791. The Structure of Some Diterpenes from Tambooti Wood, Spirostachys africana Sond.

By W. H. BAARSCHERS, D. H. S. HORN, and LE ROY F. JOHNSON.

Degradative experiments and nuclear magnetic resonance measurements are reported which establish the novel basic structure of the diterpene ketone (I), ketol (IV), and diosphenol (II) isolated from the heartwood of *Spirostachys africana* Sond. Optical rotatory measurements permit the assignment of the opposite configuration of the A/B ring junction to that of the steroids and triterpenes. Some information on the nature of the B/C ring junction is presented.

Spirostachys africana Sond. (syn. *Excoecaria africana* Muell. Arg.) is a tree of widespread occurrence in Southern Africa. The wood, generally known as " tambooti," is hard and fine-grained. It has a pleasant smell reminiscent of sandalwood, and is occasionally used for the manufacture of small articles of furniture.

Earlier investigators [1] reported the heartwood to contain an oleoresin. We have isolated [2] the following compounds from the resin: a ketone, stachenone ($C_{20}H_{30}O$) for which we propose structure (I), an α-ketol (IV), and a diosphenol (II). The interrelationship of these substances was established by autoxidizing stachenone in good yield in dry t-butyl alcohol containing potassium t-butoxide [3] to the diosphenol; the ketol was converted into the diosphenol by oxidation with bismuth oxide.[4]
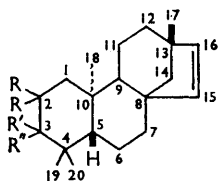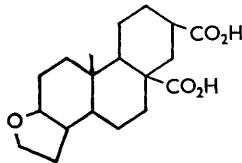

(I ; R = H, R′R″ = O)
(IV; RR = O, R′ = H, R″ = OH)
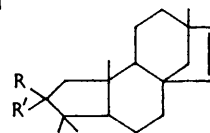(VI; R = H, R′ = OH, R″ = Me)
(VII; R = R′ = H, R″ = OH)

(II)
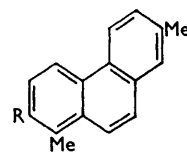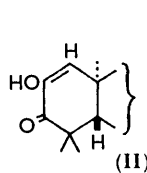
(III ; R = H)
(V ; R = Me)
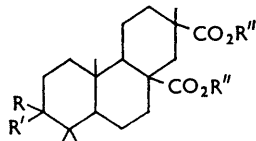
(VIII ; R = R″ = H, R′ = OH)
(XI ; R = Me, R′ = OH, R″ = H)
(XIII ; RR′ = O, R″ = H)
(XV ; RR′ = O, R″ = Me)
(XVI ; R = H, R′ = OH, R″ = Me)

(IX)

(X ; R = CO₂H, R′ = OH)
(XII ; R = CH₂·OH, R′ = OH)
(XIV; RR′ = O)

In its infrared spectrum, stachenone showed bands at 1706 and 749 cm.⁻¹, attributed to a carbonyl group in a six-membered ring and a *cis*-double bond, respectively. Bands at 1381 and 1363 cm.⁻¹ suggested the presence of a geminal dimethyl group.[5] Also, stachenone showed in its nuclear magnetic resonance spectrum (in carbon tetrachloride with tetramethylsilane as an internal standard at δ = 0·00),[6] doublet peaks ($J = 6$ c./sec.) at δ = 5·43 and 5·67 (*cis*-CH=CH), peaks at 120—150 c./sec. from tetramethylsilane

[1] Anon., *Bull. Imp. Inst.*, 1935, **33**, 136; Beckley, *E. African Agric. J.*, 1936, **1**, 469.
[2] Baarschers and Horn, Summary of papers read at the S.A. Chemical Convention, 1961; *S.A. Industrial Chemist*, 1962, **16**, 122.
[3] Bailey, Elks, and Barton, *Proc. Chem. Soc.*, 1960, 214; Barton, Pradhan, Sternhell, and Templeton *J.*, 1961, 255.
[4] Rigby, *J.*, 1951, 793.
[5] Bottomley, Cole, and White, *J.*, 1955, 2624.
[6] Djerassi, *J. Org. Chem.*, 1961, **26**, 1192.

(complex spin–spin coupling, $CO \cdot CH_2 \cdot CH_2$), $\delta = 1 \cdot 00$ (three saturated C-Me), and $\delta = 0 \cdot 90$ (one saturated C-Me).

Stachenone absorbed 1 mol. of hydrogen catalytically. The saturated ketone obtained gave no colour with tetranitromethane, and in its infrared spectrum showed no double-bond absorption. Titration of stachenone with perbenzoic acid confirmed the presence of a single double bond. Stachenone is thus tetracyclic.

Further information was obtained by dehydrogenation. Stachenone was treated with methylmagnesium iodide, and dehydrogenation of the resulting alcohol (VI) afforded, in poor yield, 1,2,7-trimethylphenanthrene (V) as the only characterizable product. When the seco-dicarboxylic acid (XI), obtained by opening the double bond of the alcohol (VI) with periodate–permanganate,[7] was dehydrogenated, 1,2,7-trimethylphenanthrene was obtained in 60% yield. In view of this high yield and the relatively mild conditions used, major alterations of the structure are unlikely and a basic perhydrophenanthrene skeleton is therefore assumed. Also, it follows that the double bond is situated in the fourth ring, which probably forms a bridge as it hinders dehydrogenation, and that one of the methyl groups marks the position of the carbonyl group.

To determine the exact position of the carbonyl group, stachenone was reduced with lithium aluminium hydride to the alcohol (VII); oxidation then led to the corresponding seco-dicarboxylic acid (VIII) and dehydrogenation afforded in 10—15% yield a 1 : 1 mixture of 1,2,7-trimethyl- and 1,7-dimethyl-phenanthrene (pimanthrene) (III). The isolation of pimanthrene indicated that the carbonyl group is in the 3-position of the perhydrophenanthrene skeleton. Stachenone, like the triterpenes with a 3-carbonyl group, gave a positive Zimmerman test.[8] The 1,2,7-trimethylphenanthrene undoubtedly arose by methyl-migration, as is common on dehydrogenation of 3-hydroxy-triterpenes which have a 4,4-dimethyl group.[9] The uncertainties in the high-temperature dehydrogenation were evident when it was found that 2-hydroxy-A-norstachene-2-carboxylic acid (X) (see below) afforded a 1 : 1 mixture of pimanthrene and 1,2,7-trimethylphenanthrene in 5—10% yield.
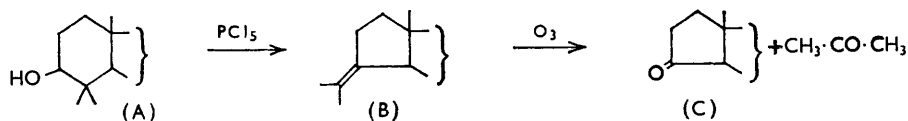
Attempts were made to confirm the presence of the 4,4-dimethyl group in stachenone by the reactions (A) ⟶ (C) involving the retropinacoline rearrangement,[10] but these failed in conditions which gave successful results with lanosterol. This failure could be attributed to the absence of a 4,4-dimethyl group or the axial orientation of the hydroxyl group.[11] However, reduction of stachenone with lithium aluminium hydride or sodium in pentyl alcohol afforded the same alcohol, which was accordingly assumed to have the desired equatorial orientation, because, as pointed out by Barton,[12] reduction of a reactive ketone with either lithium aluminium hydride or metal–alcohol should lead to the thermodynamically more stable equatorial alcohol. Conversely, in its infrared absorption spectrum, stachenol showed a band at 1012 cm.$^{-1}$, like other triterpenoids bearing equatorial 3-hydroxy-groups [13] and a 4,4-dimethyl group.

