The Euphorbia Resins. Part IX. Corresponding Isomerisations in Tirucallol and Euphorbol.*

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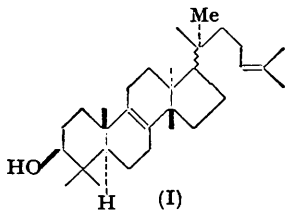
Tirucallenyl and euphorbenyl acetates are isomerised to *iso*tirucallenyl and *iso*euphorbenyl acetate respectively. These *iso*-compounds form epoxides which give dehydro*iso*-compounds. Acid isomerisation of euphorbadienyl acetate results in the movement of both double bonds to give *iso*euphorbadienyl acetate.

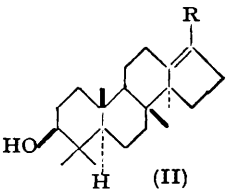
The ultraviolet extinction curves and molecular rotation differences of these compounds are compared with those reported for similar compounds from euphol.

Consideration of the data in the light of the new structure for euphol proposed by Barton, McGhie, Pradhan, and Knight (*Chem. and Ind.*, 1954, 1325; *J.*, 1955, 876) and by Arigoni, Viterbo, Dunnenberger, Jeger, and Ruzicka (*Helv. Chim. Acta*, 1954, **37**, 2306) and the identity of tirucallol and noreuphorbenol with *epi*elemenol permits complete structures for tirucallol, euphorbol, and the elemi acids to be advanced.

BARTON, MCGHIE, PRADHAN, AND KNIGHT (*Chem. and Ind.*, 1954, 1325) who have kindly sent us a copy of their full communication (*J.*, 1955, 876) have advanced convincing evidence for the complete structures of euphol and *iso*euphol. Arigoni, Viterbo, Dunnenberger, Jeger, and Ruzicka (*Helv. Chim. Acta*, 1954, **37**, 2306) have put forward similar structures and demonstrated that the configuration at $C_{(20)}$ is the same as in lanosterol. In addition, on the basis of a " concerted " reaction in the isomerisation of euphol to *iso*euphol they favour an α-orientation at $C_{(17)}$ for the side chain, which, however, Barton, McGhie, and their co-workers (*loc. cit.*) contend is yet unproved. The overall evidence, therefore, permits structures for euphol (I) and *iso*euphenol (II; R = $-CHMe\cdot[CH_2]_3\cdot CHMe_2$) whilst (III; R = C_8H_{17}) represents the diene prepared by Dunnenberger, Roth, Heusser, and Jeger (*Helv. Chim. Acta*, 1952, **35**, 1765) from *iso*euphenyl acetate. The configuration at $C_{(20)}$ is preserved throughout.



(I)



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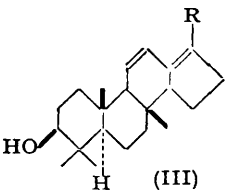


(III)

Arigoni, Wyler, and Jeger (*ibid.*, 1954, **37**, 1553) have corrected the formula of euphorbol to $C_{31}H_{52}O$ and identified noreuphorbenol and tirucallenol with *epi*elemenol, which has the side chain $-CHMe\cdot[CH_2]_3\cdot CHMe_2$ and is obtained from *epi*elemadienolic acid having the side chain $-CH(CO_2)\cdot[CH_2]_2\cdot CH{:}CMe_2$.

The structure of ring A for tirucallol, which follows from the experiments on ring A of the elemi acids (Halsall, Meakins, and Swayne, *J.*, 1953, 4141), is in agreement with our findings. Tirucallenol and euphorbenol with phosphorus pentachloride undergo a retropinacoline change to give *neo*tirucalladiene and *neo*euphorbadiene respectively. These *neo*-compounds with osmic acid give the corresponding glycols which with lead tetraacetate give acetone and trisnorketones. Trisnortirucallenone resisted all attempts at crystallisation and was isolated as its 2 : 4-dinitrophenylhydrazone, m. p. 196—197°, which is different from the corresponding derivative, m. p. 143°, from euphol. The retropinacoline change in ring A results in a *cis*-indane configuration so that the difference between euphol and tirucallol, which give different trisnorketones, cannot be attributed

* Part VIII, *J.*, 1951, 2540.

solely, if at all, to a difference in A–B ring fusion. In fact euphol and euphorbol show identical bands in the infrared for their hydroxyl and acetoxyl groups, namely, at 1022 and a single maximum at 1237 cm.$^{-1}$ respectively (Cole, *J.*, 1952, 4969). In addition the small positive molecular-rotation increase on acetylation and oxidation of euphorbol and tirucallol is consistent with an equatorial configuration on an A-type terminal ring (Klyne, *J.*, 1952, 2916; cf. also Barton and Jones, *J.*, 1944, 659; Gascoigne, Robertson, and Sims, *J.*, 1953, 1833).

