38. *The* Euphorbia *Resins. Part X.* The Structural Difference between Euphol and Tirucallol.*

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Tirucalla-8 : 24-diene has been oxidised to 7 : 11-dioxotirucall-8-enoic acid and the methyl ester subjected to the Grignard reaction with phenylmagnesium bromide. The resulting tertiary alcohol has been dehydrated and treated with *N*-bromosuccinimide, to give 24 : 24-diphenyltrisnortirucalla-8 : 20(22) : 23-triene-7 : 11-dione (V), identical with the corresponding derivative from eupha-8 : 24-diene. Further, compound (V) has been oxidised and then reduced to hexanortirucallane-7 : 11 : 20-trione (XIV) which is almost certainly identical with hexanoreuphane-7 : 11 : 20-trione of Christen, Jeger, and Ruzicka. Thus euphol is 20-*iso*tirucallol (II).

The Barbier–Wieland degradation of the side-chain of euphol (II) is reported and observations on the re-introduction of the 8 : 9-double bond by *N*-bromosuccinimide and by chromic acid are made.

The structure of euphol was put forward by Barton, McGhie, Pradhan, and Knight[1] and by Jeger and his co-workers.[2] The molecular formula of tirucallol was advanced by Arigoni, Jeger, and Ruzicka[3] as well as by Barbour, Lourens, and ourselves[4] from different evidence. These two triterpenes differed in configuration at $C_{(20)}$, and the orientation at $C_{(17)}$ remained controversial.

Jeger, Ruzicka, and their co-workers[5] have recently demonstrated the α-configuration of the side-chain of tirucallol (I; R′ = OH) by showing that the orientation at $C_{(17)}$ is opposite to that of lanosterol, the stereochemistry of which was rigidly established by Woodward, Patchett, Barton, Ives, and Kelly.[6] Further, Wolff–Kishner reduction of 3β-acetoxytirucall-8-en-21-one (III; R′ = OAc) which gave tirucallenol[3] has now been shown to give also euphenol,[5] the formation of which is attributed to inversion at $C_{(20)}$ only, so that euphol would be (II; R′ = OH). We have now eliminated the asymmetry at $C_{(20)}$ of corresponding derivatives from both tirucallol (I; R′ = OH) and euphol and

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* Part IX, *J.*, 1955, 2194.

[1] Barton, McGhie, Pradhan, and Knight, *Chem. and Ind.*, 1954, 1325; *J.*, 1955, 876.

[2] Arigoni, Viterbo, Dunnenberger, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1954, **37**, 2306.

[3] Arigoni, Jeger, and Ruzicka, *ibid.*, 1955, **38**, 222.

[4] Barbour, Lourens, Warren, and Watling, *Chem. and Ind.*, 1955, **226**; *J.*, 1955, 2194.

[5] Menard, Wyler, Hiestand, Arigoni, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1955, **38**, 1517.

[6] Woodward, Patchett, Barton, Ives, and Kelly, *J. Amer. Chem. Soc.*, 1954, **76**, 2852.

obtained identical products. Euphol, which was first isolated by Newbold and Spring[7] and has been recently reviewed by Jones and Halsall,[8] is completely defined as 20-*iso*-tirucallol (II; R′ = OH).

Tirucallol (tirucalla-8 : 24-dien-3-ol) was oxidised to tirucalladienone, characterised as its 2 : 4-dinitrophenylhydrazone, and then reduced to tirucalladiene. This diene was oxidised with chromic acid to 7 : 11-dioxotrisnortirucall-8-enoic acid (IV; R′ = H). The methyl ester (IV; R′ = Me) was reduced with zinc dust and acetic acid to methyl dioxotrisnortirucallanoate (VIII) which with phenylmagnesium bromide gave 24-hydroxy-24 : 24-diphenyltrisnortirucallane-7 : 11-dione (IX). This hydroxy-compound was readily dehydrated in boiling benzene containing a little iodine to the 23-ene (X) which with *N*-bromosuccinimide followed by boiling pyridine gave 24 : 24-diphenyltrisnortirucalla-8 : 20(22) : 23-triene-7 : 11-dione (V), m. p. 216—217°, $[\alpha]_D$ +21·6°, $\lambda_{max.}$ 301 mμ (log ε 4·61) [shoulder at λ 275 mμ (log ε 4·52)], with a strong band at 1671 cm.$^{-1}$ characteristic of the 1 : 4-diketo-ene system. Further, compound (V) was readily reduced with zinc dust and acetic acid to 24 : 24-diphenyltrisnortirucalla-20(22) : 23-diene-7 : 11-dione (XI), m. p. 199—200°, $[\alpha]_D$ −137°.

