181. *West African Timbers. Part VII.*[1] *Anthothecol, an Extractive from* Khaya anthotheca.

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Anthothecol, an extractive from *Khaya anthotheca*, has been shown to be a diosphenol, of probable structure (VIIIa). It is related chemically, and probably biologically, to substances obtained from other trees of the family Meliaceae.

Continuing our reports on the heart-wood constituents of the family Meliaceae, we now discuss anthothecol, an extractive [1] from *Khaya anthotheca* C. DC. Anthothecol, $C_{28}H_{32}O_7$, has a strong ultraviolet absorption maximum at 281 mμ (ε 11,000), which is shifted in alkaline solution to 326 mμ (ε 4600). This suggests the presence of a diosphenol grouping, which is also indicated by the fact that anthothecol gives a ferric chloride colour, and forms a monoacetate having $\lambda_{max.}$ 230 mμ (ε 10,000) and a new band attributable to an enol acetate at 1770 cm.$^{-1}$.

The position of the ultraviolet maximum is consistent with the presence of a diosphenol group in ring B of a tetracyclic triterpene, as in the partly synthetic diosphenols obtained from limonin and related compounds.[2]

Anthothecol has a further absorption maximum at 219 mμ (ε 13,000), which is similar to that shown by gedunin [3] (I) and suggests that anthothecol, like gedunin, may be an unsaturated ketone. Mild hydrogenation of anthothecol gave a dihydro-compound, still a diosphenol, in which there is a less intense maximum at 209 mμ (ε 7200). Subtraction of the curve for dihydroanthothecol from that for anthothecol leaves a difference maximum at 227 mμ (ε 9200) which is similar to the difference between gedunin and dihydrogedunin (229 mμ; ε 10,000) and in agreement with the presence of a 3-keto-Δ^1-grouping in a triterpene nucleus. A new band, at 1710 cm.$^{-1}$, appears in the infrared spectrum of dihydroanthothecol, in agreement with this assignment. Neither anthothecol nor dihydroanthrothecol gives a dinitrophenylhydrazone.

The short-wavelength maximum of dihydroanthothecol at 209 mμ is similar to that in dihydrogedunin and in khivorin [4] and suggests that anthothecol, like these compounds, contains a furan ring. This is supported by the presence of infrared bands at 1504 and 877 cm.$^{-1}$ which are characteristic of the furan ring. Unlike gedunin and khivorin, anthothecol does not yield 2-furaldehyde when boiled with alkali, but as a 7α-hydroxyl group is necessary for this elimination,[5] the failure may be accounted for by the presence of the diosphenol group, containing a 7-keto-function.

Mild alkaline hydrolysis of anthothecol gives a deacetyl compound which on acetylation gives anthothecol acetate; that deacetylanthothecol contains a new primary or secondary hydroxyl group is shown by oxidation with chromic acid in acetone to a dehydro-compound, showing a new carbonyl group by its infrared spectrum. Dihydroanthothecol reacts similarly. The new carbonyl group is present as a ketone, derived from a secondary alcohol, as in chloroform solution the compound does not show the characteristic aldehyde absorption at 2700 cm.$^{-1}$.

The presence of the groups described above leaves one oxygen atom unaccounted for. This gives no characteristic spectral absorption, and no readily detected reactions, so it seemed possible that it is present as an oxide, a feature present in all the compounds so far described from related timbers. If anthothecol contained an oxide group, it should be