A difference between the lanosterol group and the euphol group has been revealed by Dawson, Halsall, and Swayne (*J.*, 1953, 590) in the molecular rotations of the 7 : 9(11)-dienes. This difference is further exemplified by the change in the molecular rotation on the formation of 7 : 11-dioxo-compounds as shown in Table 1.

TABLE 1. *Molecular rotation differences for the* 7 : 11-*dioxo-compounds.*

	A	B	C	B − A	C − A
Lanostenyl acetate	+275° [2]	+382° [1]	+275° [6]	+107°	0°
Euphenyl acetate	+165 [5]	+100 [3]	−660 [6]	− 65	−825
Tirucallenyl acetate	− 54 [3]	− 85 [7]	−656 [7]	− 31	−602
Euphorbenyl acetate	0 [5]	−200 [7]	−758 [4]	−200	−758

Column headings: A, $[M]_D$ for enyl acetate. B, $[M]_D$ for 7 : 11-dioxo-enyl acetate. C, $[M]_D$ for 7 : 11-dioxo-anyl acetate. [1] Voser, Montavon, Gunthard, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1950, **33**, 1893. [2] Ruzicka, Denss, and Jeger, *ibid.*, 1945, **28**, 759. [3] Christen, Dunnenberger, Roth, Heusser, and Jeger, *ibid.*, 1952, **35**, 1756. [4] Vogel, Jeger, and Ruzicka, *ibid.*, p. 519. [5] Newbold and Spring, *J.*, 1944, 249. [6] Dorée, McGhie, and Kurzer, *J.*, 1949, 570. [7] Haines and Warren, *J.*, 1950, 1562. [8] *Idem*, *J.*, 1949, 2554.

Additional evidence for the stereochemistry of euphol proposed by Barton, McGhie, *et al.* (*loc. cit.*) is afforded by the large decrease in the molecular rotation on the introduction of a keto-group into ring C of euphol. This indicates that ring C is of D-type (Klyne,

TABLE 2. *Rotational differences for the introduction of* 11-*keto-groups.*

	A	B	C	B − A	C − A
Lanostenyl acetate	+275°	+651° [1]	+307° [1]	+376°	+ 32°
Euphenyl acetate	+165	+139 [2]	−248 [2]	− 26	−413

Column headings: A is $[M]_D$ for the enyl acetate, *B* is $[M]_D$ for 11-oxo-Δ^8-enyl acetate, and C is $[M]_D$ for 11-oxo-anyl acetate. [1] McGhie, Pradhan, and Cavalla, *J.*, 1952, 3176. [2] Knight and McGhie, *Chem. and Ind.*, 1953, 920.

loc. cit.) which means that the 13-methyl group is α-orientated. This large decrease is also seen in the formation of the 7 : 11-dioxoeuphanyl acetate. The similar effect of the keto-groups in the molecular-rotation differences within the euphol group is indicative of a similar ring conformation.

Similarity in the rings B and C of euphol, euphorbol, and tirucallol has also been further substantiated. Dioxotirucallenyl acetate has been oxidised with selenium dioxide to trioxotirucalladienyl acetate (cf. Barbour, Bennett, and Warren, *J.*, 1951, 2540).

The evidence advanced by Barton, McGhie, *et al.* (*loc. cit.*) for the stereochemistry at $C_{(13)}$ and $C_{(14)}$ in euphol is equally applicable to tirucallol and euphorbol. The isomerisation of euphol to *iso*euphol, which finds its exact parallel in tirucallol and euphorbol, is attributed to the " conformational driving force " due to the unfavourable configuration of the C–D ring fusion. Further these workers have pointed out that the postulated stereochemistry for euphol permits an explanation of the abnormal hydrogenation of dioxoeuphenyl acetate previously reported (Barbour and Warren, *Chem. and Ind.*, 1952, 295; Knight and McGhie, *ibid.*, 1953, 920; 1954, 24). Dioxoeuphorbenyl acetate (Barbour and Warren, *loc. cit.*) and methyl acetoxy*iso*elemenadionolate (Ruzicka, Rey, Spillman, and Baumgartner, *Helv. Chim. Acta*, 1943, **26**, 1659) was also hydrogenated abnormally to αβ-unsaturated ketones.

