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HEARTWOOD CONSTITUENTS OF *SCIADOPITYS VERTICILLATA* SIEB. ET ZUCC.—II*

THE STRUCTURE OF METHYL SCIADOPATE

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Abstract—The structure (II) is proposed for methyl sciadopate, a new diterpenoid ester, which has been correlated to agathic acid.

THE elucidation of the structure (I) for sciadin, a heartwood constituents of *Sciadopitys verticillata* Sieb. et Zucc., and the isolation of methyl sciadopate, $C_{21}H_{34}O_4$, m.p. 108·5° from the same wood have been previously described.[1] In the preliminary communication,[2] structure II was proposed for methyl sciadopate, which is closely related to the structure of sciadin (I). The present paper reports full details of the work.

The molecular formula of methyl sciadopate is supported by a mass spectral determination which shows a strong peak at 338 m/e indicating a molecular weight of 350. The IR spectrum suggests the presence of at least one hydroxyl (3344); an ester (1733); a vinylidene (1641, 896) and a trisubstituted double bond (816 cm^{-1}).

Methyl sciadopate resists hydrolysis on boiling with ethanolic potash (10%) but is saponified by boiling with diethylene glycolic potash to afford an acidic oil (III), which after treatment with diazomethane reproduces the original ester (II). The difficulty of hydrolysis suggests that the ester group is attached to a quaternary carbon atom in the axial configuration. Acetylation of methyl sciadopate with acetic anhydride in pyridine gives an oily diacetate (IV), $C_{25}H_{38}O_6$, which exhibits no IR hydroxyl absorption band. The presence of two hydroxyl groups in the molecule of methyl sciadopate is also supported by the active hydrogen determination (Zerewitinoff). Methyl sciadopate shows an intense yellow coloration on treatment with tetranitromethane and absorbs two moles of hydrogen by hydrogenation over Adams' catalyst in ethyl acetate solution to give an oily tetrahydro compound (V), $C_{21}H_{38}O_4$. Consumption of two moles of monoperphthalic acid also proves the presence of two double bonds, one of which is shown to be a vinylidene group by providing formaldehyde on ozonolysis of methyl sciadopate.

On oxidation with the Jones' reagent,[3] methyl sciadopate furnishes a dicarboxylic acid (VI), $C_{21}H_{30}O_6$, which has IR absorption at 1690 cm^{-1} and UV absorption maximum at 225·5 mμ (ϵ 7,700) suggesting the maleic acid form (VI). Boiling the

* Presented at the 7th Symposium on the Chemistry of Organic Natural Products held at Fukuoka (Oct. 1963).

[1] M. Sumimoto, *Tetrahedron* **19**, 643 (1963).

[2] M. Sumimoto, Y. Tanaka, K. Matsufuji, *Chem. & Ind.* 1928 (1963).

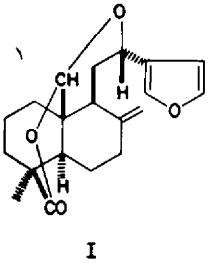
[3] A. Bowers, T. G. Halsall and E. R. H. Jones, *J. Chem. Soc.* 2555 (1953).

dicarboxylic acid (VI) in acetic anhydride for ½ hr gives an oily neutral product in quantitative yield, which shows IR absorption at 1852, 1790 cm^{-1} indicative of the maleic anhydride structure (VII).[4] The ease with which the anhydride (VII) is formed from the dicarboxylic acid (VI) is possibly a direct proof for the *cis*-relationship between the two hydroxymethyl groups in the molecule of methyl sciadopate (II). On reduction with zinc–acetic acid, the dicarboxylic acid (VI) converts to an oily acid (VIII), which has IR absorption at 1712 cm^{-1} but no UV absorption in the region over 215 mμ. These observations rationalize the partial structure (a) for methyl sciadopate, which is fully supported by the following NMR data of methyl sciadopate (II) and the diacetate (IV).