In its nuclear magnetic resonance spectrum the diosphenol showed peaks at $\delta = 6 \cdot 15$ and $5 \cdot 76$ [$CH=C \cdot (OH)$],[14] doublet peaks ($J = 6$ c./sec.) at $\delta = 5 \cdot 44$ and $5 \cdot 65$ (cis-$CH=CH$),

[7] Lemieux and von Rudloff, *Canad. J. Chem.*, 1955, **33**, 1701; von Rudloff, *ibid.*, 1956, **34**, 1415.
[8] Barton and de Mayo, *J.*, 1954, 901.
[9] Ruzicka, Schellenberg, and Goldberg, *Helv. Chim. Acta*, 1937, **20**, 791.
[10] Dorée, McGhie, and Kurzer, *J.*, 1947, 1467; Barton, Ives, and Thomas, *J.*, 1954, 903.
[11] de Mayo, " The Higher Terpenoids," Interscience Pub., Inc., New York, 1959, p. 78.
[12] Barton, *J.*, 1953, 1027.
[13] Allsop, Cole, White, and Willix, *J.*, 1956, 4868.
[14] Noller, Melera, Gut, Shoolery, and Johnson, *Tetrahedron Letters*, 1960, No. 15, 15.

peaks at $\delta = 1\cdot17$ (saturated *C*-Me), $1\cdot07$ (saturated *C*-Me), and $1\cdot02$ (two saturated *C*-Me). Peaks corresponding to protons adjacent to the carbonyl group were absent. Also, the proton at C-1 gave rise to a single peak ($\delta = 6\cdot15$), as is to be expected if C-10 is fully substituted. It is therefore likely that stachenone has the usual 10-methyl group and a 4,4-dimethyl group. The failure of stachanol to undergo the retropinacoline rearrangement may be due to a " long-range effect." [15]

Our attention was next turned to the size of the ring bearing the double bond. Reaction of stachenone with perbenzoic acid afforded a crystalline epoxide, which, on catalytic reduction, gave a mixture of isomeric diols. Further oxidation of the mixture with chromic acid afforded a mixture of isomeric diketones which in its infrared spectrum showed, in addition to the band at 1704 cm.$^{-1}$, corresponding to the original carbonyl group in the six-membered A-ring, a band of equal intensity at 1737 cm.$^{-1}$, corresponding to a ketone in a five-membered ring.

The seco-acid (VIII) obtained by cleaving the double bond of ring D was converted by means of acetic anhydride into its acetoxy-anhydride, which in its infrared spectrum showed bands at 1792 and 1749 cm.$^{-1}$, in the range of a six-membered ring anhydride.[16] This anhydride, like that derived from the seco-acid (IX) obtained from cafestol,[17] sublimed unchanged at high temperatures.

In its nuclear magnetic resonance spectrum, stachenone showed the presence of four methyl groups. These may be placed at C-4 and C-13 by dehydrogenation studies; and as on the nuclear magnetic resonance evidence it is fully substituted, C-10 probably bears the usual methyl substituent.

Wettstein and Miescher [18] found that the carboxyl groups of the di-acid (IX) differed greatly in their reactivity. Thus, the ester of only one could be saponified. The dimethyl ester (XV), on the other hand, could not be saponified at all, indicating that both carboxyl groups may be attached to quaternary carbon atoms, and this is supported by the fact that, in its nuclear magnetic resonance spectrum, the *cis*-double-bond protons of stachenone show up as a pair of doublet signals without further splitting. The positions of attachment of the five-membered unsaturated ring are thus limited to four possibilities (4,10; 5,9; 10,8; and 8,13). 4,10-Attachment is excluded because the keto-seco-acid obtained by periodate–permanganate oxidation of stachenone did not undergo β-elimination on heating. Instead, the product afforded on esterification with diazomethane the same dimethyl ester (XV) as was obtained by oxidation and esterification of the hydroxy-seco-acid (VIII). 5,9- and 10,8-Attachment are also unlikely because the hydroxy-seco-acid could not be induced to lactonize. 8,13-Attachment, as in (I), is thus most likely. Also, the biogenetic synthesis of this structure could follow along the usual lines [19] through a pimaradiene precursor,[20] as in (D) $\longrightarrow$ (E).
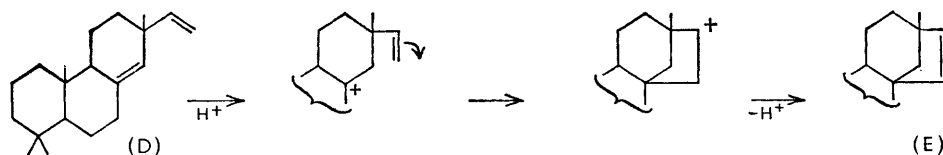
The structure of the ketol (IV) follows from its ready conversion into the diosphenol (II) and the quantitative periodate oxidation of the corresponding diol (XXI). In its nuclear magnetic resonance spectrum the ketol shows doublet peaks ($J = 6$ c./sec.) at $\delta = 5\cdot50$ and $5\cdot58$ (*cis*-CH=CH), a peak at $3\cdot72$ [CH·(OH)], doublet peaks ($J = 13$ c./sec.)

[15] Barton and Morrison in " Progress in the Chemistry of Organic Natural Products," Springer-Verlag, Vienna, 1961, p. 217.
[16] Mulholland, *J.*, 1958, 2695.
[17] Wettstein, Fritzsche, Hunziker, and Miescher, *Helv. Chim. Acta*, 1941, **24**, 332E.
[18] Wettstein and Miescher, *Helv. Chim. Acta*, 1943, **26**, 631.
[19] Ruzicka, *Experientia*, 1953, **9**, 357.
[20] Wenkert, *Chem. and Ind.*, 1955, 282.

at δ = 2·39 and 1·98 (CO·CH$_2$, *i.e.*, consistent only with the carbonyl in the 2-position), and peaks at δ = 2·21 (OH), 0·69 (two saturated *C*-Me), and 0·64 (two saturated *C*-Me).

