114. *Pristimerin. Part III.*[1] *A Modified Structure for the Chromophore.*

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The structure suggested earlier [2] for the chromophore of pristimerin has been re-examined. The " inert carbonyl " group is now shown to be contained in an ester group which is not conjugated with the main chromophore. A consequence of this change is that in the previous structure (I), the bottom ring, which was postulated to account for the existence of different naphthalenoid acid rearrangement products of pristimerin, is no longer necessary. The preferred partial formula (II) for pristimerin is related to certain triterpene structures.

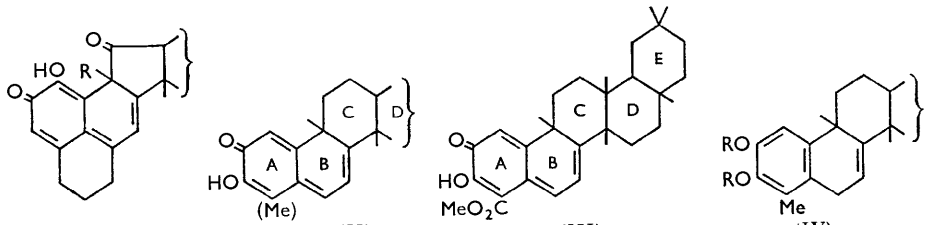
In previous papers [1,2] we described some reactions of the wood pigment pristimerin and advanced a tentative partial structure (I; R = Me or OMe). Further experimental results have led us to modify the proposed structure (I) in several important respects, and the preferred partial structure is now (II) in which the bottom ring of (I) has been deleted—the " inert carbonyl " and the methoxyl group of (I) are combined in a methoxycarbonyl group elsewhere in the molecule.

The bottom ring in structure (I) was postulated to explain the existence of two naphthalenoid acid rearrangement products one of which was believed to be conjugated with the " inert carbonyl " group. It now seems that neither of the naphthalene derivatives has its chromophore conjugated with the ester function and it is obvious that structure (II) affords enough scope for Wagner-type rearrangements to account for the formation of different naphthalenes. The phenanthrene-type skeleton is suggested on the basis of the Japanese claim [3] to have obtained a picene derivative from pristimerin after fusion with zinc dust and by analogy with the structure of other well-known natural products.

The possibility that a methoxycarbonyl group was present in pristimerin has been

[1] Part II, Grant and Johnson, *J.*, 1957, 4669.
[2] Grant and Johnson, *J.*, 1957, 4079.
[3] Nakanishi, Kakisawa, and Hirata, *J. Amer. Chem. Soc.*, 1955, **77**, 3169.

considered by other groups of workers but has been discarded partly on the grounds that celastrol (>C=O band at 1709 cm.$^{-1}$ in carbon tetrachloride solution), although converted by diazomethane into pristimerin (>C=O band at 1738 cm.$^{-1}$ in carbon tetrachloride), was considered not to be a carboxylic acid.[4] More recently Indian workers [5] claim to have proved the absence of an ester group in pristimerin by a study of the reduction with lithium aluminium hydride, but their experimental results do not accord with our own. Dr. R. S. Cooke, of the University of Melbourne, whom we thank for helpful correspondence, has also



(I) (II) (III) (IV)

concluded [6] that the evidence against the presence of a methoxycarbonyl group is not conclusive and has suggested (III) as a possible structure for pristimerin.