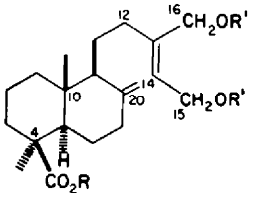
	C_{10}–CH_3	C_4–CH_3	—$OCOCH_3$	—$COOCH_3$	—OH	C_{16}–H_2	C_{15}–H_2	C_{20}–H_2	C_{14}–H
Methyl sciadopate	9·52, (s)	8·83, (s)	—,	6·42, (s)	7·08, (s)	6·00, (s)	5·93(d), J = 6·0	5·50(s), 5·16(s), J = 6·0	4·40(t)
Diacetate	9·50, (s)	8·83, (s)	7·92(s), 7·94(s),	6·44, (s)	—,	5·54, (s)	5·49(d), J = 7·0	5·54(s), 5·18(s), J = 7·0	4·46(t)

The peak (9·52 or 9·50 τ) due to C_{10}-methyl group, though it seems unusually high, is not always anomalous on the ground of a report by Miyasaka which concerns a widespread study on NMR spectra of diterpenoids.[5] The determination of these functional groups of methyl sciadopate (II) indicates that the structure contains a bicarbocylic ring.

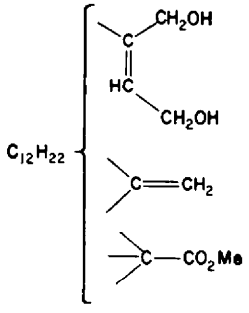
Ozonolysis of methyl sciadopate (II) gives a small amount of acidic oil (IX), the

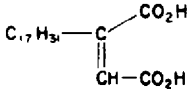


I



II R=Me, R'=H
III R=R'=H
IV R=Me, R'=Ac



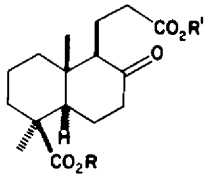


VI

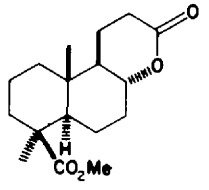
[4] L. J. Bellamy, *The IR Spectra of Complex Molecules* p. 128 (1958).

[5] S. Miyasaka; Presented at the 7th Symposium on the Chemistry of Organic Natural Products held at Fukuoka (Oct. 1963). The structure (II) for methyl sciadopate was also suggested independently by him at the Symposium.

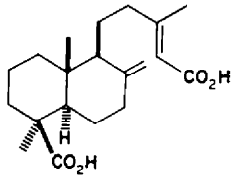
methyl ester of which has IR absorption at 1706 cm^{-1} indicating the presence of a six-membered ring ketone. This was confirmed by conversion of the ester to a 2,4-dinitrophenylhydrazone (X), $C_{24}H_{32}O_8N_4$. A neutral fraction obtained by the same treatment, on alkaline hydrolysis affords the acidic oil (IX), which, without purification, is converted to the lactonic ester (XI), $C_{17}H_{26}O_4$, by reduction with sodium borohydride. The compound (XI) has IR absorption at 1727 cm^{-1} indicative of a δ-lactone which suggests the relationship between two double bonds in the precursor, methyl sciadopate. The phenylphenacyl ester derived from the acidic oil (IX) is identical with the compound (XII) mentioned below by a mixed m.p. and IR spectrum. On ozonolysis followed by hydrogen peroxide oxidation the acid (III) provides the C_{16}-keto acid (XIII), $C_{16}H_{24}O_5$, m.p. 190°, RD curve of which shows strong negative Cotton effect, $[\alpha]_{307} - 2012$. In their study on the stereochemistry of daniellic acid, Ourisson *et al.*[6] prepared the C_{16}-keto acid (XIII) from agathic acid (XIV) and the antipodal acid (XV) from daniellic acid (XVI). Both acids (XIII and XV), m.p. 191° and 190° respectively show identical IR spectra, but they exhibit opposite signs in the RD curves; $[\alpha]_{307\cdot5} -1830$ (XIII) and $[\alpha]_{307\cdot5} +1683$ (XV). The C_{16}-keto acid, obtained by us from methyl sciadopate, is identical with XIII by comparison of mixed m.p. and IR spectra. The methyl phenylphenacyl ester (XII), $C_{31}H_{36}O_6$, derived from our C_{16}-keto acid is also identical with XII prepared from agathic acid by Ourisson *et al.*[6] These results indicating the structure II for methyl sciadopate are furthur supported by the following experiments.



