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STRUCTURE OF TURBICORYN, A NEW GLUCOSIDE FROM *TURBINA CORYMBOSA**

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Abstract—From the seeds of the plant known as Ololiuqui (*Turbina corymbosa*),† a new glucoside, turbicoryn, has been isolated and the structure of its aglucone, turbicorytin, established.[1]

THE seeds of this plant were used in precolombian times in southern Mexico as hallucinogens and the alkaloids have been investigated by Hofmann and Tscherter.[2]

A glucoside, similar to ours isolated by Cook and Keeland,[3] differs in molecular formula and in some constants, but Hofmann‡ has isolated the same glucoside and its molecular formula and constants are in good agreement with ours.

Continuing the investigations on this glucoside, in the light of new degradation products and spectroscopic data, the analysis must be interpreted differently.

With the information now available it is possible to assign the formula $C_{29}H_{50}O_{11}\cdot 1\frac{1}{2}$ H_2O for turbicoryn. Turbicorytin thus corresponds to $C_{23}H_{40}O_6\cdot \frac{1}{2}$ H_2O, this glucoside being formed with one mole of glucose.

Acetylation of turbicoryn with acetic anhydride and pyridine at 92° yields a nona-acetate from which the glucoside is regenerated upon saponification, but if acetylation is carried out at room temperature, an octa-acetate is obtained. Turbicorytin forms the corresponding hexa- or penta-acetates when acetylation is carried out at 92° or at room temperature, respectively. The NMR spectra are in agreement with the analytical data for all four of these acetates. The ease of acetylation of the tertiary hydroxyl group in the glucoside and in the aglucone is probably due to migration of an acetyl group from a hydroxyl on an adjacent carbon atom.[4]

During periodic acid degradation, turbicorytin uses three moles of periodic acid and a ketone (III) is obtained; two moles of formic acid and one of formaldehyde being produced and thus establishing the structure of a polyhydroxylated side chain.

The ketone (III) is unstable and gives high oxygen analysis corresponding to $C_{20}H_{32}O_5$, because of peroxide formation (positive test with KI and starch). The same phenomenon is observed in the analysis of its monoacetate which corresponds to $C_{22}H_{34}O_6$. This ketone gives positive Tollens and Benedict tests and readily loses the

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* F. García Jiménez, D. Sc. *Thesis*. Universidad Nacional Autónoma de Mexico.

† We wish to thank Dr. Faustino Miranda from the Instituto de Biología de la Universidad Nacional Autónoma de Mexico for the botanical classification.

‡ This information was given in a personal communication from Dr. A. Hofmann.

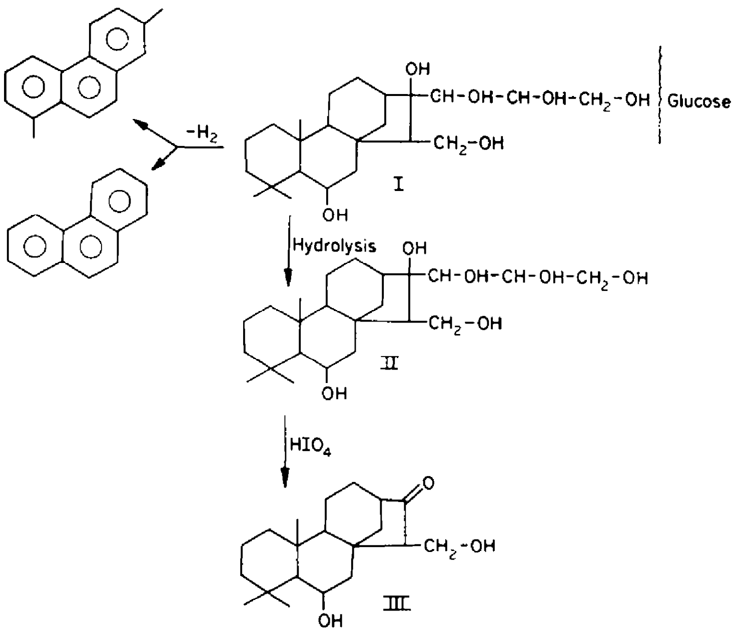
[1] M. C. Perezamador and J. Herrán, *Tetrahedron Letters* No. 7, 30 (1960).

[2] A. Hofmann und H. Tscherter, *Experientia* XVI, 414 (1960).

[3] W. B. Cook and W. E. Keeland, *J. Org. Chem.* **27**, 1061 (1962).

[4a] L. H. Briggs, B. F. Cain, R. C. Cambie and B. R. Davis, *J. Chem. Soc.* 1841 (1962);

[b] H. Hilbert and M. E. Greig, *Canad. J. Res.* **4**, 244 (1931).



elements of formaldehyde under the following conditions: (a) treatment with hydrochloric acid in aqueous methanol, gives a new ketone (IV) differing from III in one methylene and one oxygene; (b) on Tollens oxidation; (c) under conditions for oxime formation, the oxime of ketone (IV) being produced; (d) under conditions for thioketal formation, the thioketal of IV being produced; (e) mass spectrometry; strong peaks at 290, corresponding to ketone (IV) and at 302, corresponding to ketone (III) (M-18, loss of water).

Room temperature acetylation of III gives two acetates whose NMR spectra correspond to a mono- and a di-acetate, respectively. Reduction with lithium aluminum hydride of III gives the triol (VI) $C_{20}H_{34}O_3$, which forms a triacetate, in full agreement with the NMR spectrum. The same triol is obtained when the monoacetate of ketone (III) is reduced with lithium aluminum hydride.