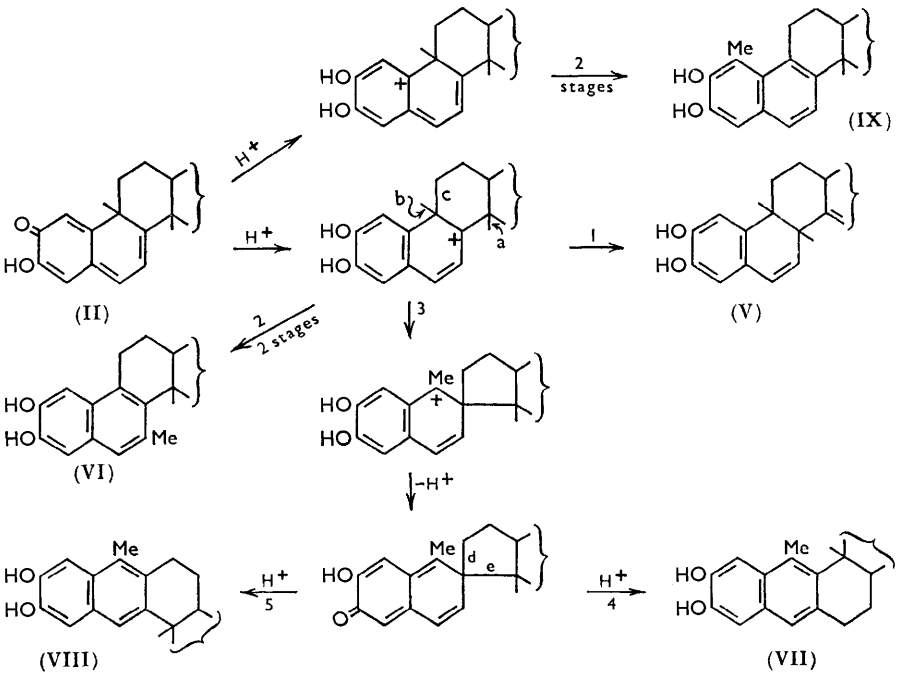
The evidence which we have obtained for the presence of the ester group is the results of the reduction of two derivatives of pristimerin with lithium aluminium hydride and of the hydrolysis of one of them. The derivatives were the benzenoid compound pristimerol dimethyl ether (partial structure IV; R = Me) and the dimethoxynaphthalene derivative (previously undescribed) obtained by hydrolysis and methylation (OAc ⟶ OH ⟶ OMe) of the Thiele acetylation product.[2] In both cases the reduction product had lost one methoxyl (Zeisel) and a carbonyl group (infrared absorption) but contained a new hydroxyl group. These results are explained by the reduction of $-CO_2Me$ to $-CH_2\cdot OH$. Alkaline hydrolysis of the naphthalenoid dimethyl ether (>C=O band at 1736 cm.$^{-1}$ in carbon tetrachloride), already referred to, gave a carboxylic acid (>C=O band at 1701 cm.$^{-1}$ in carbon tetrachloride) which could be isolated as the sparingly soluble potassium salt and with diazomethane regenerated starting material.

However we differ from Cooke and Thomson [6] in that we do not believe that the ester group is attached to the chromophore. The ultraviolet absorption spectrum of pristimerol (IV; R = H) is typical of a catechol and not of a substituted salicylic ester; moreover a hitherto unreported oxidation product of pristimerin, in which six carbon atoms have been lost with destruction of the chromophore, still contains the methoxyl group (see below). Finally the ultraviolet absorption of the dimethoxynaphthalene from pristimerin is unchanged after reduction by lithium aluminium hydride, showing that the carbonyl group cannot be conjugated with the naphthalene nucleus and hence the ester group cannot be attached to ring A or B of pristimerin. Dr. Cooke (personal communication) now concedes this point. The position of the ester-carbonyl band in the infrared spectra of solutions of pristimerin and many of its derivatives in solution is at *ca.* 1725 cm.$^{-1}$. This frequency would normally suggest the presence of an αβ-unsaturated ester and indeed such a grouping has not been entirely ruled out, but our present interpretation is that the ester is in a fully substituted position as in certain other triterpene esters (*e.g.*, methyl arjunolate; [7] >C=O ester band at 1724 cm.$^{-1}$) which show low-frequency carbonyl absorption.