The diosphenol, or the ketol in the presence of air, underwent a benzilic acid rearrangement with alkali, affording a crystalline hydroxy-acid (X) which, on reduction, afforded the diol (XII). Oxidation of the diol with periodate gave formaldehyde and A-norstachenone (XIV), the infrared spectrum of which had a band at 1737 cm.$^{-1}$ characteristic of a carbonyl group in a five-membered ring. In its nuclear magnetic resonance spectrum A-norstachenone showed doublet peaks (*J* = 6 c./sec.) at δ = 5·50 and 5·70 (*cis*-CH=CH), doublet peaks (*J* = 14 c./sec.) at δ = 2·30 and 2·80 (CO·CH$_2$), as well as δ = 1·01 (three saturated *C*-Me) and δ = 0·73 (one saturated *C*-Me). The peaks of one of the pair of protons adjacent to the carbonyl group showed a broadening of 1—2 c./sec. apparently due to spin–spin coupling. This could arise if C-10 bears a proton, *i.e.*, if methyl migration took place during the benzilic acid rearrangement, but this is unlikely in view of the work of Chaudhry, Halsall, and Jones.[21] Also the coupling constant is smaller than would be expected for a C-10 proton. Alternatively, secondary splitting could arise by four-bonded coupling of the axial C-1 proton with the axial proton at C-5, or the proton at C-9, if this has the axial configuration. The ketol (IV) has also a pair of protons adjacent to the 2-carbonyl group, and here, too, one of the protons shows slight coupling which must arise by four-bonded coupling, since, in this case, C-10 is known from nuclear magnetic resonance measurements with the corresponding diosphenol to be fully substituted.

An attempt was made to confirm the presence of a 10-substituent in A-norstachenone (XIV) by oxidizing it to the diketone (XVII) which would not be expected to be able to enolize, or by preparing A-norstachenone by another route in which migration of the methyl group is precluded. On autoxidation, in t-butyl alcohol and in the presence of potassium t-butoxide, A-norstachenone absorbed 1 mol. of oxygen and afforded a seco-aldehydo-acid (XVIII). This acid, on hydrogenation of the double bond, was identical

(XVII)   (XVIII)   (XIX)   (XX)

(XXI)   (XXII)   (XXIII)   (XXIV)

(XXV)   (XXVI)   (XXVII)   (XXVIII)
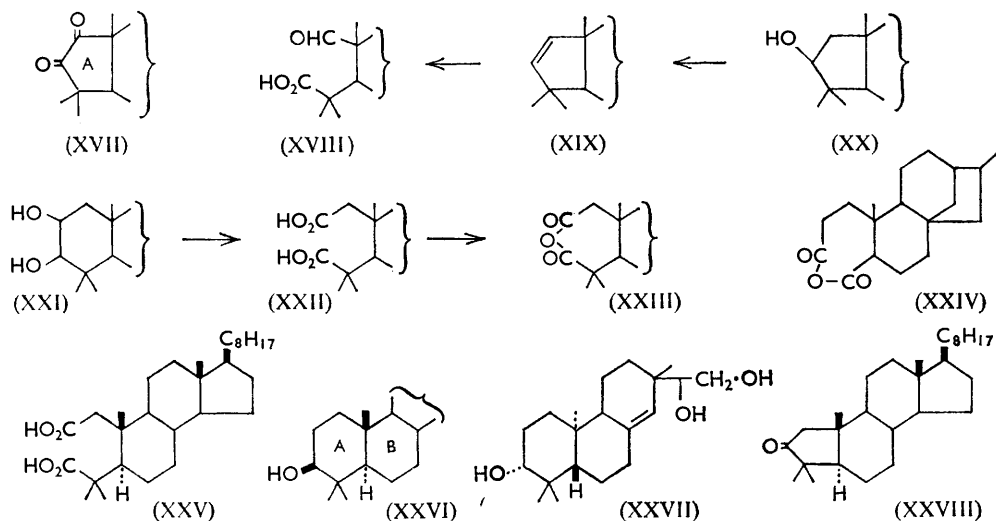
with the acid prepared by reducing dihydro-A-norstachenone with lithium aluminium hydride to the alcohol (XX), dehydrating this with potassium hydrogen sulphate to the hydrocarbon (XIX), and following this by periodate–permanganate oxidation. The hydrocarbon (XIX) showed a strong infrared band at 760 cm.$^{-1}$ characteristic of the expected *cis*-cyclopentene double bond. In its nuclear magnetic resonance spectrum the hydrocarbon showed doublet peaks (*J* = 6 c./sec.) at δ = 4·55 and 4·09 (*cis*-CH=CH). The peak due to the C-1 proton did not show any spin-spin coupling. However, even

[21] Chaudhry, Halsall, and Jones, *J.*, 1961, 2727.

if C-10 bears a proton, splitting may not arise because the dihedral angle between the 1- and the 10-substituent bonds is expected, from models, to approach 90°. The seco-aldehyde (XVIII) in its nuclear magnetic resonance spectrum had an aldehyde signal at $\delta = 9 \cdot 20$ which showed no spin–spin coupling. Position 10 of A-norstachenone is thus substituted and probably bears the usual methyl group. A-Norstachanone failed to react with selenium dioxide under mild conditions, indicating again that position 1 is sterically hindered. More drastic conditions afforded selenium-containing products.

Oxidation of stachanediol (XXI) with periodate–permanganate afforded the seco-acid (XXII) which was readily converted into the anhydride (XXIII), which had $\nu_{max.}$ 1792 and 1749 cm.$^{-1}$. The similar anhydride (XXIV) derived from cafestol showed bands at 1808 and 1745 cm.$^{-1}$. However, unlike this anhydride, or the anhydride obtained from the seco-acid (XXV),[22] our anhydride was recovered unchanged after attempted pyrolysis.

The configuration of the A/B rings of stachenone has been derived from the evidence to follow. Most natural triterpenes which have the 5α,10β-configuration (XXVI) have molecular-rotation differences between their 3-equatorial acetates and alcohols which are positive.[23] Darutigenol (XXVII), with the enantiomorphic configuration,[24] has a negative rotation difference of −90°. For stachenol and stachanol the differences are −42° and −28°, respectively. They can thus be expected to have the " unnatural " configuration like several other unusual sesqui- and di-terpenes.[25]

Confirmation of a 5β,10α-configuration was obtained by comparing the molecular rotation differences of A-norstachenone and A-norstachenol (−360°) with the large but positive rotation differences of 5α,10β-A-norsteroids and triterpenes.[26] Also, the optical rotatory dispersion curve of A-norstachenone ($[\alpha]M$, $\lambda_{max.}$ 320 $= −13\cdot3 \times 10^{-3}$) is closely similar to that of 3,3-dimethyl-A-nor-5α-cholestan-2-one (XXVIII) ($[\alpha]M$, $\lambda_{max.}$ 320 $= +11\cdot5 \times 10^{-3}$) but opposite in sign.

