Triterpenoids. Part XX. The Constitution and Stereochemistry of a Novel Tetracyclic Triterpenoid.*

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The constitution and stereochemistry of the triterpenoid α-onoceradienediol (α-onocerin), obtained from the roots of *Ononis spinosa*, have been elucidated. α-Onoceradienediol has the molecular formula $C_{30}H_{50}O_2$, containing two secondary hydroxyl groups and two exocyclic methylene groups. It must, therefore, be tetracyclic. Removal of *either* of the secondary hydroxyl groups affords the *same* deoxy-compound and demonstrates the unique symmetry of the molecule.

The secondary hydroxyl groups have been proved to be contained in the system $\cdot CH_2 \cdot CH_2 \cdot CH(OH) \cdot CMe_2 \cdot$ in a six-membered ring, and the exocyclic methylene groups to be attached as part of the system $CH_2 \cdot C(:CH_2) \cdot \overset{|}{C}H-$ in a six-membered ring.

Dehydrogenation of α-onoceradiene affords 1 : 2 : 5-trimethylnaphthalene in high yield. Ozonolysis of α-onoceradienediol diacetate followed by hydrolysis and oxidation gives a C_{28} tetraketone which on Wolff–Kishner reduction and then dehydrogenation furnishes 1 : 5-dimethylnaphthalene.

Acid-catalysed cyclisation of α-onoceradienediol affords a new series of symmetrical pentacyclic triterpenoids.

Based on these and other experiments the constitution and stereochemistry (I; R = OH) are proposed for α-onoceradienediol. This molecule is thus the first squalenoid to be detected in the vegetable kingdom; it is of importance in formulating theories of triterpenoid biogenesis.

The triterpenoid, α-onoceradienediol,† was first isolated a hundred years ago, from the roots of *Ononis spinosa* L. (the restharrow) by Hlasiwetz (*J. prakt. Chem.*, 1855, **65**, 419), Since that time its constitution has been studied in a desultory fashion, the earlier work being summarised in Elsevier's "Encyclopaedia" (Vol. XIV and supplement thereto). It has been established that α-onoceradienediol is a disecondary glycol containing two exocyclic methylene groups (or their equivalent) and having the composition $C_{30}H_{48}O_2$ or $C_{30}H_{50}O_2$. The more significant of the earlier work is that of Schulze (*Z. physiol. Chem.*, 1936, **238**, 35), who obtained 1 : 2 : 5 : 6-tetramethylnaphthalene by dehydrogenation of α-onoceradienediol, and that of J. Zimmermann (*Helv. Chim. Acta*, 1938,**21**, 853; 1940, **23**, 1110) to which more detailed reference is made below. In most respects we have had no difficulty in confirming this earlier work of Schulze and Zimmermann.

Extraction of commercial *Ononis* root gave α-onoceradienediol, conveniently isolated as its diacetate, by the procedure outlined on p. 2645, in about 0·2% yield. We express our best thanks to Messrs. Glaxo Laboratories for carrying out this extraction on a large scale. The first objective was to distinguish between the formulæ $C_{30}H_{48}O_2$ and $C_{30}H_{50}O_2$. This was done by studying the hydrogenation of the diacetate in acetic acid solution using a platinum catalyst. Zimmermann (*loc. cit.*) had reported that this afforded two onoceranediol diacetates. By thorough chromatographic fractionation of the hydrogenation product (see p. 2646) we were able to show that *three* onoceranediol diacetates were in fact produced. Onoceranediol-I diacetate, characterised by its sparing solubility, and onoceranediol-II diacetate, conveniently separated as the corresponding dibenzoate, had

* Part XIX, *J.*, 1954, 3689.

† This compound has been named onocerin or α-onocerin in the earlier literature. The solution of the structural problem, provided by the present paper, makes it opportune to put the nomenclature of the compound and its derivatives on a more systematic basis. By analogy with β-amyrenol or oleanenol for β-amyrin, we propose that α-onocerin should become α-onoceradienediol, being regarded as a derivative of the saturated tetracyclic hydrocarbon onocerane, $C_{30}H_{54}$. The naming of derivatives then follows logically.

properties in agreement with those recorded by Zimmermann. The third isomer, onoceranediol-III diacetate, further characterised as the diol, was not isolated by Zimmermann. All three onoceranediols were converted into the corresponding diketones and then, by Wolff–Kishner reduction, into the saturated onoceranes, none of which was identical with a known compound. The analytical data, particularly on the onoceranes, left no doubt that the correct molecular formula for α-onoceradienediol was $C_{30}H_{50}O_2$. The molecule must therefore be tetracyclic.

α-Onoceradienediol diacetate showed bands in the infrared spectrum at 1735 and 1240 cm.$^{-1}$ of a strength indicative of two acetate residues. The presence of two exocylic methylene groups was shown by the strength of the band at 890 cm.$^{-1}$. Other bands characteristic of exocylic methylene were present at 3110 and 1643 cm.$^{-1}$. Oxidation of α-onoceradienediol gave the known α-onoceradienedione. This compound showed no high-intensity ultraviolet absorption; the infrared spectrum exhibited bands at 1708 cm.$^{-1}$ (six-ring or aliphatic ketone; strength of band indicative of two such chromophores) and at 3100, 1642, and 892 cm.$^{-1}$ (exocyclic methylene group; strength of 892 cm.$^{-1}$ band indicative of two such chromophores). Finally ozonolysis of α-onoceradienediol diacetate afforded, in agreement with Zimmermann (*loc. cit.*), a bisnordioxo-onoceranediol diacetate in excellent yield, thus confirming chemically the presence of the two exocyclic methylene groups.

Wolff–Kishner reduction of α-onoceradienedione furnished α-onoceradiene which was not identical with any known compound. The infrared spectrum, taken in carbon tetrachloride solution, showed bands at 1390 and 1365 cm.$^{-1}$ indicative of *gem*-dimethyl groupings and at 1642 and 885 cm.$^{-1}$ (exocyclic methylene groups; strength of 885 cm.$^{-1}$ band indicative of two such groupings).

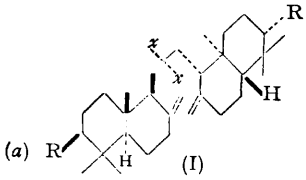
Acid-catalysed isomeration of α-onoceradienediol or its derivatives under fairly mild conditions affords compounds of the β-series (Zimmermann, *loc. cit.*) which are also diethylenic and therefore (see above) tetracyclic. According to Zimmermann (*loc. cit.*) ozonolysis of β-onoceradienediol diacetate gives acetone. In spite of numerous experiments we are unable to confirm this observation. Furthermore treatment of β-onoceradienediol diacetate with osmium tetroxide and reduction of the resultant complex with lithium aluminium hydride (cf. Barton, Ives, and Thomas, *J.*, 1954, 903) afforded an onocerane-hexaol which gave no trace of acetone on treatment with lead tetra-acetate. We conclude therefore that, contrary to the views of Zimmermann (*loc. cit.*), β-onoceradienediol does *not* contain an *iso*propylidene group.

The known β-onoceradienedione was prepared either by oxidation of β-onoceradienediol or, in a better state of purity, by acid-catalysed isomerisation of α-onoceradienedione. The ultraviolet spectrum of β-onoceradienedione showed no conjugation of the ethylenic linkages with each other or with the carbonyl groups. The infrared spectrum of β-onoceradienediol diacetate showed bands at 1730 and 1240 cm.$^{-1}$ (acetate; strength of band indicative of two such residues) but the bands characteristic of the exocyclic methylene groups (see above) had disappeared. Hydrogenation of β-onoceradienediol diacetate in acetic acid solution over a platinum catalyst gave onoceranediol-I diacetate (see above), thus showing that the transformation of the α- to the β-series very probably did not involve any skeletal rearrangement.

With these facts established, and having regard to recent views (see further below) on the nature of triterpenoid biogenesis, it was possible to deduce a hypothetical formula (I; R = OH) for α-onoceradienediol which was subsequently confirmed in every detail. We set out below the evidence for our structural proposals.