Acid-rearrangement Products of Pristimerin.—One of the most characteristic properties of the pristimerin molecule is the ease with which it undergoes rearrangement under acid

[4] Gisvold, *J. Amer. Pharm. Assoc.*, (*a*) 1939, **28**, 440; (*b*) 1940, **29**, 12; (*c*) *ibid.*, p. 432; (*d*) 1942, **31**, 529.
[5] Seshadri, Mhaskar, Kulkarni, and Shah, *J. Sci. Ind. Res., India*, 1958 **17**, *B* 111.
[6] Cooke and Thomson, *Rev. Pure Appl. Chem.*, 1958, **8**, 85.
[7] King, King, and Ross, *J.*, 1954, 3995.

conditions to aromatic derivatives with loss of the chromophoric group, and several crystalline products, including two naphthalene derivatives, from acid-rearrangements under different conditions were described in Part I.[2] A direct comparison of the dihydroxynaphthalene obtained by acid-rearrangement with the dihydroxynaphthalene obtained by hydrolysis of the Thiele acetylation product has now confirmed that they are different compounds although, as the ultraviolet absorption of the corresponding diacetates are virtually superimposable, it may be assumed that the two products are closely related. The main difference between these two dihydroxynaphthalenes is the unusually low infra-red frequency (1691 cm.$^{-1}$ in chloroform; 1703 cm.$^{-1}$ in carbon tetrachloride) of the ester-carbonyl group in the acid-rearrangement product. This has been ascribed to intramolecular hydrogen bonding with one of the hydroxyl groups and on this basis the *o*-hydroxy-groups in this product and consequently in pristimerin itself were believed to be in the 1,2- rather than 2,3-position. Further examination of the properties of these dihydroxynaphthalenes has now caused us to favour the 2,3-disposition of the hydroxyl groups. Thus the relative stability towards aerial oxidation and the failure of the Thiele hydrolysis product to give a quinone after treatment with silver oxide are more in keeping with the properties of 2,3-dihydroxynaphthalenes. Further, the Gibbs test on each of the diols was negative, from which it may be surmised that a 1,2-dihydroxynaphthalene structure was substituted in position 4; on the other hand, the coupling test with diazotised sulphanilic acid was positive and this would not normally occur in the 3-position in a 1,2-dihydroxynaphthalene. If there is any biogenetic relation between pristimerin and the triterpenes, then an oxygen atom at the 3-position in the naphthalene nucleus might be



[1] Movement of bond a. [2] Movement of bond b. [3] Movement of bond c. [4] Movement of bond d. [5] Movement of bond e.

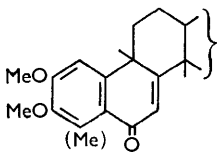
expected. The precise position of the ester group in the nucleus has not yet been determined and until this is known, a discussion of the cause of the lowered frequency of the ester-carbonyl group in the naphthalenoid acid-rearrangement product is deferred.

Another acid-rearrangement product has now been isolated after the action of methanolic sulphuric acid on pristimerin, and from spectroscopic data it appears to be a dihydroxystyrene derivative. The new diol, after purification, was obtained in about 50% yield and under Thiele acetylation conditions it failed to give the pristimerin Thiele acetylation product. However, the amorphous product from the crystallisation mother-liquors of the diol gave some of the same Thiele acetylation product as does pristimerin.

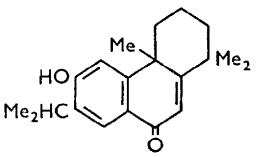
Of the various possible modes of acid-rearrangement of pristimerin the more obvious are set out below. Several possibilities exist for the position of the non-conjugated double bond in the dihydroxystyrene (V) and that illustrated is merely intended to be representative. Several naphthalenediol structures (VI, VII, VIII, IX) are shown and it is not possible to say, at present, which corresponds to the hydrolysis product from the Thiele acetylation product and which to the acid-rearrangement product.

Oxidation of Pristimerin.—On the basis of partial structure (II) for pristimerin and (IV; R = H) for pristimerol, the permanganate oxidation [2] of pristimerol dimethyl ether is no longer interpreted as involving a ring opening but, instead, as the oxidation, to a carbonyl group, of the methylene group adjacent to the aromatic ring, as in (X). The absorption of compound (X) at 249 and 301 mμ agrees well with that reported for 10-dehydro-9-oxoferruginol [8] (XI), and we are grateful to Dr. Cooke for drawing our attention to this fact.