Stachanone has unexpectedly a negative Cotton effect. Thus, comparisons in this series must be made with caution, as steric effects may play a role in determining the sign of the Cotton effect. The curve of 4,4-dimethyl-steroids and similar compounds is in any case anomalous.[27]
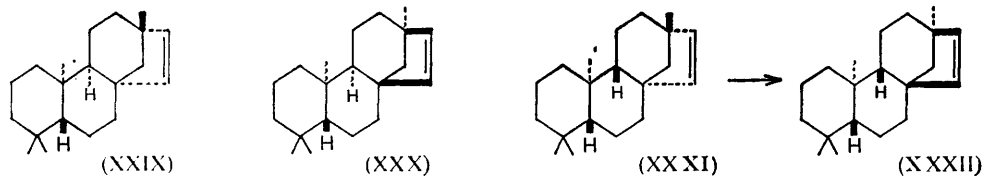
(XXIX)   (XXX)   (XXXI)   (XXXII)

With the A/B-ring configuration established, four enantiomeric structures (XXIX-XXX, XXXI, and XXXII) are possible for stachenone. Of these, (XXX) with a *syn*-backbone can be expected to have considerable steric interaction between the protons at C-1 and C-11, and would be in accord with the steric hindrance of C-1 protons found in the A-nor-series. The same configuration has been considered for cafestol.[25]

EXPERIMENTAL

Infrared spectra were measured with a Perkin–Elmer model 21 double-beam instrument, unless otherwise stated (as PE 221 and PE Infracord, etc.) $[\alpha]_D$ refer to CHCl$_3$ solutions, and ultraviolet absorption spectra to EtOH solutions.

Extraction of the Wood.—Shavings of the heartwood were extracted with boiling acetone. The solvent was distilled off *in vacuo*. The yield of the resin was 12—14%.

[22] Djerassi, Wilfred, Visco, and Lemin, *J. Org. Chem.*, 1953, **18**, 1449.
[23] Barton, *J.*, 1945, 813.
[24] Pudles, Diara, and Lederer, *Bull. Soc. chim. France*, 1959, 693.
[25] Djerassi, Cais, and Mitscher, *J. Amer. Chem. Soc.*, 1959, **81**, 2394.
[26] Klyne, *J.*, 1952, 2917.
[27] Djerassi, " Optical Rotatory Dispersion," McGraw-Hill, New York, 1960, p. 90.

Isolation of the Resin Constituents by Counter-current Distribution.—The resin (455 g.) was dissolved in hexane (1·5 l.) and extracted ten times with a solution of potassium hydroxide (6 g.) in 1 : 1 aqueous ethanol (1·5 l.). The 10 aqueous fractions were extracted four times each with hexane, and the five hexane fractions separately evaporated. Fractions 1 and 2 provided a ketone–ketol mixture (90 g.); fractions 3—5 provided mainly a diosphenol (79 g.). The aqueous layers were acidified with hydrochloric acid to pH 6 and extracted, in turn, three times with hexane. Those hexane extracts were combined and afforded uninvestigated enolizable substances (56 g.). Dilution of the aqueous layers with water (200 ml.) and two more extractions with hexane afforded uninvestigated acidic material (80 g.).

3-Hydroxystach-15-en-2-one (IV).—Fractions 1 and 2 in hexane were cooled to 0° and the crystals filtered off (25 g.). Recrystallization from hexane afforded *3-hydroxystach-15-en-2-one* as needles, m. p. 129°, $[\alpha]_D$ +30° (c 3·3), $\nu_{max.}$ (in CS_2) 3466, 1712, and 739 cm.$^{-1}$ $\lambda_{max.}$ 203 (ε 7550), 285 mμ (ε 41) (Found: C, 79·4; H, 9·8. $C_{20}H_{30}O_2$ requires C, 79·4; H, 10·0%).

Stach-15-en-3-one (I).—The mother-liquors of fractions 1 and 2 (70 g. of solid) were chromatographed on alumina (activated at 110° for 15 hr., 0·5% of water added). Elution with hexane afforded a ketone (16 g.), which was rechromatographed and recrystallized from hexane, to give *stach-15-en-3-one*, as needles, m. p. 35—36·5°, $[\alpha]_D$ +22° (c 5·2), R.D. (c 0·37 in $CHCl_3$) $[\alpha]_{589}$ +29°, $[\alpha]_{325}$ +228° $\nu_{max.}$ (in CS_2, PE 221) 1706, 1381, 1363, and 749 cm.$^{-1}$, $\lambda_{max.}$ 285 mμ (ε 49) (Found: C, 84·1; H, 10·7. $C_{20}H_{30}O$ requires C, 83·9; H, 10·6%). The 2,4-*dinitrophenylhydrazone* (formed in ethanol–sulphuric acid) recrystallized from ethanol as orange needles, m. p. 194—196° (Found: C, 66·7; H, 7·3. $C_{26}H_{34}N_4O_4$ requires C, 66·9; H, 7·4%). On hydrogenation over palladised calcium carbonate stachenone absorbed 1 mol. of hydrogen, giving *stachan-3-one* as needles (from hexane), m. p. 62—64°, $[\alpha]_D$ −58° (c 2·6), $[\alpha]_{589}$ −55°, $[\alpha]_{310}$ −1323° (both c 0·03, in chloroform), $\nu_{max.}$ (in CS_2, PE Infracord) 1704 and 1385 cm.$^{-1}$ (Found: C, 83·3; H, 11·2. $C_{20}H_{32}O$ requires C, 83·3; H, 11·2%).

2-Hydroxystacha-1,15-dien-3-one (II).—Fractions 3—5 (79 g.) were dissolved in hexane (300 ml.) and extracted five times with a solution of potassium hydroxide (1 g.) in 2 : 3 aqueous ethanol (300 ml.). The five aqueous layers were each extracted with the same 5 batches of hexane (300 ml.). The first three hexane extracts were combined, evaporated to ~50 ml., and cooled to 0°, and the crystals were filtered off (15 g.). Recrystallization from hexane afforded *2-hydroxystacha-1,15-dien-3-one* as prisms, m. p. 132°, $[\alpha]_D$ +49° ± 3° (c 3·2), $\nu_{max.}$ (in CS_2) 3420, 1670, 1648, 1405, 1379, 1362, and 750 cm.$^{-1}$ (Found: C, 80·1; H, 9·6. $C_{20}H_{28}O_2$ requires C, 80·0; H, 9·4%). A neutral solution in ethanol had $\lambda_{max.}$ 270 mμ (ε 10,000), and a solution in alkaline ethanol (0·02N-KOH) had $\lambda_{max.}$ 315 mμ (ε 6250).