Halsall *et al.* (*loc. cit.*) report that elemenic acid was not isomerised by chloroformic hydrogen chloride which had been used successfully by Dawson, Halsall, and Swayne (*loc. cit.*) to convert euphol into *iso*euphol. It is significant that we have found that tirucallenyl and euphorbenyl acetate are readily isomerised by sulphuric acid to *iso*tirucallenyl and *iso*euphorbenyl acetate respectively, in which the infrared spectra indicate a

tetrasubstituted double bond. The intensity values for the low-wavelength ultraviolet extinction of *iso*euphorbenyl acetate (λ 220, ε 2800; λ 223; ε 2400) and *iso*euphorbadienyl acetate (λ 220, ε 2500; λ 223, ε 1400) are consistent with a tetrasubstituted double bond exocyclic to one ring (cf. Bladon, Henbest, and Wood, *J.*, 1952, 2741) as was found by Dawson *et al.* (*loc. cit.*) for *iso*euphenyl acetate.

These *iso*-compounds gave epoxides which with sulphuric acid yielded conjugated dienes; and the ultraviolet extinction curve of dehydro*iso*euphorbenyl acetate showed maximal absorption at 247, 254, and 264 mμ (log ε 4·3, 4·33, and 4·24 respectively). This absorption is identical with that found by Dunnenberger *et al.* (*loc. cit.*) for the diene from *iso*euphenyl acetate (247, 255, and 265 mμ, log ε 4·26, 4·32, and 4·12 respectively).

The methylene group in euphorbol is assumed by Arigoni *et al.* (*loc. cit.*) to be at position 24 on biogenetic grounds. We have now established the correctness of this assumption. Isomerisation of euphorbadienyl acetate gave *iso*euphorbadienyl acetate having no strong infrared bands characteristic of a methylene link. Ozonisation of *iso*euphorbadienyl acetate gave acetone in agreement with the isomerisation $-C(:CH_2)\cdot CHMe_2 \longrightarrow -CMe:CMe_2$.

TABLE 3. *Molecular-rotation differences for the* iso*-compounds.*

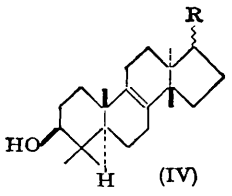
	Euphol	Tirucallol	Euphorbol
$[M]_D$ ene acetate	+193° [1]	− 79° [1]	0° [2]
$[M]_D$ *iso*ene acetate	− 47 [3]	+ 44 [4]	+ 10 [4]
$[M]_D$ dehydro*iso*ene acetate	+ 84 [3]	+267 [4]	+178 [4]
$[M]_D$ *iso*ene minus $[M_D]$ ene	−240	+123	+ 10
$[M]_D$ dehydro*iso*ene minus $[M]_D$ ene	−107	+346	+178
$[M]_D$ dehydro*iso*ene minus $[M]_D$ *iso*ene	+131	+223	+168

[1] Haines and Warren, *J.*, 1949, 2554. [2] Newbold and Spring, *J.*, 1944, 249. [3] Dawson, Halsall, and Swayne, *J.*, 1953, 590. [4] This paper.

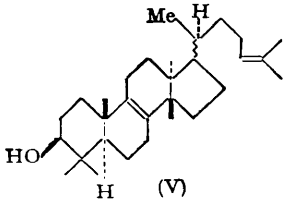
The molecular-rotation differences of derivatives of euphol, tirucallol, and euphorbol are shown in Table 3. The conversion of the *iso*enes of these three compounds into the corresponding dehydro*iso*enes results in a positive change in rotation of the same order. This is in agreement with the conclusions above that the *iso*-compounds have similar tetrasubstituted double bonds and that the dehydro*iso*-compounds have similar chromophores. The isomerisation of tirucallenyl and euphorbenyl acetate into their *iso*-compounds, however, results in a positive change in rotation whilst the formation of *iso*euphenyl acetate produces a negative change. The inert double bond in all three compounds has been placed at position 8 : 9 from the ready formation of the dioxo-enes (Haines and Warren, *J.*, 1950, 1562; Barbour, Warren, and Wood, *J.*, 1951, 2537), so that one difference between tirucallol and euphorbol on the one hand, and euphol on the other, involves the geometry of the groupings associated with the conversion of the ene into the *iso*ene.

