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REACTIONS IN HIGH BOILING SOLVENT–II

EFFECT OF RANEY NICKEL ON TRITERPENOIDS

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Abstract—The effect of Raney nickel on triterpenoids in boiling *p*-cymene has been studied. The following three different types of reactions have been observed: (a) dehydrogenation (oxidation) of the 3-OH group, (b) saturation of the easily reducible double bond, and (c) shifting of the double bond to an adjacent position as in allylic shift. The shift is of reversible nature. A 3-hydroxytriterpenehydrochloride is converted to 3-keto-triterpene by this reaction, the Cl atom being removed by hydrogenolysis. A mechanism is also proposed.

IN THE course of our investigation on reactions in high boiling solvents a study was made on the effect of Raney nickel on steroids.[1-4] It may, however, be mentioned that the Me groups in one of the two halves of the dimer (VII) in reference 4 are sterically in the opposite side to those of the other half. In view of the interesting results obtained on the effect of Raney nickel on steroids in boiling *p*-cymene solution, this reaction was extended to the field of triterpenoids.[5-6] Some of these triterpenes were directly obtained from known sources and some were prepared from other triterpenes.

In this study α-amyrin (I), a pentacyclic triterpene, was heated with Raney nickel in *p*-cymene solution and the product that could be isolated was α-amyrone (II). β-Amyrin (III) on similar treatment gave the corresponding ketone, β-amyrone (IV). Taraxerol (V) when refluxed with Raney Ni in *p*-cymene solution yielded taraxerone (VI).

When lupeol (VII) was heated with an excess of Raney Ni in *p*-cymene solution the product isolated was the saturated ketone, lupanone (VIII). With a small amount of the catalyst no appreciable conversion took place. Lupanone (VIII) was also obtained when the reaction was carried out with the saturated alcohol, dihydrolupeol (IX).

The action of Raney Ni on ursolic acid and betulinic acid appeared to be rather complex. Methyl ursolate (X), however, gave methyl ursonate (XI) under similar experimental conditions. Also, methyl betulate (XII) on treatment with Raney Ni in boiling *p*-cymene solution afforded the saturated keto-ester, methyldihydrobetulonate (XIII). Epifriedelinol (XIV), a saturated pentacyclic triterpene alcohol, when refluxed with Raney Ni in *p*-cymene solution, yielded friedelin (XV).Germanicol (XVI) on similar treatment afforded germanicone (XVII).

Cycloartenol was prepared from cycloartenone, isolated from the latex of *Artocarpus integrifolia*[7] by treating it with aluminium isopropoxide in isopropanol according to Meerwein-Pondorf-Verley reduction.[8] The naturally occurring cycloartenol has 3β-OH group. MPV reduction of cycloartenone yields two epimeric alcohols, cycloarten-3α-ol (9, 19-cyclolanost-24-en-3α-ol) and cycloarten-3β-ol (9, 19-cyclolanost-24-en-3β-ol), the latter epimer being obtained in larger proportions.[8] When cycloarten-3β-ol (XVIII), $C_{30}H_{50}O$, was heated with a small amount of Raney Ni in *p*-cymene solution,

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two unsaturated ketones, ketone A and ketone B, having the same molecular formula were obtained in addition to a small amount of the saturated ketone, cycloartanone. Both the ketones showed C=O stretching frequencies at 1713 cm^{-1} in the IR spectrum. Ketone A was found to be identical with cycloartenone (XIX). The other ketone, ketone B, which was obtained in small yields, had an almost identical polarity on alumina or silica gel although a TLC on silica gel revealed that the ketone B had a slightly lower R_f value than that of cycloartenone. Cycloartenone was separated from ketone B by repeated chromatography on a large column of alumina, cycloartenone travelling somewhat faster than ketone B. On hydrogenation over platinum oxide catalyst in glacial acetic acid ketone B took up one mole of hydrogen yielding a saturated ketone which was found to be identical with cycloartanone. Thus this ketone differs from cycloartenone only in the position of the double bond. Apparently, during the course of the reaction with Raney Ni the double bond of cycloartenol had migrated from its usual 24:25 position. The shift of double bond under the effect of Raney Ni was observed by Chakravarti and Robinson in the conversion of strychnine into neostrychnine.[9] The ketone B on ozonolysis yielded formaldehyde. Formation of formaldehyde from ketone B coupled with the fact that it shows an absorption at 890 cm^{-1} in the IR spectrum clearly indicates the presence of a terminal double bond in the molecule. Evidently, during the course of the reaction, the double bond had migrated. This migration may be visualised as a hydrogenation *cum* dehydrogenation from 24:25 position possibly through a free radical mechanism. Thus the ketone B is to be represented by the structure (XX).