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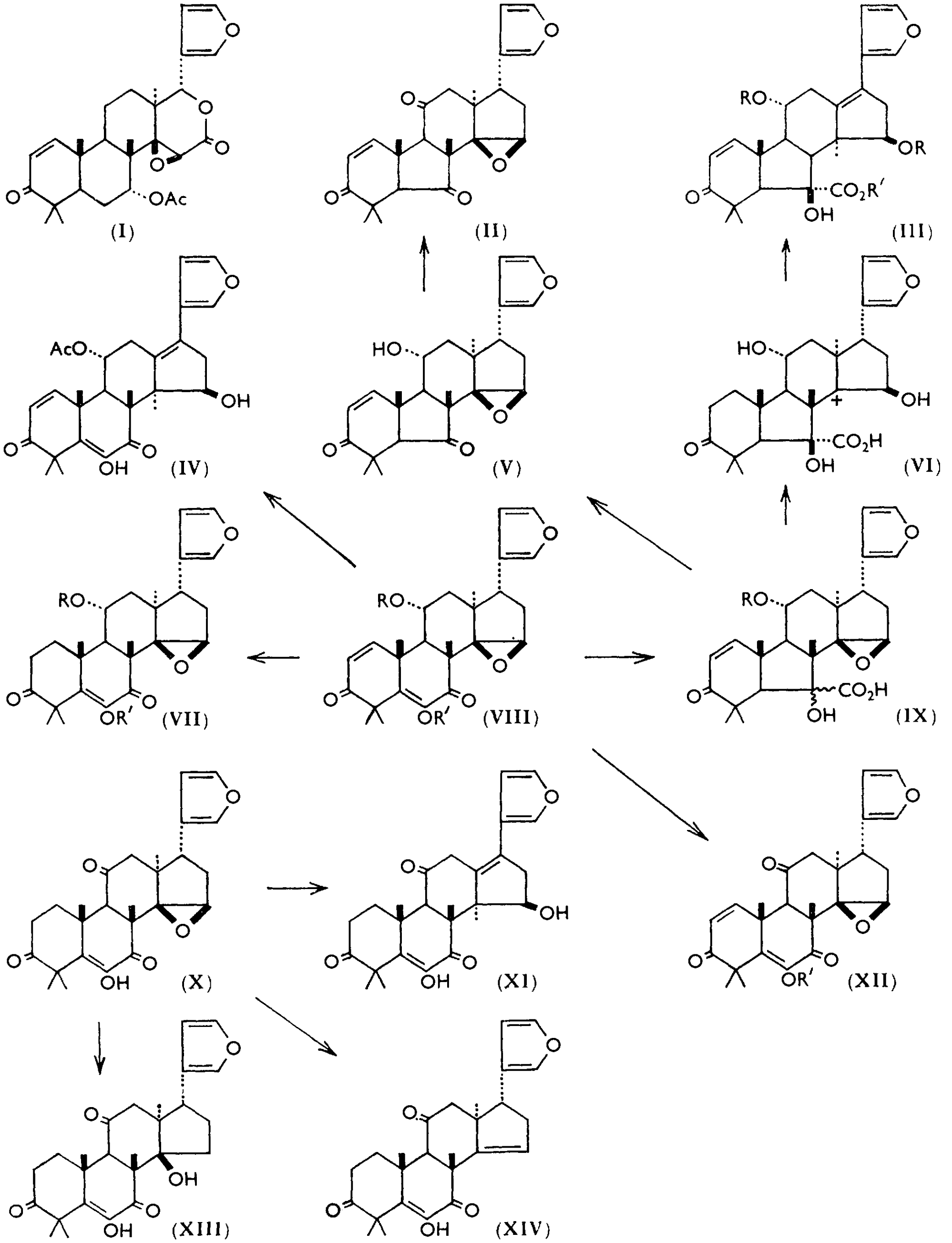
[1] Part VI, preceding paper.
[2] Barton, Pradhan, Sternhell, and Templeton, *J.*, 1961, 255.
[3] Akisanya, Bevan, Halsall, Powell, and Taylor, *J.*, 1961, 3705.
[4] Bevan, Halsall, Nwaji, and Taylor, *J.*, 1962, 768.
[5] Melera, Schaffner, Arigoni, and Jeger, *Helv. Chim. Acta*, 1957, **40**, 1420.

reduced by chromous chloride to a deoxy-compound, as are gedunin and related compounds.[4] This was investigated on the ketone obtained by chromic acid oxidation of deacetyldihydroanthothecol. Reduction of this compound with chromous chloride gave a deoxy-compound having spectral properties similar to those of the starting material. This shows that deacetyldehydrodihydroanthothecol contains an epoxide group which is



(a) R = Ac, R′ = H. (b) R = R′ = Ac. (c) R = R′ = H. (d) R = Ac, R′ = CH_3. (e) R = H, R′=CH_3.

not adjacent to an unsaturated function or to a carbonyl group, as the deoxy-compound shows no spectral evidence of new conjugated unsaturation. On this basis, and by analogy with gedunin (I), the structure (VIIIa) is proposed for anthothecol. The position of the acetoxyl group in this formula is at present assigned arbitrarily, and it is discussed below: the stereochemistry is derived by analogy with gedunin, but is supported by evidence to be discussed below.