Reduction of 3-Hydroxystach-15-en-2-one.—The ketol (IV) (500 mg.) in ether (50 ml.) was added to a suspension of lithium aluminium hydride (600 mg.) in ether (50 ml.). The mixture was refluxed with stirring for 1 hr., then cooled, and 10% sulphuric acid (50 ml.) was added. Extraction with ether afforded *stach-15-ene-2,3-diol* (XXI) (480 mg.), which recrystallized from methanol as needles, m. p. 181—182°, $[\alpha]_D$ +12° (c 3·1), $\nu_{max.}$ (in CS_2) 3539 and 3391 cm.$^{-1}$ (Found: C, 78·9; H, 10·7. $C_{20}H_{32}O_2$ requires C, 78·9; H, 10·6%). On catalytic hydrogenation as above the diol absorbed 1 mol. of hydrogen and afforded *stachane-2,3-diol* as needles (from ethanol), m. p. 200—205°, $[\alpha]_D$ −32° (c 3·1) (Found: C, 78·5; H, 11·2. $C_{20}H_{34}O_2$ requires C, 78·4; H, 11·2%).

Oxidation of 3-Hydroxystach-15-en-2-one.—To the ketol (IV) (411 mg.) in acetic acid (5 ml.) was added freshly prepared bismuth oxide (430 mg.).[4] The mixture was heated on a water-bath for 45 min., cooled, poured into water, and extracted with hexane. The product (483 mg.), recrystallized from hexane, had m. p. 132° alone or mixed with 2-hydroxystacha-1,15-dien-3-one.

Rearrangement of 2-Hydroxystacha-1,15-dien-3-one.—The diosphenol (II) (518 mg.) was refluxed with potassium hydroxide (4 g.) in ethanol (50 ml.) for 6 hr. Part of the ethanol was removed under reduced pressure and the residue diluted with water, acidified with hydrochloric acid, and extracted with ether. The ether solution was extracted with dilute sodium hydrogen carbonate solution. The aqueous extract was acidified with hydrochloric acid and extracted with ether, which removed material (480 mg.) that recrystallized from ethanol to give *2-hydroxy-A-norstach-15-ene-2-carboxylic acid* (X) as needles, m. p. 242—243°, $[\alpha]_D$ +8° (c 1·5 in EtOH), $\nu_{max.}$ (in KBr, PE Infracord) 3731, 1733, and 746 cm.$^{-1}$, $\lambda_{infl.}$ 265 mμ (ε 15) (Found: C, 75·1; H, 9·3. $C_{20}H_{30}O_3$ requires C, 75·4; H, 9·5%). Catalytic hydrogenation as above afforded *2-hydroxy-A-norstachane-2-carboxylic acid* as needles (from ethanol), m. p. 252—254°, $[\alpha]_D$ −23° (c 1·2 in EtOH) (Found: C, 74·8; H, 10·0. $C_{20}H_{32}O_3$ requires C, 75·0; H, 10·1%).

Rearrangement of 3-Hydroxystach-15-en-2-one.—The ketol (IV) (75 mg.) was refluxed with

4052 *Baarschers* et al.: *The Structure of Some Diterpenes from*

potassium hydroxide (0·6 g.) in ethanol (10 ml.) for 6 hr. The mixture was worked up as for the diosphenol above, and the product (43 mg.), on recrystallization from ethanol, afforded the hydroxy-acid, m. p. 241—243°, mixed m. p. with 2-hydroxy-A-norstach-15-ene-2-carboxylic acid 240—242°.

Oxidation of Stach-15-en-3-one with Selenium Dioxide.—To the ketone (I) (351 mg.) in ethanol (6 ml.) was added a solution of selenium dioxide (2·5 g.) in water (1·5 ml.) and ethanol (6 ml.). The mixture was refluxed for 15 min., cooled, filtered, and evaporated, and the residue was extracted with hexane. The hexane solution was evaporated to 50 ml. and extracted with potassium hydroxide (0·2 g.) in 3 : 2 aqueous ethanol (5 × 50 ml.). The aqueous layers were acidified with hydrochloric acid and extracted with ether. The residue (70 mg.) from the ether, when crystallized from hexane, had m. p. 128—129° alone or mixed with 2-hydroxystacha-1,15-dien-3-one.

Autoxidation of Stach-15-en-3-one in the Presence of Potassium t-Butoxide.—The ketone (I) (567 mg.) in t-butyl-alcoholic 0·35N-potassium t-butoxide solution (2 ml.) was shaken in oxygen (atm. pressure) for 1 hr. The solidified mixture was dissolved in 2 : 3 aqueous ethanol (100 ml.) and extracted with hexane. The aqueous layer was acidified with hydrochloric acid and extracted with hexane and the residue (460 mg.) from this extract recrystallized five times from hexane; it then had m. p. 128—129·5° alone or mixed with 2-hydroxystacha-1,15-dien-3-one.

Reduction of Stach-15-en-3-one with Lithium Aluminium Hydride.—Stachenone (4·14 g.) in ether (60 ml.) was added to a suspension of lithium aluminium hydride (6·68 g.) in ether (70 ml.) and refluxed with stirring for 1 hr., cooled, and treated with 10% sulphuric acid (100 ml.). Extraction with ether afforded *stach-15-en-3-ol* (VII) (4·02 g.), which recrystallized from methanol as needles, m. p. 164°, $[\alpha]_D$ +28° (*c* 6·2), $\nu_{max.}$ (in CS_2) 3470, 1385, 1364, 1041, 1012, and 749 cm.$^{-1}$ (Found: C, 83·5; H, 11·2. $C_{20}H_{32}O$ requires C, 83·3; H, 11·2%). On catalytic hydrogenation as above the alcohol absorbed 1 mol. of hydrogen, to give *stachan-3-ol*, needles (from methanol), m. p. 158—159°, $[\alpha]_D$ −4° (*c* 5·1), $\nu_{max.}$ (in CS_2) 3571, 1381, 1365, 1041, and 1016 cm.$^{-1}$ (Found: C, 82·6; H, 11·9. $C_{20}H_{34}O$ requires C, 82·7; H, 11·8%).

3-Acetoxystach-15-ene and 3-Acetoxystachane.—Stachenol (VII) (100 mg.) was refluxed with acetic anhydride (20 ml.) for 2 hr., the excess of anhydride removed *in vacuo*, and the residue, on crystallization from methanol, afforded *3-acetoxystach-15-ene* as plates, m. p. 117·5—119·5°, $[\alpha]_D$ +12° (*c* 5·3), $\nu_{max.}$ (in CS_2) 1728, 1243, and 751 cm.$^{-1}$ (Found: C, 79·7; H, 10·4. $C_{22}H_{34}O_2$ requires C, 80·0; H, 10·4%). On catalytic hydrogenation as above the acetate absorbed 1 mol. of hydrogen and afforded *3-acetoxystachane*, as plates (from methanol), m. p. 146—147°, $[\alpha]_D$ −12° (*c* 6·9), $\nu_{max.}$ (in CS_2, PE Infracord) 1733 and 1245 cm.$^{-1}$ (Found: C, 79·6; H, 11·1. $C_{22}H_{36}O_2$ requires C, 79·5; H, 10·9%).