Ketone (IV) has a molecular formula $C_{19}H_{30}O_2$ with a mol. wt. 290, determined by mass spectrometry. It has a carbonyl band at 1740 cm^{-1}, corresponding to a five membered ring ketone. The NMR spectrum shows in the high field zone signals for three methyl groups at 0·87, 0·95 and 1·14 ppm. In addition there are two signals for three protons alpha to the carbonyl group, one a singlet at 1·97 ppm which integrates for two protons and the other, at 2·4 ppm, is a multiplet and integrates for one proton. Two of these protons are exchangeable with deuteurium (NMR and M.S. of the deuterated ketone which gives a molecular peak at 292). The bridgehead proton in the bicyclooctane system does not exchange, in accordance with Bredt's rule. The signal for the OH proton appears at 1·86 ppm and disappears upon addition of deuterated water; there is also a multiplet for *H*—C—OH at 3·94 which integrates for one proton.

On acetylation this ketone gives a product that could not be crystallized but in accordance with the NMR spectrum corresponds to a monoacetate. The ketone (IV) forms a monoxime, $C_{19}H_{31}O_2N$, which on hydrolysis regenerates IV. Reduction with lithium aluminum hydride of IV gives a diol (VII) $C_{19}H_{32}O_2$, which forms a diacetate, $C_{23}H_{36}O_4$, in agreement with the IR and NMR spectra.

Jones oxidation[5] of this diol (VII) gives a diketone (VIII) $C_{19}H_{28}O_2$, identical with the product obtained by direct oxidation of ketone (IV) with the same reagent. This diketone shows carbonyl absorption at 1747 and 1712 cm^{-1}, corresponding to a five and a six membered ring ketone. The NMR spectrum shows six protons alpha to the keto groups, and as expected only five of them are exchangeable by deuterium. This is confirmed in the NMR and mass spectra of the deuterated ketone which has a mol. wt. of 293. Treatment with hydroxylamine hydrochloride gives the corresponding dioxime, which on Wolff-Kishner reduction yields a hydrocarbon (XII).

The oxime of ketone (IV), on Wolff-Kishner reduction, gives the alcohol (IX) $C_{19}H_{32}O$, with a mol. wt. of 276 (M.S.), identical with the product obtained when the thioketal, $C_{21}H_{34}OS_2$, of ketone (IV) is treated with Raney nickel. This alcohol was dehydrated with P_2O_5 to the olefin (XI), with only one vinyl proton giving a multiplet in the NMR. This hydrocarbon (XI) yields the hydrocarbon (XII) on hydrogenation with PtO_2 in acetic acid.

Jones oxidation of alcohol (IX) produces ketone (X), $C_{19}H_{30}O$, mol. wt. of 274 (M.S.). This ketone shows in the IR a maximum at 1725 cm^{-1} corresponding to a six membered ring ketone. The original NMR shows three protons alpha with respect to carbonyl which are exchangeable with deuterium as confirmed by NMR and M.S. (mol. wt. 277) of the deuterated ketone (X). The oxime of X gives, on Wolff-Kishner reduction, the hydrocarbon (XII).

This hydrocarbon (XII) has a molecular formula $C_{19}H_{32}$ and when compared with 17-norphyllocladane* (XIII), they cannot be separated on thin layer chromatography, using silica gel as adsorbent. Their NMR and IR spectra are also very similar.

Dehydrogenation of turbicoryn with selenium gives phenanthrene and 1,7-dimethylphenanthrene which were identified by their UV and IR spectra, m.ps and picrates. In addition, from 1,7-dimethylphenanthrene the trinitrobenzene adduct was prepared.

DISCUSSION

The fundamental nucleus of the glucoside is suggested by the dehydrogenation products; 1,7-dimethylphenanthrene establishes the position of sixteen carbon atoms. By Kuhn-Roth oxidation of the glucoside and of the aglucone, only one C-methyl group was detected and the NMR of the acetates indicate the presence of three; therefore, two are probably *gem* C-methyls. There are two possible positions for these groups, C-4 or C-13. The latter position is excluded because the hydroxyl group in ketone (IV) in accordance with the observed results, can not be placed at any other position. This hydroxyl must have three protons in carbons alpha to the C—OH and has to be near the *gem* methyl group, as later explained.

Furthermore, the comparison of the NMR spectra of hydrocarbon (XII) and 17-norphyllocladane shows two superimposable signals at 0·81 and 0·86 ppm for two methyl groups. The signal for the other methyl group at 0·94 ppm is displaced by 5 c/s to lower field in XII. The IR spectra of these two compounds are identical in the region between 3400 and 5000 cm^{-1} differing only in some bands in the fingerprint