Catalytic hydrogenation of the ketone obtained by the oxidation of deacetyldihydroanthothecol, to which ketone the structure (X) can now be assigned, gave a different product from that obtained by reduction with chromous chloride. This product gave analyses for a dihydro-derivative and still contained the diosphenol group and the furan ring. It was not oxidised by chromic acid in acetone. It is considered that it is obtained by the opening of the epoxide ring without dehydration, to give a tertiary alcohol, and that it has structure (XIII).

On treatment with sodium hydroxide in aqueous methanol, anthothecol undergoes a benzilic acid rearrangement, giving a complex mixture of acid products. After acetylation and esterification with diazomethane, a methyl ester, $C_{31}H_{38}O_9$, was isolated, containing two acetyl groups. This ester showed an infrared absorption band at 1680 cm.$^{-1}$, due to the unsaturated ketone grouping in ring A, and had ultraviolet absorption maxima at 209 (ε 25,000), 215 (ε 23,000), and 234 mμ (ε 20,600). We account for these facts by supposing that the epoxide ring is opened by internal attack by the newly formed carboxylate ion to give a 15-hydroxy-compound (VI) with a carbonium ion at position 14. A Wagner–Meerwein rearrangement then follows in which the 13-methyl group moves to position 14 and a 13(17)-double bond is formed, in conjugation with the furan ring. This vinylfuran group accounts for the new absorption maximum at 234 mμ, the maximum being displaced somewhat to shorter wavelength by the absorption due to the unsaturated ketone. A comparison of the absorption curves of the benzilic ester and gedunin, to allow for the effect of the unsaturated ketone, gives a difference maximum, due to the vinylfuran chromophore alone, at 243 mμ (ε 13,000).

The stereochemistry assigned to anthothecol is in agreement with the requirements for this rearrangement, which are that the 13-methyl group and the epoxide ring should be *trans*-related. The *cis*-relation of the 13-methyl group and the furan ring results in a steric interaction which may provide the driving force for the rearrangement. If the opening of the epoxide ring in the benzilic acid is to be initiated by attack at C-14 by the carboxylate ion, as we consider to be probable, then it is necessary for the carboxyl group to be in the α-configuration, and the new 15-hydroxyl group will retain the β-configuration. The methyl benzilate acetate can then be represented by structure (IIId). Dihydroanthothecol, in contrast, does not undergo a benzilic acid transformation, the only reaction after prolonged boiling with alkali being hydrolysis of the acetyl group.

A similar isomerisation occurs when anthothecol is treated with hydrochloric acid in acetic acid. The product, isoanthothecol, still shows absorption due to the diosphenol group at 281 mμ and to the unsaturated ketone in the infrared region, but the short-wavelength ultraviolet absorption maximum is spread out, an unresolved peak appearing at 210—230 mμ (ε *ca.* 12,000). The difference maximum between anthothecol and isoanthothecol was at 241 mμ (ε 13,000). This is accounted for as opening of the epoxide ring by hydrochloric acid, followed by Wagner–Meerwein transformation. Isoanthothecol is then represented by the formula (IV).

It remains to discuss the position of the acetoxyl group. Since it has been shown to be hydrolysed to a secondary alcohol, oxidised to a ketone, only position 11, 12, or 16 is possible for it. If it were in position 2 or 1 hydrolysis would give an α- or a β-diketone, which is not the case; and all other secondary positions are already substituted. If the acetoxyl group were at position 16, then hydrolysis and oxidation would give an $\alpha\beta$-epoxyketone, which would be expected on reduction by chromous chloride to lose an oxygen atom and give an unsaturated ketone. This is not the case, for the ultraviolet absorption spectrum of the chromous chloride reduction product (XIV) of deacetyldehydrodihydroanthothecol (X), referred to earlier, shows that it is not an unsaturated ketone. Further, if anthothecol were a 16-acetoxyl compound, then the ketone (X) in which the original acetoxyl has been converted into a ketone group would be a cyclopentanone, whereas its infrared spectrum is consistent with the new carbonyl group in a 6-membered ring.