Reduction of Stach-15-en-3-one with Sodium in n-Pentyl Alcohol.—To a boiling solution of stachenone (516 mg.) in n-pentyl alcohol (40 ml.; distilled over sodium) was added sodium (1·75 g.) in small portions. The mixture, after refluxing until all the metal dissolved, was steam-distilled, and the aqueous residue extracted with ether that removed stach-15-en-3-ol (495 mg.), needles, m. p. and mixed m. p. 162—163° (from methanol).

Reaction of Stach-15-en-3-one with Methylmagnesium Iodide, and Dehydrogenation of the Product.—Stachenone (2·57 g.) in ether (100 ml.) was added to the Grignard reagent from methyl iodide (3 g.) and magnesium in ether (50 ml.). The mixture was refluxed for 1 hr., then cooled, and 10% sulphuric acid (100 ml.) was added. Extraction with ether afforded a slightly yellow product, which was heated *in vacuo* with potassium hydrogen sulphate (2·5 g.) at 160—170° for 1 hr. After cooling, the mixture was extracted with ether and the extracted product (2·28 g.) was chromatographed on alumina. Elution with hexane afforded a colourless liquid (1·22 g.), which was heated with selenium (2 g.) at 300—310° (vac.) for 18 hr. The product was extracted with ether and afforded a residue which was partly soluble in ethanol. The soluble part (825 mg.), with picric acid (1 g.) in ethanol, afforded a picrate, plates (from ethanol), m. p. 146—148°. This was decomposed by chromatography on alumina. Elution with benzene gave a hydrocarbon that, recrystallized five times from ethanol, afforded 1,2,7-trimethylphenanthrene as leaflets, m. p. 122—123°, $\lambda_{max.}$ 353, 337, 322, 301, 290, 282, and 259 mμ (ε 451, 594, 473, 1415, 1351, 1755, and 879,300) (Found: C, 92·3; H, 7·6. Calc. for $C_{17}H_{16}$: C, 92·7; H, 7·3%). The styphnate recrystallized from ethanol as needles, m. p. 169°. The hydrocarbon chromatographed in the gas phase (Pye Argon Chromatograph, 5% of silicone Dow 550 on Chromosorb, 225°), as did an authentic specimen.

Oxidation of 3-Methylstach-15-en-3-ol.—The alcohol (VI) (984 mg.) (prepared from stachenone as above), potassium carbonate (1·6 g.), sodium metaperiodate (6·6 g.), 0·01M-aqueous potassium permanganate (7·7 ml.), and 7 : 3 aqueous t-butyl alcohol (800 ml.) were shaken at room temperature for 20 hr. Solid sodium metabisulphite was added until the solution was slightly yellow, and then the pH was adjusted to ~8 with solid potassium hydroxide. The butyl alcohol was removed *in vacuo*, and the remaining aqueous solution acidified with hydrochloric acid and extracted with ether. The ether solution was extracted with aqueous potassium hydroxide solution, and the alkaline layer acidified with hydrochloric acid and again extracted with ether. The residue (1·05 g.) recovered from ether as a white foam, crystallized from methanol, afforded 3-*hydroxy-3-methyl*-15,16-*secostachane*-15,16-*dioic acid* (XI) as needles, m. p. 211—216° (Found: C, 69·1; H, 9·5. $C_{21}H_{34}O_5$ requires C, 68·8; H, 9·4%).

Dehydrogenation of the Hydroxy-diacid (XI).—The diacid (730 mg.) was heated with potassium hydrogen sulphate (1 g.) *in vacuo* for 1 hr., then extracted with ether, and the residue (610 mg.) therefrom was heated with selenium (800 mg.) at 300—310° (vac.) for 14 hr. The product (420 mg.) was extracted with ether and crystallized from ethanol as leaflets, m. p. 112—114°. The picrate, prepared with picric acid (400 mg.), separated from ethanol as red plates, m. p. 148—149°, which on chromatography on alumina, elution with benzene, and recrystallization from ethanol, gave 1,2,7-trimethylphenanthrene as plates, m. p. 121—122° (mixed m. p. 121—123°).

*Reduction of 2-Hydroxy-*A-*norstach-15-ene-2-carboxylic Acid* (X).—The acid (2·48 g.) was refluxed with a suspension of lithium aluminium hydride (3 g.) in ether (150 ml.) for 1 hr. 10% Sulphuric acid (100 ml.) was added and the mixture extracted with ether. The residue (2·38 g.), on crystallization from ethanol, afforded 2-*hydroxymethyl*-A-*norstach-15-en-2-ol* (XII) as needles, m. p. 160—161°, $[\alpha]_D$ +17° (c 7·8) (Found: C, 79·2; H, 10·7. $C_{20}H_{32}O_2$ requires C, 78·9; H, 10·6%).

Oxidation of the Diol (XII) *with Periodic Acid.*—The diol (619 mg.) in 3 : 7 aqueous ethanol (80 ml.) was mixed with 0·5M-aqueous periodic acid (10 ml.) and left overnight; crystals (477 mg.) were filtered off and recrystallized from 3 : 7 aqueous ethanol, giving A-*norstach-15-en-2-one* (XIV) as prisms, m. p. 83—84°, $[\alpha]_D$ −100° (c 3·5), R.D. (c 0·11 in MeOH) $[\alpha]_{589}$ −16°, $[\alpha]_{319}$ −3682° (the maximum did not decrease on addition of acid), $\nu_{max.}$ (in CCl_4, Beckman 7) 1738, 1386, 1362, and 746 cm.$^{-1}$, $\lambda_{max.}$ 295 mμ (ε 40) (Found: C, 83·9; H, 10·5. $C_{19}H_{28}O$ requires C, 83·8; H, 10·4%). The 2,4-*dinitrophenylhydrazone* (formed in ethanol–sulphuric acid) recrystallized from ethanol as orange needles, m. p. 195—196° (Found: C, 66·2; H, 7·2. $C_{25}H_{32}N_4O_4$ requires C, 66·4; H, 7·1%). Formaldehyde was recovered from the filtrate as its dimedone complex, m. p. and mixed m. p. 190—191°. On catalytic hydrogenation (1 mol.) as above the norketone (XIV) afforded A-*norstachan-2-one* as prisms (from 3 : 7 aqueous ethanol), m. p. 84—85·5°, $[\alpha]_D$ −137° (c 3·2), R.D. (c 0·13 in $CHCl_3$), $[\alpha]_{589}$ −148°, $[\alpha]_{320}$ −4792° $\nu_{max.}$ (in CCl_4), Beckman 7) 1738 and 1386 cm.$^{-1}$, $\lambda_{max.}$ 300 mμ (ε 27) (Found: C, 83·1; H, 11·1. $C_{19}H_{30}O$ requires C, 83·2; H, 11·0%).

