195. *Eburicoic Acid.*

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Eburicoic acid, isolated as its acetyl derivative from the naturally grown fungus, *Polyporus anthracophilus* Cooke, is shown to be a tetracyclic hydroxy-acid of the triterpene series, of formula $C_{30}H_{48}O_3$ and not $C_{27}H_{44}O_3$ as suggested by Gascoigne, Holker, Ralph, and Robertson (*Nature*, 1950, **166**, 652). It contains one reactive and one inert ethylenic linkage, and the presence of the system $\cdot CH_2\cdot C{:}C\cdot CH_2\cdot$ has been established by oxidation to the chromophore $\cdot CO\cdot C{:}C\cdot CO$ recognised by its characteristic absorption spectrum.

By conversion of the carboxyl group into a methyl group a new triterpene alcohol, eburicol, has been prepared.

The report by Gascoigne, Holker, Ralph, and Robertson (*Nature*, 1950, **166**, 652) of the occurrence of eburicoic acid in the fungus *Polyporus anthracophilus* Cooke makes it desirable to publish our results on this acid obtained from the same source. Mr. J. L. Somerville, Australian Newsprint Mills, Boyer, Tasmania, observed several years ago that the " white rot " in a sample of decayed *Eucalyptus regnans*, on extraction with alcohol, yielded a crystalline acid, and he very kindly made this acid and supplies of the fungus available to us for further investigation. We have isolated from the mycelium of the fungus, in yields of up to 70%, the acetyl derivative of a monobasic acid recorded by Gascoigne *et al.* We were unaware of the identity of this acid with eburicoic acid which now appears to have been established by the Liverpool workers. We accept this identification and adopt the name given to the acid by the earlier workers, Kariyone and Kuruno (*J. Pharm. Soc. Japan*, 1940, **60**, 110, 318).

On the basis of analytical figures obtained for eburicoic acid and four of its derivatives, Gascoigne *et al.* put forward a formula $C_{27}H_{44}O_3$ for the acid. However, the present communication describes twenty-seven derivatives and degradation products, analyses of which clearly indicate the formula $C_{30}H_{48}O_3$ originally suggested by Kariyone and Kuruno; but for consistent analyses figures we found it necessary to sublime the free acid under a high vacuum.

Hydrolysis of the acetate gave the free acid, m. p. 292—293°, $[\alpha]_D^{17}$ +34° (in pyridine), in good agreement with the values given by Gascoigne *et al.* [m. p. 293°, $[\alpha]_D^{17}$ +35·6° (in pyridine)]. Three of the four derivatives recorded by these workers have also been prepared by us and there is reasonable agreement between our results (see Experimental).

Eburicoic acid is a weak acid which can be titrated with standard alkali in alcohol solution. Its methyl ester, readily prepared by the action of diazomethane, is very stable towards alkali, indicating that the carboxyl group is attached to a tertiary carbon atom. Benzoylation of the methyl ester proceeded readily, but benzoyleburicoic acid resisted methylation by diazomethane in ether although it took place slowly in acetone. This suggests that the carboxyl and the hydroxyl group are close together, resistance to methylation being caused by steric hindrance by the large benzoyl group.

Eburicoic acid and its simple derivatives gave a yellow colour with tetranitromethane in chloroform and positive tests in the Liebermann–Burchard and Salkowski reactions. Thus we concluded that eburicoic acid is a monohydroxy-carboxylic acid, $C_{30}H_{48}O_3$, of the triterpene series, and thus isomeric with a number of well-defined acids of this class.

Eburicoic acid on mild oxidation with chromic acid yielded a ketonic acid, eburiconic acid, $C_{30}H_{46}O_3$, m. p. 232° (semicarbazone, m. p. 223°). The alcoholic group present in eburicoic acid is thus secondary, and probably at position 2 in the triterpene nucleus in common with most of the triterpenes of known structure, although proof of this has not yet been obtained.