A similar series of reactions on eupha-8 : 24-diene reported by Christen, Jeger, and Ruzicka[9] confirms the physical properties of all the products. The action of *N*-bromosuccinimide on 24 : 24-diphenyltrisnoreuph-23-ene-7 : 11-dione and dehydration of the product gave the yellow compound, m. p. 214—216°, $[\alpha]_D$ +21·6°, which, however, is 24 : 24-diphenyltrisnoreupha-8 : 20(22) : 23-triene-7 : 11-dione (V) and not the diene (XI) as previously reported.[9] By using two equivalents of *N*-bromosuccinimide higher yields were obtained and the difficult separation was avoided. This trisnoreuphatriene (V) showed ultraviolet and infrared absorption characteristic of the diketone structure and its infrared spectrum was identical with that of the trisnortirucallatriene (V) with which it showed no melting-point depression.

Oxidation of 24 : 24-diphenyltrisnortirucalla-8 : 20(22) : 23-triene-7 : 11-dione (V) with chromic acid gave hexanortirucall-8-ene-7 : 11 : 20-triene (VII) as yellow needles, m. p. 189—190° which was reduced to the corresponding hexanortirucallanetrione (XIV), m. p. 223—225°, $[\alpha]_D$ −244°. This compound (XIV) is almost certainly identical with hexanoreuphanetrione, m. p. 223—225°, $[\alpha]_D$ −232°, of Christen, Jeger, and Ruzicka,[9] and was further characterised as its 2 : 4-dinitrophenylhydrazone. Compound (XIV) could not, however, have been obtained directly from pure 24 : 24-diphenyltrisnoreupha-8 : 20(22) : 23-triene-7 : 11-dione (V), which is now the structure assigned to the starting material; and it is probable that these authors oxidised the mixture of diene and triene or omitted to record the reduction stage.

The action of *N*-bromosuccinimide in re-introducing the 8 : 9-double bond was repeated on 7 : 11-dioxoeuphanyl acetate[10] to give 7 : 11-dioxoeuph-8-enyl acetate.[11]

Before this reaction with *N*-bromosuccinimide was fully appreciated, and in view of the difficulties associated with the isolation of the large quantities of tirucallol necessary for the separation of the butadiene (XII), a study was made of the Barbier–Wieland stepwise degradation of the side-chain of euphol. 24 : 24-Diphenyltrisnoreuph-23-ene-7 : 11-dione (X) was oxidised with chromic acid to 7 : 11-dioxotetranoreuph-8-enoic acid (VI; R′ = H), and the methyl ester (VI; R′ = Me) reduced to methyl 7 : 11-dioxotetranoreuphanoate (XII; R′ = Me). The Grignard reaction with phenylmagnesium bromide on compound (XII; R′ = Me), dehydration of the product, and then oxidation with chromic acid gave a yellow oily acid, which on reduction with zinc dust and acetic acid yielded 7 : 11-dioxopentanoreuphanoic acid (XIII; R′ = H) characterised further

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[7] Newbold and Spring, *J.*, 1944, 249.

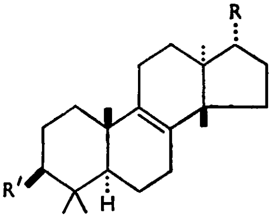
[8] Jones and Halsall, *Fortshr. Chem. org. Naturstoffe*, 1955, **12**, 101; see also ref. 1.

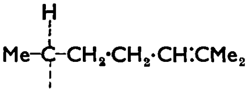
[9] Christen, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1951, **34**, 1675.

[10] Christen, Dunnenberger, Roth, Heussen, and Jeger, *ibid.*, 1952, **35**, 1771.

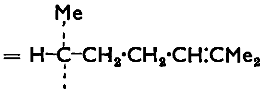
[11] Haines and Warren, *J.*, 1950, 1563.

as its methyl ester. Oxidation of 24 : 24-diphenyltrisnortirucall-23-ene-7 : 11-dione (X) also gave only an oily acid; but reduction of the acid resulted in crystalline 7 : 11-dioxo-tetranortirucallanoic acid (XII; R′ = H), isolated also as its methyl ester.