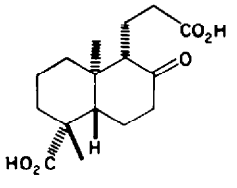
IX R = Me, R' = H
XII R = Me, R' = $CH_2COC_6H_4C_6H_5$
XIII R = R' = H



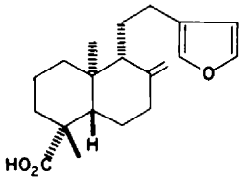
XI



XIV



XV



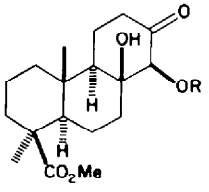
XVI

On ozonolysis followed by zinc–acetic acid reduction, diacetyl methyl sciadopate (IV) furnishes the ketodiolmonoacetate (XVII), $C_{20}H_{30}O_6$, the functional groups of which are indicated by IR absorption at 3515, 3400 (hydroxyl), 1757 (acetate), 1736 (ester) and 1716 cm^{-1} (six membered ring ketone) and UV absorption at 281 mμ (ϵ 45). The compound (XVII) resists either acetylation with acetic anhydride in

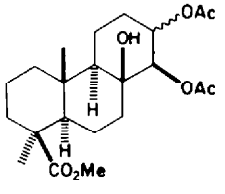
[6] J. Haeuser, R. Lombard, F. Lederer and G. Ourisson, *Tetrahedron* **12**, 205 (1961).

pyridine or oxidation with chromic acid in pyridine suggesting that the hydroxyl group is tertiary. Sodium borohydride reduction of XVII followed by acetylation affords two diastereomeric trioldiacetates, $C_{22}H_{34}O_7$, presumably represented by XVIII and XIX, only one of which could be isolated in a pure state. The conformation of the acetoxyl groups at C-13 of both compounds was not determined. Since XVII should be tricarbocyclic, the compound appears to be an aldol condensation product of the diketone (XX). Hydrolysis of XVII with dilute methanolic potash provides two products, one of which is the ketodiol (XXI), $C_{18}H_{28}O_5$, a simple hydrolysis product, for acetylation of XXI regenerates the ketodiolmonoacetate (XVII). The other, giving a positive ferric chloride test, is a diosphenol (XXII), $C_{18}H_{26}O_4$, the IR (3435, 3340, 1660, 1643 cm^{-1}) and UV absorption of which ($\lambda_{max}^{Neutral}$ 278 mμ, $\lambda_{max}^{Alkaline}$335 mμ) demonstrate the presence of a grouping C—C=C—CO—,[7]

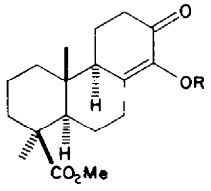
though IR spectrum accompanies the complex absorption bands in the region near 6 μ. The diosphenol acetate (XXIII), $C_{20}H_{28}O_5$, obtained in the usual way from the diosphenol (XXII) has IR (1770, 1690, 1638 cm^{-1}) and UV absorption (246 mμ) which are in good accord with those in a literature.[7] The possible conversion of the diosphenol, on ozonolysis followed by sodium borohydride reduction, to the lactonic ester (XI) substantiates the structure XXII.