One of the most striking properties of the structure (I; R = OH) is its complete symmetry about the $x \ldots . x$ axis. This was established rigidly by showing that both hydroxyl groups of α-onoceradienediol were structurally equivalent. For convenience of exposition these two hydroxyl groups are arbitrarily designated (*a*) and (*b*) (see I). Partial hydrolysis of α-onoceradienediol *ab*-diacetate gave, besides unchanged diacetate and α-onoceradienediol, *a*-acetoxy-β-onoceradiene-*b*-ol. This was oxidised by chromic acid to furnish *a*-acetoxy-β-onoceradien-*b*-one, Wolff–Kishner reduction of which afforded α-onoceradien-*a*-ol further characterised as its acetate. *a*-Acetoxy-α-onoceradiene-*b*-ol

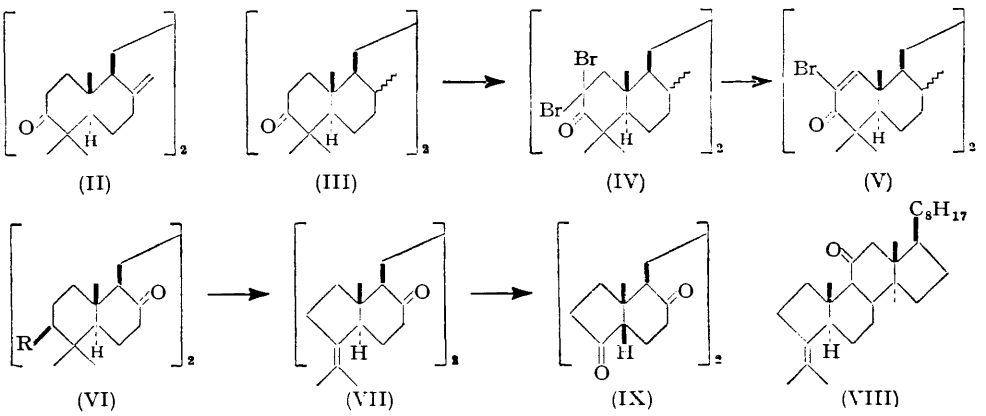
was also converted into the *a*-acetate *b*-benzoate which on partial hydrolysis gave *b*-benzoyloxy-α-onoceradien-*a*-ol. This, in turn, was oxidised to *b*-benzoyloxy-α-onoceradien-*a*-one. Wolff–Kishner reduction furnished α-onoceradien-*b*-ol, further characterised as the acetate. These compounds were identical with α-onoceradien-*a*-ol and its acetate (see above). Furthermore, hydrolysis of *a*-acetoxy-α-onoceradien-*b*-one gave the corresponding alcohol and thence *a*-benzoyloxy-α-onoceradien-*b*-one, identical in all respects, including the infrared spectrum, with the *b*-benzoyloxy-α-onoceradien-*a*-one referred to above.



(I)

The unique symmetry of (I; R = OH) also explains why only *three* onocerane derivatives are obtained on catalytic hydrogenation of (I; R = OAc) (see above). The two methyl groups produced by hydrogenation must be respectively equatorial-equatorial, axial-axial, equatorial-axial, and axial-equatorial. From the symmetrical structure (I) the last two stereoisomers would, of course, be identical.

The nature of the rings containing the hydroxyl groups of α-onoceradienediol was investigated as follows. α-Onoceradienedione (II) (see above) gave a positive Zimmermann test (W. Zimmermann, *Z. physiol. Chem.*, 1935, **233**, 257; 1936, **245**, 47; Barton and de Mayo, *J.*, 1954, 887; Broadbent and Klyne, *Biochem.*, *J.*, 1954, **56**, xxx). In view of the symmetry, we take this as indicative of two CH_2·CO groups. In agreement bromination of onoceranedione-II (III) furnished a tetrabromo-dione (IV) which was resistant to further bromination. That the bromination was not accompanied by rearrangement was shown by reduction with zinc dust and acetic acid which gave back the parent onoceranedione-II. Treatment of tetrabromo-onoceranedione-II with collidine afforded the bismonobromo-enone (V), the absorptiom spectrum of which was indicative of the presence of *two* chromophores of the type (·CO·CBr:CH·) (Nussbaum, Mancera, Daniels, Rosenkranz, and Djerassi, *J. Amer. Chem. Soc.*, 1951, **73**, 3263; Arya, Barton, and Cookson, unpublished observations). α-Onoceradienediol contains, therefore, two groupings of the type ·CH(OH)·CH_2·CH_2·.

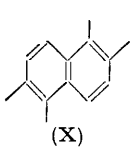


As mentioned above ozonolysis of α-onoceradienediol diacetate affords a diketone which must now be formulated as (VI; R = OAc). Alkaline hydrolysis gave the known (Zimmermann, *loc. cit.*) dihydroxy-diketone (VI; R = OH). On treatment with phosphorus pentachloride this diol underwent the usual dehydration with rearrangement to furnish the diketone (VII), the presence of two *iso*propylidene groups per mol. being demonstrated by ozonolysis which gave acetone, isolated as the 2 : 4-dinitrophenylhydrazone in 48% of the theoretical yield for two moles of acetone per mole of (VII) : ozonolysis of *iso*lanosten-11-one (VIII) (Voser, White, Heusser, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1952, **35**, 830) under the same conditions gave 46% of acetone. The second product (IX) of the ozonolysis of the diketone (VII) could not be obtained

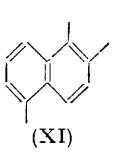
crystalline. These experiments prove the presence in α-onoceradienediol of two groupings $\cdot CMe_2\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot$ in six-membered rings.

The evidence outlined above characterises the two terminal rings of α-onoceradienediol. The other two rings were investigated in part as follows. It is clear that the two ketone groups of the diacetate (VI; R = OAc) cannot be contained in the terminal rings. They must therefore be present in the other two rings. The dione-diacetate (VI; R = OAc) showed bands at 1735 and 1240 (acetate; strength of band indicative of two acetates) and at 1710 cm.$^{-1}$. The 1710-cm.$^{-1}$ band was of a strength indicative of two ketone groups which, from the frequency, must be placed in six-membered rings. The dione-diacetate (VI; R = OAc) gave a positive Zimmermann test and therefore must contain two groupings of the type $\cdot CH_2\cdot CO\cdot$. In agreement, quantitative bromination showed that it consumed about five mols. of bromine. Although a crystalline product was not isolated it is clear, from the symmetry of the molecule, that at least six replaceable α-hydrogen atoms must be present. The second two rings of α-onoceradienediol contain therefore the grouping $\cdot CH_2\cdot C(:CH_2)\cdot CH<$ in a six-membered ring in agreement with formula (I; R = OH).

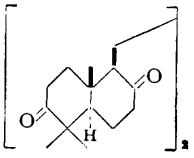
Further evidence on the nature of the carbon skeleton of α-onoceradienediol was obtained by dehydrogenation. In agreement with Schulze's findings (*loc. cit.*) selenium dehydrogenation of α-onoceradienediol itself gave 1 : 2 : 5 : 6-tetramethylnaphthalene (X). However, selenium dehydrogenation of α-onoceradiene (I; R = H), where the possibility of a rearrangement of *gem*-dimethyl groups is minimised, afforded 1 : 2 : 5-trimethylnaphthalene (XI) in remarkably high yield [68% based on two moles of (XI) from one mole of (I; R = H)]. Proof of the position of attachment of the exocyclic methylene groups of α-onoceradienediol was obtained as follows. The dione-diol (VI; R = OH) was oxidised to the tetra-ketone (XII), which was also available by ozonolysis of α-onoceradienedione (II). This tetraketone was reduced by the Wolff–Kishner method to the hydrocarbon (XIII) which gave on dehydrogenation 1 : 5-dimethylnaphthalene (XIV) only.



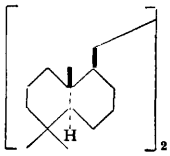
(X)



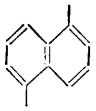
(XI)



(XII)



(XIII)

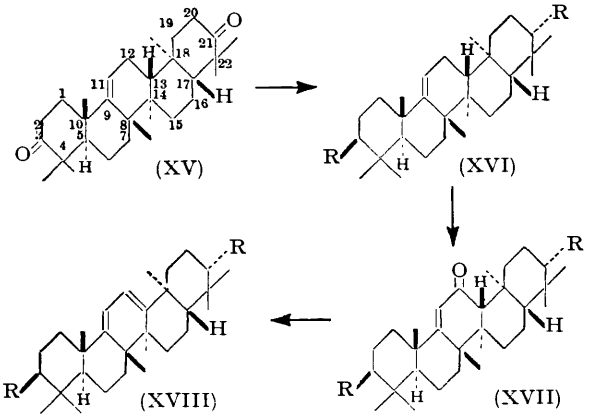


(XIV)