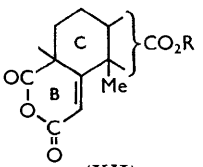
Oxidation of pristimerin itself in acetone solution with permanganate has given a colourless crystalline product, $C_{24}H_{34}O_5$, *i.e.*, six carbon atoms have been lost. This is soluble in aqueous sodium hydroxide solution but insoluble in aqueous sodium hydrogen carbonate and the ester group is retained. The infrared spectrum of the oxidation product (in Nujol) showed strong bands in the carbonyl region at 1802, 1754, and 1733 cm.$^{-1}$ and the ultraviolet absorption spectrum showed a single peak at 228 mμ (log ε 3·85). The substance was stable to further oxidation, being recovered largely unchanged from further treatment with neutral permanganate or even boiling nitric acid. However the oxidation product was hydrolysed by hot 10% aqueous sodium hydroxide (and by hot alkaline permanganate in another attempted oxidation) to give a related compound, $C_{23}H_{32}O_5$ which did not contain a methoxyl group but with diazomethane regenerated the original oxidation



(X)



(XI)



(XII)

product. Thus it appears that the methoxycarbonyl group of pristimerin is retained in the oxidation product which is formulated tentatively as an ester anhydride (partial formula XII; R = Me), and the hydrolysis product as the corresponding acid-anhydride (XII; R = H). Further examination of these anhydrides is in progress.

Experimental

Pristimerol Monomethyl Ether.—The crude methylation product of pristimerol (from 250 mg. of pristimerin) was dissolved in ether, chromatographed on alumina (Spence type H), and eluted with ether. The eluate was collected in fractions (10 c.c.), the first containing pristimerol dimethyl ether, m. p. 214—215°,[2] and the second after removal of the solvent giving a colourless gum (25 mg.) which crystallised on trituration with methanol. After two crystallisations from methanol, the pristimerol monomethyl ether formed colourless plates, m. p. 195—197° (lit.,[5] m. p. 194—195°) (Found: C, 77·2; H, 9·3. Calc. for $C_{31}H_{44}O_4$: C, 77·45; H, 9·25%), $\lambda_{max.}$

[8] Bredenberg, *Acta Chem. Scand.*, 1957, **11**, 932.

283—284 mμ (log ε 3·45), $\lambda_{min.}$ 253 mμ (log ε 2·49), $\nu_{max.}$ (KBr disc) 3439, 3046, 2947, 2913, 2872, 2809, 1720, 1660, 1622, 1499, 1469, 1380, 1320, 1297, 1259, 1243, 1209, 1158, 1121, 1099, 1022, 999, 954, 945, 883, 855, 842, 809, and 683 cm.$^{-1}$.

Reduction of Pristimerol Dimethyl Ether by Lithium Aluminium Hydride.—Pristimerol dimethyl ether (70 mg.) in ether (30 c.c.) was added to a suspension of excess of lithium aluminium hydride in ether (30 c.c.). The suspension was kept, with occasional shaking, for 40 min. The excess of hydride was decomposed with water, and the solution treated with dilute sulphuric acid. The ether layer was separated, washed with aqueous sodium hydrogen carbonate, and dried, and the solvent removed. The colourless crystalline residue (45 mg.) was repeatedly crystallised from aqueous ethanol; it formed colourless needles, m. p. 105—115°, of the reduction *product* [Found: (i) on a sample dried at 95°: C, 77·2; H, 10·1; OMe, 13·2; loss at 120°, 3·85. $C_{31}H_{46}O_3,H_2O$ requires C, 76·8; H, 10·0; 2OMe, 13·3; H_2O, 3·7. (ii) On a sample dried to constant weight at 120°: C, 80·0, 79·8; H, 10·7, 10·6. $C_{31}H_{46}O_3$ requires C, 79·8; H, 9·95%], $\lambda_{max.}$ (anhydrous sample) 280—281 mμ (log ε 3·33), $\lambda_{min.}$ 250—251 mμ (log ε 2·76), $\nu_{max.}$ (KBr) 3439 cm.$^{-1}$ (OH) but no carbonyl band.

