neutral oil, devoid of hydroxyl or carbonyl absorption in the infrared region (Found: C, 87·0; H, 12·4. $C_{19}H_{32}$ requires C, 87·6; H, 12·4%).

Dihydrorosenol.—Reduction of methyl dihydrorosenate (2 g.) in ether (80 ml.) with lithium aluminium hydride (0·6 g.) for 48 hr. gave *dihydrorosenol* (1·4 g.), b. p. 160°/0·5 mm., with an orange tetranitromethane reaction in chloroform, $[\alpha]_D^{22}$ +97° (*c* 0·4), $\lambda_{max.}$ 239 mμ (log ε 4·15) (Found: C, 84·2; H, 11·2; OMe, 0. $C_{20}H_{32}O$ requires C, 83·3; H, 11·2%). Oxidation of this alcohol (1 g.) in benzene (12 ml.) and *tert.*-butyl alcohol (4 ml.), containing chromic oxide (1 g.), occurred in 8 days. The yellow neutral product furnished *dihydrorosenal semicarbazone* which separated from methanol in needles (0·3 g.), m. p. 218° (Found: C, 73·4; H, 9·5; N, 12·4. $C_{21}H_{33}ON_3$ requires C, 73·4; H, 9·7; N, 12·2%).

Dehydration of Dihydrorosenol.—When dihydrorosenol (2 g.) and naphthalene-2-sulphonic acid (0·02 g.) were gradually heated at 0·1 mm. dehydration occurred and an oil distilled at 160°. A solution of the distillate in ether was washed with N-aqueous sodium hydroxide, and water, dried, and distilled, giving a *product* (1 g.), b. p. 152—154°/0·1 mm., $[\alpha]_D^{24}$ −24° (*c* 1·2) (Found: C, 88·7; H, 11·1. $C_{20}H_{30}$ requires C, 88·8; H, 11·2%). Dehydrogenated with powdered selenium (12 g.) at 330—335° for 48 hr., this hydrocarbon (6 g.) gave a product which on purification by chromatography from light petroleum (b. p. 60—80°) on aluminium oxide was obtained as an oil. A solution of this oil in the minimum quantity of alcohol slowly deposited a solid (24 mg.) which on crystallisation from benzene–light petroleum (b. p. 60—80°) gave the anthracene derivative, m. p. and mixed m. p. 240°, described in Part XXXI [1] having the same infrared absorption spectrum.

After the isolation of the crude anthracene derivative the residual methanolic solution was evaporated, leaving an oil (1·2 g.) whose ultraviolet absorption was of the phenanthrene type. After distillation in a vacuum this gave 1 : 7-dimethylphenanthrene picrate which after repeated crystallisation had m. p. and mixed m. p. 128° (85 mg.) and the requisite infrared absorption.

allo- *and* neo-*Hydroxyrosanoic Lactone.*—A solution of tetrahydrorosenic acid (0·28 g.) in sulphuric acid (4 ml.) at −10° was stirred during 45 min., then poured on ice and extracted with ether, and the ethereal solution was washed with N-aqueous sodium hydroxide. There was no acidic fraction. Purification of the neutral fraction from methanol gave *allo*hydroxyrosanoic lactone in prisms (0·1 g.), m. p. 138°, $[\alpha]_D^{20}$ +28·9° (*c* 1 in EtOH) identical with *allo*hydroxyrosanoic lactone prepared from *iso*(?)ros-11 : 12-en-16-oic acid (preceeding paper) and having the requisite infrared spectrum.

Concentration of the methanolic mother-liquors from the purification of *allo*hydroxyrosanoic lactone furnished a more soluble neutral product, neo*hydroxyrosanoic lactone*, which separated from aqueous methanol in needles (30 mg.), m. p. 123°, $[\alpha]_D^{24}$ −19° (*c* 3·5 in EtOH), having an infrared spectrum identical with that of the second lactone derived from *iso*(?)ros-11 : 12-en-16-oic acid (Found: C, 79·3; H, 10·6. $C_{20}H_{32}O_2$ requires C, 78·9; H, 10·6%).

The ultraviolet absorption spectra were determined in 95% EtOH with a Unicam S.P. 500 Spectrophotometer; the infrared spectral data were obtained for CCl_4 solutions with a Perkin-Elmer Model 21 Spectrophotometer. [α] refer to $CHCl_3$ solutions unless otherwise stated. The analyses were performed by Mr. A. S. Inglis, M.Sc., and his associates of this Department.

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