Reduction of methyl acetyleburicoate, m. p. 157—158°, with hydrogen at high temperature and pressure in the presence of Raney nickel yielded an unsaturated (tetranitromethane) product, m. p. 157—158°, which did not depress the melting point of the starting material. The product was, however, methyl acetyldihydroeburicoate, also produced by quantitative hydrogenation at atmospheric temperature and pressure in the presence of Adams's catalyst in which one mole of hydrogen was absorbed. Furthermore, methyl acetyleburicoate absorbed two atoms of oxygen per molecule from perbenzoic acid, indicating the presence of two ethylenic linkages, and methyl acetyldihydroeburicoate absorbed only one.

From the reaction of perbenzoic acid on methyl acetyleburicoate an "oxide," m. p. 208°, of probable formula $C_{33}H_{52}O_6$ was isolated which gave no colour with tetranitromethane. On the other hand, the product of the same reaction on methyl acetyldihydroeburicoate had the composition, $C_{33}H_{52}O_4$, and is thus isomeric with methyl acetyleburicoate; this product gave an intense yellow colour with tetranitromethane, and its ultra-violet absorption spectrum, (maxima at 243 and 251 mμ.) points to the presence of two conjugated double bonds, the formation of which can readily be explained by loss of water from an unstable oxide intermediate. Birchenough and McGhie (*J.*, 1949, 2038) have shown that perbenzoic acid reacted with α-dihydrolanosteryl acetate to give a labile intermediate " oxide " which readily passed into a diene during recrystallisation. The $\lambda_{max.}$ values of the absorption spectrum of α-dihydroagnosteryl acetate thus formed are identical with those of our product which we have termed methyl acetyl*iso*eburicoate.

From the evidence so far considered we conclude that eburicoic acid is a tetracyclic triterpene acid and that since it has no characteristic ultra-violet absorption spectrum the two double bonds present are not conjugated. Other tetracyclic acids to which eburicoic acid may bear some relation are polyporenic acid A (Cross and Jones *J.*, 1940, 1491) and the elemadienolic acids (α- and β-elemolic acids) (Ruzicka, Rey, Spillmann, and Baumgartner, *Helv. Chim. Acta*, 1943, **26**, 1638). Further reactions were carried out in an endeavour to establish such a relationship.

With ozone methyl acetyleburicoate yielded 0·5 mole of formaldehyde, indicating an exocyclic methylene group. This double bond is that which is readily reduced, as methyl acetyldihydroeburicoate gave no formaldehyde on ozonolysis. These results are in close agreement with those obtained by Cross and Jones (*loc. cit.*) with polyporenic acid A. The non-volatile product from the ozonolysis of methyl acetyleburicoate was a ketonic methyl ester acetate, $C_{32}H_{50}O_5$.

Oxidation of dihydroeburicoic acid with chromic acid at 40° gave dihydroeburiconic acid, but methyl acetyldihydroeburicoate gave a product, $C_{33}H_{50}O_6$, as bright yellow prisms having an intense absorption maximum at 270—272 mμ. The replacement of four hydrogen atoms by two oxygen atoms and the light absorption indicated the chromophore ·CO·C:C·CO, formed by oxidation of $\cdot CH_2\cdot C{:}C\cdot CH_2$, so the product must be methyl acetyldihydrodiketoeburicoate. This arrangement of two ketone groups with a conjugated double bond between them has been established for other yellow compounds formed in the triterpene series (*Helv. Chim. Acta*, 1942, **25**, 1394, 1405; *Annalen*, 1939, **539**, 219; *J.*, 1950, 1562). As well as supplying valuable structural evidence this oxidation confirms the presence of the second, the inert, double bond which had previously been indicated by perbenzoic acid titration.

The oxidation of methyl acetyleburicoate with chromic acid at 70° gave a mixture, from which two well-defined yellow crystalline solids were readily separated by chromatography. For one, $C_{33}H_{48}O_6$, yellow prisms, m. p. 143—145°, the absorption spectrum with a maximum at 264—267 mμ. again indicated the presence of the chromophore ·CO·C:C·CO. The main product, $C_{32}H_{46}O_7$, crystallised in yellow needles, m. p. 195° ($\lambda_{max.}$ 268—270 mμ.); in the formation of this compound oxidation has taken place also at the reactive double bond with the elimination of the methylene group, forming a new keto-group not in close proximity to the main chromophore; the product is therefore a methyl triketo-ester acetate.