If the acetoxyl group were at position 12, then the rearranged benzilic acid (III) and isoanthothecol (IV) would be allyl alcohol derivatives, and it seems unlikely that these would survive the conditions of formation without dehydration to a furylbutadiene. The spectral properties expected for such a compound would be widely different from those found. Moreover, if the acetoxyl group were at position 12, then the compound (X) in which the acetoxyl is converted into a ketone group would be expected to rearrange under acid conditions to a compound in which the furan ring is conjugated through the 13(17)-double bond with the 12-carbonyl group. Such a conjugated system would be expected to show an absorption maximum at ~314 mμ, similar to that shown by furfurylideneacetone. In fact, acidic rearrangement of compound (X) gave a non-crystalline isocompound (XI) whose ultraviolet absorption spectrum showed maxima at 211, 237, and 284 mμ, the difference maximum between this compound and (X) being at about 237 mμ, very similar to the corresponding maxima for isoanthothecol and the benzilic ester. This indicates that the rearrangement product of compound (X) has the vinylfuran structure (XI) and is not the isomeric conjugated furfurylidene ketone, which it would be if the acetoxyl in anthothecol were at position 12. For these reasons we consider that the acetoxyl group is not at position 12 or 16, and so we place it at position 11 by elimination. Since it is readily hydrolysed and reacetylated we assign it the 11α-configuration. We have not yet obtained direct evidence that it is in this position.

Some other transformation products of anthothecol have been obtained. Methylation with methyl iodide and sodium in toluene, or better with methyl iodide and potassium t-butoxide, gave a monomethyl ether (VIIId). In another experiment in which sodium and toluene containing a little methanol were used, deacetylanthothecol methyl ether (VIIIe) was obtained, which on acetylation gave anthothecol methyl ether. Reduction of anthothecol methyl ether with sodium borohydride in methanol gave a dihydro-derivative (VIId) in which the double bond conjugated with the 3-ketone group was reduced, as shown by the spectral properties. The corresponding deacetyl ether (VIIe) was also obtained. Oxidation of deacetylanthothecol methyl ether (VIIIe) with chromic acid in acetone gave a ketone (XIIe), analogous to that obtained by the oxidation of deacetylanthothecol itself.

When the crude mixture of acids obtained by alkali treatment of anthothecol was oxidised with lead tetra-acetate, a crystalline product was obtained which had the analysis to be expected if the α-hydroxy-acid is converted into a ketone [$>C(OH)\cdot CO_2H \longrightarrow >CO$]. The infrared spectrum showed a band at 1754 cm.$^{-1}$, in agreement with the presence of a cyclopentanone nucleus in the molecule, and the unsaturated ketone and furan bands were still present. There was no spectral evidence of the presence of a vinylfuran, and so it is considered that this substance has structure (V) and arises by oxidation of the unrearranged benzilic acid (IX), in which the oxide ring has not opened. It may be that this is produced from a stereoisomeric benzilic acid, which is unable to rearrange as the carboxyl group is in the unfavourable β-configuration. Alternatively, it may merely be that opening of the epoxide ring is slower than the benzilic acid transformation and had to compete with it.