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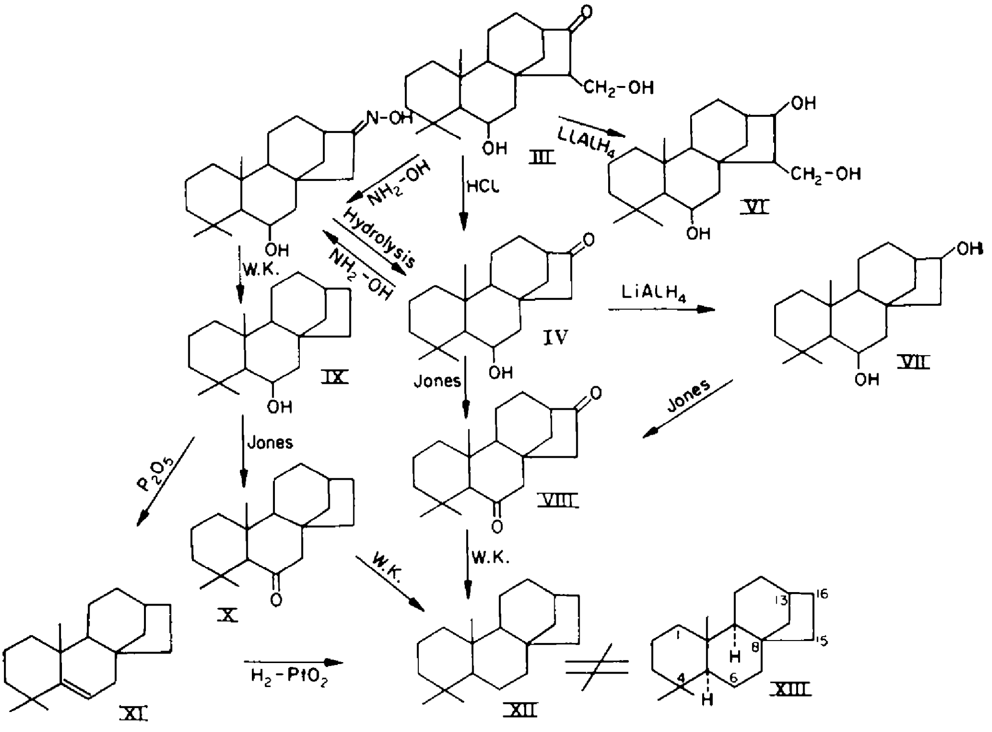
* We wish to thank Dr. L. H. Briggs of the University of Auckland, New Zealand, for the sample of phyllocladene that he kindly sent to us.

[5] A. Bowers, T. G. Hassall, E. R. H. Jones and A. J. Lemin, *J. Chem. Soc.* 2555 (1953).



17 Norphyllocladane

region. The characteristic double band for a *gem* methyl group appears in both compounds at 1380 and 1366 cm^{-1}.

The assignment for the signal of the isolated C-methyl group is based on the observation that, elimination of the carbonyl group in ketone (IV) displaces the position of the C-methyl 5 c/s at 1·14 ppm in ketone (IV) with respect to the same C-methyl group in alcohol (IX.) The positions of the other two methyls, at 0·95 and 0·87 ppm, remains the same.

With the position of the three methyl groups fixed, there are only positions 13–8 left for ring D closure because this ring must be attached to a tertiary and a secondary carbon atom, since ketone (IV) has by NMR three protons alpha to the carbonyl.

The interpretation of the spectra as well as the evidence of the chemical reactions are in keeping with structure III for the ketone obtained by periodic oxidation of turbicorytin.

In the IR spectrum there is a strong wide band corresponding to a primary alcoholic group between 1010 and 1100 cm^{-1}. At 3400 cm^{-1} only one wide band for hydroxyl groups appears; this band shows no modification on dilution, in accordance with intramolecular association. The carbonyl band at 1740 cm^{-1} indicates that ring D is five membered.

The NMR shows three C-methyl groups at 0·90, 0·98 and 1·17 ppm; between 2 and 2·6 ppm a multiplet appears, corresponding to two protons alpha to the carbonyl and one OH; between 3·17 and 5·3 ppm there is a complex multiplet which integrates for four protons, two of the —CH_2OH, one of the H—COH and one of the other OH.

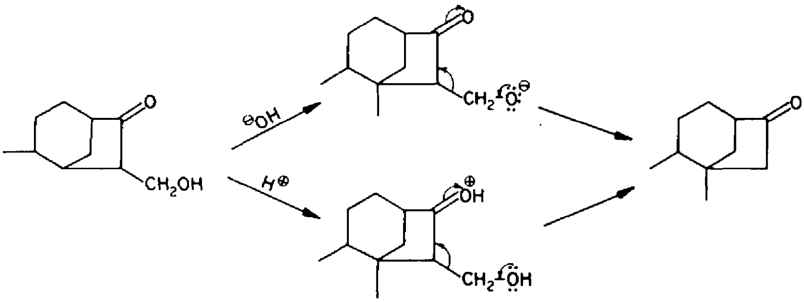
The position of the carbonyl group in ketone (IV), which corresponds to that in ketone (III), is assigned to position 16 because this is the only position in which a five

POSITION OF THE MAIN PEAKS IN THE NMR SPECTRA, SHOWING CHEMICAL SHIFTS

	3 C—CH_3	Hα to C=O
Turbicorytin acetate	0·84; 0·92; 1·03	
Ketone III	0·90; 0·98; 1·17	2·00 (2 H^+; s) 2·44 (1 H^+; m)
Monoacetate III	0·90; 0·96; 1·17	
Diacetate III	0·89; 0·95; 1·15	
Ketone IV	0·87; 0·95; 1·14	1·97 (2 H^+; s) 2·40 (1 H^+; m)
Acetate IV	0·95; 0·95; 1·20	1·88 (2 H^+; s) 2·36 (1 H^+; m)
Diketone VIII	1·20; 0·92; 1·20	2·00 (2 H^+; s) 2·23 (2 H^+; s) 2·40 (1 H^+; m) 2·62 (1 H^+; m)
Alcohol VII	0·88; 0·94; 1·09	
Acetate VII	0·93; 0·93; 1·13	
Thioketal	0·85; 0·92; 1·07	
Alcohol IX	0·87; 0·95; 1·09	
Acetate IX	0·92; 0·92; 1·11	
Ketone X	1·00; 0·89; 1·04	2·13 (2 H^+; s) 2·33 (1 H^+; m)
Hydrocarbon XI	0·87; 0·92; 1·03	
Hydrocarbon XII	0·81; 0·86; 1·02	
Norphyllocladane	0·81; 0·86; 0·94	

membered ring ketone can have three alpha protons, with only two exchangeable by deuterium.