Consideration of the above permits the partial structures put forward by Arigoni *et al.* (*loc. cit.*) to be elaborated on the basis of the formula for euphol (I).

Tiruculladienol	IV	R = $-CHMe\cdot[CH_2]_3\cdot CH:CMe_2$
Euphorbadienol	IV	R = $-CHMe\cdot[CH_2]_3\cdot C(:CH_2)\cdot CHMe_2$
*epi*Elemadienolic acid	IV	R = $-CH(CO_2H)\cdot[CH_2]_3\cdot CH:CMe_2$
*iso*Tirucallenol	II	R = $-CHMe\cdot[CH_2]_3\cdot CHMe_2$
Dehydro*iso*tirucallenol	III	
*iso*Euphorbenol	II	R = $-CHMe\cdot[CH_2]_3\cdot CHMe\cdot CHMe_2$
Dehydro*iso*euphorbenol	III	
*iso*Euphorbadienol	II	R = $-CHMe\cdot[CH_2]_3\cdot CMe:CMe_2$



(IV)



(V)

The group R in tirucallol and euphorbol is envisaged as having a configuration at $C_{(17)}$ opposite to that in euphol (I), this difference

being lost on isomerisation. *iso*Euphenol (II) and *iso*tirucallenol (II) would then differ in configuration at $C_{(20)}$. Tirucallol is accordingly (V) and is 17-*iso* : 20-*iso*euphol. It also follows that euphorbol has this same configuration at $C_{(20)}$ as in (IV). [Since this paper was presented, Arigoni, Jeger, and Ruzicka (*Helv. Chim. Acta*, 1955, **38**, 222) have advanced irrefutable evidence for the identity of the ring systems, and the difference in configuration at $C_{(20)}$, of euphol and tirucallol. Since they again favour an α-orientation of the side-chain in both these triterpenes they consider tirucallol as 20-*iso*euphol.]

The degradation of the side chain of the elemi acids was effected by Arnold, Koller, and Jeger (*Helv. Chim. Acta*, 1951, **34**, 555) and Mazur, Koller, Jeger, and Ruzicka (*ibid.*, 1952, **35**, 181) by the reactions

$$R{\cdot}CH(CO_2H){\cdot}[CH_2]_3{\cdot}CHMe_2 \longrightarrow R{\cdot}CH(CO{\cdot}N_3){\cdot}[CH_2]_3{\cdot}CHMe_2 \longrightarrow$$
$$R{\cdot}CH(NH_2){\cdot}[CH_2]_3{\cdot}CHMe_2 \longrightarrow R{\cdot}CH(NH{\cdot}CS{\cdot}NH{\cdot}C_6H_5){\cdot}[CH_2]_3{\cdot}CHMe_2 \longrightarrow$$
$$R{\cdot}CH{:}CH{\cdot}[CH_2]_2{\cdot}CHMe_2$$

The thermal elimination of the phenylthiourea gave only one product. Halsall *et al.* (*loc. cit.*) have attributed this to attachment of the side chain to the remainder of the molecule at a tertiary carbon. The formula now advanced for thee lemi acids is consistent with the non-formation of a 17 : 20-ethylenic linkage. The thermal elimination of phenylthiourea will involve a vicinal *cis*-hydrogen atom and it is unlikely that the amino-group will be able to assume a position favourable for the elimination with the 17-hydrogen atom owing to the proximity of the 13- or 14-methyl group (cf. Fieser and Fieser, *Experientia*, 1948, **4**, 286), according to the orientation at $C_{(17)}$.

Experimental.

Microanalyses are by Yvonne Merchant, ultraviolet data are by Margorie von Klemperer, and infrared data by Dr. E. C. Leisegang and A. J. Rossouw. [α] refer to chloroform solutions.