Oxidation of this cyclopentanone (V) with chromic acid in acetone gave a dehydro-derivative (II) in which the secondary hydroxyl group corresponding to the original acetate is oxidised to a ketone. Hydrogenation of the crude benzilic acid mixture gave a non-crystalline product, the infrared absorption of which showed that both the unsaturated ketone and the furan ring had been reduced. Oxidation of this with lead tetra-acetate gave a crystalline product whose analysis indicated the expected hexahydro-derivative of compound (V). However, the spectrum was not in accordance with this structure, as it did not show the band at 1754 cm.$^{-1}$ expected for the cyclopentanone and had only one carbonyl maximum, at 1720 cm.$^{-1}$, presumably due to the 3-ketone group. Oxidation of the substance with chromic acid in acetone gave a dehydro-derivative which showed no hydroxyl band in the infrared spectrum but had a new band at 1754 cm.$^{-1}$, probably attributable to a cyclopentanone group; this derivative had an ultraviolet absorption maxima at 219 mμ (ε 3162); the nature of this substance is not known. There was also obtained a smaller amount of a substance which is probably the expected hexahydro-derivative of compound (V).

The formula (VIIIa) assigned to anthothecol is that of the 11α-acetoxy-derivative of cedrelone, whose structure has been disclosed in preliminary notes by two groups of workers.[6] Cedrelone is obtained from *Cedrela toona*, which also belongs to the Meliaceae. The reported chemistry of cedrelone closely parallels our findings with anthothecol.

EXPERIMENTAL

Optical rotations refer to chloroform, and ultraviolet spectra to methanol, solutions and infrared spectra to Nujol mulls, unless otherwise stated. Only infrared maxima which are different from those in the starting material are recorded.

Anthothecol (VIIIa).—Anthothecol[1] had $\lambda_{max.}$ 219 (ε 13,000) and 281 mμ (ε 11,000) in methanol, 224 (ε 8320) and 326 mμ (ε 4600) in alkaline methanol, and $\nu_{max.}$ 3400, 1740, 1670, 1655, 1620, 1504, 1235, and 877 cm.$^{-1}$. The *acetate* formed needles, m. p. 234°, from toluene (Found: C, 68·95; H, 6·6; O, 24·3; OAc, 15·8. $C_{30}H_{34}O_8$ requires C, 68·95; H, 6·6; O, 24·5; 2OAc, 16·5%), $[\alpha]_D^{20}$ $-67°$, $\lambda_{max.}$ 230 mμ (ε 10,000), $\nu_{max.}$ 1770 cm.$^{-1}$.

Dihydroanthothecol (VIIa).—Anthothecol was hydrogenated over palladium–charcoal or Adams catalyst in methanol, giving *dihydroanthothecol*, needles, m. p. 188° (from propanol) (Found: C, 69·5; H, 6·8; OAc, 9·0. $C_{28}H_{34}O_7$ requires C, 69·7; H, 7·1; 1OAc, 9·0%), $[\alpha]_D^{20}$ $-86°$, $\lambda_{max.}$ 209 (ε 7200) and 281 mμ (ε 11,000), unchanged in alkali, $\nu_{max.}$ 1710 cm.$^{-1}$. The compound gave a greenish-brown ferric chloride colour. The *acetate* (VIIb) crystallised from methanol in prisms, m. p. 144° (Found: C, 68·7; H, 7·0. $C_{30}H_{36}O_8$ requires C, 68·7; H, 7·0%), $[\alpha]_D^{20}$ $-106°$, $\lambda_{max.}$ 249 mμ (ε 10,000), $\nu_{max.}$ 1770 cm.$^{-1}$.

Deacetylanthothecol (VIIIc).—Anthothecol (1·4 g.) in methanol (100 ml.) was refluxed for 10 min. with 2N-sodium hydroxide solution (25 ml.). The solution was acidified and the product chromatographed on alumina; the main fraction crystallised from benzene–cyclohexane to give *deacetylanthothecol*, m. p. 218° (Found: C, 71·1; H, 6·6; O, 21·5; OAc, 0. $C_{26}H_{30}O_6$ requires C, 71·2; H, 6·9; O, 21·9%), $[\alpha]_D^{20}$ $-59°$. The infrared spectrum lacked the band at 1740 cm.$^{-1}$, and that at 1235 cm.$^{-1}$ was much weaker. Reacetylation gave anthothecol acetate, identical with an authentic specimen.