The possibility existed that the alcohol resulting from the conversion of the carboxyl group of eburicoic acid into a methyl group might be identical with one of the well-defined tetracyclic alcohols. This conversion was attempted by the standard procedure. Thionyl chloride reacted with acetyleburicoic acid to form an acid chloride, but hydrogen chloride was added at the double bond, forming a compound $C_{32}H_{50}O_3Cl_2$; but use of oxalyl chloride gave a compound, in poor yield, which was probably the required acid chloride. We found, however, that the conversion of the carboxyl group into the aldehyde group could be accomplished readily by another route. Lithium aluminium hydride converted either methyl eburicoate or methyl acetyleburicoate into a new crystalline diol containing one secondary and one primary hydroxyl group. Its diacetate on careful hydrolysis was converted into the monoacetate, having a free primary alcohol group which was then oxidised to the corresponding aldehyde. Wolff–Kishner reduction then yielded eburicol $C_{30}H_{50}O$, m. p. 158—159°, $[\alpha]_D^{17}$ $+66°$, isomeric but not identical with any known triterpene alcohol. Catalytic reduction of its acetate gave dihydroeburicyl acetate, which on hydrolysis gave dihydroeburicol. These are not identical with dihydro-β-tritelemol and its acetate (Ruzicka and Häusermann, *Helv. Chim. Acta*, 1942, **25**, 439) formed by a similar conversion from dihydro-β-elemolic acid. Like polyporenic acid A (Cross and Jones, *loc. cit.*), eburicoic acid is not readily isomerised. Other points of similarity with polyporenic acid A have been established in this paper and this acid may perhaps be a hydroxy-eburicoic acid.

EXPERIMENTAL.

All m. p.s are corrected. Rotations were measured in chloroform solution unless otherwise stated.

Extraction of the Fungus.—Dried mycelium of *Polyporus anthracophilus* Cooke (150 g.) was refluxed with alcohol (*ca.* 1 l.) for 10 minutes and filtered hot with suction. The residue was extracted twice more with smaller volumes of alcohol. The combined alcoholic extracts deposited the crude triterpene on storage. By filtration and concentration, several crops of crystalline material were obtained, of unchanged physical properties. The yield of crude triterpene thus obtained varied from 58 to 70% of the weight of fungus. It was recrystallised three times from alcohol, then twice from glacial acetic acid, and finally from alcohol. After being dried in a vacuum at 140° for 12 hours acetyleburicoic acid melted at 259° and had $[\alpha]_D^{16}$ +42° (*c*, 0·42) (Found : C, 76·8; H, 9·8. Calc. for $C_{32}H_{50}O_4$: C, 77·1; H, 10·0%). Gascoigne *et al.* report m. p. 256—257°, $[\alpha]_D^{20}$ +35·8°.

Eburicoic Acid.—Acetyleburicoic acid was heated with aqueous-alcoholic potassium hydroxide at 40° for 24 hours and worked up in the usual way. Crystallisation three times from alcohol and finally from chloroform–ethanol gave minute needles of *eburicoic acid*, m. p. 292—293°, $[\alpha]_D^{17}$ +34° (*c*, 1·2 in pyridine), +50° (*c*, 0·25 in chloroform) [Found : C, 78·5; H, 10·5%; equiv., 458 (cholic acid used for standardisation). Calc. for $C_{30}H_{48}O_3$: C, 78·9; H, 10·6%; equiv., 456]. The Liebermann–Burchard test gave an intense red colour and the Salkowski test an orange-red colour.