Rearrangement of Pristimerin with Dilute Sulphuric Acid.—2N-Sulphuric acid (6 drops) was added to a solution of pristimerin (100 mg.) in methanol (15 c.c.). The dark red solution was heated under reflux for 20 min. The colour changed to orange-yellow. Sufficient warm water was added to the boiling solution to produce a slight turbidity and, after cooling, a pale yellow product (41 mg.) crystallised. Repeated crystallisation from aqueous methanol (charcoal) or light petroleum (b. p. 60—80°) gave very pale yellow needles of the rearrangement *product*, m. p. 236—238° (Found: C, 77·4; H, 8·7; OMe, 8·65. $C_{30}H_{40}O_4$ requires C, 77·55; H, 8·7; 1OMe, 6·7%). $\lambda_{max.}$ 309 and 256 mμ (log ε 3·74 and 4·58), $\lambda_{infl.}$ 250 mμ (log ε 4·57), $\lambda_{min.}$ 277 and 217 mμ (log ε 3·48 and 3·89), $\nu_{max.}$ (in $CHCl_3$) 3559, 3276, 2942, 2859, 1727, 1608, 1581, 1388, 1301, 1111, 1095, and 1007 cm.$^{-1}$.

The *dimethyl ether* was prepared by heating a solution of dimethyl sulphate (1·3 c.c.) and the acid-rearrangement product (61 mg.) in acetone (16 c.c.) under reflux in the presence of anhydrous potassium carbonate (1 g.) for 5½ hr. The mixture was diluted with water, most of the acetone removed under reduced pressure, and the resulting yellow gelatinous precipitate separated. The ethereal solution of the product was chromatographed on alumina (Spence, activated type " H "); removal of the solvent from the eluate gave a colourless gum (41 mg.) which crystallised on contact with methanol. Repeated crystallisation from methanol gave colourless flat rods of the methylation product, m. p. 197—198° (Found: C, 77·9; H, 9·2; OMe, 17·8. $C_{32}H_{44}O_4$ requires C, 78·0; H, 9·0; 3OMe, 18·9%), $\lambda_{max.}$ 299, 255, and 248 mμ (log ε 3·82, 4·61, and 4·60 respectively), $\lambda_{min.}$ 270, 251—252, and 215 mμ (log ε 3·53, 4·59, and 3·96 respectively), $\nu_{max.}$ (in $CHCl_3$) 3009, 2948, 2871, 1731, 1596, 1569, 1482, 1471, 1459, 1440, 1382, 1337, 1325, 1259, 1169, 1161, 1112, 1095, 1079, 1062, 1007, 965, 935, 856, and 821 cm.$^{-1}$. On another occasion a methylation product, m. p. 161—162°, was obtained which resolidified above the m. p. and remelted at 196—197°. This product had the same analysis and spectra as the former compound and was probably a dimorphic form.

The *diacetyl derivative* of the acid rearrangement product (60 mg.) was prepared by keeping a solution in acetic anhydride (2 c.c.) containing pyridine (1·5 c.c.) overnight. The product was isolated in the usual way and, if chromatographed on alumina as before, gave the acetyl derivative which crystallised from aqueous methanol as colourless needles, m. p. 207—208° (Found: C, 74·7; H, 7·85; OMe, 6·2. $C_{34}H_{44}O_6$ requires C, 74·4; H, 8·1; 1OMe, 5·65%), $\lambda_{max.}$ 288 and 248 mμ (log ε 3·76 and 4·55), $\lambda_{min.}$ 270 and 214 mμ (log ε 3·61 and 3·94), $\nu_{max.}$ (in $CHCl_3$) 2947, 1768, 1725, 1647, 1599, 1467, 1377, 1314, 1112, 1096, and 903 cm.$^{-1}$.