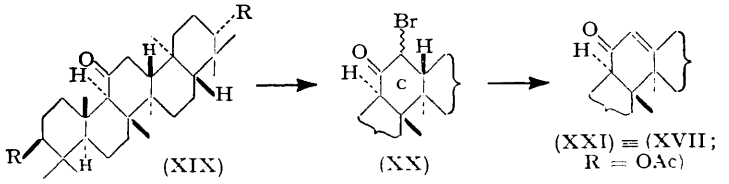
Further evidence as to the nature of the carbon skeleton of α-onoceradienediol was secured by a study of acid-catalysed isomerisation under more vigorous conditions than those required to produce the β-series (see above). Treatment of α-onoceradienedione (II) in benzene solution with acetic–sulphuric acid at room temperature (cf. Ames, Halsall, and Jones, *J.*, 1951, 450) gave a crystalline isomerisation product (XV) which we designate γ-onocerenedione. This diketone consumed per-acid at about the same rate as β-amyrin. Wolff–Kishner reduction afforded γ-onocerene (XVI; R = H). Similar acid-catalysed isomerisation of α-onoceradienediol diacetate afforded γ-onocerenediol diacetate (XVI; R = OAc), oxidised by chromic acid to the unsaturated ketone (XVII; R = OAc), $\lambda_{max.}$ 247 mμ (ε 9200) indicative of the chromophore (>C:CH·CO·) (see Woodward, *J. Amer. Chem. Soc.*, 1941, **63**, 1123; 1942, **64**, 76). Reduction of this compound with lithium aluminium hydride followed by dehydration with toluene-*p*-sulphonic acid in acetic anhydride furnished a conjugated diene (XVIII; R = OAc). This contained the two ethylenic linkages in one ring, as shown by the ultraviolet absorption maximum at 281 mμ (ε 10,600) which is identical in position with that of analogous ring-C homoannular dienes in the α- and β-amyrin series.

That the γ-series of compounds contained only one ethylenic linkage, and therefore they were pentacyclic, was proved in the following way. Treatment of γ-onocerene (XVI; R = H) with hydrogen peroxide in acetic acid–chloroform gave a ketone (XIX; R = H) which was saturated to tetranitromethane. This ketone resisted Wolff–Kishner reduction under normal conditions, which is in agreement with the degree of steric

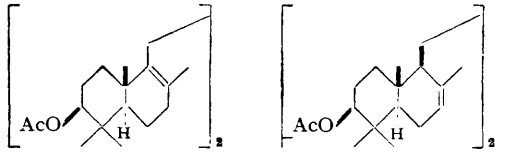
hindrance expected of such a carbonyl group (Barton and Holness, *J.*, 1952, 78; Budziarek, Johnston, Manson, and Spring, *J.*, 1951, 3019; Barton, *J.*, 1953, 1027). In a similar manner γ-onocerenediol diacetate was converted into the corresponding saturated ketone



(XIX; R = OAc). This was smoothly brominated to the bromo-ketone (XX; R = OAc) which on dehydrobromination with collidine furnished an unsaturated ketone (XXI; R = OAc) which was identical with the ketone (XVII; R = OAc). The identity



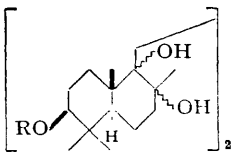
was confirmed by catalytic hydrogenation to γ-onocerenediol diacetate (XVI; R = OAc). These identities show that the unique symmetry of the α-onoceradienediol molecule is preserved in the γ-series and provides strong support for the structures proposed. It also explains why only one cyclised compound results, since the 9(11)-position of (XVI) is identical with the 12(13)-position.



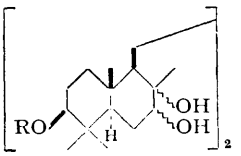
The final structural problem in the chemistry of α-onoceradienediol is the position of the ethylenic linkage in the β-series of compounds. β-Onoceradienediol diacetate must be represented by (XXII) or (XXIII), and the derived hexaol by (XXIV; R = H) or (XXV; R = H). In agreement with (XXIII), acetylation of the hexaol with pyridine and acetic anhydride gave a diacetate (XXV; R = Ac), which on oxidation with chromium trioxide rapidly consumed two atoms of oxygen. Further acetylation with acetic anhydride–sodium acetate gave a tetra-acetate (XXVI), or equivalent structure, as would be expected on the basis of (XXV). The placing of the ethylenic linkage in the β-series as in (XXIII) is somewhat unexpected (cf. Dietrich, E. Lederer, and Mercier, *Helv. Chim. Acta*, 1954, **37**, 705; Burn and Rigby, *Chem. and Ind.*, 1955, 386).

There remains for discussion the stereochemistry of α-onoceradienediol and its derivatives. Reduction of α-onoceradienedione (II) with sodium and propan-1-ol gave back

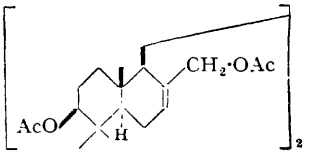
α-onoceradienediol in good yield. The two hydroxyl groups of the diol must, therefore, be equatorial. The molecular-rotation increments produced by acetylation of the hydroxyl groups of α-onoceradienediol and its derivatives are all positive (see Table). Such values are consistent with a 3β-configuration (Barton and Jones, *J.*, 1944, 659; Klyne and Stokes, *J.*, 1954, 1979), not a 3α-configuration which would give large negative Δ_1 values (Klyne and Stokes, *loc. cit.*). Now if the ring fusion in α-onoceradienediol were *trans* the equatorial



(XXIV)



(XXV)



(XXVI)

configuration would be β-, if *cis* it would be α- (cf. Barton, *Experientia*, 1950, **6**, 316). The molecular-rotation data are consistent therefore with a *trans*-fusion of rings, as in all other triterpenoids containing the same structural feature. It is hoped to advance more conclusive chemical evidence on this point shortly. The ozonolysis of α-onoceradienediol diacetate to furnish the bisnordione (VI; R = OAc) has been carried out under very mild

Parent alcohol	$[M]_D$ (in $CHCl_3$) Alcohol	Acetate	Δ_1 (per acetate residue)
α-Onoceradienediol (I; R = OH)	+ 80°	(mono) +121°	+ 41°
		(di) +147	+ 34
β-Onoceradienediol	+491	(di) +600	+ 55
Onoceranediol-II	+102	(di) +297	+ 98
Onoceranediol-III	+ 36	(di) +329	+147
α-Onoceradienol	+ 90	+140	+ 50
Bisnordionediol (VI; R = OH)	−303	−175	+ 64

conditions such as to minimise the danger of inversion of the connecting bridge at the centres adjacent to the newly formed ketone groups. The diketone formed was identical with that already described by Zimmermann (*loc. cit.*) (see above). Further, this diketone was not isomerised on vigorous treatment with base (see p. 2647). On these grounds we regard the connecting bridge of α-onoceradienediol as attached to the two bicyclic moieties in the more stable configuration. This is to be regarded (cf. Barton, *Chem. and Ind.*, 1953, 664) as equatorial, and therefore β-, attachment. The proposed stereochemistry has already been summarised in (I; R = OH).

The stereochemical situation in the γ-series of cyclised derivatives is simply derived. Since the molecules retain the unique symmetry (see above) of the parent α-series the two methyl groups at $C_{(8)}$ and $C_{(14)}$ must be *anti* with respect to each other. The very strong positive rotation of the diene (XVIII; R = OAc) ($[\alpha]_D$ +227°) is comparable with rotations recorded on numerous occasions for ring-C dienes in the α- and β-amyrin series and implies, in our opinion, a similar stereochemical environment. That is, the 8-methyl group must be β- and the 14-methyl group α-oriented. As already mentioned, the ketone (XIX; R = H) was not inverted at position 9, even on vigorous alkaline treatment : on conformational grounds then the configuration there must be α and therefore, on the basis of symmetry, the configuration at $C_{(13)}$ must be β. The proposed stereochemistry of the γ-series is therefore as already summarised in (XVI; R = OH) and derived formulæ. From the conformational point of view the compounds of the γ-series show a remarkable symmetry : this symmetry is reflected in the very high melting points of the γ-series of compounds. Indeed the symmetry of the α-onoceradienediol molecule itself also gives rise to m. p.s. which are anomalously high for tetracyclic compounds.

The absolute configuration of the α-onoceradienediol molecule is not defined by the above arguments, except that we consider that the high positive rotation of the ring-C

diene in the γ-series is indicative of a normal absolute configuration as depicted in (I; R = OH). Modern concepts of biogenesis (see below) are fully in accord with this view.