The ketone XX was converted to the corresponding alcohol (XXa) in the usual way and this on treatment with Raney Ni in boiling *p*-cymene yielded a mixture of cycloartenone (XIX), the ketone (XX) and cycloartanone (XXI), thus indicating the reversible nature of this Raney Ni reaction.

Ketone XX is less stable than its isomer, cycloartenone (XIX) from thermodynamic consideration and, therefore, its formation requires absorption of energy, evidently supplied by the reaction. The ketone (XX) is believed to be formed by a free-radical mechanism, first knocking out on allylic H atom which then adds to the olefinic carbon (Fig I).

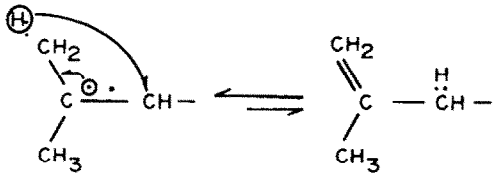


Fig. – I

But when cycloartenol (3β-alcohol) was treated with an excess of the catalyst in a similar manner, the product obtained was the saturated ketone, cycloartanone. Cycloarten-3α-ol (XXII), which was obtained in small amounts from the reduction product of cycloartenone, when heated with moderately large amount of Raney Ni in *p*-cymene solution, yielded the saturated ketone (XXI). No unsaturated ketone could, however, be isolated from the reaction mixture. It is highly probable that some unsaturated ketone, cycloartenone (XIX) and/or 9:19-cyclolanost-25-en-3-one (XX) would also

result, particularly when the reaction is carried out with a small amount of the catalyst. This, however, could not be experimentally verified due to paucity of the material.

$\Delta^{9(11)}$-Lanostenol (XXIII), prepared from cycloartanyl acetate according to method of Spring et al,[10] when refluxed with Raney Ni in boiling *p*-cymene solution furnished $\Delta^{9(11)}$-lanostenone (XXIV), irrespective of the catalyst being used in small quantity or in excess. $\Delta^{9(11)}$-lanostenone (XXIV) was characterised by its strong ketonic absorption at 1712 cm^{-1} and preparation of semicarbazone.

Thus the effect of Raney Ni on triterpenoids in boiling *p*-cymene solution involving three different types of reactions may be summarized as follows:

Type I. dehydrogenation (oxidation) of the 3α-or 3β-OH group
Type II. saturation of the easily reducible double bond
Type III. shifting of the double bond to an adjacent position as in allylic shift.

Type III reaction was observed only in two cases, although this may take place in other triterpenes having a similar system. It may be noted that in comparison with reactions of Raney Ni with steroids, the reaction of Raney Ni with triterpenes requires a larger amount of the catalyst. Type I reaction usually requires the use of a small amount of the catalyst whereas with excess of the catalyst the saturated ketone is obtained by a combination of type I and type II reactions. The types I and II are quite in conformity with the results obtained on the effect of Raney Ni on steroids in boiling *p*-cymene solution.

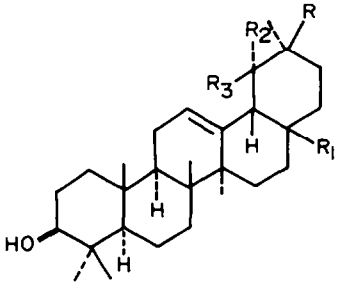
Halsall *et al*[11] prepared 18-iso-β-amyranol (XXVI) by reducing lupeol hydrochloride (XXV) catalytically or with sodium and isopropanol. With a view to examining the course of the effect of Raney Ni on lupeol hydrochloride (XXV), this was heated with Raney Ni in boiling *p*-cymeme and the product isolated was a new ketone, 18-iso-β-amyranone (XXVII) (C=O stretching frequency at 1710 cm^{-1}). The latter product was also obtained when the reaction was carried out with 18-iso-β-amyranol (XXVI), prepared according to the method of Halsall.[11] 18-Iso-β-amyranone (XXVII) was characterised by converting it to the corresponding alcohol (XXVI) by sodium/n-propanol reduction and preparation of the oxime. Thus heating with Raney Ni in *p*-cymene solution can also bring about hydrogenolysis of triterpene chloride.