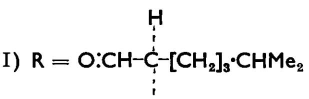


(I) R =  (Tirucallol)

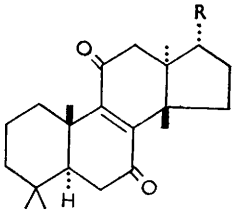
$\mathrm{Me{-}\overset{H}{\underset{\vdots}{C}}{-}CH_2{\cdot}CH_2{\cdot}CH{:}CMe_2}$

(II) R =  (Euphol)

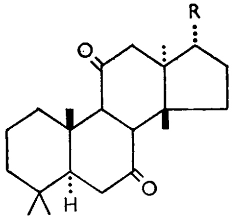
$\mathrm{H{-}\overset{Me}{\underset{\vdots}{C}}{-}CH_2{\cdot}CH_2{\cdot}CH{:}CMe_2}$

(III) R = 

$\mathrm{O{:}CH{-}\overset{H}{\underset{\vdots}{C}}{-}[CH_2]_3{\cdot}CHMe_2}$



(IV) R = $-\mathrm{CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2R'}$
(V) R = $-\mathrm{CMe{:}CH{\cdot}CH{:}CPh_2}$
(VI) R = $-\mathrm{CHMe{\cdot}CH_2{\cdot}CO_2R'}$
(VII) R = $-\mathrm{COMe}$



(VIII) R = $-\mathrm{CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Me}$
(IX) R = $-\mathrm{CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}CPh_2{\cdot}OH}$
(X) R = $-\mathrm{CHMe{\cdot}CH_2{\cdot}CH{:}CPh_2}$
(XI) R = $-\mathrm{CMe{:}CH{\cdot}CH{:}CPh_2}$
(XII) R = $-\mathrm{CHMe{\cdot}CH_2{\cdot}CO_2R'}$
(XIII) R = $-\mathrm{CHMe{\cdot}CO_2R'}$
(XIV) R = $-\mathrm{COMe}$

It is to be noted that the chromic acid oxidation of the diphenylethylenes from tirucallol and euphol to corresponding acids is accompanied by partial restoration of the 8 : 9-double bond, and the resulting mixture was difficult to separate. Reduction of the mixture with zinc dust and acetic acid immediately gave crystalline acids. The dehydrogenation of euphane-7 : 11-diones with *N*-bromosuccinimide and with chromic acid parallels the dehydrogenation by selenium dioxide and by aerial oxidation accelerated by alkaline conditions reported by Barton and McGhie and their co-workers.[12,1] These are other examples of the difference between euphane-7 : 11-dione and lanostane-7 : 11-dione series which have rings B/C *cis*- and *trans*-fused respectively.

EXPERIMENTAL

Rotations are for $CHCl_3$ solutions. Ultraviolet data were determined by Marjorie E. von Klemperer, and infrared spectra by Mr. A. J. Rossouw. Microanalyses were by Yvonne Merchant, analytical samples being dried at 100°/0·1 mm. for 6 hr. unless otherwise stated.

Tirucalla-8 : 24-*dien*-3-*one*.—Tirucall-8-en-3-ol (3·2 g.), benzene (200 ml.), chromic acid

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[12] Knight and McGhie, *Chem. and Ind.*, 1953, 920; 1954, 24.

(4 g.), water (40 ml.), and acetic acid (100 ml.) were stirred for 36 hr. at room temperature. The neutral fraction (3·2 g.) in light petroleum was chromatographed over alumina (70 g.; Grade I); the resulting colourless oil, dissolved in hot methanol, deposited an oil on cooling. The mother-liquors gave after 48 hr. *tirucalla*-8 : 24-*dien*-3-*one* as laminæ, m. p. 62°, $[\alpha]_D^{20}$ +13·7° (Found: C, 84·8; H, 11·5. $C_{30}H_{48}O$ requires C, 84·8; H, 11·4%). The 2 : 4-*dinitrophenylhydrazone* crystallised from methanol–chloroform (6 : 1) as orange laminæ, m. p. 175—176° (Found: C, 71·5; H, 8·9. $C_{36}H_{52}O_4N_4$ requires C, 71·5; H, 8·7%).