A satisfactory mechanism for the elimination of the —CH_2OH is only possible if this group is in position 15:[6]



The position of the hydroxyl group at C-6 is determined by the oxidation of alcohol (IX) which gives a six membered ring ketone with three vicinal protons exchangeable by deuterium. In addition, dehydration of this alcohol gives an olefin with only one vinyl proton.

Position 11 for the OH group is excluded because of the effect that acetylation of

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[6] C. Djerassi, W. Ritell, A. L. Nussbaum, P. W. Donovan and J. Herrán, *J. Amer. Chem. Soc.* **76**, 6410 (1954).

this group has on one of the *gem* methyls as shown by NMR. In ketone (IV) the NMR spectrum exhibits two signals for the *gem* methyl group at 0·95 and 0·87 ppm while the acetate gives only one signal at 0·95 ppm, corresponding to a shift of the second methyl group.

A similar effect is observed in the oxidation of the hydroxyl group to carbonyl in ketone (IV). While one of the methyl groups has a displacement of only 1 c/s, the other one is displaced by 13 c/s.

All this is only possible with the hydroxyl in position 6, because at a greater distance both methyls would be similarly affected.

On the basis of all the observed facts, formula I is proposed for turbicoryn and formula II for turbicorytin.

Further work is being carried out to establish the stereochemistry of turbicorytin.

EXPERIMENTAL

Isolation of tubicoryn (I)

The ground seeds of *Turbina corymbosa* (250 g) were defatted with hexane in a Soxhlet. The dry powder was extracted with ethanol and the extract evaporated to dryness *in vacuo* yielding a yellow extract (47·5 g; 18·70% with respect to dry seeds). The yellow residue (20 g) was dissolved in methanol (80 ml) and water (1000 ml) added. Lead subacetate was added the precipitate removed by filtration and the solution treated with H_2S to eliminate excess Pb salts. These were filtered off and the filtrate concentrated *in vacuo* to approx. 50 ml. After several days, 5·5 g of a white crystalline powder separated (27·5% with respect to the original extract and 5·2% with respect to the dry seeds). This powder was crystallized 4 times from methanol–water until the product (2·05 g, 37·4% with respect to the precipitated glucoside) gave one spot on a chromatoplate, run with butanol–acetic acid–water (5:1:4). The analytical sample, crystallized from methanol–water, m.p. 244–45°, $[\alpha]_D^{22}$ −48·3° (*c* = 5·7; pyridine). (Found: C, 59·42; H, 8·48. $C_{29}H_{50}O_{11}\cdot 1\frac{1}{2}\ H_2O$ requires: C, 59·67; H, 8·80%).

Acetylation of turbicoryn

(a) *Nona-acetate.* Turbicoryn (500 mg, m.p. 244–45°) was acetylated with acetic anhydride (5 ml) and anhydrous pyridine (5 ml), by heating 3 hr at steam bath temp (92°). The solution was poured into water and the solid product washed twice with 5% HClaq and then with water. The acetate (740 mg, m.p. 204–10°) gave only one spot on a chromatoplate run with ethyl acetate. For the analytical sample it was crystallized 3 times from methanol–ethyl acetate, m.p. 239–240°. (sealed tube), 248–250° (Kofler), $[\alpha]_D^{23}$ −29·4° (*c* = 3·195; $CHCl_3$). (Found: C, 58·62; H, 7·16; acetyl, 41·9 $C_{47}H_{68}O_{20}\cdot 1$ MeOH requires: C, 58·52; H, 7·36; acetyl, 39·32%).

(b) *Octa-acetate.* Turbicoryn (100 mg, m.p. 244–245°) was acetylated by allowing the mixture to stand for 24 hr at room temp. The product (150 mg) gave only one spot on a chromatoplate. The analytical sample was crystallized from methanol–ethyl acetate, m.p. 239–240° (sealed tube), $[\alpha]_D^{22}$ −28·2° (*c* = 3·11; $CHCl_3$). (Found: C, 58·16; H, 7·18; acetyl, 35·9 $C_{45}H_{66}O_{19}\cdot 1$ MeOH requires: C, 58·58; H, 7·48; acetyl, 36·51%).

Saponification of the nona-acetate

The acetate (200 mg, m.p. 239–240°) was saponified under the usual conditions. The product (110 mg), m.p. 243–245° was crystallized from methanol–water and had an IR spectrum and m.p. and mixed m.p. identical with turbicoryn.

M.ps were determined on a Kofler block, unless otherwise specified, and are uncorrected. IR spectra were determined on a Perkin-Elmer model 21 spectrophotometer in $CHCl_3$ and the UV spectra with a Beckman D-K 2 spectrophotometer in ethanol solution, unless otherwise specified. The NMR spectra were determined in $CDCl_3$ containing T.M.S. as internal standard using a Varian A-60 machine. The mass spectra were run by the Stanford University, Dep. of Chemistry, Calif. and by the Institut de Chimie des Substances Naturelles, Gifsur-Yvette, France. Microanalyses were determined by Dr. F. Pascher, Bonn, Germany. Alumina Woelm was used for chromatography and Silica Gel G Merck for chromatoplates.