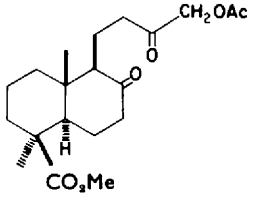
XVII R=Ac
XXI R=H



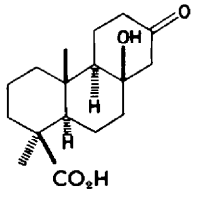
XVIII and XIX



XXII R=H
XXIII R=Ac



XX

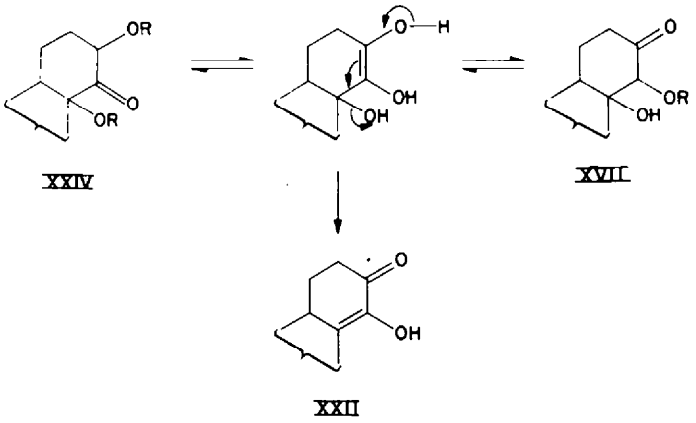


XXV

Of the two possible routes to a diosphenol (XXII) as shown, the one from XXIV has been reported in the steroid field by Wendler,[8] but the other from XVII is as yet unknown.

The ketodiolmonoacetate in question gives a positive Fehling's test, which may suggest the formula XXIV rather than XVII. The former possibility may be excluded as oxidation of XVII with periodate or with lead tetraacetate yields quantitatively the starting material unchanged. The compound XVII also cannot be

[7] D. H. R. Barton, S. K. Pradhan, S. Sternhell and J. F. Templeton, *J. Chem. Soc.* 255 (1961).
[8] N. Wendler, *Chem. & Ind.* 20 (1959).



XXIV XVII XXII

dehydrated in boiling acetic anhydride or with phosphoryl chloride in pyridine. Furthermore, the formation of XXIV by the intramolecular condensation of the diketone (XX) is improbable because a diketone generally condenses to a β-ketol but not to an α-ketol. Thus the preferred structure for the ketodiolmonoacetate is XVII rather than XXIV.

The *trans* B/C ring junction of XVII and accordingly the β-configuration of the tertiary hydroxyl group at C-8 are presumed by the condensation mechanism of the diketone (XX) to XVII. This is supported by the strong positive Cotton effect ($[\alpha]_{307}$ +1255) of the RD curve of XVII which is similar to that of the ketol (XXV), ($[\alpha]_{307\cdot5}$ +1517) shown by Ourisson *et al.*[6] Determination of the IR absorption band (3584 cm^{-1}) due to the C-8 hydroxyl group of XVII shows the presence of a hydrogen bond between the hydroxyl and the C_{13}-acetoxyl groups.[9] The configuration of the acetoxyl group is thus indicated to be β- and on the same side as the C_8-hydroxyl group.

EXPERIMENTAL

M.ps were determined on a hot stage and are uncorrected; IR and UV spectra were for nujol mulls and ethanol solutions respectively and optical rotations for chloroform solutions unless otherwise stated; the NMR spectra in deuterochloroform solutions with tetramethyl silane as internal reference at 60 MC.

Methyl sciadopate (II)

The method[1] described in the preceding paper for the isolation of methyl sciadopate was improved as follows. A condensed methanol extract of powdered heartwood of *Sciadopitys verticillata* (5 kg) was macerated with pet. ether (2 l.) and ether (2 l.) successively. The ethereal solution was washed with 1 N NaOH aq and water, dried and evaporated. The neutral residue (84 g) was fractionally distilled. A fraction (17 g b.p. 220–250/4 mm Hg) was dissolved in benzene and to the mixture pet. ether was added until the solution was slightly turbid. After standing for a week in a refrigerator, the crystals deposited (7·6 g) were collected and recrystallized from isopropyl ether affording methyl sciadopate identified by m.p., mixed m.p. and IR spectrum. Mass spectral determination showed a strong peak at 332 m/e indicating the mol. wt of 350. Determinations of active hydrogen by Zerewitinoff's method gave the value 2·03 moles.

Acetylation of methyl sciadopate (0·5 g) with acetic anhydride in pyridine in the usual way yielded an oil (0·51 g), which was distilled to give the diacetate (IV), b.p. 160–185° (bath temp)

[9] L. P. Kuhn, *J. Amer. Chem. Soc.* **74**, 2492 (1952); cf. A. Nickon, *Ibid.* **79**, 243 (1957).

and 10^{-3} mm Hg. This had ν_{max} 1758, 1731, 1655, 893 cm^{-1}. (Found: C, 69·0; H, 8·8. $C_{25}H_{36}O_6$ requires: C, 69·09; H, 8·81%)

Hydrolysis of methyl sciadopate

Methyl sciadopate (206 mg) was heated with diethylene glycolic potash (10%, 2 cc) under reflux for 2 hr. Water (15 cc) was added and the mixture washed with pet, ether and then with ether. The aqueous layer was acidified with dil. HCl and extracted with ether. Evaporation of the solvent gave an acidic oil (III, 190 mg). This had ν_{max} 3350, 1703, 1641, 892 cm^{-1}.