Tirucalla-8 : 24-*diene*.—Tirucalladienone (2·4 g.), absolute alcohol (100 ml.), and 50% hydrazine hydrate (2 ml.) were refluxed for 1 hr. Diethylene glycol (100 ml.) and potassium hydroxide (2 g.) were added, and the solution was concentrated under reflux until the temperature reached 200° and then refluxed for 4 hr. The product in light petroleum was chromatographed over alumina (50 g.; Grade I) to yield a colourless oil (2 g.). The sample was sublimed to give fine needles of *tirucalla*-8 : 24-*diene*, m. p. 54°, $[\alpha]_D^{24}$ −21° (Found: C, 88·3; H, 12·5. $C_{30}H_{50}$ requires C, 87·7; H, 12·3%).

7 : 11-*Dioxotrisnortirucall*-8-*enoic Acid* (IV).—Tirucalladiene (2 g.), chloroform (3 ml.), acetic acid (100 ml.), chromium trioxide (4 g.), and water (5 ml.) were kept at 50—60° for 4 hr. and set aside at room temperature overnight. The solution was worked up in the usual way. The solid acid fraction (1·8 g.), crystallised three times from methanol, gave 7 : 11-*dioxotrisnortirucall*-8-*enoic acid* as yellow needles, m. p. 268—270°, $[\alpha]_D^{19}$ −16°. A sample was dried at 76° for 6 hr. for analysis (Found: C, 75·9; H, 9·75. $C_{27}H_{40}O_4$ requires C, 75·7; H, 9·4%) Action of diazomethane on the acid and recrystallisation three times from methanol gave the *methyl ester* as yellow needles, m. p. 171—172°, $[\alpha]_D^{19}$ −16·5° (Found: C, 76·0; H, 9·7. $C_{28}H_{42}O_4$ requires C, 76·0; H, 9·6%).

Methyl 7 : 11-*Dioxotrisnortirucallanoate* (VIII).—Methyl dioxotrisnortirucallenoate (2 g.), glacial acetic acid (100 ml.), and zinc dust (3 g.) were refluxed for 1 hr. The solid product was recrystallised from methanol–chloroform (10 : 1), to give *methyl dioxotrisnortirucallanoate* as needles, m. p. 258—260°, $[\alpha]_D^{19}$ −176° (Found: C, 75·3; H, 10·2. $C_{28}H_{44}O_4$ requires C, 75·6; H, 10·0%).

24-*Hydroxy*-24 : 24-*diphenyltrisnortirucallane*-7 : 11-*dione* (IX).—Methyl dioxotrisnortirucallanoate (3·2 g.) in benzene (50 ml.) and the Grignard reagent, prepared from magnesium (3·8 g.), dry ether (100 ml.), bromobenzene (25 g.), and benzene (100 ml.), were refluxed for 4 hr. The complex was treated with 2N-sulphuric acid and extracted with ether, to yield a gum which solidified on lixiviation with methanol which dissolved the diphenyl. Three crystallisations from acetone gave 24-*hydroxy*-24 : 24-*diphenyltrisnortirucallane*-7 : 11-*dione* as needles, m. p. 210—212°, $[\alpha]_D^{20}$ −113° (Found: C, 82·3; H, 9·4. $C_{39}H_{52}O_3$ requires C, 82·35; H, 9·2%).

24 : 24-*Diphenyltrisnortirucall*-23-*ene*-7 : 11-*dione* (X).—The hydroxy-compound, iodine (100 mg.), and benzene (100 ml.) were refluxed for 1 hr. The product, crystallised three times from methanol–chloroform (6 : 1), gave 24 : 24-*diphenyltrisnortirucall*-23-*ene*-7 : 11-*dione* as laminæ, m. p. 196—197°, $[\alpha]_D^{19}$ −163° (Found: C, 85·0; H, 9·5. $C_{39}H_{50}O_2$ requires C, 85·0; H, 9·2%).

24 : 24-*Diphenyltrisnortirucall*-8 : 20(22) : 23-*triene*-7 : 11-*dione* (V).—Diphenyltrisnortirucallenedione (3·0 g.), dry carbon tetrachloride (100 ml.), and 85% *N*-bromosuccinimide (2·5 g.) were refluxed with slow distillation for 20 min. in a quartz flask in bright sunlight. Copious evolution of hydrogen bromide started after 5 min. and ceased after 20 min. The solution, filtered and evaporated under reduced pressure, gave an oil which was heated with pyridine at 100° for 1 hr. The product in ether was washed with acid, the solvent evaporated, and the residue crystallised twice from acetone, to give 24 : 24-*diphenyltrisnortirucalla*-8 : 20(22) : 23-*triene*-7 : 11-*dione* (1·3 g.) as stout yellow needles, m. p. 216—217°, $[\alpha]_D^{20}$ +21·6°, $\lambda_{max.}$ 301 mμ (log ε 4·61) with a shoulder at 275 mμ (log ε 4·52), showing absorption at 1671 cm.$^{-1}$ (Found: C, 86·0; H, 8·45. $C_{39}H_{46}O_2$ requires C, 85·7; H, 8·5%).