Methyl eburicoate. Eburicoic acid was methylated with diazomethane in ether, and the product crystallised three times from methanol from which it separated as white needles, m. p. 127—129°. After being dried in a vacuum at 80° for 4 hours it had m. p. 142—145°. Recrystallisation from ethyl acetate then gave the ester, m. p. 146—147°, $[\alpha]_D^{15}$ +45° (*c*, 1·83) (Found : C, 79·1; H, 10·4; OMe, 6·6. Calc. for $C_{31}H_{50}O_3$: C, 79·2; H, 10·6; OMe, 6·6%). The sample for analysis was sublimed in a high vacuum. Attempted hydrolysis of methyl eburicoate with N-alcoholic alkali yielded unchanged material. With tetranitromethane in chloroform it gave a deep yellow colour. Gascoigne *et al.* report m. p. 140—141°.

Methyl acetyleburicoate. This was prepared either by methylation of acetyleburicoic acid with diazomethane in ether or by acetylation of methyl eburicoate with acetic anhydride and pyridine, and was isolated in the usual way. After three crystallisations from methanol the methyl ester separated in long, slender, glistening needles which, after being dried in a vacuum at 120° for 24 hours, had m. p. 157—158°, $[\alpha]_D^{16}$ +48° (*c*, 0·52) (Found : C, 77·4; H, 10·3; OMe, 5·9%. Calc. for $C_{33}H_{52}O_4$: C, 77·3; H, 10·2; OMe 6·1%). Gascoigne *et al.* report m. p. 153—154°.

Benzoyleburicoic acid. Eburicoic acid and benzoyl chloride in pyridine were kept at room temperature for 24 hours. The product, crystallised twice from acetone, gave *benzoyleburicoic acid* in squat prisms, m. p. 166°, $[\alpha]_D^{15}$ +57° (*c*, 0·912) (Found : C, 79·8; H, 9·1. $C_{37}H_{52}O_4$ requires C, 79·3; H, 9·3%).

Attempts to methylate this with diazomethane in ether yielded unchanged starting material. When benzoyleburicoic acid in acetone was treated with excess of diazomethane in ether and kept for 48 hours at 0° *methyl benzoyleburicoate* was formed, which after crystallisation from acetone formed needles, m. p. 200—201°, $[\alpha]_D^{15}$ +71° (*c*, 0·418). For analysis a sample was dried in a vacuum at 140° for 8 hours (Found : C, 79·7; H, 9·2; OMe, 5·5. $C_{38}H_{54}O_4$ requires C, 79·4; H, 9·4; OMe, 5·4%). The same product was obtained by benzoylating methyl eburicoate.

Eburiconic Acid.—To eburicoic acid (1·82 g.) in purified glacial acetic acid (60 ml.) at 40° was added chromic acid in acetic acid (12 ml. of N.) during 1 hour. Next morning the solution was treated with a few drops of methanol to destroy excess of chromic acid and then poured into water (400 ml.). The product was filtered off, washed with water, and crystallised twice from acetone. *Eburiconic acid* separated in fine white needles, m. p. 232°, $[\alpha]_D^{20}$ +49° (*c*, 0·512) (Found : C, 79·1; H, 10·2. $C_{30}H_{46}O_3$ requires C, 79·3; H, 10·1%).

The semicarbazone, formed in the normal way, melted at 223° (Found : C, 72·8; H. 9·8. $C_{31}H_{49}O_3N_3$ requires C, 72·8; H, 9·6%).

Methyl Acetyldihydroeburicoate.—Methyl acetyleburicoate (1 g.) in methanol (100 ml.) was reduced with hydrogen in the presence of Raney nickel at 100°/100 atm. for 2 hours. The filtered solution was concentrated, yielding *methyl acetyldihydroeburicoate*, needles, m. p. 157—158°, $[\alpha]_D^{18}$ +56° (*c*, 2·8) (Found : C, 76·9; H, 10·7. $C_{33}H_{54}O_4$ requires C, 77·0; H, 10·5%), which gave a distinct yellow colour with tetranitromethane. The same reduction was effected with Adams's platinum catalyst in ethanol at atmospheric pressure : reduction ceased after the uptake of one mole of hydrogen.