α-Onoceradienediol now takes its place, along with squalene (Heilbron *et al.*, *J.*, 1929, 873, 883, and earlier papers; Karrer and Helfenstein, *Helv. Chim. Acta*, 1931, **14**, 78) and ambrein (Ruzicka and Lardon, *ibid.*, 1946, **29**, 913; E. Lederer *et al.*, *ibid.*, p. 1354; E. Lederer and Mercier, *Experientia*, 1947, **3**, 188) in the small group of squalenoid triterpenoids. It represents the first tetracyclic squalenoid compound and, more important, the first representative of this class detected in the vegetable kingdom. In so far as recent concepts of the biogenesis of steroids and triterpenoids (see Ruzicka, *Experientia*, 1953, **9**, 357) place special emphasis on the cyclisation of squalene in ways which (see Woodward and Bloch, *J. Amer. Chem. Soc.*, 1953, **75**, 2023; Dauben *et al.*, *ibid.*, p. 3038; Ruzicka, *loc. cit.*) are not mechanistically self-evident, the elucidation of the constitution of α-onoceradienediol may be taken as welcome support for these concepts.

Experimental

For general experimental conditions see Part VII (*J.*, 1952, 2339). Rotations were determined in $CHCl_3$ solution unless otherwise specified. Ultraviolet absorption spectra were taken in EtOH solution with the Unicam S.P. 500 Spectrophotometer. Infrared spectra were kindly determined by Messrs. Glaxo Laboratories in CS_2 solution unless stated to the contrary. Alumina for chromatography was Messrs. Peter Spence's Grade H; silica gel for the same purpose was obtained from Messrs. Hopkin and Williams Ltd. Light petroleum of b. p. 40—60° was used throughout unless stated to the contrary.

Extraction of α-Onoceradienediol (α-Onocerin).—Commercial *Ononis spinosa* root (1 kg.; small chips) was refluxed with 95% ethanol (3 l.) for 3 hr. The extraction was repeated with two further portions (3 l. each) of the same solvent. The combined extracts were concentrated *in vacuo* to about 500 ml. and potassium hydroxide (10 g.) in water (50 ml.) was added. After refluxing for a further hour the solution was diluted with water (500 ml.) and left at room temperature overnight. The crude onocerin was collected, dried at 100° (7—8 g.), suspended in dry pyridine (50 ml.) and acetic anhydride (25 ml.), and heated on the steam-bath for 30 min. (clear dark brown solution). On cooling, α-onoceradienediol diacetate (α-onocerin diacetate) separated. After being washed thoroughly with methanol this was filtered through alumina in 1 : 1 benzene–light petroleum. Crystallisation from chloroform–acetone gave pure α-onoceradienediol diacetate (1·35 g.) as well-formed rods, m. p. 222—224°, $[\alpha]_D$ +29° (*c* 3·84), +28° (*c* 1·74), $\lambda_{max.}$ 205 mμ (ε 9500), no selective absorption above 220 mμ (Found: C, 77·2, 77·2, 77·6, 77·65; H, 10·35, 10·45, 10·85, 10·75. Calc. for $C_{34}H_{54}O_4$: C, 77·5; H, 10·35%). Working up the pyridine–acetic anhydride mother-liquors in the same way gave a further quantity of α-onoceradienediol diacetate (860 mg.) of m. p. 216—218°. Grinding the *Ononis* root to a fine powder did not increase the yield of α-onoceradienediol diacetate. Hydrolysis of the diacetate with potassium hydroxide (6%) in 1 : 1 dioxan–methanol gave α-onoceradienediol. Recrystallised from chloroform–methanol, this had m. p. 202—203°, $[\alpha]_D$ +18° (*c* 0·287; 4-dm. tube), +1° (*c*, 0·92 in pyridine).

α-Onoceradienedione.—α-Onoceradienediol (1·42 g.) in "AnalaR" benzene (50 ml.) and "AnalaR" acetic acid (150 ml.) was treated with chromium trioxide (465 mg.) in 95% aqueous acetic acid (10 ml.) overnight at room temperature. After addition of methanol, the solution was concentrated to half its volume and diluted with water on the steam-bath until crystallisation commenced. Filtration afforded α-onoceradienedione (1·12 g.), m. p. (from chloroform–methanol) 183—185°, $[\alpha]_D$ −2° (*c* 2·31), −2° (*c* 1·61), unchanged on further recrystallisation and on chromatography. The diketone gave a strongly positive Zimmermann reaction. Reduction of α-onoceradienedione (50 mg.) with sodium–propanol under reflux for 2 hr. gave back α-onoceradienediol (m. p. and mixed m. p.) in almost quantitative yield. The identity was confirmed by conversion into the diacetate {m. p., mixed m. p., and rotation, $[\alpha]_D$ +29° (*c* 1·03)}.

α-Onoceradiene.—α-Onoceradienedione (200 mg.) was heated at 180° for 18 hr. with anhydrous hydrazine (1·0 ml.) and ethanol (5 ml.) containing dissolved sodium (400 mg.). Working up in the usual way and crystallisation from chloroform–methanol gave *α-onoceradiene*, m. p. 195—197°, $[\alpha]_D$ +29° (*c* 2·27 or 1·13) (Found: C, 87·6; H, 12·5. $C_{30}H_{50}$ requires C, 87·75;

H, 12·25%). The hydrocarbon was more conveniently obtained by the Wolff–Kishner reduction procedure of Barton, Ives, and Thomas (*J.*, 1955, 2056). α-Onoceradienedione (8·0 g.) in diethylene glycol (250 ml.; redistilled) containing dissolved sodium (5·0 g.) was treated with anhydrous hydrazine in the usual way (Barton, Ives, and Thomas, *loc. cit.*). Working up and filtration in light petroleum through alumina gave α-onoceradiene (4·3 g.).

Hydrogenation of α-Onoceradienediol Diacetate.—The diacetate (2·0 g.) in ethyl acetate (150 ml.) was hydrogenated overnight with a platinum catalyst (500 mg.) until the solution was saturated to tetranitromethane. Crystallisation from benzene–methanol afforded onoceranediol-I diacetate (190 mg.), m. p. 216—218°, $[\alpha]_D$ +55° (*c* 1·38) (Found : C, 77·0; H, 11·0. Calc. for $C_{34}H_{58}O_4$: C, 76·95; H, 11·0%). Hydrolysis of this diacetate (250 mg.) with dioxan–methanolic potassium hydroxide afforded onoceranediol-I (212 mg.), m. p. (from aqueous methanol) 259—263°. For these two compounds Zimmermann (*Helv. Chim. Acta*, 1938, **21**, 853) recorded m. p. 218°, $[\alpha]_D$ +57°, and m. p. 255° respectively.

After removal of the onoceranediol-I diacetate the combined mother-liquors were evaporated to dryness *in vacuo* and the residue carefully chromatographed on alumina (60 g.) in light petroleum. The column was eluted by gradually increasing the content of benzene in the eluant from 0 to 100% (26 fractions). Fractions 24—26 inclusive, eluted with pure benzene, gave (from chloroform–methanol) onoceranediol-I diacetate (127 mg.), identified by m. p., mixed m. p., and rotation {$[\alpha]_D$ +55° (*c* 1·73)}. Fractions 4—8 inclusive, eluted with 15% benzene–light petroleum, were combined (320 mg.) and rechromatographed over alumina (15 g.), with elution as before (23 fractions). Crystallisation of the later fractions, eluted with 50% benzene–light petroleum, gave *onoceranediol-III diacetate* (250 mg.), long needles (from methanol), m. p. 150—151°, $[\alpha]_D$ +62° (*c* 1·53) (Found : C, 75·8; H, 11·05. $C_{34}H_{58}O_4,\frac{1}{2}MeOH$ requires C, 75·8; H, 11·0%). Hydrolysis with dioxan–methanolic potassium hydroxide afforded *onoceranediol-III*, long rods (from ethanol), m. p. 200—201°, $[\alpha]_D$ +8° (*c* 2·63 or 2·90) (Found : C, 80·1, 79·95; H, 11·85, 11·9. $C_{30}H_{54}O_2,\frac{1}{2}EtOH$ requires C, 79·5; H, 11·9%).

Careful examination of combined fractions 14—22 of the original chromatogram did not lead to a substance of authenticated homogeneity. The fractions were therefore combined (770 mg.) and hydrolysed with dioxan–methanolic potassium hydroxide, and the product was benzoylated with dry pyridine (5 ml.) and benzoyl chloride (1·54 ml.) overnight at room temperature. Crystallisation from methanol furnished *onoceranediol-II dibenzoate* (460 mg.), m. p. (plates) 200—201°, $[\alpha]_D$ +54° (*c* 3·44) (Found : C, 80·45; H, 9·5. $C_{44}H_{62}O_4$ requires C, 80·7; H, 9·55%). Hydrolysis in the usual way gave onoceranediol-II, m. p. 176—177° (from aqueous methanol and after drying overnight at 95° under 0·5 mm.), $[\alpha]_D$ +23° (*c* 1·98) (Found : C, 80·2; H, 12·0. Calc. for $C_{30}H_{54}O_2$: C, 80·65; H, 12·2%). Acetylation with pyridine–acetic anhydride at room temperature overnight furnished the diacetate, m. p. 171—172° (from chloroform–methanol), $[\alpha]_D$ +56° (*c* 3·22 or 1·54) (Found : C, 76·8; H, 10·9. Calc. for $C_{34}H_{58}O_4$: C, 76·95; H, 11·0%). For these two compounds Zimmermann (*loc. cit.*) recorded m. p. 187° and m. p. 170°, $[\alpha]_D$ +55°, respectively.