24 : 24-*Diphenyltrisnortirucalla*-20(22) : 23-*diene*-7 : 11-*dione* (XI).—The above triene (200 mg.), glacial acetic acid (40 ml.), and zinc dust (0·4 g.) were refluxed for 30 min. The product, crystallised five times from methanol, gave 24 : 24-*diphenyltrisnortirucalla*-20(22) : 23-*diene*-7 : 11-*dione* as silky needles, m. p. 199—200°, $[\alpha]_D^{20}$ −137°, $\lambda_{max.}$ 305 mμ (log ε 4·36), $\nu_{max.}$ 1700 cm.$^{-1}$ (Found: C, 85·4; H, 9·1. $C_{39}H_{48}O_2$ requires C, 85·35; H, 8·8%).

7 : 11-*Dioxotetranortirucallanoic Acid* (XII; R′ = H).—Diphenyltrisnortirucallenedione (2 g.) in carbon tetrachloride (20 ml.) was added to chromium trioxide (3 g.), water (3 ml.), and acetic acid (190 ml.) at 0°, and the temperature allowed to rise to 40° at which it was maintained

for 4 hr. The oily product was reduced with zinc dust and boiling acetic acid. The solid product, crystallised three times from methanol, gave 7 : 11-*dioxotetranortirucallanoic acid* as fine needles, m. p. 212—214°, $[\alpha]_D^{22}$ $-157°$ (Found: C, 74·5; H, 10·0. $C_{26}H_{40}O_4$ requires C, 75·0; H, 9·7%). Esterification with methanol and dry hydrogen chloride and crystallisation four times from methanol gave the *methyl ester* as fine needles, m. p. 216—217°, $[\alpha]_D^{22}$ $-169°$ (Found: C, 75·5; H, 9·9. $C_{27}H_{42}O_4$ requires C, 75·3; H, 9·8%).

24 : 24-*Diphenyltrisnoreupha*-8 : 20(22) : 23-*triene*-7 : 11-*dione* (V).—This was prepared from 24 : 24-diphenyltrisnoreuph-23-ene-7 : 11-dione [9] (3 g.) and 90% *N*-bromosuccinimide (1·2 g.) as described for the tirucallatriene derivative. The oil was chromatographed in light petroleum–benzene (3 : 1) over alumina (60 g.) to give an oil (2 g.) which was rechromatographed. The first 300 ml. eluted a yellow gum (0·7 g.) and the next 500 ml. gave a yellow oil (1·1 g.) which, crystallised three times from methanol, gave 24 : 24-*diphenyltrisnoreupha*-8 : 20(22) : 23-*triene*-7 : 11-*dione* as yellow needles, m. p. 214—216°, $[\alpha]_D^{22}$ $+21·6°$ (Found: C, 85·8; H, 8·8. $C_{39}H_{46}O_2$ requires C, 85·7; H, 8·5%). Christen *et al.*[9] give m. p. 212—213°, $[\alpha]_D$ $+20°$, for (XI).

7 : 11-*Dioxotetranoreuph*-8-*enoic Acid* (VI).—Diphenyltrisnoreuphenedione (8 g.) in carbon tetrachloride (30 ml.) was treated with chromium trioxide (8 ml.) in acetic acid (270 ml.) and water (3 ml.) at 0° and set aside at 20° overnight. The acid product was an oil (5 g.) which, crystallised three times from methanol, gave 7 : 11-*dioxotetranoreuph*-8-*enoic acid* as yellow needles, m. p. 230—232°, $[\alpha]_D^{20}$ $+10°$ (Found: C, 74·8; H, 9·3. $C_{26}H_{38}O_4$ requires C, 75·3; H, 9·2%). Esterification with methanol and hydrogen chloride and four crystallisations from methanol gave the *methyl ester* as yellow needles, m. p. 140—142°, $[\alpha]_D^{22}$ $+9·5°$ (Found, after drying at 76°/0·1 mm.: C, 75·8; H, 9·6. $C_{27}H_{40}O_4$ requires C, 75·7; H, 9·4%).