Methyl acetyldihydroeburicoate (100 mg.) was dissolved in ethanol (20 ml.) to which was added 2 ml. of N-potassium hydroxide, and the solution kept overnight. The product isolated by dilution with water and filtration was crystallised from chloroform–methanol, yielding *methyl dihydroeburicoate*, m. p. 135—136°, $[\alpha]_D^{20}$ +44° (*c*, 1·1) (Found : C, 78·5; H, 11·2. $C_{31}H_{52}O_3$ requires C, 78·8; H, 11·0%).

Acetyldihydroeburicoic Acid.—Catalytic reduction of acetyleburicoic acid (1 g.) in ethanol (100 ml.) with Raney nickel at 100°/100 atm. yielded this *acid*, which crystallised from methanol in fine small needles, m. p. 268—270°, $[\alpha]_D^{20}$ +47° (*c*, 1·384) (Found : C, 76·5; H, 10·5. $C_{32}H_{52}O_4$ requires C, 76·8; H, 10·4%). Hydrolysis of a sample with aqueous-alcoholic alkali gave *dihydroeburicoic acid* in fine needles (after crystallisation from chloroform–methanol), m. p. 286—288°, $[\alpha]_D^{17}$ +55° (*c*, 0·22) (Found : C, 78·3; H, 11·1. $C_{30}H_{50}O_3$ requires C, 78·6; H, 10·9%).

Titrations with Perbenzoic Acid.—To a solution of methyl acetyleburicoate (1 g.) in chloroform at 0°, a 200% excess of perbenzoic acid in chloroform was added and the mixture kept at 0°. Aliquot portions were withdrawn at intervals and treated with excess of potassium iodide, the solutions acidified with acetic acid, and the iodine was titrated with 0·1N-sodium thiosulphate. After 24 hours 2 atoms of oxygen per molecule were absorbed and no further reaction took place. The bulk of the solution was then treated with excess of potassium iodide and sodium thiosulphate with shaking, and the chloroform layer separated, washed with sodium carbonate solution and water, then dried, and distilled. The residue was crystallised twice from methanol, giving the "*oxide*," long white needles, m. p. 208°, $[\alpha]_D^{17}$ +4° (*c*, 2·416) (Found: C, 73·3; H, 9·5. $C_{33}H_{52}O_6$ requires C, 72·8; H, 9·6%). The product gave no colour with tetranitromethane in chloroform.

Methyl acetyldihydroeburicoate on perbenzoic acid titration as above absorbed 1 atom of oxygen per molecule after 24 hours; reaction then ceased. Working up the product in the usual way gave *methyl acetyl*iso*eburicoate*, m. p. 167°, $[\alpha]_D^{20}$ +59° (*c*, 0·8) (Found: C, 77·2; H, 10·2. $C_{33}H_{52}O_4$ requires C, 77·3; H, 10·1%), $\lambda_{max.}$ 243 and 251 mμ., $\varepsilon_{max.}$ 17,300 and 11,700. With tetranitromethane in chloroform it gave a bright yellow colour.

Ozonolysis of Methyl Acetyleburicoate.—Methyl acetyleburicoate (1 g.) in glacial acetic acid (80 ml.) was treated with ozone and oxygen for 1 hour. The solution was then diluted with 1 l. of water and distilled. The distillate (approx. 800 ml.), when treated with 2 : 4-dinitrophenylhydrazine hydrochloride, gave formaldehyde 2 : 4-dinitrophenylhydrazone, m. p. 167° undepressed on admixture with an authentic sample. The yield was 0·2 g. (50%). The residue from the distillation was extracted with ether, the ethereal solution dried and distilled, and the residue crystallised twice from methanol. The *product* separated in needles, m. p. 181—183°, $[\alpha]_D^{18}$ +51° (*c*, 1·48) (Found: C, 74·9; H, 10·1. $C_{32}H_{50}O_5$ requires C, 74·7; H, 9·7%).

Dihydroeburiconic Acid.—Dihydroeburicoic acid (100 mg.) was oxidised with chromic acid, as in the preparation of eburiconic acid above, yielding *dihydroeburiconic acid* as leaflets, m. p. 240—243°, $[\alpha]_D$ +50° (*c*, 0·3) (Found: C, 78·6; H, 10·8. $C_{30}H_{48}O_3$ requires C, 78·9; H, 10·6%).