Onocerane-I.—Onoceranediol-I (200 mg.) in " AnalaR " acetic acid (10 ml.) and " AnalaR " benzene (10 ml.) was treated with chromium trioxide (100 mg.) in 95% aqueous acetic acid (10 ml.) added dropwise with stirring at room temperature. Filtration of the product in benzene through alumina and crystallisation from chloroform–ethanol, afforded onoceranedione-I, m. p. 212—213°, $[\alpha]_D$ +67° (*c* 1·57). For this compound Zimmermann (*loc. cit.*) recorded m. p. 209—211°. Onoceranedione-I (120 mg.) was heated at 180° for 16 hr. in anhydrous hydrazine (1·0 ml.) and ethanol (2·5 ml.) containing dissolved sodium (200 mg.). Filtration of the product through alumina in light petroleum solution gave *onocerane-I* (63 mg.), m. p. (from chloroform–methanol) 232—235° (evacuated capillary), 234—235° (Köfler block), $[\alpha]_D$ +51° (*c* 1·61) (Found : C, 86·7; H, 12·9. $C_{30}H_{54}$ requires C, 86·9; H, 13·1%).

Onocerane-II.—Onoceranediol-II (245 mg.) in " AnalaR " acetic acid (15 ml.) was treated with chromium trioxide (95 mg.) in 95% aqueous acetic acid (10 ml.) at room temperature for 48 hr. Filtration of the product in benzene through alumina and crystallisation from chloroform–methanol afforded onoceranedione-II, m. p. 160—162°, $[\alpha]_D$ +23° (*c* 1·20) (Found : C, 81·3; H, 11·05. Calc. for $C_{30}H_{50}O_2$: C, 81·4; H, 11·35%). Zimmermann (*loc. cit.*) recorded m. p. 154°. The diketone (140 mg.) was heated with anhydrous hydrazine (1·0 ml.) and ethanol (2·5 ml.) containing dissolved sodium (200 mg.) at 180° for 18 hr. After filtration of the product, in light petroleum through alumina, crystallisation from ethanol furnished *onocerane-II*, m. p. 135—136°, $[\alpha]_D$ +33° (*c* 2·95), +32° (*c* 1·15) (Found : C, 86·6; H, 12·9%).

Onocerane-III.—Onoceradienediol-III (120 mg.) in " AnalaR " acetic acid (3 ml.) and " AnalaR " benzene (2·5 ml.) was treated with chromium trioxide (50 mg.) in water (1·0 ml.)

overnight at room temperature. Crystallisation of the product from aqueous ethanol afforded onoceranedione-III, plates, m. p. 168—169°, $[\alpha]_D$ −6° (*c* 1·64) (Found: C, 81·2; H, 11·3%). The diketone (75 mg.) was heated with 100% hydrazine hydrate (0·6 ml.) and ethanol (2·5 ml.) containing dissolved sodium (150 mg.) at 180° for 16 hr. Filtration of the product through alumina in light petroleum solution and crystallisation from ethanol afforded *onocerane-III*, m. p. (needles) 123—124°, $[\alpha]_D$ +12° (*c*, 1·75) (Found: C, 86·9; H, 13·05%).

β-Onoceradienediol (β-Onocerin) and its Derivatives.—α-Onoceradienediol diacetate (1·0 g.) in acetic acid (200 ml.) was treated with concentrated sulphuric acid (2·0 ml.) in the same solvent (50 ml.) at 40° for 3 hr. Crystallisation from benzene–methanol afforded β-onoceradienediol diacetate (435 mg.), m. p. 231—236° (changes from plates to needles), 261—264° (evacuated capillary after drying for 45 min. at 110°/0·1 mm.), $[\alpha]_D$ +114° (*c* 1·89), +113° (*c* 1·24). Zimmermann (*Helv. Chim. Acta*, 1938, **21**, 853) gives m. p. 260° $[\alpha]_D$ +106°.

β-Onoceradienediol diacetate (200 mg.) was hydrolysed with potassium hydroxide (3·0 g.) in dioxan (15 ml.) and methanol (35 ml.) under reflux for 2 hr. Dilution with water gave β-onoceradienediol, m. p. 233—236° (from aqueous–methanol), $[\alpha]_D$ +111° (*c* 1·95) (157 mg.). This was taken up in "AnalaR" acetic acid (10 ml.) and treated with chromium trioxide (50 mg.) in 95% aqueous acid (3·0 ml.) at room temperature for 48 hr. Crystallisation of the product from methanol gave somewhat impure β-onoceradienedione, needles, m. p. 162—164°, $[\alpha]_D$ +166° (*c* 1·19), $\lambda_{max.}$ 245 mμ (ε 2600). Contamination with αβ-unsaturated ketone is clearly indicated. A more satisfactory specimen of the β-diketone was prepared as follows. α-Onoceradienedione (200 mg.) was refluxed with acetic acid–concentrated hydrochloric acid (9 : 1; 50 ml.) for 18 hr. Chromatography of the product over alumina and crystallisation from methanol gave pure β-onoceradienedione (32 mg.), m. p. 168—170°, $[\alpha]_D$ +187° (*c* 0·94). Zimmermann (*loc. cit.*) recorded m. p. 170°.

Hydrogenation of β-Onoceradienediol Diacetate.—The diacetate (325 mg.) was hydrogenated in "AnalaR" acetic acid with a platinum catalyst for 2 days. The product was chromatographed over alumina (8·0 g.) in 1 : 1 light petroleum–benzene (five fractions). All but the first fraction consisted of pure onoceranediol-I diacetate, identified by m. p., mixed m. p., and rotation {$[\alpha]_D$ +49° (*c* 2·02)}.

Ozonolysis of α-Onoceradienediol Diacetate.—α-Onoceradienediol diacetate (3·0 g.) in dry methylene chloride (50 ml.) was cooled to −70° and ozonised until a test portion was negative to tetranitromethane. Acetic acid (25 ml.) was added and zinc dust (5 g.) was stirred in portionwise during 2 hr., the temperature being held at −20°. Crystallisation from aqueous ethanol afforded diacetoxydinoronoceranedione (VI; R = OAc) (2·11 g.), m. p. 120—125° (resolidified) and 162—164°, $[\alpha]_D$ −33° (*c*, 3·56, 2·42, or 1·15), $\lambda_{max.}$ 286 mμ (ε 75). After drying at 100/0·1 mm. for 14 hr. the compound melted at 164—166°.

The diketone diacetate (VI; R = OAc) (350 mg.) was refluxed with 5% methanolic potassium hydroxide solution (25 ml.) for 2 hr. Crystallisation of the product from benzene–light petroleum (b. p. 60—80°) gave the dihydroxy-diketone (VI; R = OH), rods, m. p. 216—218°, $[\alpha]_D$ −68° (*c* 2·40). For this compound and for its parent diacetate (see above) Zimmermann (*Helv. Chim. Acta*, 1940, **23**, 1110) recorded m. p. 217° and 165° respectively.

In further experiments the diketone diacetate (350 mg.) was refluxed (*a*) with 10% methanolic potassium hydroxide overnight and (*b*) with 20% methanolic potassium hydroxide for 3 hr. In both cases the same dihydroxy-diketone was formed. Reacetylation with pyridine–acetic anhydride at room temperature overnight gave back the parent diketone diacetate, identified by m. p., mixed m. p., and rotation {$[\alpha]_D$ −34° (*c* 1·37)}.

The diketone gave an immediate response in the Zimmermann colour reaction.

The diketone diacetate (107 mg.) in "AnalaR" acetic acid (11·7 ml.) was mixed with a solution of bromine (256 mg.; 8 mols.) in "AnalaR" acetic acid (8·3 ml.) with addition of one drop of 50% hydrobromic–acetic acid. The consumption of bromine (in mols.) after the stated times (in parentheses) was as follows: 0·94 (20 min.), 2·03 (60 min.), 3·87 (90 min.) 4·44 (16 hr.), 4·78 (22 hr.), 4·91 (44 hr.). A duplicate experiment with a higher concentration of hydrobromic acid as catalyst led to an uptake of 4·90 mols. of bromine in 75 min.