Trioxotirucalladienyl Acetate.—Dioxotirucallenyl acetate (600 mg., 1 mol.), acetic acid–acetic anhydride (1 : 1; 25 ml.), and saturated aqueous selenium dioxide (600 mg., 4·5 mols.) were refluxed for 4 hr. The ether extract, worked up in the usual way, gave a crystalline solid (600 mg.), which, dissolved in light petroleum (200 ml.), was filtered through a column of alumina (activity II; 20 g.). Light petroleum–benzene (2 : 1) eluted a yellow solid (390 mg.) which when crystallised four times from methanol gave *trioxotirucalladienyl acetate* as deep yellow plates, m. p. 183—184°, $\lambda_{max.}$ 285 mμ (log ε 3·95), infrared bands at 1659 s, 1683 s, 1709 sh., 1749, s, broad, $cm.^{-1}$. After sublimation at 150° in a high vacuum, the sample, m. p. 184—186°, was analysed (Found : C, 75·1; H, 8·9 $C_{32}H_{46}O_5$ requires C, 75·25; H, 9·1%).

neo*Euphorbadiene.*—Euphorbenol (1 g.) in light petroleum (300 ml.) was treated with phosphorus pentachloride (1 g.) at room temperature for 4 hr. whilst dry nitrogen was bubbled through the solution. The clear solution, diluted with light petroleum, washed with sodium carbonate solution, and dried (Na_2SO_4), gave a yellow solid (1 g.). A solution of this solid in light petroleum was chromatographed over alumina (activity II; 30 g.). Light petroleum eluted a colourless solid which, crystallised twice from acetone–methanol (1 : 3) and finally from acetone, gave neo*euphorbadiene* (500 mg.) as needles, m. p. 98·5—99°, $[\alpha]_D^{23}$ +15° (*c*, 1) (Found : C, 87·4; H, 12·3. $C_{31}H_{52}$ requires C, 87·7; H, 12·3%).

neo*Tirucalladiene.*—Tirucallenol (2·0 g.) was treated with phosphorus pentachloride as described above. The product, crystallised from acetone, gave neo*tirucalladiene* as needles, m. p. 107·5—108°, $[\alpha]_D^{17}$ +16·6° (*c*, 1) (Found : C, 87·8; H, 21·1. $C_{30}H_{50}$ requires C, 87·7; H, 12·3%). When nitrogen was not passed during the reaction a chlorine-containing compound was also obtained and the yield was smaller.

neo*Euphorbenediol.*—*neo*Euphorbadiene (500 mg.) in anhydrous ether (70 ml.) was treated with osmium tetroxide (350 mg.), and the dark liquid set aside for 6 days. The product was worked up in the usual way (cf. Dorée, McGhie, and Kurzer, *J.*, 1949, 167). The benzene extract was chromatographed over alumina with light petroleum–benzene (1 : 1) to give a solid which crystallised twice from acetone–water to give neo*euphorbenediol* (300 mg.) as needles, m. p. 122—123° (Found : C, 80·8; H, 11·9. $C_{31}H_{54}O_2$ requires C, 81·1; H, 11·9%).

Oxidation of neo*Euphorbenediol,*—The diol (100 mg.), chloroform (0·5 ml.), glacial acetic acid (5 ml.), and lead tetra-acetate (0·2 g.) were set aside at room temperature overnight. The

product was treated with water and distilled. The distillate afforded acetone 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 124—126°.

Formation and Oxidation of neo*Tirucallenediol.*—*neo*Tirucalladiene (1·0 g., 1 mol.) was treated with osmium tetroxide as described above, to give a very small quantity of *neo*tirucallenediol, m. p. 117—118°, which was not further purified. This was treated with lead tetra-acetate (1 mol.) as above. Water was added and a small quantity distilled into an aqueous perchloric acid solution of 2 : 4-dinitrophenylhydrazine (Neuber, Grauer, and Pisha, *Analyt. Chim. Acta*, 1952, **7**, 238) to give yellow crystals, m. p. 124°, undepressed when mixed with acetone 2 : 4-dinitrophenylhydrazone. The residue was treated with Girard's reagent P. The ketone fraction, having infrared bands at 1670 sh. and 1745 s cm.$^{-1}$, failed to crystallise and was treated with 2 : 4-dinitrophenylhydrazine. The product, crystallised from a large volume of methanol or light petroleum, gave *trisnor*neo*tirucallenone* 2 : 4-*dinitrophenylhydrazone* in needles, m. p. 196—197° (Found : C, 70·6; H, 8·9; N, 9·9. $C_{33}H_{48}O_4N_4$ requires C, 70·2; H, 8·6; N, 9·9%).