The Raney Ni reaction appears essentially to be a hydrogenation *cum* dehydrogenation process. When a conjugated steroid ketone like cholest-4-en-3-one was heated with Raney Ni in *p*-cymene no reduction of the double bond took place and the ketone could be recovered unchanged. It was thought that the double bond in conjugation with the carbonyl group, being stabler than isolated double bond, where no delocalization of the π-orbitals is possible, might have resisted the hydrogenation under this reaction condition. Therefore, the reaction was carried out with a few triterpene ketones with easily reducible isolated double bond like cycloartenone, lupenone, methyl ketobetulate, etc. In these cases also no saturation of the double bond occurred and the ketones were recovered unchanged. Even unsaturated acetates like cholesteryl acetate, cycloartenyl-acetate, were unaffected by this reaction. But unsaturated 3-hydroxy steroids or triterpenoids smoothly furnished the saturated ketones on treatment with Raney Ni in boiling *p*-cymene solution. Thus the hydrogen necessary for the reduction of the double bond appears to be supplied from the reacting molecules and not from the Raney Ni itself. The hydrogen evolved on dehydrogenation of the alcohols actually brings about

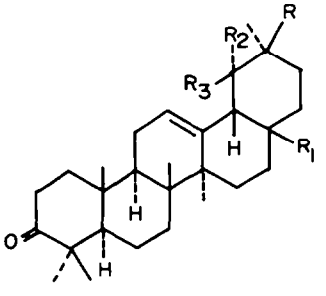
the saturation of the double bond in presence of the catalyst. The solvent perhaps consumes some amount of this liberated hydrogen.

The fact that for the formation of saturated ketone larger amount of the catalyst is necessary, seems to suggest that with the increase in the amount of the catalyst, the availability of the surface, where reduction of the double bond with the liberated hydrogen takes place, increases—thus increasing the availability of the gas for reduction of the dehydrogenated product, the unsaturated ketone, on the surface of the catalyst. This mechanism holds good for steroids also.

One interesting point to note in this connection is that triterpene alcohols with a reducible double bond on heating with Raney Ni in *p*-cymene yield in most cases the saturated ketone, whilst in the case of sterols with 5 : 6-double bond both unsaturated and saturated ketones are obtained. This may be explained as follows. Dehydrogenation of 3-OH group of steroids having 5 : 6-double bond promotes a shift of the double bond to 4 : 5-position to attain stabilization by delocalizing the π-orbitals. With triterpenes hydrogenation of the isolated double bond involving the breaking of π-bond is much easier than the hydrogenation of the more stable conjugated steroid ketone. Although the solvent *p*-cymene is quite stable, it probably consumes an appreciable amount of the liberated hydrogen because here the lower reactivity is compensated by a higher probability of successful collision on account of the quantity of the solvent used.

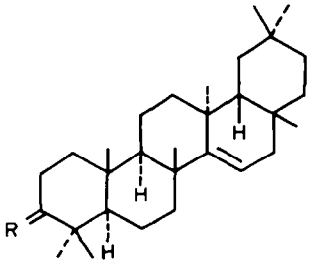


I, III, X

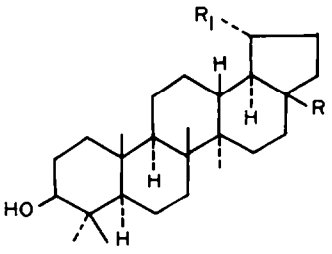


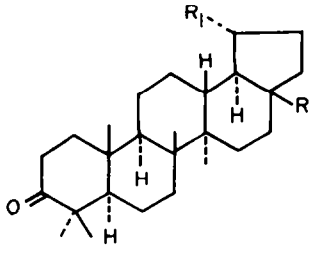
II, IV, XI

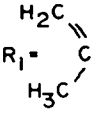
I & II : $R = R_2 = H$, $R_1 = R_3 = CH_3$
III & IV : $R_2 = R_3 = H$, $R = R_1 = CH_3$
X & XI : $R = R_2 = H$, $R_3 = CH_3$, $R_1 = COOCH_3$