Acetylation of the Naphthalenoid Acid-rearrangement Product of Pristimerin.—A solution of the naphthalenoid acid-rearrangement product [2] (30 mg.) in acetic anhydride (0·75 c.c.) containing pyridine (0·5 c.c.) was kept at room temperature for 23 hr. The *product* was isolated in the usual way and crystallised repeatedly from methanol, forming colourless needles, m. p. 173—174° (Found: C, 74·5; H, 8·1; OMe, 6·65. $C_{34}H_{44}O_6$ requires C, 74·4; H, 8·1; 1OMe, 5·65%), $\lambda_{max.}$ 324, 288, and 233 mμ (log ε 2·94, 3·87, and 4·91 respectively), $\lambda_{infl.}$ 280—281 mμ (log ε 3·81) $\lambda_{min.}$ 321 and 254 mμ (log ε 2·81 and 3·37), $\nu_{max.}$ (in $CHCl_3$) 3070, 2944, 2867, 1772, 1722, 1638, 1609, 1513, 1469, 1439, 1416, 1373, 1250, 1202, 1178, 1115, 1095, 1065, 1037, 1016, 899, and 819 cm.$^{-1}$.

Deacetylation of the Thiele Acetylation Product of Pristimerin.—A solution of the Thiele acetylation product [2] (110 mg.) in methanol (17 c.c.) was heated under reflux with 20% hydrochloric

acid (4 c.c.) for 8 hr. The solution was diluted with water, and most of the methanol removed by distillation. The product which separated as a cream-coloured resin was removed, dissolved in ether, washed with aqueous sodium hydrogen carbonate, and dried. After removal of the solvent the residue, crystallised repeatedly from aqueous methanol, gave the deacetylation *product* as long colourless needles, m. p. 70—75° (Found: C, 77·3; H, 8·65; OMe, 8·9. $C_{30}H_{40}O_4$ requires C, 77·55; H, 8·7; 1OMe, 6·7%), $\lambda_{max.}$ 333, 317, 295, and 239 mμ (log ε 3·44, 3·42, 3·83, and 4·75) with inflections at 306 and 285 mμ (log ε 3·74 and 3·76), $\lambda_{min.}$ at 324, 316, and 261 mμ (log ε 3·22, 3·41, and 3·33), $\nu_{max.}$ (in $CHCl_3$) 3518, 3280, 2958, 2875, 1723, 1639, 1529, 1467, 1443, 1407, 1351, 1318, 1280, 1172, 1129, 1086, 1025, 957, and 850 cm.$^{-1}$.

The methylation product of the diol (55 mg.) was obtained by heating a solution in acetone (15 c.c.) and dimethyl sulphate (1 c.c.) in the presence of anhydrous potassium carbonate (0·8 g.) for 5½ hr. The mixture was diluted with water, most of the acetone removed under reduced pressure, and the resulting yellowish gum separated, dissolved in ether, and chromatographed on alumina. Removal of the solvent from the eluate gave a *product* which after repeated crystallisation from methanol gave colourless needles, m. p. 92·5—93·5° (Found: C, 77·7; H, 9·0; OMe, 19·9. $C_{32}H_{44}O_4$ requires C, 78·0; H, 9·0; 3OMe, 18·9%), $\lambda_{max.}$ 328, 291, and 239 mμ (log ε 3·24, 3·85, and 4·85) with inflections at 315, 300, and 281 mμ (log ε 3·23, 3·74, and 3·80), $\lambda_{min.}$ at 320 and 255 mμ (log ε 3·07 and 3·34), $\nu_{max.}$ (in CCl_4) 3075, 2955, 2874, 1736, 1618, 1566, 1511, 1483, 1467, 1415, 1314, 1265, 1218, 1188, 1174, 1159, 1114, 1086, 1064, and 1017 cm.$^{-1}$.