Reduction of A-*Norstach-15-en-2-one.*—The ketone (2·90 g.) was reduced with lithium aluminium hydride (3 g.) in ether (100 ml.) as for reduction of the ketol (IV) above. The product (2·64 g.) recrystallized from hexane, affording stereoisomeric A-norstach-15-en-2-ols (XX) as needles, m. p. 93·6—96·6°, $[\alpha]_D$ +30° (c 1·0) (Found: C, 82·7; H, 11·1. Calc. for $C_{19}H_{30}O$: C, 83·2; H, 11·0%). On catalytic hydrogenation (1 mol.) as above the alcohols gave stereoisomeric A-norstachan-2-ols as needles (from hexane), m. p. 95—104°, $[\alpha]_D$ +12° (c 2·1) (Found: C, 82·8; H, 11·7. Calc. for $C_{19}H_{32}O$: C, 82·5; H, 11·7%).

Dehydration of the A-*Norstachan-2-ols.*—The alcohols (2·24 g.) and potassium hydrogen sulphate (2·5 g.) were heated *in vacuo* at 160—170° for 1 hr. Extraction with ether afforded a product (1·65 g.) which was distilled *in vacuo*. The main fraction (805 mg.; b. p. 115—135°/0·1 mm.) was chromatographed on alumina. Elution with hexane afforded A-*norstach-1-ene* (XIX) as a colourless liquid, $\nu_{max.}$ (in CS_2, PE Infracord) 760 cm.$^{-1}$ (Found: C, 87·9; H, 11·6. $C_{19}H_{30}$ requires C, 88·3; H, 11·7%).

Oxidation of A-*Norstach-1-ene.*—The hydrocarbon (800 mg.), potassium carbonate (1·37 g.), sodium periodate (5·55 g.), 0·01M-aqueous potassium permanganate (6·65 ml.), and 7 : 3 aqueous t-butyl alcohol (822 ml.) were shaken at room temperature for 20 hr. The product was recovered as for the hydroxy-acid (XI) above, and recrystallized from aqueous ethanol to give 1-*oxo*-1,2-*seco*-A-*norstachane-2-carboxylic acid* (XVIII) as needles, m. p. 180·5—181·5°, $[\alpha]_D$ −6°

± 2° (*c* 2·5), $\nu_{max.}$ (in CS_2, PE Infracord) 3322, 1736, and 1695 cm.$^{-1}$, $\lambda_{infl.}$ 275 mμ (ε 48) (Found: C, 74·2; H, 9·8. $C_{19}H_{30}O_3$ requires C, 74·5; H, 9·9%). Esterification with diazomethane afforded the *methyl ester*, prisms (from hexane), m. p. 119·5—120·5°, $[\alpha]_D$ +66° (*c* 3·7), $\nu_{max.}$ (in CS_2, PE Infracord) 1727, shoulder at 1733 cm.$^{-1}$ (Found: C, 75·0; H, 10·0. $C_{20}H_{32}O_3$ requires C, 75·0; H, 10·1%).

Autoxidation of A-*Norstach*-15-*en*-2-*one*.—The ketone (XIV) (570 mg.) in t-butyl-alcoholic 0·35N-potassium t-butoxide (5 ml.) was shaken in oxygen. The mixture solidified after 7 hr. and was then dissolved in 2 : 3 aqueous ethanol (50 ml.) and extracted with hexane. The aqueous layer was acidified with hydrochloric acid and extracted with hexane. The crystalline residue (235 mg.), recrystallized from aqueous ethanol, had m. p. 205—207°. On catalytic hydrogenation (1 mol.) as above the substance gave the seco-aldehydo-acid (XVIII), m. p. and mixed m. p. 178—181°, with the previous infrared spectrum.

*Dehydrogenation of 2-Hydroxy-*A-*norstach-*15-*ene-*2-*carboxylic Acid.*—The acid (X) (3·96 g.) was heated with selenium (4·35 g.) at 290—310° (vac.) for 15 hr., then extracted with pentane, and the residue (2·32 g.) from the pentane was distilled *in vacuo*. To the main fraction (800 mg.; b. p. 150—200°/0·8 mm.) was added picric acid (1 g.) in ethanol. The picrate was recrystallized once from ethanol and decomposed by chromatography on alumina. Elution with benzene afforded a mixture of hydrocarbons, which was subjected to reversed-phase partition chromatography.[28] It was resolved into two fractions. Fraction I (60% of the mixture), when recrystallized from ethanol, had m. p. 80—82° (mixed m. p. with 1,7-dimethylphenanthrene 81—84°); the derived picrate had m. p. and mixed m. p. 133°. Fraction II likewise afforded pure 1,2,7-trimethylphenanthrene (V), m. p. and mixed m. p. 118—119° (picrate, m. p. and mixed m. p. 148°).

Attempt to Prepare the A-*Norketone* (XIV) *through the Ring-*A *Anhydride.*—The dihydro-diol (XXI) (470 mg.), potassium carbonate (750 mg.), sodium metaperiodate (3·05 g.), 0·01M-aqueous potassium permanganate (3·7 ml.), and 7 : 3 aqueous t-butyl alcohol (450 ml.) were shaken at room temperature for 20 hr. The product (357 mg.), recovered as for the hydroxy-diacid (XI) above, recrystallized from ethyl acetate to give 2,3-*secostachane*-2,3-*dioic acid* (XXII) as needles, m. p. 212°, $[\alpha]_D$ −25° (*c* 7·4), $\nu_{max.}$ (in $CHCl_3$, PE Infracord) 1718 cm.$^{-1}$ (Found: C, 71·2; H, 9·5. $C_{20}H_{32}O_4$ requires C, 71·4; H, 9·6%). This acid (372 mg.) was refluxed with acetic anhydride (10 ml.) for 1 hr. The excess of acetic anhydride was removed *in vacuo* and the residue recrystallized from hexane (250 mg.), affording the *anhydride* (XXIII) as needles, m. p. 123—124°, $\nu_{max.}$ (in $CHCl_3$) 1792 and 1749 cm.$^{-1}$ (Found: C, 75·6; H, 9·5. $C_{20}H_{30}O_3$ requires C, 75·4; H, 9·5%). The anhydride was pyrolyzed *in vacuo* at 190° for 1 hr., but was unchanged (m. p. and mixed m. p. 121—122°).

*Oxidation of Stach-*15-*en-*3-*one with Potassium Permanganate and Sodium Periodate.*—Stachenone (878 mg.), potassium carbonate (1·31 g.), sodium metaperiodate (5·40 g.), 0·01M-aqueous potassium permanganate (6·4 ml.), and 7 : 3 aqueous t-butyl alcohol (790 ml.) were shaken at room temperature for 20 hr. The product (848 mg.) was recovered as for the hydroxy-acid (XI) above, and afforded 3-*oxo-*15,16-*secostachane-*15,16-*dioic acid* (XIII) as a white foam. With diazomethane this afforded its *dimethyl ester* (XV), prisms (from hexane), m. p. 119·5—121°, R.D. (*c* 0·435 in $CHCl_3$) $[\alpha]_{589}$ −22°, $[\alpha]_{310}$ −678°, $\nu_{max.}$ (in CS_2, PE Infracord) 1730 and 1709 cm.$^{-1}$ (Found: C, 69·8; H, 9·1. $C_{22}H_{34}O_5$ requires C, 69·8; H, 9·1%). The ester (28 mg.) was saponified for 7 hr. with potassium hydroxide (30 mg.) in 1 : 4 aqueous ethanol (5 ml.) but, in comparison with a control experiment, no alkali was consumed, and non-acid material was recovered (27 mg.).