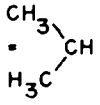


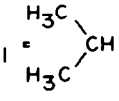
V : R = H, OH (β)
VI R = O

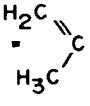


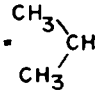


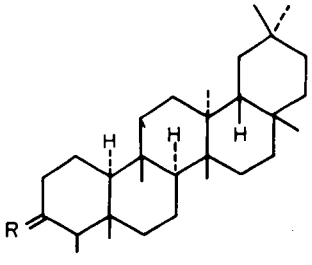
VII : R = CH_3, R_1 = 

VIII : R = CH_3, R_1 = 

IX : R = CH_3, R_1 = 

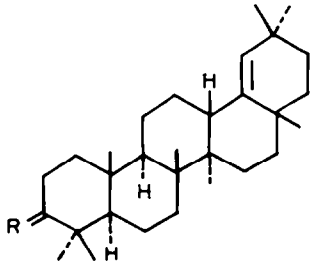
XII : R = $COOCH_3$, R_1 = 

XIII : R = $COOCH_3$, R_1 = 



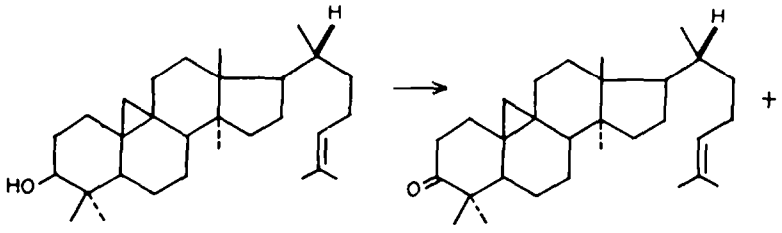
XIV : R = H, OH (β)

XV : R = O

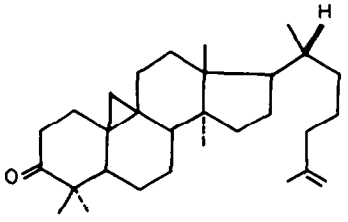


XVI : R = H, OH (β)