Reactions of the Naphthalenoid Dimethyl Ether Derived from the Thiele Acetylation Product.—(i) *Reduction by lithium aluminium hydride.* A solution of the dimethyl ether (90 mg.) from the foregoing experiment was added to a suspension of excess of lithium aluminium hydride in ether (25 c.c.), and the suspension was kept at room temperature, with occasional stirring, for 35 min. The excess of reagent was decomposed with water, the solution treated with 10% sulphuric acid, and the ethereal layer separated, washed with sodium hydrogen carbonate, and dried. Removal of the solvent gave a colourless gum which solidified on trituration with light petroleum (b. p. 60—80°) and was crystallised repeatedly from light petroleum; the reduction *product* formed colourless needles, m. p. 55—56° (Found: C, 80·4; H, 9·7; OMe, 11·3. $C_{31}H_{44}O_3$ requires C, 80·15; H, 9·55; 2OMe, 13·3%), $\lambda_{max.}$ 329, 291, and 239 mμ (log ε 3·19, 3·78, and 4·84) with inflections at 315 and 282 mμ (log ε 3·17 and 3·73), $\lambda_{min.}$ at 320 and 254 mμ (log ε 2·99 and 3·29), $\nu_{max.}$ (KBr) 3428, 2932, 2858, 1618, 1578, 1490, 1466, 1411, 1384, 1366, 1322, 1257, 1210, 1184, 1110, 1081, 1036, 1010, 990, 971, 949, 911, 833, 806, and 780 cm.$^{-1}$.

(ii) *Alkaline hydrolysis.* A solution of the dimethyl ether (100 mg.) in 10% methanolic potassium hydroxide (5 c.c.) was heated under reflux for 10 hr. The potassium salt of the product was precipitated with water and was separated, washed with a small volume of water, and dried. The infrared spectrum showed max. at 2900, 1625, 1560, 1475, 1412, 1390, 1255, 1212, 1110, 1084, 1018, 830, and 810 cm.$^{-1}$.

In another experiment the cold hydrolysis product was diluted and then acidified with concentrated hydrochloric acid, and the precipitate (75 mg.) separated and crystallised from light petroleum (b. p. 60—80°); this *product* formed colourless needles, m. p. 115—126° (Found: C, 77·9; H, 8·8; OMe, 12·6. $C_{31}H_{42}O_4$ requires C, 77·8; H, 8·8; 2OMe, 12·9%), $\lambda_{max.}$ 329, 291, and 239 mμ (log ε 3·21, 3·85, and 4·85) with an inflection at 281 mμ (log ε 3·81), $\lambda_{min.}$ 321 and 256 mμ (log ε 3·10 and 3·34), $\nu_{max.}$ (CCl_4) 2950, 2870, 2720, 2625, 1750, 1701, 1610, 1606, 1510, 1482, 1468, 1456, 1414, 1388, 1373, 1335, 1318, 1291, 1263, 1218, 1184, 1177, 1144, 1112, 1085, 1016, 975, 953, and 900 cm.$^{-1}$.

The acid was methylated by reaction with an excess of ethereal diazomethane. After removal of excess of reagent and the solvent, the residue was repeatedly crystallised from methanol, to give colourless needles, m. p. 92·5—93·5°, alone and mixed with the Thiele methylation product.

Permanganate Oxidation of Pristimerin.—A solution of pristimerin (0·97 g.) in acetone (150 c.c.) was shaken vigorously while finely powdered potassium permanganate (3·8 g.) was added at intervals until a pink colour persisted (48 hr.). The manganese dioxide sludge was separated, washed free from potassium permanganate with acetone, and exhaustively extracted with hot water (12 × 50 c.c.) until no precipitate was obtained after acidification of the filtrate. The combined aqueous filtrates were acidified and extracted with ether (6 × 80 c.c.), and the combined ethereal extracts were shaken with saturated aqueous sodium hydrogen carbonate (4 × 70 c.c.). The neutral fraction (260 mg.) was thus separated from the acidic fraction (520 mg.) which was obtained from the sodium hydrogen carbonate extracts by acidification and