Enzymatic hydrolysis of turbicoryn

Turbicoryn (10 g, m.p. 244–245°) in 50 ml methanol, was evaporated to approx. 20 ml and diluted to 2000 ml with distilled water. To this solution, 100 ml acetate buffer pH 4·9 was added, which contained the emulsin from 30 g pulverized almonds, and then incubated for 24 hr at 37°. The reaction mixture was concentrated *in vacuo* to 200 ml. The precipitate was filtered off and the aglucone dissolved from the filter with acetone. The acetone solution was dried (Na_2SO_4) filtered and concentrated under N_2 until turbicorytin II (5·45 g; 81·84% of theoretical) crystallized out. These crystals gave one spot on a chromatoplate run with 1:1 ethyl acetate–methanol. An analytical sample was crystallized from methanol–water and dried *in vacuo* the product being highly hygroscopic, m.p. 151–153°, transition 270–273°; $[\alpha]_D^{22}$ $-52{\cdot}4°$ ($c = 3{\cdot}0$; pyridine); end absorption at 206 mμ, $\varepsilon = 7{\cdot}65$. (Found: C, 65·45; H, 9·42. $C_{23}H_{40}O_8{\cdot}\frac{1}{2}\ H_2O$ requires: C, 65·53; H, 9·80. Kuhn-Roth determination: 4·43%. 1 C—CH_3 requires: 3·62%).

Acetylation of turbicorytin

(a) *Hexa-acetate*. Turbicorytin (300 mg, m.p. 151–153°) was acetylated as for turbicoryn nona-acetate yielding 480 mg of the hexa-acetate. On a chromatoplate run with 3% chloroform–methanol one main spot was observed with another more polar. An analytical sample was purified by thin layer chromatography, crystallized from methanol and had m.p. 236–238°. (Found: C, 61·95; H, 7·72; acetyl, 39·8 $C_{35}H_{52}O_{14}{\cdot}1$ MeOH requires: C, 62·04; H, 8·09; acetyl, 37·06%).

(b) *Penta-acetate*. Turbicorytin (375 mg, m.p. 151–153°) was acetylated as for turbicoryn octa-acetate yielding 500 mg of the penta-acetate. On a chromatoplate there was one main spot and another due to a less polar compound. An analytical sample was purified by thin layer chromatography, crystallized from methanol and had m.p. 202–204°, $[\alpha]_D^{22}$ $-32{\cdot}9°$ ($c = 3{\cdot}075$; $CHCl_3$). (Found: C, 62·10; H, 7·85; acetyl, 32·87 $C_{33}H_{50}O_{11}{\cdot}1$ MeOH requires: C, 62·36; H, 8·31; acetyl, 32·86%).

Periodic acid degradation of turbicorytin

(a) *Moles of periodic acid used*. To a solution of 103 mg turbicorytin (m.p. 151–153°) in 10 ml methanol, 50 ml of an aqueous solution of H_5IO_6 (6·8385 g in 1000 ml) was added and allowed to react 12 hr. At the same time a blank was prepared. To both flasks 5 g KI in 50 ml water and 10 ml 1:10 H_2SO_4 were added and titrated with 0·1N $Na_2S_2O_3$, using 13·8 ml which corresponds to 2·82 moles HIO_4.

(b) *Moles of formic acid produced*. Turbicorytin (194·5 mg, m.p. 151–153°) was oxidized with 3 moles periodic acid. The resulting solution was diluted with 20 ml water and potentiometrically titrated, using 8·9 ml which corresponds to 1·95 moles formic acid.

(c) *Moles of formaldehyde produced*. Turbicorytin (192·65 mg, m.p. 151–153°) was subjected to oxidation with 3 moles periodic acid. The reaction mixture was steam distilled and to 250 ml of distillate, 50 ml of 50% alcoholic aqueous solution with 1% dimedone was added. It was allowed to stand 12 hr and then 107·2 mg filtered off, m.p. 189–190°. No depression was observed on mixed m.p. with an authentic sample of formaldimedone. These 107·2 mg correspond to 0·80 moles formaldehyde.

Periodic acid oxidation of turbicorytin

Turbicorytin (2·785 g, m.p. 151–153°) in 80 ml methanol, was treated with 5·45 g periodic acid in 35 ml water. The mixture was stirred 1 hr and allowed to stand 12 hr at room temp. The reaction liquid was poured into 150 ml water and neutralized with $NaHCO_3$. It was extracted with ether and after washing the extract with water, the solvent was evaporated to dryness yielding a white foamy product (2·0 g). This solid could not be induced to crystallize but gave one spot on a chromatoplate run with 35% ethyl acetate–benzene and positive Benedict and Tollens tests. On storage it had an odor similar to formaldehyde and liberated I_2 when treated with a KI solution. An analytical sample was purified by thin layer chromatography. The product was eluted from the plate with 20% ethyl acetate–methanol and after evaporation of the solvents yielded a white powder, ketone (III), m.p. 98–100°, $[\alpha]_D^{20}$ $-35{\cdot}8°$ ($c = 2{\cdot}48$; pyridine). (Found: C, 67·63; H, 8·71. $C_{20}H_{32}O_5$ requires: C, 68·15; H, 9·15%).