Deacetyldehydroanthothecol (XIIa).—Deacetylanthothecol was oxidised with a slight excess of 8N-chromic acid in acetone. *Deacetyldehydroanthothecol*, isolated with chloroform and crystallised from methanol, had m. p. 203° (Found: C, 71·8; H, 6·9. $C_{26}H_{28}O_6$ requires C, 71·55; H, 6·5%), $[\alpha]_D^{20}$ $-74°$, $\lambda_{max.}$ 217 (ε 10,000) and 279 mμ (ε 12,000), $\nu_{max.}$ 1724 cm.$^{-1}$.

Deacetyldihydroanthothecol (VIIc).—Alkaline hydrolysis of dihydroanthothecol gave *deacetyldihydroanthothecol*, m. p. 230° (from propanol) (Found: C, 70·65; H, 7·1. $C_{26}H_{32}O_6$ requires C, 70·9; H, 7·3%), $[\alpha]_D^{20}$ $-75°$, $\lambda_{max.}$ 213 (ε 6300) and 281 mμ (ε 10,000), unchanged by alkali.

Deacetyldehydrodihydroanthothecol (X).—Oxidation of deacetyldihydroanthothecol with chromic acid in acetone gave *deacetyldehydrodihydroanthothecol*, crystallising in prisms, m. p. 248—250°, from methylene chloride–methanol (Found: C, 71·3; H, 6·9. $C_{26}H_{30}O_6$ requires C, 71·2; H, 6·9%), $[\alpha]_D^{20}$ $-61°$, $\lambda_{max.}$ 211 (ε 8000) and 281 mμ (ε 10,000), $\nu_{max.}$ 1724 cm.$^{-1}$.

Reduction of Deacetyldehydrodihydroanthothecol by Chromous Chloride.—The dihydro-ketone (X) (3·0 g.) was dissolved in acetone (200 ml.) and acetic acid (200 ml.) in a 500-ml. flask. The air was displaced by butane, and ~20% aqueous chromous chloride added to fill the flask, which was then stoppered and left overnight. The contents were diluted with water and chloroform, and the chloroform layer was washed with sodium carbonate solution and with water, and evaporated. The residue crystallised from methanol, to give the *deoxy-derivative* (XIV) (0·75 g.), m. p. 214° (Found: C, 73·4; H, 7·3. $C_{26}H_{30}O_5$ requires C, 73·9; H, 7·2%), $[\alpha]_D^{20}$

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[6] Hamor, Hodges, McGeachin, Raphael, Robertson, and Sim, *Proc. Chem. Soc.*, 1961, 444; Gopinath, Govindachari, Parthasarathy, Viswanathan, Arigoni, and Wildman, *Proc. Chem. Soc.*, 1961, 446.

$-118°$, $\lambda_{\max.}$ 206 (ε 10,000) and 279 mμ (ε 10,000). The compound gave a ferric chloride colour. It was recovered unchanged after treatment with chromic acid in acetone.

Catalytic Hydrogenation of Deacetyldehydrodihydroanthothecol.—Hydrogenation of the ketone (X) over Adams catalyst in glacial acetic acid was very slow. The product crystallised from propanol, to give the *dihydro-compound* (XIII), m. p. 282—283° (Found: C, 70·7; H, 7·7. $C_{26}H_{32}O_6$ requires C, 70·9; H, 7·3%), $[\alpha]_D^{20}$ $-28°$, $\lambda_{\max.}$ 210 (ε 6000) and 282 mμ (ε 10,000). The infrared spectrum was similar to that of the starting material, except for the presence of a more intense hydroxyl bond. The compound gave a positive ferric chloride test and was unchanged by chromic acid in acetone.

Benzilic Acid Transformation on Anthothecol.—Anthothecol (5 g.) was refluxed for 3 hr. with methanol (50 ml.), water (50 ml.), and sodium hydroxide (5 g.). After cooling, the solution was acidified, and the precipitate collected and dried. Acetylation with pyridine and acetic anhydride gave a product which partly crystallised in very soluble prisms, m. p. 278°. These were not purified, but the whole was esterified with diazomethane in ether to give the *ester acetate* (IIId) (1·6 g.), crystallising from methylene chloride–methanol in prisms, m. p. 226—228° (Found: C, 67·1; H, 7·1. $C_{31}H_{38}O_9$ requires C, 67·1; H, 6·9%), $[\alpha]_D^{20}$ $-115°$, $\lambda_{\max.}$ 209 (ε 25,000), 215 (ε 22,000) (inflexion), and 234 mμ (ε 20,000).