extraction into ether. An ethereal solution of the acidic fraction was kept overnight, then re-extracted with aqueous sodium hydrogen carbonate; it thus yielded a further quantity (130 mg.) of the neutral material. Trituration of the combined neutral fractions with ether precipitated crystals which, after decolorisation with charcoal and repeated crystallisation from ether and then ether–light petroleum (b. p. 40—60°), gave colourless needles (220 mg.) of *anhydride A*, m. p. 220—221°, and a further quantity (30 mg.) of the same product was obtained by chromatography on alumina of the residue from the crystallisation mother-liquors [Found: C, 71·6, 71·5, 71·5; H, 8·35, 8·7, 8·2; OMe, 9·2%; *M* (*X*-ray), 391. $C_{24}H_{34}O_5$ requires C, 71·6; H, 8·5; 1OMe, 7·7%; *M*, 402]. Light absorption: (i) max. at 228 mμ (log ε 3·85); (ii) after a solution of the anhydride in ethanol–0·1N-sodium hydroxide (1 : 1) had been kept overnight, only end absorption was observed. Infrared absorption max. (Nujol): 1802, 1754, 1733, 1307, 1280, 1253, 1220, 1203, 1156, 1138, 1100, 1088, 1064, 1056, 1037, 1025, 1002, 984, 959, 949, 907, 864, 844, 835, 784, 768, and 719 cm.$^{-1}$.

Alkaline Hydrolysis of Anhydride A: *Anhydride B*.—(i) Anhydride A (60 mg.) dissolved in 10% aqueous sodium hydroxide (17 c.c.) when heated under reflux for 1 hr. The cool solution was acidified and extracted with ether; next morning the ethereal extract was washed with aqueous sodium hydrogen carbonate, dried, and evaporated. The neutral fraction (*anhydride B*) (25 mg.) crystallised from light petroleum (b. p. 40—60°) as colourless needles, m. p. 259—262° (Found: C, 70·8, 70·9; H, 7·95, 8·1. $C_{23}H_{32}O_5$ requires C, 71·1; H, 8·3%), $\lambda_{max.}$ 227—229 mμ (log ε 4·00). After being kept overnight a solution of anhydride B in ethanol–0·1N-aqueous sodium hydroxide (1 : 1) showed only end-absorption. Infrared absorption max. (Nujol) were at 3300, 1800, 1737, 1723, 1615, 1308, 1288, 1140, 1098, 1085, 1057, 1018, 1003, 964, 944, 878, 860, and 777 cm.$^{-1}$.

(ii) A solution of anhydride A (64 mg.) in benzene (15 c.c.) was shaken with 10% aqueous sodium hydroxide (20 c.c.) for 48 hr. while a slight excess of finely powdered potassium permanganate was added at intervals. The benzene layer was removed and the manganese dioxide sludge separated and extracted with hot water. The alkaline solution and the aqueous filtrates were combined and acidified and the precipitate was dissolved in ether. The ethereal solution was shaken with saturated aqueous sodium hydrogen carbonate, and the acidic fraction (53 mg.) and the neutral fraction (15 mg.) were isolated in the usual manner. Keeping a solution of the acid fraction overnight and then re-extracting it with aqueous sodium hydrogen carbonate yielded a further quantity (25 mg.) of the neutral material, which crystallised from ether, and then ether–light petroleum (b. p. 60—80°), in colourless crystals of anhydride B, m. p. and mixed m. p. with the neutral product from the alkaline hydrolysis of anhydride A, 263°.

Methylation of Anhydride B.—Excess of ethereal diazomethane was added to anhydride B (20 mg.) in ether (2 c.c.), and the solution was kept overnight. After removal of the excess of reagent and the ether, the residue was repeatedly crystallised from light petroleum (b. p. 40—60°), giving colourless needles of anhydride A, m. p. 219—220° alone and mixed with the oxidation product from pristimerin.

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