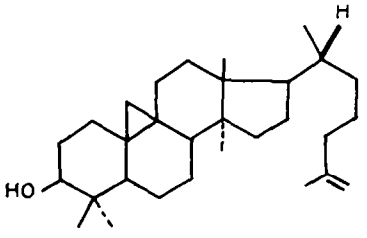
XVII : R = O



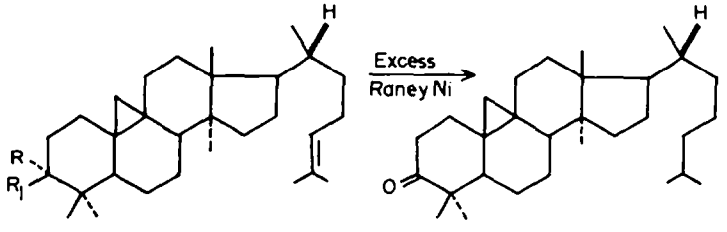
XVIII XIX



XX

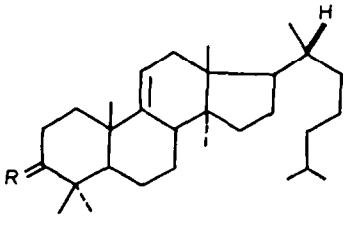


XXa

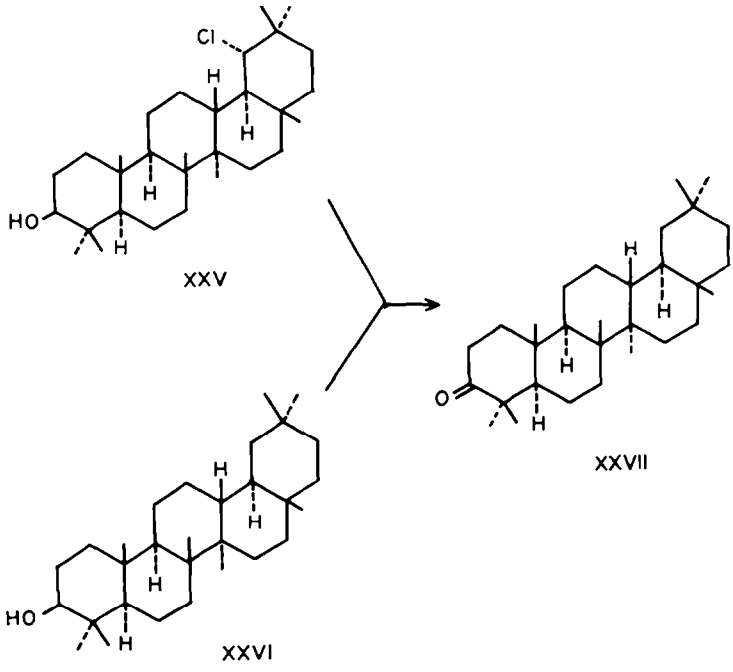


XVIII: R = H, R_1 = OH
XXII: R_1 = H, R = OH

XXI



XXIII: R = H, OH (β)
XXIV: R = O



EXPERIMENTAL

Preparation of Raney Ni *catalyst.* Raney Ni, W—2, was prepared by the action of NaOH aq on Raney N aluminium alloy according to the method of Mozingo.[14] The catalyst was generally used within a month of its preparation.

Purification of the solvent. *p*-Cymene used in this reaction was prepared by refluxing the technical *p*-cymene with Raney Ni ct for 2–3 hr followed by distillation.

General procedure. The triterpene taken in a ground joint flask was dissolved in *p*-cymene and to this was added Raney Ni ct previously washed with *p*-cymene. The flask was fitted with a distillation arrangement. The mixture was heated on a sand-bath and a few ml *p*-cymene was distilled so as to ensure complete removal of water and alcohol by azeotropic process. The mixture was then heated under reflux on the sand bath for 10 hr. After the reaction the mixture was filtered hot and the filtrate distilled in steam to remove *p*-cymene. The residue obtained was taken up in ether, benzene or chloroform and separated from the aqueous layer. The residue left after removal of the solvent was chromatographed over a column of neutral Brockmann alumina using solvents successively in the order of increasing polarities (pet ether→pet ether–benzene mixtures→benzene→benzene–ether mixtures→ether→ethanol). The products obtained from different fractions were examined.

The light petroleum used had b.p. 40–60°. Chromatographic separations were carried out over a column of neutral Brockmann alumina. The weights of the catalyst were taken after the reactions were over although the approximate amounts of the catalyst taken for a reaction were determined by taking the catalyst in a small spoon of known capacity. All m.ps were taken in open capillary tubes and are uncorrected. Rotations were determined in chloroform solns at the room temp. IR spectra were recorded as Nujol mulls on a Perkin–Elmer 137 spectrometer.

Action of Raney Ni *on α-amyrin.* α-Amyrin (0·25 g) in *p*-cymene (12 ml) and Raney Ni (0·5 g) were used and worked up as described above under "general procedure". The product (0·22 g) from a chloroform extract of the residue after steam distillation was chromatographed on alumina (15 g). The light petroleum yielded a colourless glassy residue which on crystallization from aqueous MeOH yielded α-amyrone (0·11 g), m.p. 126°(undepressed on admixture with an authentic sample). (Found: C, 84·67; H, 11·43; Calc. for $C_{30}H_{48}O$: C, 84·84;H, 11·39%); semicarbazone, m.p. 205–206° (dec). (Found: N, 8·48; Calc. for $C_{31}H_{51}ON_3$:N, 8·72%).

Action of Raney Ni *on β-amyrin.* β-Amyrin (0·25 g), prepared from taraxerol by the method of Spring *et al*, *p*-cymene (12 ml) and Raney Ni (0·5 g) were used and the reaction product (0·22 g) isolated in the usual way was chromatographed on alumina (15 g). The material eluted with light petroleum-benzene (8:1) on crystallization from 90% EtOH afforded *β*-amyrone (0·11 g), m.p. and mixed m.p. with an authentic sample of *β*-amyrone 177–179°. (Found; C, 84·62; H, 11·41; Calc. for $C_{30}H_{48}O$:C, 84·84; H, 11·39%); semicarbazone, m.p. 245–246° (dec).