Methyl Acetyldihydrodiketoeburicoate.—A solution of methyl acetyldihydroeburicoate (0·6 g.) in acetic acid (50 ml.), kept at 70°, was treated during 1 hour with chromic acid (0·7 g.) in acetic acid (10 ml.). The solution was then set aside overnight, whereafter methanol was added to destroy excess of chromic acid, and the whole poured into water and extracted thoroughly with ether. The ethereal extract was washed with sodium carbonate solution, then water, and dried (Na_2SO_4). The residue after removal of the ether was crystallised from methanol and the *methyl acetyldihydrodiketoeburicoate* after two more crystallisations from the same solvent was obtained as large yellow prisms, m. p. 174°, $[\alpha]_D^{17}$ +81° (*c*, 0·34) (Found: C, 73·0; H, 9·4. $C_{33}H_{50}O_6$ requires C, 73·1; H, 9·2%), $\lambda_{max.}$ (in alcohol) 270—272 mμ.; $\varepsilon_{max.}$ 7500.

Oxidation of Methyl Acetyleburicoate.—This ester (4 g.) in acetic acid (300 ml.) was oxidised by the dropwise addition of chromic acid (5 g.) in acetic acid at 70°. The mixture was kept overnight and worked up as in the preceding experiment. The crude product was a yellow resinous mass which failed to crystallise. It was dissolved in light petroleum–benzene (1 : 1) (50 ml.) and filtered through neutralised alumina (80 g.). Light petroleum–benzene (1 : 1) removed *methyl acetyldiketoeburicoate* (50 mg.) which after several recrystallisations from methanol and acetone formed bright yellow prisms, m. p. 143—145°, $[\alpha]_D^{18}$ +70° (*c*, 0·9) (Found: C, 73·2; H, 9·0. $C_{33}H_{48}O_6$ requires C, 73·3; H, 8·9%), $\lambda_{max.}$ (in alcohol) 264—267 mμ.; ε 6900. Benzene or benzene–ether (3 : 1) removed a second yellow *constituent* (2·1 g.) which after four crystallisations from methanol separated as fine yellow needles, m. p. 195°, $[\alpha]_D^{18}$ +67° (*c*, 1·04), $\lambda_{max.}$ (in alcohol) 268—270 mμ.; ε = 7900. For analyses a sample was sublimed in a high vacuum (Found: C, 71·0; H, 8·4. $C_{32}H_{46}O_7$ requires C, 70·9; H, 8·5%).

Acid Chloride Formation.—Acetyleburicoic acid (1·5 g.) was treated with thionyl chloride (15 ml.) at room temperature. The mixture was kept for 3 hours, excess of thionyl chloride removed in a vacuum, and the residue kept in a vacuum-desiccator over solid sodium hydroxide for 48 hours. The *product* crystallised from *n*-hexane in white needles, m. p. 193—195° (Found: C, 69·6; H, 9·1; Cl, 12·6. $C_{32}H_{50}O_3Cl_2$ requires C, 69·6; H, 9·0; Cl, 12·8%).

When acetyleburicoic acid (2 g.) was heated under reflux with oxalyl chloride (5 ml.) for 4 hours and the excess of oxalyl chloride removed under reduced pressure a product was obtained which dissolved readily in *n*-hexane and from this a small amount of crystalline material of rather indefinite m. p. separated which was thought to be the desired acid chloride. It was not analysed or used further.

Eburicodiol.—A suspension of lithium aluminium hydride (0·5 g.) in dry ether (20 ml.) was gently boiled under nitrogen for 15 minutes, then ground, and further heated for 5 minutes. Methyl eburicoate (1·6 g.) in ether (50 ml.) was then run in during 15 minutes. The mixture was set aside for 30 minutes and then treated with sodium hydroxide solution, followed by excess of dilute hydrochloric acid. The ethereal layer was separated, washed with water, dried, and concentrated to 20 ml. Small clusters of needles separated which, after crystallisation from alcohol or acetone, gave *eburicodiol*, m. p. 212—213°, $[\alpha]_D^{17}$ +55° (*c*, 1) (Found: C, 80·9; H, 11·4. $C_{30}H_{50}O_2$ requires C, 81·4; H, 11·3%). The same product was obtained from methyl acetyleburicoate. Attempts to form an *iso*propylidene derivative failed.