Ketone (III) *acetates*

Ketone (III) (200 mg m.p. 98–100°) was acetylated at room temp for 24 hr. After the usual isolation process, 210 mg of an oil was obtained, which gave two spots on a chromatoplate run with

80% ethyl acetate–benzene. These two fractions were separated by thin layer chromatography: (a) The less polar fraction consisted of an oil, giving positive Tollens and Benedict tests, and showed two acetyl groups in the NMR and no hydroxyl band in the IR. (b) The more polar fraction was a crystalline product also giving positive Tollens and Benedict tests and showed one acetyl group in the NMR and an hydroxyl band in the IR. The analytical sample was crystallized from methanol, m.p. 293–295°. (Found: C, 66·87; H, 8·35. $C_{22}H_{34}O_6$ requires: C, 66·98; H, 8·69%).

Reduction of ketone (III)

Ketone (III) (3 g, m.p. 98–100°) in 50 ml anhydrous tetrahydrofurane was added to 1 g $LiAlH_4$ in 250 ml anhydrous ether and refluxed 12 hr. The product was isolated as usual and 2·8 g of the triol (VI) obtained. The analytical sample was crystallized from ethyl acetate, m.p. 156–158°. (Found: C, 67·62; H, 10·05. $C_{20}H_{34}O_3 \cdot 2$ AcOEt requires: C, 67·43; H, 10·11%).

Triol (VI) *acetate*

The triol (VI) (m.p. 156–158°) was acetylated 4 hr on the steam bath, giving an oily product which showed only one spot on a chromatoplate run with 40% benzene–ethyl acetate. The NMR showed three acetyl groups.

Oxime from ketone (III)

Ketone (III) (250 mg, m.p. 98–100°) and hydroxylamine hydrochloride (250 mg) in anhydrous pyridine (5 ml) and anhydrous methanol (5 ml) was refluxed 2 hr. The oxime (165 mg) crystallized from methanol. It gave only one spot on a chromatoplate run with 10% chloroform–methanol and had m.p. 268–270° (sealed tube). (Found: C, 74·35; H, 10·14; N, 4·82. $C_{19}H_{31}O_2N$ requires: C, 74·71; H, 10·23; N, 4·59%).

Thioketal from ketone (III)

Ketone (III) (900 mg, m.p. 98–100°) was dissolved in 15 ml anhydrous benzene and 5 ml ethanedithiol, 7 ml of an ethereal solution of BF_3 and 2 g anhydrous Na_2SO_4 added. The reaction mixture was allowed to stand 48 hr at room temp, then filtered, and the filtrate after evaporation to dryness, diluted with ice water and extracted with chloroform. The extract was washed with 5% NaOHaq and then with water, dried with Na_2SO_4 and evaporated to dryness. A crude product (850 mg) was obtained which gave two spots on a chromatoplate run with 40% benzene–ethyl acetate. This product was chromatographed on 50 g neutral alumina II, eluting with benzene. A white crystalline substance was obtained which gave only one spot on a chromatoplate and crystallized from methanol, m.p. 227–228°. The analytical sample was crystallized twice from methanol and had m.p. 230–231°. (Found: C, 68·76; H, 9·41; S, 17·22; M, 364 (osmometer). $C_{21}H_{34}OS_2$ requires: C, 68·79; H, 9·34; S, 17·48%; M, 366·6).

Desulfuration of the thioketal

The thioketal (320 mg, m.p. 230–231°) was dissolved in 200 ml ethanol and 1·5 ml Raney nickel W-7, in the same solvent, added. The mixture was refluxed 10 hr, filtered and evaporated to dryness, giving 230 mg of a crystalline product, m.p. 120–128°. The analytical sample of this alcohol (IX) was sublimed *in vacuo* at 95°/0·01 mm and had m.p. 143–145°, $[\alpha]_D^{21}$ $-41{\cdot}8°$ ($c = 7{\cdot}0$; $CHCl_3$). (Found: C, 82·63; H, 11·76; M, 276 (M.S.). $C_{19}H_{32}O$ requires: C, 82·54; H, 11·66%; M, 276·04).

Alcohol (IX) *acetate*

Alcohol (IX) (40 mg, m.p. 143–145°) was dissolved in 0·5 ml acetic anhydride and 0·5 ml anhydrous pyridine and heated 3 hr on a steam bath. After the usual isolation, 40 mg of an homogeneous oil was obtained which gave one spot on a chromatoplate run with 25% benzene–hexane. The NMR showed one acetyl group.

Ketone (IV)

Ketone (III) (250 mg, m.p. 98–100°) was dissolved in 25 ml 50% aqueous methanol with 10% HCl and refluxed 4 hr. After cooling, a white crystalline product precipitated (130 mg; m.p. 143–147°). On a chromatoplate run with 35% ethyl acetate–benzene one main spot was observed with a spot due to a trace of a less polar substance. The product was purified by thin layer chromatography run with the same mixture of solvents and extracted with 20% ethyl acetate–methanol. It did not give a positive Tollens or Benedict test. The analytical sample was crystallized from acetone–water and had m.p. 165–166°, $[\alpha]_D^{22}$ −54·2° (c = 2·1; $CHCl_3$). (Found: C, 78·14; H, 10·06; M, 290 (M.S.). $C_{19}H_{30}O_2$ requires: C, 78·57; H, 10·41%; M, 290·43).