Action of Raney Ni *on taraxerol.* Taraxerol (0·35 g) in *p*-cymene (15 ml) and Raney Ni (1 g) were used and the benzene extract of the crystalline residue (0·31 g) after the steam distillation was chromatographed on alumina (15 g). Light petroleum-benzene (8:1) eluate yielded a white crystalline residue which on crystallization from chloroform-EtOH mixture afforded taraxerone, as leaflets (0·26 g), m.p. and mixed m.p. with an authentic sample 240–241°, $[\alpha]_D^{25}+7·1°$ (strong ketonic absorption at 1709 cm^{-1}). (Found:C, 84·81; H, 11·41; Calc. for $C_{30}H_{48}O$:C, 84·84; H, 11·39%).

Action of Raney Ni *on lupeol.* Lupeol (1·5 g) in *p*-cymene (30 ml) and Raney Ni (6 g) were used. The product (1·32 g) after separation of the catalyst and the solvent was chromatographed over alumina (45 g). The residue from benzene eluate on crystallization from EtOH-chloroform (4:1) yielded lupanone, as flakes (0·85 g), m.p. 202–203° (undepressed on admixture with an authentic sample), $[\alpha]_D^{25}+16°$; IR spectrum was superimposable on that of an authentic sample of lupanone (C=O stretching frequency at 1710 cm^{-1}). (Found: C, 84·38; H, 11·77; Calc. for $C_{30}H_{50}O$:C, 84·44; H, 11·81%): oxime, m.p. 270°.

Action of Raney Ni *on dihydrolupeol.* Dihydrolupeol (0·5 g) in *p*-cymene (20 ml) and Raney Ni (0·75 g) were used and the product (0·43 g) isolated in the usual way was chromatographed on alumina (15 g). The material eluted with benzene on crystallization from EtOH containing a little chloroform yielded lupanone (0·29 g) m.p. 202–203°.

Action of Raney Ni *on methyl ursolate.* Methyl ursolate (1 g) in *p*-cymene (25 ml) and Raney Ni (4 g) were used. Working up in the usual way the reaction product (0·91 g) was chromatographed on alumina (30 g). Light petroleum-benzene (1:1) eluted a solid material which on crystallization from light petroleum afforded methyl ursonate, in fine needles (0·45 g), m.p. 192–193°, $[\alpha]_D^{25}+78°$. (Found: C, 79·35; H, 10·16; Calc. for $C_{31}H_{48}O_3$:C, 79·43; H, 10·32%); oxime, m.p. 240–241° (Found: N, 2·68; Calc. for $C_{31}H_{49}O_3N$:N, 2·90%).

Action of Raney Ni *on methyl betulate.* Methyl betulate (0·5 g) in *p*-cymene (15 ml) and Raney Ni (2·5 g) were used. The residue (0·42 g) from ether extract was chromatographed on alumina (15 g). The residue from light petroleum-benzene (1:1) eluate on crystallization from MeOH-ether afforded methyl dihydrobetulonate in fine needles (0·25 g), m.p. 188–189°, undepressed on admixture with an authentic sample, $[\alpha]_D^{25}+7°$ (Found: C, 79·19; H, 10·61; Calc. for $C_{31}H_{50}O_3$:C, 79·10; H, 10·71%); oxime, m.p. 248–250° (dec).

Action of Raney Ni *on epifriedelinol.* Epifriedelinol (0·25 g) in *p-cymene* (10 ml) and Raney Ni (0·5 g) were used. Working up in the usual way the product (0·42 g) was chromatographed on alumina (10 g). The material eluted with light petroleum-benzene (4:1) on crystallization from EtOH containing a little chloroform yielded friedelin, as flakes (80 mg), m.p. 261–262°.

Action of Raney Ni *on germanicol.* Germanicol required for this work was prepared from lupeol by the method of Halsall *et al.* Germanicol (0·5 g) in *p*-cymene (15 ml) and Raney Ni (2 g) were used. The ethreal extract (0·42 g) after removal of the solvent and chromatographic purification followed by crystallization from EtOH-chloroform afforded germanicone in plates (0·27 g) m.p. and mixed m.p. with an authentic specimen 188–189°, $[\alpha]_D^{25}+36°$. (Found: C, 84·69; H, 11·26; Calc. for $C_{30}H_{48}O$:C, 84·84; H, 11·39%); 2:4-dinitrophenylhydrazone, m.p. 240° (dec).