Attempted Decarboxylation of the Keto-dicarboxylic Acid from Stachenone.—The acid (XIII) (245 mg.) was refluxed in methanol (10 ml.) containing concentrated sulphuric acid (2 drops) for 4 hr., then was diluted with water, and extracted with ether. The extract (233 mg.), when treated with diazomethane, gave the keto-dimethyl ester (XV), m. p. 117—119° (from hexane) (mixed m. p. 118—120°).

Oxidation of Stachenol with Potassium Permanganate and Sodium Periodate.—Stachenol (650 mg.), potassium carbonate (1·08 g.), sodium metaperiodate (4·40 g.), 0·01M-aqueous potassium permanganate (5·1 ml.), and 7 : 3 aqueous t-butyl alcohol (500 ml.) were shaken at room temperature for 20 hr. The product (545 mg.), a white foam, recovered as for the hydroxy-acid (XI) above, afforded 3-*hydroxy-*15,16-*secostachane-*15,16-*dioic acid* (VIII) as

[28] Enslin and Rivett. (*a*) *Chem. and Ind.*, 1956, 23; (*b*) *J.*, 1956. 3682.

prisms (from methanol), decomp. from 160° (Found: C, 68·4; H, 9·2. $C_{20}H_{32}O_5$ requires C, 68·2; H, 9·2%). With diazomethane this afforded its *dimethyl ester* (XVI), prisms (from hexane), m. p. 197—198° (Found: C, 69·4; H, 9·5. $C_{22}H_{36}O_5$ requires C, 69·4; H, 9·5%).

Oxidation of the Hydroxy-diester (XVI).—To the ester (101 mg.), in acetone (15 ml.), was added 0·12 ml. of a solution of chromium trioxide (2·67 g. in 2·3 ml. of concentrated sulphuric acid, made up to 10 ml. with water).[29] After 15 min. at 10°, a few drops of methanol were added. The mixture was diluted with water and extracted with ether that removed a keto-ester (72 mg.), prisms (from hexane), m. p. 121—122° (mixed m. p. with dimethyl 3-oxo-15,16-secostachane-15,16-dioate 119—121°).

Dehydrogenation of the Hydroxy-diacid (VIII).—The acid (440 mg.) was heated with selenium (520 mg.) for 15 hr. at 290—310° (vac.). The mixture was extracted with ether and the product (306 mg.) chromatographed on alumina. The main fraction (170 mg.), eluted with hexane, was converted into the picrate. This was recrystallized once from ethanol and decomposed by chromatography on alumina; elution with benzene afforded a crystalline hydrocarbon (50 mg.). A 2% solution of this in hexane was chromatographed in the gas phase [6-ft. column, 170°, 0·75% of silicone polymer SE-30 on " Gaschrom " P (100—140 mesh)], and shown to be identical with a 2% solution of a 1 : 1 mixture of 1,7-dimethylphenanthrene and 1,2,7-trimethyl-phenanthrene.

3-Acetoxy-15,16-secostachane-15,16-*dioic Anhydride*.—The hydroxy-diacid (VIII) (163 mg.) was refluxed with acetic anhydride (10 ml.) for 1 hr. The acetic anhydride was removed *in vacuo* and the residue afforded 3-acetoxy-15,16-*secostachane*-15,16-*dioic anhydride* as needles (from ethyl acetate), m. p. (sealed tube) 308°, $\nu_{max.}$ (in $CHCl_3$) 1792, 1753, 1722, and 1252 cm.$^{-1}$ (Found: C, 70·1; H, 8·6. $C_{22}H_{32}O_5$ requires C, 70·2; H, 8·6%). The anhydride sublimed *in vacuo* at 280° (m. p. and mixed m. p. after sublimation 310°).

15,16-Epoxystachan-3-one.—To stachenone (970 mg.) in chloroform (2 ml.) was added, with cooling, a solution of perbenzoic acid (7·99 ml., 0·067 g./ml. in chloroform). The whole was allowed to come to room temperature overnight. Potassium iodide (1 g.) in water (50 ml.) and glacial acetic acid (5 ml.) were added and the mixture was titrated with 0·01N-sodium thio-sulphate. In comparison with a control 1·15 mol. of perbenzoic acid were consumed. The mixture was then extracted with chloroform, and the chloroform solution dried and evaporated. The residue, in ether, was washed several times with dilute sodium carbonate solution, then evaporated and the ether residue (1·04 g.) was chromatographed on alumina. Elution with hexane afforded 15,16-*epoxystachan-3-one*, needles (from hexane), m. p. 114—114·5°, $\nu_{max.}$ (in CS_2, PE Infracord) 1700 and 852 cm.$^{-1}$ (Found: C, 79·3; H, 9·9. $C_{20}H_{30}O_2$ requires C, 79·4; H, 10·0%).

Reduction of the Epoxide and Oxidation of the Product.—The epoxide (231 mg.) in acetic acid (15 ml.) was hydrogenated (2 mol.) with Adams catalyst. The mixture was filtered, the acetic acid removed *in vacuo*, and the residue (240 mg.), which had no carbonyl absorption in its infrared spectrum, was oxidized in acetone (10 ml.) with chromic acid reagent (0·7 ml.) as for the hydroxy-diester (XVI) above. Methanol was added, and the mixture was poured into water (50 ml.) and extracted with hexane. The extract gave a residue (200 mg.) that, recrystal-lized from hexane, afforded a mixture of stachane-3,15- and -3,16-dione, m. p. not sharp, $\nu_{max.}$ (in CS_2) 1730 and 1700 cm.$^{-1}$ (equal intensity) (Found: C, 79·6; H, 9·9. Calc. for $C_{20}H_{30}O_2$: C, 79·4; H, 10·0%).

NATIONAL CHEMICAL RESEARCH LABORATORY,
    COUNCIL FOR SCIENTIFIC AND INDUSTRIAL RESEARCH,
        PRETORIA, SOUTH AFRICA.
VARIAN ASSOCIATES, PALO ALTO, CALIFORNIA, U.S.A.
    [Present address of D. H. S. H.: ORG. CHEM. DIV., C.S.I.R.O.,
        MELBOURNE, AUSTRALIA.]   [*Received, April 2nd*, 1962.]

[29] Djerassi, Engle, and Bowers, *J. Org. Chem.*, 1956, **21**, 1547.