Acetylation with acetic anhydride–pyridine gave the *diacetate* in fine needles, m. p. 134° after crystallisation from methanol and drying in a vacuum at 100° for 24 hours. Unless thus dried, the product melted at 115°, resolidified, and remelted at 134°. It had $[\alpha]_D^{17}$ +45° (*c*, 1) (Found: C, 77·3; H, 10·2. $C_{34}H_{54}O_4$ requires C, 77·6; H, 10·3%).

To the diacetate (2 g.) in alcohol (70 ml.) and water (3 ml.) was added 0·023N-KOH (190 ml.). The resulting solution was refluxed for 2 hours and worked up in the usual way. The product was dissolved in benzene–light petroleum (b. p. 40—60°) and filtered through neutralised alumina (40 g.). Benzene eluted the main product, *eburicodiol 2-acetate*, which after three crystallisations from chloroform–methanol formed small white needles, m. p. 166—167°, $[\alpha]_D^{17}$ +56° (*c*, 1) (Found: C, 79·3; H, 10·8. $C_{32}H_{52}O_3$ requires C, 79·3; H, 10·7%).

Eburicalyl Acetate.—To the above monoacetate (0·666 g.) in acetic acid (100 ml.) and ether (350 ml.) was added chromic acid (150 mg.) in acetic acid (4·8 ml.) during 1 hour. The whole was set aside for 2 hours, then diluted largely with water, and the ethereal layer separated. The aqueous layer was further extracted with ether, and the extracts were combined, washed with sodium carbonate solution and water, and dried. After removal of the ether, the residue, dissolved in light petroleum (b. p. 40—60°), was filtered through neutralised alumina. Benzene–light petroleum (1 : 1) eluted *eburicalyl acetate* which after three crystallisations from methanol melted over the range 140—144°. It had $[\alpha]_D^{17}$ +53° (*c*, 0·42) (Found : C, 79·1; H, 10·6. $C_{32}H_{50}O_3$ requires C, 79·7; H, 10·4%).

Eburicyl Acetate.—The above aldehyde (100 mg.), sodium ethoxide (from Na, 1·5 g., and alcohol, 15 ml.), and hydrazine hydrate (100%; 2·5 ml.) were heated at 200° for 17 hours. The crude product, isolated in the usual way, was acetylated with acetic anhydride–pyridine and the product, in light petroleum (b. p. 40—60°), filtered through neutralised alumina. Light petroleum–benzene (9 : 1) eluted *eburicyl acetate* (40 mg.) which crystallised from methanol in plates, m. p. 138—139°, $[\alpha]_D^{17}$ +66° (*c*, 0·25) (Found : C, 82·2; H, 11·4. $C_{32}H_{52}O_2$ requires C, 82·1; H, 11·1%).

Hydrolysis of this acetate yielded *eburicol*, m. p. 158—159°, $[\alpha]_D^{17}$ +66° (*c*, 0·3) (Found : C, 84·6; H, 11·9. $C_{30}H_{50}O$ requires C, 84·5; H, 11·7%).

Eburicyl acetate (20 mg.), hydrogenated in alcohol solution with hydrogen in the presence of Adams's catalyst, yielded *dihydroeburicyl acetate* which crystallised from methanol in flat needles, m. p. 127°, $[\alpha]_D^{17}$ +79° (*c*, 0·22) (Found : C, 81·7; H, 11·7. $C_{32}H_{54}O_2$ requires C, 81·7; H, 11·5%). Hydrolysis of this gave *dihydroeburicol*, leaflets (from methanol), m. p. 164—165°, $[\alpha]_D^{20}$ +40° (*c*, 0·2) (Found : C, 83·8; H, 12·4. $C_{30}H_{52}O$ requires C, 84·1; H, 12·2%).

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