Methyl 7 : 11-*Dioxotetranoreuphanoate* (XII; R′ = Me).—The above ester was reduced with zinc dust and acetic acid. The solid product, crystallised three times from methanol, gave *methyl* 7 : 11-*dioxotetranoreuphanoate* as needles, m. p. 217—218°, $[\alpha]_D^{20}$ $-164°$ (Found: C, 75·25; H, 10·0. $C_{27}H_{42}O_4$ requires C, 75·3; H, 9·8%).

7 : 11-*Dioxopentanoreuphanoic Acid* (XIII; R′ = H).—Methyl dioxotetranoreuphanoate (10 g.) was treated with phenylmagnesium bromide as described above and refluxed for 8 hr. The brown oily product was refluxed with glacial acetic acid for 1 hr. and steam-distilled to remove diphenyl. The residual oil in light petroleum–benzene (3 : 1) was chromatographed over alumina (200 g.). The eluant (1·5 l.) gave an oil (6 g.) which failed to crystallise and was oxidised with chromium trioxide as described above. The acid fraction failed to crystallise and was reduced with zinc dust and acetic acid. The solid product in benzene was chromatographed over alumina (30 g.; Grade II) and crystallised three times from methanol, to give 7 : 11-*dioxopentanoreuphanoic acid* as needles, m. p. 234—236°, $[\alpha]_D^{20}$ $-144°$ (Found: C, 74·8; H, 9·7. $C_{25}H_{38}O_4$ requires C, 74·6; H, 9·5%). Esterified with diazomethane, chromatographed in light petroleum over alumina (grade II), and crystallised three times from methanol, this gave the *methyl ester* as needles, m. p. 196—197°, $[\alpha]_D^{20}$ $-103°$ (Found, after drying at 120°/0·1 mm.: C, 75·0; H, 9·8. $C_{26}H_{40}O_4$ requires C, 75·0; H, 9·7%).

Hexanortirucall-8-*ene*-7 : 11 : 20-*trione* (VII).—Diphenyltrisnortirucallatrienedione (1·3 g.) in carbon tetrachloride (20 ml.) was treated at 0° with chromium trioxide (2·5 g.), water (5 ml.), and acetic acid (150 ml.). The solution was set aside at 40° for 4 hr. The neutral oil (1·2 g.) in benzene was steam-distilled. The residual solid, crystallised three times from methanol, gave *hexanortirucall*-8-*ene*-7 : 11 : 20-*trione* as yellow needles, m. p. 189—190°, $[\alpha]_D^{17}$ $-34°$ (Found: C, 78·1; H, 9·6. $C_{24}H_{34}O_3$ requires C, 77·8; H, 9·25%).

Hexanortirucallane-7 : 11 : 20-*trione* (XIV).—Reduction of hexanortirucallenetrione with zinc dust and acetic acid and four crystallisations of the product from methanol and one from acetone gave hexanortirucallane-7 : 11 : 20-trione as needles, m. p. 223—225°, $[\alpha]_D^{22}$ $-244°$ (Found: C, 77·6; H, 10·05. Calc. for $C_{24}H_{36}O_3$: C, 77·4; H, 9·7%). The 2 : 4-*dinitrophenylhydrazone* crystallised from methanol–chloroform in orange needles, m. p. 251—253° (Found: C, 65·2; H, 7·35. $C_{30}H_{40}O_6N_4$ requires C, 65·2; H, 7·3%).

Dioxoeuphanyl Acetate.—Christen *et al.*[10] give m. p. 156—157°, $[\alpha]_D$ $-132°$. Prepared by the same method the dioxoeuphanyl acetate crystallised from methanol in plates, $[\alpha]_D^{22}$ $-127°$ (*c* 0·7) (Found: C, 77·0; H, 10·4. Calc. for $C_{32}H_{52}O_4$: C, 76·8; H, 10·4%). In a capillary tube these melted on rapid heating at 131—132°, whilst with slow heating there was partial melting at 132° and flowing at 157°. Slow heating on Kofler stage between crossed Nicol prisms showed m. p. 130—132° with immediate solidification to birefringent crystals, m. p. 144—152°.

N-Bromosuccinimide and 7 : 11-*Dioxoeuphanyl Acetate.*—Dioxoeuphanyl acetate[10] (3·2 g.), m. p. 131°, was treated with *N*-bromosuccinimide (1·2 g.) and then with pyridine as above. The product was chromatographed over alumina with light petroleum and crystallised from methanol, to give 7 : 11-dioxoeuph-8-enyl acetate, m. p. 112°, undepressed on admixture with an authentic specimen.[11]

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