Methylation of the acidic oil by treatment with ethereal diazomethane reproduced methyl sciadopate identified by m.p., mixed m.p. and IR spectrum.

Hydrogenation of methyl sciadopate

Methyl sciadopate (203 mg) in ethyl acetate (20 cc) was hydrogenated over Adams' catalyst (20 mg). After absorption of 2·23 moles hydrogen; the reaction ceased yielding an oily neutral product, which was chromatographed on alumina. Elution with ether gave a product (110 mg), distilled at b.p. 170–180° (bath temp and 10^{-3} mm Hg) which had ν_{max} 3362, 1728 cm^{-1} and showed a negative tetranitromethane test. (Found: C, 71·2; H, 10·8. $C_{31}H_{36}O_4$ requires: C, 71·14; H, 10·80%).

Chromic acid oxidation of methyl sciadopate to the dicarboxylic acid (VI)

To a solution of methyl sciadopate (1·0 g) in acetone (90 cc) the Jones' reagent[3] (6·0 cc) was added with occasional shaking. After standing 1 hr at room temp, the reaction mixture was poured into water (300 cc), the acetone removed *in vacuo* and the deposited crystals (922 mg) chromatographed on silica gel (30 g). Elution with ether–pet. ether (1:1) gave a product, m.p. 201° (516 mg) which crystallized in needles from ether–pet. ether, m.p. 210°, $[\alpha]_D^{EtOH}$ +21·7, λ_{max} 225·5 mμ (ϵ 7,700), ν_{max} 1728, 1690, 1655, 1640, 896, 816 cm^{-1}. (Found: C, 66·8; H, 8·05. $C_{31}H_{30}O_6$ requires: C, 66·64; H, 7·99%).

Formation of anhydride (VII)

The dicarboxylic acid (105 mg) was boiled with acetic anhydride (1·0 cc) for 30 min, and the reaction mixture poured into water. The ether extract was washed with $NaHCO_3$ aq and then with water, dried and evaporated. The resulting viscous oil (93 mg) was distilled at b.p. 195–210° (bath temp and 10^{-3} mm Hg) yielding a slightly yellow oil (60 mg) with ν_{max} 1852, 1790, 1730, 1640, 890 cm^{-1}.

Zinc–acetic acid reduction of the dicarboxylic acid (VI)

To a solution of the dicarboxylic acid (VI, 103 mg) in acetic acid (7·0 cc) powdered zinc (1·2 g) was added gradually and the mixture stirred on a water bath for 2 hr. Excess zinc was removed by filtration, the acetic acid evaporated *in vacuo* and water (20 cc) added. After acidification the mixture was extracted with ether. The extract (87 mg) was chromatographed on silica gel (3·0 g). The main fraction was an oil (VIII; 58 mg) which had ν_{max} 1728, 1710, 1643, 895 cm^{-1} and no UV absorption in the region over 215 mμ.

Ozonolysis of methyl sciadopate

(a) A solution of methyl sciadopate (152 mg) in methylene chloride (20 cc) was saturated with ozone at −70° and the solvent evaporated *in vacuo* without heating. The residue was steam distilled and dimedone (180 mg) added to the distillate (pH adjusted at ca. 7). Crystallization of the product afforded a formaldehyde-dimedone compound (62 mg) identified by m.p. and mixed m.p.

(b) Methyl sciadopate (1·2 g) in chloroform (40 cc) was treated with ozone at −70° as usual. Water (5 cc) was added to the solution and the mixture heated under reflux for 20 min. An acidic oil (IX; 108 mg) from the chloroform layer was methylated with ethereal diazomethane and the product chromatographed on a short column of alumina. 2,4-Dinitrophenylhydrazone (86 mg) of the oily methyl ester prepared in the usual way was crystallized repeatedly from dil. methanol, m.p. 85°. (Found: C, 56·9; H, 6·3; N, 10·9. $C_{34}H_{32}N_4O_8$ requires: C, 57·13; H, 6·39; N, 11·11%).