Action of Raney Ni *on cycloartenol.* Cycloartenol (1 g) in *p*-cymene (25 ml) and Raney Ni (0·7 g) were used. Working up in the usual way the product (0·91 g) was chromatographed on alumina (30 g).

The material (0·61 g) eluted with light petroleum-benzene (4:1) and (1:1) was rechromatographed on alumina (25 g). Fractions were collected in 35 ml. The results are indicated below:

Fraction	*Eluate*
Light petroleum	
1–2	nil
3–4	Cryst. (0·13 g)
5	Cryst. (0·04 g)
6–8	Cryst. (0·15 g)
9	Cryst. (0·04 g)
10–14	Cryst. (0·24 g)

Fractions 3–4 were rechromatographed over alumina. Light petroleum-benzene (4 : 1) eluate yielded a residue which on crystallization from MeOH–$CHCl_3$ yielded cycloartanone, in needles (13 mg), m.p. 106–107°.

Fractions 6-8 were combined and crystallized from MeOH-chloroform to give cycloartenone, in needles (0·11 g), m.p. and mixed m.p. with an authentic sample 108–109° $[\alpha]_D^{25}$ + 24°, strong ketonic absorption at 1713 cm^{-1} in the IR spectrum (Found: C, 84·73; H, 11·28; Calc. for $C_{30}H_{48}O$:C, 84·84; H, 11·39%); semicarbazone m.p. 206°.

Fractions 10–14 were mixed and chromatographed again. The later fractions (0·17 g) eluted with light petroleum-benzene (2 : 1), which appeared to be homogenous on TLC, on crystallization from MeOH-chloroform afforded XX in fine needles (0·12 g), m.p. 99–100°, $[\alpha]_D^{20}$+19°. (Found: C, 84·74; H, 11·27; $C_{30}H_{48}O$ requires: C, 84·84; H, 11·39%). The IR spectrum of the compound exhibited absorption peaks at 1713 cm^{-1} (6-ring ketone), 1380 cm^{-1} (c-methyl), 3045 cm^{-1} (unsubstituted methylene group in cyclopropane ring), 890 cm^{-1} (=CH_2); *semicarbazone*, m.p. 214° (dec). (Found: N, 8·34; $C_{31}H_{51}ON_3$ requires: N, 8·72%).

Hydrogenation. The ketone XX (40 mg) was dissolved in glacial AcOH (75 ml) and hydrogenated in presence of Adams catalyst (10 mg) at room temp for 6 hr. On completion of hydrogenation, the product was worked up in the usual way and crystallized from MeOH containing a little chloroform to yield cycloartanone, in needles (25 mg), m.p. 106–107° (undepressed on admixture with an authentic sample), $[\alpha]_D^{20}$+20·2°. (Found; C, 84·34; H, 11·72; Calc. for $C_{30}H_{50}O$:C, 84·44; H, 11·81%).

Ozonolysis. Through a soln of XX (0·15 g) in dry chloroform (30 ml) dry ozonized O_2 was passed at ice-cold temp till the gas gave tests for O_3. The solvent was removed under reduced pressure, the ozonide decomposed with water on a water-bath. The volatile carbonyl compound was swept with a current of N_2 into a flask containing 0·1% aqueous acidic soln of 2,4-dinitrophenyl-hydrazine. The yellow ppt was collected by filtration and washed free from acid and dried. It had m.p. 166°, undepressed on admixture with an authentic specimen.

Cycloartenol (0·5 g) in *p*-cymene (20 ml) and Raney Ni (1·5 g) were used and the product isolated in the usual way was chromatographed on alumina (15 g). The material eluted with light petroleum-benzene (1 : 1) on crystallization fron MeOH containing a little chloroform afforded cycloartanone (0·20 g), m.p. 106–107°, $[\alpha]_D^{20}$ + 20°; 2, 4-dinitrophenylhydrazone, m.p. 240° (dec).

Action of Raney Ni *on* 9, 19-*cyclolanost*-25-*en*-3β-*ol* (XXa). Compound XXa (0·15 g) in *p*-cymene (8 ml) and Raney Ni (0·1 g) were used. After working up in the usual way and on repeated chromatographic separation cycloartenone (19 mg), m.p. 109°, ketone XX (12 mg), m.p. 99–100°, and cycloartanone (6 mg), m.p. 106–107°, were obtained.