Isoanthothecol (IV).—Anthothecol (1 g.), acetic acid (3 ml.), and concentrated hydrochloric acid (0·15 ml.) were heated at 100° for 3 hr. After cooling, the solution was diluted with chloroform and water, the chloroform layer was dried, and the product chromatographed on alumina. Chloroform eluted *isoanthothecol* (220 mg.), m. p. 125° (from chloroform–hexane) (Found: C, 69·8; H, 6·9. $C_{28}H_{32}O_7$ requires C, 70·0; H, 6·7%), $\lambda_{\max.}$ 210—230 mμ (ε 12,000—14,000).

Acid Rearrangement of Deacetyldehydrodihydroanthothecol.—Isomerisation of the ketone (X), carried out as described for anthothecol, gave a gum, probably (XI), which did not crystallise after chromatography and had $\lambda_{\max.}$ 211, 237, and 284 mμ (ε *ca.* 10,000).

Anthothecol Methyl Ether (VIIId).—Potassium (1 g.) was dissolved in t-butyl alcohol (100 ml.), and anthothecol (12 g.) was added. Methyl iodide (20 ml.) was then added, and the solution refluxed for ½ hr. After cooling, the solution was diluted with water and chloroform, and the chloroform layer evaporated. Crystallisation of the residue from methanol–methylene chloride gave *anthothecol methyl ether* (9·2 g.), m. p. 175° (Found: C, 70·7; H, 6·95; O, 22·45; OMe, 6·5. $C_{29}H_{34}O_7$ requires C, 70·4; H, 6·9; O, 22·65; 1OMe, 6·3%), $[\alpha]_D^{20}$ $-24°$, $\lambda_{\max.}$ 222 (ε 12,000) and 266 mμ (ε 8900). The compound gave no ferric chloride colour.

Deacetylanthothecol Methyl Ether (VIIIe).—Anthothecol (3 g.) was boiled for 2 hr. with sodium (250 mg.) in toluene (50 ml.) containing a little methanol. Methyl iodide was then added, and the solution boiled for 1 hr. longer. After being washed with water, the toluene layer was evaporated, and the product crystallised from methanol, to give *deacetylanthothecol methyl ether*, m. p. 210° (Found: C, 71·9; H, 7·2; OMe, 5·75. $C_{27}H_{32}O_6$ requires C, 71·65; H, 7·1; 1OMe, 6·85%), $[\alpha]_D^{20}$ $-28°$. The compound gave no ferric chloride colour. Reacetylation gave anthothecol methyl ether, identical with the above specimen.

Dihydroanthothecol Methyl Ether (VIId).—Anthothecol methyl ether in methanol was treated with aqueous sodium borohydride. After 1 hr. the solution was acidified and extracted with chloroform. Evaporation of the extract gave *dihydroanthothecol methyl ether*, crystallising from methanol in needles, m. p. 173° (Found: C, 70·55; H, 7·4. $C_{29}H_{36}O_7$ requires C, 70·15; H, 7·3%), $[\alpha]_D^{20}$ $-51°$, $\lambda_{\max.}$ 219 (ε 6000) and 266 mμ (8000), $\nu_{\max.}$ 1724 cm.$^{-1}$. On another occasion, under similar conditions, *deacetyldihydroanthothecol methyl ether* (VIIe) was obtained, having m. p. 222° (from methanol) (Found: C, 71·65; H, 7·65; OMe, 6·75. $C_{27}H_{34}O_6$ requires C, 71·35; H, 7·5; 1OMe, 6·8%); $[\alpha]_D^{20}$ $-31°$ $\lambda_{\max.}$ 220 (ε 5600) and 266 mμ (ε 7900) $\nu_{\max.}$ 3450, 1724 cm.$^{-1}$. The acetate peak at 1740 cm.$^{-1}$ was missing. Reacetylation gave dihydroanthothecol methyl ether.