Formation of the Tetraketone (XII).—(*a*) The dihydroxy-diketone (VI; R = OH) (82 mg.) in "AnalaR" acetic acid (3·0 ml.) was treated overnight at room temperature with chromium trioxide (30 mg.) in the same solvent (6·0 ml.). Crystallisation of the product from methanol furnished the *dinoronoceranetetraone* (XII), stout rods, m. p. 196—198°, $[\alpha]_D$ −104° (*c* 2·45) (Found: C, 75·7; H, 9·35. $C_{28}H_{42}O_4$ requires C, 75·95; H, 9·55%).

(*b*) α-Onoceradienedione (500 mg.) in methylene dichloride (50 ml.) was ozonised at −70° until a test portion was negative to tetranitromethane. After working up with acetic

acid and zinc dust as outlined above, filtration of the product in benzene through alumina gave the same tetraketone (417 mg.), identified by m. p., mixed m. p., and rotation {$[\alpha]_D$ −106° (*c* 2·57)}.

Action of Phosphorus Pentachloride on the Dihydroxy-diketone (VI; R = OH).—A solution of the dihydroxy-diketone (450 mg.) in " AnalaR " benzene (200 ml.) was concentrated to half its volume *in vacuo*. To this solution, cooled to 0°, there was added phosphorus pentachloride (700 mg.) in one portion with stirring. The stirring was continued with passage of a stream of dry oxygen-free nitrogen and exclusion of moisture for 30 min. (all phosphorus pentachloride in solution). Chromatography over alumina (15 g.) gave a crystalline *dinoronoceradienedione*, plates (from chloroform–methanol), m. p. 156—160°, $\lambda_{max.}$ 205 mμ (ε 17,500), $[\alpha]_D$ −113° (*c* 2·28), −112° (*c* 1·25) (Found : C, 81·9; H, 9·35. $C_{28}H_{42}O_2$ requires C, 81·9; H, 10·3%). Fractionation from chloroform–methanol did not alter the rather diffuse m. p.

Ozonolysis of the product (163 mg.) (obtained with phosphorus pentachloride) at −60° in methylene dichloride (10 ml.) and working up by addition of zinc dust and acetic acid as outlined above gave acetone. This was determined in the following way. The solution of acetone in methylene dichloride–acetic acid was distilled over into a solution of 2 : 4-dinitrophenylhydrazine (250 mg.) in ethanol (50 ml.) and concentrated hydrochloric acid (1·0 ml.). During the distillation ethanol was added to the original solution so that the final volume of the distillate was 200 ml. The solvent was removed from the distillate *in vacuo* and the residue chromatographed over alumina (5·0 g.) on benzene. Elution with benzene gave acetone 2 : 4-dinitrophenylhydrazone (84 mg., 48% based in two *iso*propylidene groups), identified by m. p., mixed m. p., and analysis (Found : C, 45·8; H, 4·45; N, 25·2, 22·9. Calc. for $C_9H_{10}O_4N_4$: C, 45·4; H, 4·25; N, 23·5%).

In another experiment the ozonolysis product was decomposed at low temperature with zinc dust and acetic acid. Careful chromatography of the product did not give any crystalline product.

In a model experiment *iso*lanosten-11-one (500 mg.), kindly provided by Mr. D. A. J. Ives, was ozonised in the same way to give acetone 2 : 4-dinitrophenylhydrazone (135 mg., 46%), identified by m. p. and mixed m. p.

Ozonolysis of β-*Onoceradienediol Diacetate*.—β-Onoceradienediol diacetate (135 mg.) was ozonised and the product worked up essentially as described above. In spite of extensive examination the formation of acetone, claimed by Zimmermann (*Helv. Chim. Acta*, 1940, **23**, 1110), could not be confirmed.

Hydroxylation of β-*Onoceradienediol Diacetate with Osmium Tetroxide*.—The diacetate (300 mg.) in dry pyridine (5 ml.) was treated with osmium tetroxide (375 mg.) in dry ether (5 ml.) in the dark for 5 days. Lithium aluminium hydride (600 mg.) in dry ether (20 ml.) was then added and the solution refluxed for 1 hr. The excess of lithium aluminium hydride was destroyed with ethyl acetate. Crystallisation of the product from methanol–benzene furnished the desired *onoceranehexaol* (XXV; R = H) (100 mg.), silky needles, m. p. 268—271° (evacuated capillary), $[\alpha]_D$ +20° (*c* 3·18) (Found : C, 70·0; H, 10·7. $C_{30}H_{54}O_6$ requires C, 70·55; H, 10·65%). The hexaol (95 mg.) in acetic acid (2 ml.) was treated with lead tetra-acetate (200 mg.) in acetic acid (10 ml.) for 18 hr. at room temperature. The solution was diluted with water (150 ml.) and distilled into a solution of 2 : 4-dinitrophenylhydrazine (250 mg.) in ethanol (50 ml.) and concentrated hydrochloric acid (1·0 ml.). The distillate was evaporated to dryness *in vacuo* and the residue chromatographed for acetone 2 : 4-dinitrophenylhydrazone (see above). None of this compound could be detected.

The hexaol (XXV; R = H) (230 mg.) was acetylated with pyridine–acetic anhydride overnight at room temperature, furnishing the diacetate (XXV; R = Ac), plates (from chloroform–methanol), m. p. 268—271° (evacuated capillary), $[\alpha]_D$ +37° (*c* 1·67) (Found : C, 68·60; H, 9·65. $C_{34}H_{58}O_8$ requires C, 68·65; H, 9·80%).

Further acetylation of the diacetate (110 mg.) in refluxing acetic anhydride (containing 5% of anhydrous sodium acetate) for 1 hr. afforded, after chromatography over alumina, the tetra-acetate (XXVI), rods (from methanol), m. p. 234—237° (evacuated capillary), $[\alpha]_D$ +21° (*c* 0·57) (Found : C, 70·95; H, 9·5; Ac, 24·3. $C_{38}H_{58}O_8$ requires C, 71·0; H, 9·1; Ac, 26·8%).

When the hexaol diacetate, after rigorous drying *in vacuo*, was treated with chromium trioxide (2·2 atom-equiv. of oxygen) in aqueous (2%) acetic acid at room temperature overnight, 2 atom-equivs. of oxygen were consumed rapidly. Neither the resulting diketone nor its dioxime could be obtained crystalline.

Treated with lead tetra-acetate in acetic acid at room temperature, the hexaol diacetate (XXV; R = Ac) consumed 2 mols. within 5 min., and no more during a further 19 hr.

Bromination of Onoceranedione-II.—The diketone (42 mg.) in " AnalaR " acetic acid (5 ml.) containing one drop of hydrobromic–acetic acid was treated dropwise with a solution of bromine in acetic acid (0·53% w/v) at 50°. Two mols. of bromine were rapidly absorbed, a further two mols. more slowly; there was no additional uptake after 2 hr. at the same temperature in the presence of a further 2 mols. of bromine. Crystallisation of the product from chloroform–methanol gave *tetrabromo-onoceranedione-II*, needles, m. p. 194—196° (decomp.), $[\alpha]_D$ −20° (*c* 2·90) (Found: C, 48·15; H, 6·2; Br, 43·05. $C_{30}H_{46}O_2Br_4$ requires C, 47·5; H, 6·1; Br, 42·15%). This tetrabromo-compound (15 mg.) in " AnalaR " acetic acid (1 ml.) was kept with a solution of bromine in acetic acid (5 ml.; 8·16 mg. per ml.) for 5 days at room temperature. Back-titration showed that less than 0·1 mol. of bromine had been consumed.

Tetrabromo-onoceranedione-II (20 mg.) in " AnalaR " acetic acid (3 ml.) was refluxed with zinc dust (150 mg.) for 2 hr. Crystallisation of the product from chloroform–methanol gave back onoceranedione-II (m. p. and mixed m. p.).

Tetrabromo-onoceranedione-II (210 mg.) in redistilled collidine (3 ml.) was heated in a sealed tube at 180° for 2 hr. Chromatography of the product over alumina (5 g.) in 10—50% benzene–light petroleum (six fractions) gave *bisdehydrodibromo-onoceranedione-II*, m. p. (from chloroform–methanol) 221—223°, $[\alpha]_D$ +34° (*c* 1·88), $\lambda_{max.}$ 255 mμ (ε 17,500) (Found: C, 60·65; H, 7·5; Br, 26·9. $C_{30}H_{44}O_2Br_2$ requires C, 60·4; H, 7·4; Br, 26·85%).