iso*Tirucallenyl Acetate.*—Tirucallenyl acetate (2 g.) in glacial acetic acid (50 ml.) was treated with 2N-sulphuric acid (2 ml.) and refluxed for 5 hr., during which the colourless solution changed through orange to a deep purple. The product in light petroleum was chromatographed over alumina to give an oil which, crystallised three times from methanol, gave iso*tirucallenyl acetate* as laminæ, m. p. 95—96°, $[\alpha]_D^{17}$ +9·3° (*c*, 1) (Found : C, 81·7; H, 11·3. $C_{32}H_{54}O_2$ requires C, 81·6; H, 11·6%). It gave a yellow colour with tetranitromethane.

iso*Euphorbenyl Acetate.*—Euphorbenyl acetate (1·1 g.) was isomerised with dilute sulphuric acid as above. The product, crystallised from methanol, gave iso*euphorbenyl acetate*, m. p. 108—110°, $[\alpha]_D^{20}$ +2° (*c*, 1) (Found : C, 81·5; H, 11·6. $C_{33}H_{56}O_2$ requires C, 81·75; H, 11·6%).

*Epoxy*iso*tirucallanyl Acetate.*—*iso*Tirucallenyl acetate (700 mg.) with perbenzoic acid (250 mg., 1·25 mols.) in chloroform was set aside at 0°. After 29 hr. 0·91 mol. of oxygen had been absorbed and the product, worked up after 2 days, gave *epoxy*iso*tirucallanyl acetate* as a colourless gum, $[\alpha]_D^{20}$ +21·1° (*c*, 1) (Found : C, 78·8; H, 11·2. $C_{32}H_{54}O_3$ requires C, 78·9; H, 11·2%). This failed to crystallise even after chromatography and gave no colour with tetranitromethane.

*Epoxy*iso*euphorbanyl Acetate.*—*iso*Euphorbenyl acetate (0·5 g.) with perbenzoic acid in chloroform was set aside for 8 days. The product in light petroleum, filtered through alumina (grade I) and crystallised twice from methanol, gave *epoxy*iso*euphorbanyl acetate*, m. p. 60—61°, $[\alpha]_D^{20}$ −13° (*c*, 1) (Found : C, 79·3; H, 11·1. $C_{33}H_{56}O_3$ requires C, 79·1; H, 11·3%).

*Dehydro*iso*tirucallenyl Acetate.*—Epoxy*iso*tirucallanyl acetate (400 mg.) in acetic acid (58 ml.) was treated with concentrated sulphuric acid (six drops) and heated for 2 hr. on a water-bath. The product, crystallised four times from methanol, gave *dehydro*iso*tirucallenyl acetate* as rhombohedra, m. p. 85°, $[\alpha]_D^{21}$ +57° (*c*, 1), $\lambda_{max.}$ 250 mμ (log ε 3·80 in EtOH) (Found : C, 82·1; H, 11·2. $C_{32}H_{52}O_2$ requires C, 82·0; H, 11·2%).

*Dehydro*iso*euphorbenyl Acetate*—Epoxy*iso*euphorbanyl acetate (200 mg.), glacial acetic acid (20 c.c.), and concentrated sulphuric acid (3 drops) were set aside overnight at room temperature. The product in light petroleum was chromatographed over alumina. The first fraction gave a waxy solid which, crystallised from methanol, gave *dehydro*iso*euphorbenyl acetate* as laminæ, m. p. 106·5—107°, $[\alpha]_D^{22}$ +37° (*c*, 1) (Found : C, 82·2; H, 11·3. $C_{33}H_{54}O_2$ requires C, 82·1; H, 11·3%). The crystals showed in alcohol absorption max. at 247, 254, 264 mμ (log ε 4·3, 4·33, 4·24 respectively) and were coloured dark brown with tetranitromethane.

iso*Euphorbadienyl Acetate.*—Euphorbadienyl acetate (1 g.), glacial acetic acid, and 2N-sulphuric acid were refluxed and worked up as above. The product, crystallised three times from acetone, gave iso*euphorbadienyl acetate* as needles, m. p. 129—130°, $[\alpha]_D^{20}$ 0° (*c*, 1) (Found : C, 82·0; H, 11·2. $C_{33}H_{54}O_2$ requires C, 82·1; H, 11·3%). Ozonolysis of this product gave acetone characterised as its 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 120—122°.

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