A neutral oil (950 mg) from the chloroform layer was hydrolysed by refluxing with methanolic

potash (0·1 N, 18 cc) for 1 hr. Water was added and the methanol evaporated. The ether extract gave an acidic product (702 mg), a part of which (300 mg) was dissolved in methanol (20 cc) and NaOH aq (1 N, 4 cc). To the solution $NaBH_4$ (205 mg) was added and the mixture left at room temp for 24 hr. The solvent was evaporated and the residue extracted with ether. The ether extract gave a neutral oil (147 mg), which was chromatographed on alumina. Crystallization of the product from isopropyl ether afforded the lactonic ester (XI; 62 mg), m.p. 131°, $[\alpha]_D$ +29·9, ν_{max} 1727 cm^{-1}. (Found: C, 69·2; H, 8·8. $C_{17}H_{26}O_4$ requires: C, 69·36; H, 8·90%).

To a methanolic solution of another part of acidic hydrolysis product (402 mg) Na_2CO_3 (59 mg) and *p*-phenylphenacylbromide (375 mg) were added and the mixture heated under reflux for 90 min. After cooling, the product was crystallized from ether–pet. ether providing the phenylphenacyl ester (XII; 114 mg) identified by m.p., mixed m.p. and IR spectrum.

C_{16}-Keto acid (XIII) *from methyl sciadopate*

Methyl sciadopate (1·0 g) was hydrolysed as described above to afford an oily acid (III; 0·96 g), which was ozonized in methylene chloride at −70°. To the resulting mixture, H_2O_2 (30%, 10 cc) and KOH aq (10%, 10 cc) were added gradually and the mixture stirred for 24 hr. The acidic product (780 mg) was chromatographed on silica gel (25 g). Elution with ether–pet. ether (1:2) gave the product (224 mg), which after several recrystallizations from ether–pet. ether and isopropyl ether yielded the pure C_{16}-keto acid (XIII), m.p. 190°, $[\alpha]_{307}$ −20, $[\alpha]_{307}$ −2012. (Found: C, 64·7; H, 8·25. $C_{16}H_{24}O_5$ requires: C, 64·84; H, 8·16%). The identity with Ourisson's C_{16}-ketoacid from agathic acid was confirmed by mixed m.p. and IR spectrum.

The phenylphenacyl ester (XII) from the C_{16}-ketoacid (XIII) was prepared by the Ourisson's method,[6] m.p. 140°, $[\alpha]_D$ O. (Found: C, 73·6; H, 7·3. $C_{31}H_{36}O_6$ requires: C, 73·73,; H, 7·19%). The ester (XII) was identified with an authentic sample by mixed m.p. and IR spectrum.

Ozonolysis of diacetyl methyl sciadopate (IV)

A solution of diacetyl methyl sciadopate (IV; 540 mg) in methylene chloride (30 cc) was saturated with ozone at −70° as usual. To the reaction mixture, acetic acid (15 cc) and zinc dust (6 g) were added and the mixture stirred for 3 hr. Excess zinc was removed by filtration, the methylene chloride evaporated and water (120 cc) added. An ether extract yielded a neutral residue (460 mg), which was chromatographed on silica gel (15 g). Elution with ether–pet. ether (1:1) gave the product (352 mg), crystallization of which from ether–pet. ether furnished the ketodiolmonoacetate (XVII), m.p. 201°, $[\alpha]_D$ +54·3, $[\alpha]_{307}$ +1255, λ_{max} 280 mμ (ϵ 45), ν_{max} 3515, 3400, 1757, 1736, 1716 cm^{-1}. (Found: C, 65·7; H, 8·2. $C_{30}H_{30}O_6$ requires: C, 65·55; H, 8·25%).

Hydrogen bond determination by IR spectrum was carried out in a 2 mm cell in CCl_4 solution and 2·8 × 10^{-3} molar concentration, $\nu_{max}^{CCl_4}$ 3584, 1763, 1741, 1730 cm^{-1}.