Deuterium exchange in ketone (IV)

Ketone (IV) (100 mg, m.p. 165–166°) was dissolved in 5 ml deuteromethanol (MeOD) in which 2 mg of metallic Na had been previously dissolved. The solution was heated ½ hr and allowed to stand at room temp 48 hr. The methanol was evaporated, water added and the mixture neutralized with HClaq to pH 6. The product was filtered off and dissolved in ethyl acetate–chloroform, decolorized with 100 mg activated charcoal and filtered. The filtrate was evaporated to dryness, giving 106 mg of a white crystalline product, m.p. 160–163°, mol. wt. 292 (M.S.).

Acetate of ketone (IV)

Ketone (IV) (100 mg, m.p. 165–166°) was acetylated 3 hr on a steam bath, giving an oil (110 mg) which on a chromatoplate run with 20% benzene–ethyl acetate showed only one spot. The NMR showed only one acetyl group.

Ketone (IV) *oxime*

Ketone (IV) (250 mg, m.p. 165–166°) was converted to an oxime (225 mg) identical in m.p. (268–270°) and IR spectrum with the oxime from ketone (III).

Hydrolysis of ketone (IV) *oxime*

To the above oxime (200 mg) dissolved in 10 ml ethanol, 6 ml pyruvic acid and 6 g sodium acetate were added. After refluxing the mixture 16 hr and evaporating the solvent *in vacuo*, the product was extracted with ethyl acetate and washed with $NaHCO_3$aq and with water. By fractional crystallization from methanol two products were separated, 150 mg of the recovered oxime and 16 mg of a product identical with ketone (IV) by IR spectrum, m.p. and mixed m.p.

Alcohol (IX)

The oxime of ketone (IV) (250 mg, m.p. 268–270°) was sealed in a thick glass tube with 2·5 ml 95% hydrazine and 25 mg metallic Na dissolved in 7·5 ml ethylene glycol. The tube was heated 2 hr at 200–205°. The product crystallized in the tube on cooling. The entire contents of the tube were poured into water and the white crystalline product (218 mg), m.p. 150–165° filtered off. It gave only one spot on a chromatoplate run with 40% hexane–ethyl acetate. Purified by sublimation at 130°/0·05 mm, it melted at 143–145° and was identical with the alcohol obtained by desulphuration of the thioketal (m.p., IR spectrum and mixed m.p.).

Dehydration of alcohol (IX)

Alcohol (IX) (140 mg, m.p. 143–145°) was dissolved in 15 ml anhydrous benzene and P_2O_5 (300 mg) added. After 4 hr heating under reflux the benzene solution was evaporated to dryness, leaving an oily residue which gave two spots on a chromatoplate run with benzene. This product was chromatographed on 50 g basic alumina I and in the first fractions 106 mg of an oil was obtained producing only one spot on chromatoplate. This product (hydrocarbon (XI)) gave a positive test with tetranitromethane and the NMR showed only one vinyl proton.

Hydrogenation of hydrocarbon (XI)

The olefinic hydrocarbon (100 mg) was hydrogenated with 10 mg PtO_2 in 30 ml acetic acid and 10 ml ethyl acetate. After 2 hr the calculated amount of H_2 for one double bond had been absorbed with no more absorptions during 2 hr additional stirring. After the usual isolation the liquid residue was distilled at 170°/0·01 mm. A colorless liquid was obtained which was purified by gas chromatography at 200° in a 2 m × 6 mm copper column filled with 30% silicon DC on Chromosorb 60/80. Two main fractions were obtained: a crystalline solid (32 mg, m.p. 74–75°), identical with hydrocarbon (XII) obtained by Wolff-Kishner reduction of ketone (X) (m.p., IR spectrum and mixed m.p.); and a non homogeneous fraction which was not further investigated.

Jones oxidation of alcohol (IX)

Alcohol (IX) (218 mg, m.p. 143–145°) was oxidized[5] yielding a colorless oil (170 mg) which gave only one spot on a chromatoplate run with 25% hexane–ethyl acetate. This oil was distilled at 170°/0·05 mm and a crystalline product (156 mg) was obtained, m.p. 78–79°, mol. wt. 274 (M.S.) which corresponded to ketone (X).

Deuterium exchange with ketone (X)

Ketone (X) (100 mg, m.p. 78–79°), treated as for ketone (IV) yielded 95 mg of the deuterated ketone (X), m.p. 78–79°, mol. wt. 277 (M.S.).

Hydrocarbon (XII) *from ketone* (X)

Ketone (X) (50 mg, m.p. 78–79°) was treated with 50 mg hydroxylamine hydrochloride and 50 mg sodium acetate in 20 ml ethanol. After the usual isolation the oxime was crystallized from methanol, giving 45 mg, m.p. 169–170°. This substance was subjected to a Wolff-Kishner reduction as described for the oxime of ketone (IV) and yielded 30 mg of hydrocarbon (XII). For an analytical sample it was dissolved in hexane and distilled at 170°/0·05 mm. The product had m.p. 74–75° and $[\alpha]_D^{25}$ $-44{\cdot}1°$ ($c = 2{\cdot}02$; $CHCl_3$). (Found: C, 87·57; H, 12·14. $C_{19}H_{32}$ requires: C, 87·62; H, 12·38%).