Oxidation of Deacetylanthothecol Methyl Ether.—The methyl ether was oxidised in acetone with a slight excess of chromic acid; the *product* (XIIe), isolated in the usual way, had m. p. 220° (from propanol) (Found: C, 71·6; H, 6·7. $C_{27}H_{30}O_6$ requires C, 72·0; H, 6·7%), $[\alpha]_D^{20}$ $-46°$, $\lambda_{\max.}$ 218 (ε 12,900) and 267 mμ (ε 6310).

Oxidation of the Crude Benzilic Acid by Lead Tetra-acetate.—Anthothecol (4 g.), 10% aqueous sodium hydroxide (25 ml.), and methanol (50 ml.) were refluxed for 1 hr. Acidification gave the crude benzilic acid (3·8 g.). This was dissolved in chloroform and treated with lead tetra-acetate (4·5 g.). After 30 hr. the solution was diluted with water, the chloroform layer washed and evaporated, and the residue crystallised from methanol. Recrystallisation from propanol gave a *diketone*, probably (V), m. p. 284° (Found: C, 73·5; H, 7·3; O, 19·3. $C_{25}H_{30}O_5$ requires C, 73·15; H, 7·4; O, 19·5%), $[\alpha]_D^{20}$ $-30°$, $\lambda_{max.}$ 223 mμ (ε 12,000), $\nu_{max.}$ 1754 (cyclopentanone) and 1681 cm.$^{-1}$ (ring A ketone). Evaporation of the methanol mother-liquors gave a *substance* (of unknown structure), m. p. 245° (from methyl ethyl ketone) (Found: C, 72·6; H, 7·3; O, 19·5%), $\nu_{max.}$ 3333, 1724, 1681, and 877 cm.$^{-1}$.

Oxidation of Compound (V).—Oxidation of compound (V) with chromic acid in acetone, as usual, gave a *ketone*, probably (II), m. p. 193° (from methanol) (Found: C, 72·9; H, 6·9; O, 20·0. $C_{25}H_{28}O_5$ requires C, 73·5; H, 6·9; O, 19·6%), $[\alpha]_D^{20}$ $-50°$, $\lambda_{max.}$ 220 mμ (ε 14,000), $\nu_{max.}$ 1754, 1724 (new, probably 11-ketone), and 1681 cm.$^{-1}$.

Hydrogenation of the Crude Benzilic Acid.—The crude mixture of benzilic acids, prepared as described above, was hydrogenated in methanol over palladised charcoal. The infrared spectrum of the amorphous product showed no furan or unsaturated ketone bands. Oxidation with lead tetra-acetate as described above gave a *product*, crystallising from methanol in needles, m. p. 232° (Found: C, 71·7, 72·0; H, 8·65, 8·7; O, 19·3, 19·4. $C_{25}H_{36}O_5$ requires C, 72·1; H, 8·7; O, 19·2%), $[\alpha]_D^{20}$ $-103°$, $\lambda_{max.}$ 219 (ε 1995) and 303 mμ (ε 158), $\nu_{max.}$ 3333 and 1720 cm.$^{-1}$. Chromatography of the mother-liquors gave another *substance*, possibly the hexahydro-derivative of (V), m. p. 255° (from methanol) (Found: C, 71·0; H, 8·7. $C_{25}H_{36}O_5,\frac{1}{2}CH_3{\cdot}OH$ requires C, 70·8; H, 8·85%), $[\alpha]_D^{20}$ $-123°$, $\lambda_{max.}$ 210 mμ (ε 2000), $\nu_{max.}$ 3340, 1745 and 1724 cm.$^{-1}$ (not 887 cm.$^{-1}$).

Oxidation of the main product, m. p. 232°, with chromic acid in acetone gave a *substance*, m. p. 219° (from methanol) (Found: C, 71·8; H, 7·8. $C_{24}H_{32}O_5$ requires C, 72·0; H, 8·0%), $\lambda_{max.}$ 219 (ε 3162) and 280 mμ (ε, 749) $\nu_{max.}$ 1754 and 1724 cm.$^{-1}$ (no OH band).

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