Sodium borohydride reduction of the ketodiolmonoacetate (XVII)

To a solution of the ketodiolmonoacetate (196 mg) in methanol (20 cc), NaOH aq (1 N, 5 cc) and $NaBH_4$ (120 mg) were added. After standing 24 hr at room temp, the reaction mixture was acidified with dil. HCl aq and the methanol evaporated. An ether extract provided a neutral product (192 mg), which was acetylated with acetic anhydride in pyridine in the usual way. The resulting product (200 mg) was chromatographed on silica gel (8 g). Elution with ether–pet. ether (1:2) gave two components, the first of which (48 mg) was crystallized from isopropyl ether and sublimed affording one of the isomers of the ketotrioldiacetate (XVIII and XIX), m.p. 248°, $[\alpha]_D$ +36·0, ν_{max} 3455, 1742, 1717 cm^{-1}. (Found: C, 64·3; H, 8·4. $C_{32}H_{44}O_7$ requires: C, 64·37; H, 8·35%).

The second fraction (120 mg) was crystallized from ether–pet. ether and yielded a mixture of two isomers (XVIII and XIX), m.p. 98–105°, ν_{max} 3295, 1749, 1725 cm^{-1}. (Found: C, 64·5; H, 8·5. $C_{32}H_{34}O_7$ requires: C, 64·37; H, 8·35%).

Hydrolysis of the ketodiolmonoacetate (XVII)

A solution of the ketodiolmonoacetate (604 mg) in methanol (25 cc) containing KOH (200 mg) was heated under reflux for 30 min. After acidification with dil. HCl, water (30 cc) was added and the methanol evaporated. The ether extract gave a product (590 mg), which was chromatographed on silica gel (30 g). Elution with ether–pet. ether (1:2) yielded two fractions. Crystallization of the first (305 mg) from pet. ether gave the diosphenol (XXII), m.p. 137°, $[\alpha]_D$ +11·5, $\lambda_{max}^{Neutral}$ 278 mμ

(ϵ 12,100), $\lambda_{max}^{0.1\,N\,KOH\,in\,EtOH}$ 335 mμ (ϵ 6,500), ν_{max} 3435, 3340, 1727, 1670, 1660, 1643, 1632 cm^{-1}. (Found: C, 70·4; H, 8·6. $C_{18}H_{26}O_4$ requires: C, 70·56; H, 8·55%) The ferric chloride test showed a violet coloration.

The diosphenol acetate (XXIII) was prepared by acetylation of the diosphenol with acetic anhydride in pyridine in the usual way and crystallized in needles from isopropyl ether, m.p. 160°, $[\alpha]_D$ +60·8, λ_{max} 246 mμ (ϵ 12,800), ν_{max} 1770, 1732, 1690, 1638 cm^{-1}. (Found: C, 69·3.; H, 8·2. $C_{20}H_{28}O_5$ requires: C, 68·94; H, 8·10%).

Crystallization of the second fraction (125 mg) from ether–pet. ether yielded the ketodiol (XXI), m.p. 180°, ν_{max} 3495, 3410, 1722 cm^{-1}. (Found: C, 66·8; H, 8·8. $C_{18}H_{28}O_5$ requires: C, 66·64; H, 8·70%). The compound showed a positive Fehling's test.

Acetylation of the ketodiol (XXI) with acetic anhydride in pyridine furnished the ketodiolmonoacetate (XVII) identified by m.p., mixed m.p. and IR spectrum.

Ozonolysis of the diosphenol (XXII)

A solution of the diosphenol (280 mg) in methylene chloride (30 cc) was saturated with ozone at −70°. To the reaction mixture, NaOH aq. (10%, 4 cc) and H_2O_2 (30%, 3·5 cc), were added under cooling and the mixture stirred for 20 hr at room temp. The ether extract gave an acidic oil (255 mg), to which methanol (15 cc), NaOH aq. (1 N, 4 cc) and $NaBH_4$ (140 mg) were added. After standing 24 hr, water (15 cc) was added, the solution acidified and the methanol evaporated. The ether extract was washed with aqueous alkali and water, dried, evaporated and the resulting product (140 mg) chromatographed on alumina (4 g). Elution with ether–pet. ether (1 : 2) provided the lactonic ester (XI; 122 mg) identified by m.p., mixed m.p., and IR spectrum.

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