Jones oxidation of ketone (IV)

Ketone (IV) (300 mg, m.p. 165–166°) was oxidized and the product sublimed at 125°/0·07 mm yielding a crystalline substance (250 mg, m.p. 137–139°) which was sublimed again under similar conditions, giving 200 mg, m.p. 139–140°. It gave only one spot, corresponding to ketone (VIII), on a chromatoplate run with 25% hexane–ethyl acetate. (Found: C, 78·71; H, 9·50; mol. wt., 288 (M.S.). $C_{19}H_{28}O_3$ requires: C, 79·12; H, 9·79%; mol. wt., 288·41).

The deuterium exchange of this ketone was carried out as for the other ketones and a product with m.p. 139–140° and mol. wt., 293 (M.S.) obtained.

Hydrocarbon (XII) *from ketone* (VIII)

The dioxime of ketone (VIII), prepared using the procedure for ketone (X), had m.p. 228–230° and on Wolff-Kishner reduction, using conditions as previously described, yielded hydrocarbon (XII).

Reduction of ketone (IV)

To a suspension of 70 mg $LiAlH_4$ in 20 ml anhydrous ether, 220 mg of the ketone (m.p. 165–166°) in 20 ml anhydrous ether was slowly added and the mixture refluxed 10 hr. The crystalline product, 213 mg, gave only one spot on a chromatoplate run with 5% ethyl acetate–methanol. The analytical sample of this diol (VII) was crystallized from acetone, m.p. 184–185°. (Found: C, 77·59; H, 11·05; mol. wt. 292 (M.S.). $C_{19}H_{32}O_2$ requires: C, 78·03; H, 11·03%; mol. wt. 292·45).

Diol (VII) *acetate*

Diol (VII) (100 mg, m.p. 184–185°) was acetylated 2 hr on a steam bath, giving the acetate (110 mg) which showed only one spot on a chromatoplate run with 5% ethyl acetate–methanol. The analytical sample was crystallized from methanol, m.p. 154–155°. (Found: C, 73·39; H, 9·69; mol. wt., 376 (M.S.). $C_{23}H_{36}O_4$ requires: C, 73·36; H, 9·64%; mol. wt., 376·52). The NMR integrated for two acetyl groups.

Dehydrogenation of turbicoryn

The glucoside (10 g, m.p. 244–245°) was mixed with 40 g Se powder and placed in a thick glass tube 60 cm long and 3 cm in diameter. The tube was heated at 360° for 24 hr. The gases produced were collected and only 7 ml (s.t.p.) obtained. The formation of H_2Se was confirmed with lead acetate which was added to the liquid in the collection system. The products of dehydrogenation were extracted with benzene and decolorized with 1 g activated charcoal. The solvent was evaporated to dryness, yielding 2·8 g of an oily residue with a dark brown colour.

This oil was treated with 3 g Zn dust and after heating 2 hr at 320° yielded 133 ml (s.t.p.) evolved gas. As the oil resulting showed in the IR spectrum only partial aromatization, it was again dehydrogenated with 1 g 10% Pd–C, heating 24 hr at 350°. After this time a fluorescent substance began to sublime in the tube. The product was dissolved in benzene and the solution filtered. On evaporation of the solvent 250 mg of a slightly yellow oil with a violet fluorescence was obtained.

This oil was distilled *in vacuo* at 180°/0·01 mm. On a chromatoplate run with hexane, 3 spots appeared; from these, the two more polar ones could be seen with UV light; the one with the smallest R_f value gave a light green colour with $Ce(SO_4)_2$ and had the same R_f and aspect as that of phenanthrene.

The distilled oil (206 mg) was chromatographed on basic alumina I and eluted first with hexane. This fraction, 95 mg, was not fluorescent and appeared as a partially aromatic hydrocarbon in the IR and NMR.

The fraction eluted with benzene was fluorescent and weighed 102 mg. The trinitrobenzene complex was prepared and crystallized 3 times from methanol to m.p. 155–161°. It was reduced with $SnCl_2$ and HCl, poured into water and extracted with hexane. The hydrocarbon fraction was purified by fractional sublimation at 120–140°/0·05 mm. Two fractions were obtained: the first, m.p. 86–88° and a UV (in hexane) corresponded to 1,7-dimethylphenanthrene.[7] The picrate of this product, m.p. 132° and the trinitrobenzolate, m.p. 160–162°, were in agreement with those reported for 1,7-dimethylphenanthrene;[8] the second fraction was a mixture of phenanthrene hydrocarbons, difficult to separate.

The mother liquors from the crystallization of the trinitrobenzolate were reduced with $SnCl_2$ and HCl and the hydrocarbon obtained purified by fractional sublimation at 120°/0·05 mm, giving 20 mg of a crystalline fraction, m.p. 97–99°, picrate, m.p. 143–145°. The UV, IR and NMR spectra corresponded to phenanthrene; there being no depression on mixed m.p.

17-*Norphyllocladane*

The semicarbazone (m.p. 230–231°) was prepared from 17-norphyllocladan-17-one,[9] obtained by permanganate–periodate oxidation[10] of phyllocladene. This semicarbazone (100 mg) was subjected to a Wolff-Kishner reduction as for ketone IV oxime but with 0·5 ml hydrazine and 5 ml ethylene glycol in which 5 mg of metallic Na had been dissolved. After the usual procedure, extraction with hexane and evaporation yielded 70 mg of a hydrocarbon, m.p. 79–81° and $[\alpha]_D^{25}$ $+8{\cdot}5$ ($c = 1{\cdot}35$; $CHCl_3$) which was used as a model compound for comparison with hydrocarbon (XII).

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