γ-Onocerenedione.—α-Onoceradienedione (3·0 g.) in " AnalaR " benzene (30 ml.) and 15 : 85 concentrated sulphuric acid–" AnalaR " acetic acid (300 ml.; mixed with cooling) was kept at room temperature for 3 days. After dilution with water, extraction with ether, and washing with sodium hydroxide solution, evaporation of the ethereal solution *in vacuo* and treatment of the residue with light petroleum (b. p. 60—80°) gave a crystalline product. This was filtered through alumina in benzene solution to furnish *γ-onocerenedione* (525 mg.), stout prisms (from benzene–light petroleum), m. p. 291—293° (evacuated capillary), $[\alpha]_D$ +104° (*c* 2·07) (Found: C, 81·8; H, 10·45. $C_{30}H_{46}O_2$ requires C, 82·1; H, 10·55%). In a further experiment the α-onoceradienedione was treated for only 15 hr. Chromatography of the product over alumina gave γ-onocerenedione and then β-onoceradienedione in a ratio of approximately 1 : 2.

γ-Onocerenedione reacted with ethereal monoperphthalic acid at 0°, consuming 34% of the theoretical amount for one ethylenic linkage in 4 days. A solution of β-amyrin benzoate of the same concentration treated in the same way consumed 29% in the same time.

γ-Onocerene.—γ-Onocerenedione (52 mg.) was heated with anhydrous hydrazine (0·5 ml.) and ethanol (2 ml.) containing dissolved sodium (100 mg.) at 180° for 20 hr. Filtration of the product in light petroleum through alumina gave *γ-onocerene*, rods (from methanol), m. p. 254—256° (Köfler block), $[\alpha]_D$ +83° (*c* 1·58) (Found: C, 87·65; H, 12·3. $C_{30}H_{50}$ requires C, 87·75; H, 12·3%).

γ-Onocerenediol Diacetate.—α-Onoceradienediol diacetate (250 mg.) in " AnalaR " benzene (2·5 ml.) and 15 : 85 concentrated sulphuric acid–" AnalaR " acetic acid (25 ml.) was kept at room temperature overnight. Chromatography of the product over alumina (8 g.) in light petroleum and elution with 30—100% benzene–light petroleum (six fractions) afforded *γ-onocerenediol diacetate*. Purified by vacuum-sublimation and crystallisation from chloroform–methanol this (27 mg.) had m. p. 333—336° (evacuated capillary), $[\alpha]_D$ +79° (*c* 1·55), +80° (*c* 1·45) (Found: C, 77·4; H, 10·5. $C_{34}H_{54}O_4$ requires C, 77·5; H, 10·35%).

Diacetoxy-γ-onocerenone.—γ-Onocerenediol diacetate (100 mg.) in refluxing " AnalaR " acetic acid (20 ml.) was treated with chromium trioxide (80 mg.) in 95% aqueous acetic acid (10 ml.) added dropwise during 1 hr. The refluxing was continued for a further hour. Filtration of the crude product in benzene through alumina and crystallisation from benzene–ethanol gave diacetoxy-γ-onocerenone, large hexagonal plates, m. p. 356—360° (evacuated capillary), $[\alpha]_D$ +86° (*c* 2·27), $\lambda_{max.}$ 247 mμ (ε 9200) (Found: C, 75·2; H, 9·8. $C_{34}H_{52}O_5$ requires C, 75·5; H, 9·7%).

γ-Onoceradienediol Diacetate.—Oxo-γ-onocerenediol diacetate (250 mg.) in anhydrous ether (30 ml.) was refluxed with lithium aluminium hydride (300 mg.) for 2 hr. Excess of lithium aluminium hydride was decomposed by addition of ethyl acetate, and the crude product, obtained in the usual way, refluxed with toluene-*p*-sulphonic acid (25 mg.) in acetic anhydride (5 ml.) for 1 hr. Crystallisation from chloroform–methanol afforded *γ-onoceradienediol diacetate*, m. p. 350—353° (evacuated capillary), $[\alpha]_D$ +221° (*c* 3·45), $\lambda_{max.}$ 281 mμ (ε 10,800) (Found: 77·75, 77·7; H, 9·55, 9·95. $C_{34}H_{52}O_4$ requires C, 77·8; H, 10·0%).

γ-Onoceranone.—γ-Onocerene (190 mg.) in " AnalaR " acetic acid (15 ml.) was heated on the steam-bath and treated with hydrogen peroxide (30%; 3 ml.) in " AnalaR " acetic acid

(3 ml.) added portionwise during 2·5 hr. A little chloroform was added from time to time to ensure a clear solution. Crystallisation of the product from chloroform–methanol gave *γ-onoceranone*, plates, m. p. 295—298°, $[\alpha]_D$ +25° (*c* 1·27) (Found: C, 82·75; H, 11·5. $C_{30}H_{50}O,\frac{1}{2}CH_4O$ requires C, 82·8; H, 11·85. Found, after drying at 120°/0·1 mm. for 5 days: C, 83·65; H, 12·2. $C_{30}H_{50}O$ requires C, 84·45; H, 11·8%). This ketone (45 mg.) was recovered unchanged (m. p. and mixed m. p.) after being subjected to the normal sealed-tube Wolff–Kishner reduction conditions.

Transformations with γ-Onocerenediol Diacetate.—γ-Onocerenediol diacetate (200 mg.) in "AnalaR" acetic acid (15 ml.), heated on the steam-bath, was treated with hydrogen peroxide (30%; 3·5 ml.) in "AnalaR" acetic acid (3·5 ml.) added portionwise during 2·5 hr. A little chloroform was added from time to time to ensure a clear solution (internal temp. 85°). Crystallisation of the product from chloroform–methanol afforded *diacetoxy-γ-onoceranone*, hexagonal plates, m. p. >370°, $[\alpha]_D$ +32° (*c* 1·46), $\lambda_{max.}$ 296 mμ (ε 30) (Found: C, 75·15; H, 10·05. $C_{34}H_{54}O_5$ requires C, 75·25; H, 10·05%). The homogeneity of this compound was confirmed by chromatography.

Diacetoxy-γ-onoceranone (156 mg.) in "AnalaR" acetic acid (50 ml.) containing 2 drops of hydrobromic–acetic acid was treated at 75° with bromine in "AnalaR" acetic acid (5·87 ml.; 8·62 mg. of bromine per ml.; 1·1 mols.) added in ½-ml. portions as rapidly as it was consumed (2 hr.). Crystallisation of the product from chloroform–methanol afforded *bromodiacetoxy-γ-onoceranone*, rods, m. p. about 320° (decomp.), $[\alpha]_D$ +15° (*c* 1·60) (Found: C, 65·55; H, 8·65; Br, 13·2. $C_{34}H_{53}O_5Br$ requires C, 65·7; H, 8·6; Br, 12·9%).

The bromo-ketone (80 mg.) was heated with redistilled collidine (2 ml.) in a sealed tube at 180° for 1·5 hr. Crystallisation of the product from chloroform–ethanol gave diacetoxy-γ-onocerenone, identified by m. p., mixed m. p., absorptiom [$\lambda_{max.}$ 247 mμ (ε 9000)], and rotation {$[\alpha]_D$ +89° (*c* 1·63)}. The identity was further checked by hydrogenation of the unsaturated ketone (45 mg.) in "AnalaR" acetic acid over platinum at room temperature for 2 days. Crystallisation from chloroform–methanol gave γ-onocerenediol diacetate, identified by m. p., mixed m. p., and rotation {$[\alpha]_D$ +73° (*c* 1·66)}.

Semihydrolysis of α-Onoceradienediol Diacetate.—α-Onoceradienediol diacetate (1·1 g.) in dioxan (25 ml.), water (10 ml.), and 40% aqueous dioxan (11·8 ml.) containing potassium hydroxide (9 mg. per ml.; 0·9 mole) was refluxed overnight. The addition of phenolphthalein showed that this time was required for the complete consumption of the potassium hydroxide. Chromatography of the product over alumina (30 g.) in benzene solution gave unchanged α-onoceradienediol diacetate (235 mg.), identified by m. p. and mixed m. p. Elution with 9 : 1 ether–methanol gave a mixture which was further chromatographed over silica gel (45 g.) in light petroleum. Elution with 9 : 1 light petroleum–benzene (four fractions) afforded *α-onoceradienediol monoacetate* (560 mg.), needles [from benzene–light petroleum (b. p. 60—80°)], m. p. 156—158°, $[\alpha]_D$ +25° (*c* 1·37), +26° (*c* 0·70) (Found: C, 79·1; H, 10·5. $C_{32}H_{52}O_3$ requires C, 79·3; H, 10·8%). Elution with methanol gave a small amount of α-onoceradienediol (m. p. and mixed m. p.).