Action of Raney Ni *on cycloarten*-3α-*ol*. Cycloarten-3α-ol (0·15 g) in *p*-cymene (10 ml) and Raney Ni (0·25 g) were used and the chromatographic separation of the product yielded cycloartanone (40 mg), m.p. 106–107° (undepressed on admixture with an authentic sample).

Action of Raney Ni *on cycloartanol*. Cycloartanol (0·15 g) in *p*-cymene (10 ml) and Raney Ni (0·25 g) were used. After working up as above cycloartanone was obtained (45 mg), m.p. 106–107°.

Action of Raney Ni *on* $\Delta^{9(11)}$-*lanostenol*. $\Delta^{9(11)}$-Lanostenol (0·75 g) in *p*-cymene (20ml) and Raney Ni (2·5 g) were used. Working up in the usual way the residue was chromatographed on alumina (25 g). Light petroleum-benzene (1 : 1) eluate yielded a residue which on crystallization from MeOH-chloroform yielded $\Delta^{9(11)}$-lanostenone, in plates (0·45 g), m.p. 117–118°, $[\alpha]_D^{20}$+47°; the IR spectrum showed strong absorption peak at 840 cm^{-1}(trisubstituted double bond). (Found: C, 84·36; H, 11·74; $C_{30}H_{50}O$ requires: C, 84·44; H, 11·81%); semicarbazone, m.p. 225–226° (dec); the ketone was characterized by converting it to $\Delta^{9(11)}$-lanostenol by sodium-n-propanol reduction.

Action of Raney Ni *on lupeol hydrochloride*. Lupeol hydrochloride (0·5 g) in *p*-cymene (20 ml) and RaneyNi (2·5 g) were used. The ether extract yielded a solid residue which was chromatographed on alumina (15 g). The residue from light petroleum-benzene (1 : 1) on crystallization from EtOH-chloroform yielded 18-*iso*-β-amyranone, in plates (0·27 g), m.p. 235–236°, $[\alpha]_D^{20}$+58·6°, strong peaks at 1710 cm^{-1}, 1380 cm^{-1}. (Found: C, 84·36; H, 11·77; $C_{30}H_{50}O$ requires: C, 84·44; H, 11·81%), oxime, m.p. 275–276° (dec). The ketone was characterised by its conversion to the corresponding alcohol, 18 iso-β-amyranol by sodium-n-propanol reduction.

Action of Raney Ni *on* 18-*iso*-β-*amyranol*. 18-iso-β-amyranol (0·1 g) in *p*-cymene (7 ml) and Raney Ni (0·25 g) were used. After working up as above 18-iso-β-amyranone was obtained (23 mg). m.p. 235–236°.

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REFERENCES

[1] D. Chakravarti, R.N. Chakravarti and M. N. Mitra. *Nature Lond* **193**, 1071 (1962).
[2] R. N. Chakravarti, M. N. Mitra and Debi Chakravarti, *Bull. Cal. School Trop. Med.* **11**, 147 (1963)
[3] R. N. Chakravarti, M. N. Mitra and Debi Chakravarti, *Ibid.* **12**, 112 (1964).
[4] S. K. Banerjee, D. Chakravarti, R. N. Chakravarti and M. N. Mitra, *Tetrahedron* **24**, 6459 (1968)
[5] S. K. Banerjee and R. N. Chakravarti, *Bull. Cal. School Trop. Med.* **13**, 60 (1965)
[6] S. B. Mahato, S. K. Banerjee and R. N. Chakravarti, *Ibid.* **16**, 122 (1968)
[7] D. H. R. Barton, *J. Chem. Soc.* 1444 (1951)
[8] A. R. H. Cole, D. E. White and R. L. S. Willix, *Ibid.* 4868 (1956)
[9] R. N. Chakravarti and R. Robinson, *Ibid.* 78 (1947)
[10] H. R. Bentley, J. A. Henry, D. S. Irvine and F. S. Spring, *Ibid.* 3673 (1953)
[11] T. G. Halsall, E. R. H. Jones and G. D. Meakins, *Ibid.* 2862 (1952)
[12] R. Mozingo, *Organic Syntheses* Coll. Vol. III, P. 181. Wiley, New York (1955)