α-Onoceradienediol monoacetate (339 mg.) in "AnalaR" acetic acid (10 ml.) was treated with chromium trioxide (50 mg.) in 95% aqueous acetic acid (5 ml.) at room temperature overnight. Filtration of the product through alumina in benzene gave the *monoacetate ketone*, needles (from chloroform–methanol), m. p. 187—189°, $[\alpha]_D$ +18° (*c* 1·98) (Found: C, 78·6; H, 10·25. $C_{32}H_{50}O_3,\frac{1}{2}CH_4O$ requires C, 78·3; H, 10·5%).

α-Onoceradienediol monoacetate (700 mg.) in dry pyridine (5 ml.) and benzoyl chloride (0·7 ml.) was left overnight at room temperature. Chromatography of the product over alumina (20 g.) in light petroleum and elution with 1 : 10 benzene–light petroleum to pure benzene (10 fractions) gave *α-onoceradienediol acetate benzoate*, m. p. 133—135° (from chloroform–methanol), $[\alpha]_D$ +30° (*c* 1·39), $\lambda_{max.}$ 229 mμ (ε 15,500) (Found: C, 77·6; H, 9·5. $C_{39}H_{56}O,\frac{1}{2}CH_4O$ requires C, 77·4; H, 9·75%).

α-Onoceradienol.—(*a*) The monoacetate ketone (180 mg.) was heated with anhydrous hydrazine (0·9 ml.) in ethanol (4·5 ml.) containing dissolved sodium (350 mg.) at 180° for 14 hr. Crystallisation of the product from aqueous ethanol gave *α-onoceradienol*, fine needles, m. p. 182—184°, $[\alpha]_D$ +21° (*c* 1·70) (Found: C, 84·3; H, 12·0. $C_{30}H_{50}O$ requires C, 84·4; H, 11·8%). Acetylation with pyridine–acetic anhydride at room temperature furnished *α-onoceradienyl acetate*, needles (from chloroform–methanol), m. p. 141—143°, $[\alpha]_D$ +30° (*c* 1·52) (Found: C, 82·3; H, 11·5. $C_{32}H_{52}O_2$ requires C, 82·0; H, 11·2%).

(*b*) α-Onoceradienediol acetate benzoate (610 mg.) in dioxan (10 ml.) and 2 : 3 aqueous dioxan (6·7 ml.) containing potassium hydroxide (9 mg. per ml.; 1·0 mol.) was heated under

reflux for 16 hr. Chromatography of the product over alumina (20 g.) in benzene and elution with 1—→4 : 10 ether–benzene gave *α-onoceradienediol monobenzoate*, rods (from chloroform methanol), m. p. 222—224°, $[\alpha]_D$ +25° (*c* 1·54), $\lambda_{max.}$ 229 mμ (ε 15,100) (Found : C, 81·1; H, 9·75. $C_{37}H_{54}O_3$ requires C, 81·25; H, 9·95%). Oxidation of this monobenzoate (233 mg.) in " AnalaR " acetic acid (20 ml.) with chromium trioxide (32 mg.) in 95% aqueous acetic acid (5 ml.) overnight at room temperature gave the *monobenzoate ketone*, needles (from methanol), m. p. 152—154°, $[\alpha]_D$ +23° (*c* 1·56) (Found : C, 81·5; H, 9·55. $C_{37}H_{52}O_3$ requires C, 81·55; H, 9·5%). This monobenzoate ketone (112 mg.) was heated with anhydrous hydrazine (1·0 ml.) and ethanol (3·0 ml.) containing dissolved sodium (200 mg.) at 180° for 14 hr. Crystallisation of the product from aqueous ethanol gave α-onoceradienol identical {m. p., mixed m. p., crystal form, and rotation, $[\alpha]_D$ +20° (*c* 2·11)} with material described under this name above. The identity was confirmed by acetylation to α-onoceradienyl acetate {m. p., mixed m. p., and rotation, $[\alpha]_D$ +29° (*c* 1·35)}.

Further Correlation of the Hydroxyl Groups of α-Onoceradienediol.—The monoacetate ketone from α-onoceradienediol (775 mg.) in dioxan (15 ml.) and 2 : 3 aqueous dioxan (11·35 ml.) containing potassium hydroxide (9 mg. per ml.; 1·1 mols.) was heated under reflux for 14 hr. The product was chromatographed over alumina (30 g.) in benzene. Elution with benzene gave unchanged monoacetate ketone (56 mg.) (m. p. and mixed m. p.). Elution with ether afforded the desired *hydroxyonoceradienone* (530 mg.), needles (from chloroform–methanol), m. p. 175—177°, $[\alpha]_D$ +6° (*c* 1·90) (Found : C, 80·65; H, 11·15. $C_{30}H_{48}O_2,\frac{1}{2}CH_4O$ requires C, 80·25; H, 11·05%). Treatment of this compound (365 mg.) in dry pyridine (5 ml.) with benzoyl chloride (0·365 ml.) at room temperature for 14 hr. and filtration of the product in light petroleum through alumina furnished a monobenzoate ketone identical {m. p., mixed m. p., crystal form, rotation—$[\alpha]_D$ +21° (*c* 1·93 or 2·48)—and infrared spectrum (*c* 2·0 in CS_2)} with the corresponding compound described above.

Dehydrogenation of α-Onoceradienediol.—α-Onoceradienediol (4·2 g.) was heated in a metal bath at 240—260°/0·2 mm. for 45 min. The flask was cooled, black selenium (8·4 g.) added, and the mixture heated for 23 hr. at 310—320°/1 atm. The flask and its contents were powdered in a mortar and extracted (Soxhlet) with ether. The ethereal solution was evaporated to dryness and the product chromatographed over alumina (15 g.) in light petroleum. Elution with this solvent gave crude 1 : 2 : 5 : 6-tetramethylnaphthalene (180 mg.) characterised as its picrate.

Dehydrogenation of α-Onoceradiene.—α-Onoceradiene (3·56 g.) was heated at 195°/0·2 mm. for 1 hr. Black selenium (6·2 g.) was stirred into the melt, and the mixture heated in a stream of nitrogen at 310—320° for 24 hr. Soon after the mixture had attained this temperature there was a vigorous evolution of gas. This had ceased after 24 hr. The residue was extracted as described above and the product chromatographed over alumina (100 g.) in light petroleum. Elution with this solvent (four fractions) gave 1 : 2 : 5-trimethylnaphthalene (1·91 g., 68% based on two moles from one mole of α-onocerene), characterised as the picrate (2·42 g.), m. p. 137—139° alone or mixed with an authentic specimen of m. p. 135—137°, as the styphnate, m. p. 129—131° alone or mixed with an authentic specimen of m. p. 129—131°, and as the trinitrobenzene adduct, m. p. 158—159° (Ruzicka *et al.*, *Helv. Chim. Acta*, 1930, **13**, 1411, give m. p. 159°).

Dehydrogenation of Dinoronocerane.—Freshly dried anhydrous hydrazine was distilled over in an all-glass apparatus into diethylene glycol (250 ml.; redistilled) until the solution boiled evenly at 180° (see Barton, Ives, and Thomas, *J.*, 1955, 2056). The tetra-ketone (XII) (see above) (5·0 g.) was added and the solution refluxed at 180° for 14 hr. Excess of hydrazine was distilled out until the temperature reached 210°, and the solution refluxed for 6 hr. Filtration of the product in light petroleum through alumina and crystallisation from chloroform–methanol gave *dinoronocerane* (2·3 g.), long needles, m. p. 117—119°, $[\alpha]_D$ +62° (*c* 2·47 or 2·62) (Found : C, 86·8; H, 13·0. $C_{28}H_{50}$ requires C, 86·95; H, 13·0%). When the tetraketone was reduced under standard Wolff–Kishner conditions in a sealed tube only intractable products resulted.

Dinoronocerane was not dehydrogenated by twice its weight of selenium at 310—320° for 16 hr. (70% recovery of crystalline starting material). The hydrocarbon was, however, smoothly dehydrogenated as follows. It (1·0 g.) was kept at 160—170°/0·2 mm. for 1 hr., well mixed with black selenium (2·0 g.), and then heated in a metal bath at 355—365° for 18 hr. Gas evolution, marked during the first hour, had ceased at the end of this period. The product was extracted with ether and processed as above. Elution with light petroleum and vacuum-sublimation gave 1 : 5-dimethylnaphthalene (213 mg.), identified by m. p. (79·5—80·5°) and mixed m. p. (79—80°) with an authentic specimen (m. p. 78—79·5°). The identity was

confirmed by a comparison of ultraviolet absorption spectra, $\lambda_{max.}$ 275, 286, and 297 mμ (ε 7100, 8800, and 6100), with that of the authentic specimen.

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