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CHEMISTRY OF THE PODOCARPACEAE—XII[1]

OXIDATION OF O-METHYLPODOCARPIC ACID WITH LEAD TETRA-ACETATE

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Abstract—Six products have been obtained from the oxidation of O-methylpodocarpic acid (I, R = Me) with lead tetra-acetate. These are a mixture of alkenes VIII, IX and X, the tertiary acetate XI (R = Ac), and the lactones XV (R = Ac), and XVII. Evidence for their stereochemistry is presented and pathways for their formation are suggested. Ozonolysis, and permanganate or osmium tetroxide–periodate oxidations of the alkene mixture give *inter alia* the *cis*-A/B-ring fused ketone, 12-methoxy-16-norpodocarpa-8,11,13-trien-4-one (IV), a potential intermediate for steroidal synthesis.

AMONG the resin acids,[2] podocarpic acid (I, R = H) provides a potential source of an abundant and cheap natural product for the conversion to intermediates suitable for the synthesis of steroidal compounds. This acid is readily obtained from the New Zealand trees, *Dacrydium cupressinum* Lamb. ("rimu")[3] and *Podocarpus dacrydioides* A. Rich. ("kahikatea")[4] where it frequently occurs in the heartshakes from whence it can be collected directly without extraction in a high state of purity.[5] Considerable work has been directed towards the utilization of the related C_4-equatorially substituted dehydroabietic acid (II, R = H)[6–11] for the synthesis of steroids and recently, the modification of ring C of podocarpic acid and its derivatives has received increased attention.[12,13] However, only one modification of the A-ring of podocarpic acid which

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[1] Part XI: C. R. Bennett and R. C. Cambie, *Tetrahedron* **22**, 2845 (1966).

[2] M. Tsutsui and E. A. Tsutsui, *Chem. Rev.* **59**, 1031 (1959).

[3] T. H. Easterfield and B. C. Aston, *Trans. N.Z. Inst.* **36**, 483 (1903).

[4] T. H. Easterfield, *Trans. N.Z. Inst.* **43**, 53 (1910); L. H. Briggs, R. C. Cambie, R. N. Seelye and A. D. Warth, *Tetrahedron* **7**, 270 (1959).

[5] For a comprehensive bibliography of the literature pertaining to podocarpic acid see S. G. Brooker, R. C. Cambie and M. A. James, *Trans. Roy. Soc. N.Z.* **1**, 205 (1966).

[6] A. Brossi, H. Gutmann and O. Jeger, *Helv. Chim. Acta* **33**, 1730 (1950).

[7] R. P. Jacobsen, *J. Amer. Chem. Soc.* **75**, 4709 (1953).

[8] H. H. Zeiss and W. B. Martin, *J. Amer. Chem. Soc.* **75**, 5935 (1953).

[9] J. W. Huffman and R. F. Stockel, *J. Org. Chem.* **28**, 506 (1963); R. F. Stockel, *Canad. J. Chem.* **41**, 834 (1963).

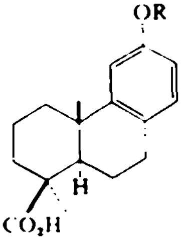
[10] H. Kanno, *J. Chem. Soc. Japan* **82**, 113 (1961), *Chem. Abstr.* **56**, 10195 (1962); P. F. Ritchie, T. F. Sanderson and L. F. McBurney, *J. Amer. Chem. Soc.* **75**, 2610 (1953), **76**, 723 (1954); H. H. Zeiss and M. Tsutsui, *J. Amer. Chem. Soc.* **77**, 6707 (1955); H. H. Zeiss, U.S. Pat. 2,803,645 (1957), *Chem. Abstr.* **52**, 2921 (1958); M. Ohta and L. Ohmori, *Pharm. Bull. Tokyo* **5**, 91, 96 (1957); E. Wenkert and B. G. Jackson, *J. Amer. Chem. Soc.* **80**, 211 (1958); E. Wenkert and J. W. Chamberlin, *J. Amer. Chem. Soc.* **81**, 688 (1959); E. Wenkert, R. W. J. Carney and C. Kaneko, *J. Amer. Chem. Soc.* **83**, 4440 (1961).

[11] J. W. Huffman and P. G. Arapakos, *J. Org. Chem.* **30**, 1604 (1965).

[12] R. H. Bible and R. R. Burtner, *J. Org. Chem.* **26**, 1174 (1961); H. L. Dryden, G. M. Webber, R. R. Burtner and J. A. Cella, *J. Org. Chem.* **26**, 3237 (1961); F. Sondheimer and M. Gibson, *Bull. Res. Council Israel* **9A**, 204 (1960), *Chem. Abstr.* **55**, 6520 (1961); E. Wenkert, V. I. Stenberg and P. Beak, *J. Amer. Chem. Soc.* **86**, 96 (1964); N. N. Girotra and L. H. Zalkow, *Tetrahedron* **21**, 101 (1965); K. Mori and M. Matsui, *Tetrahedron Letters* No. 28, 2347 (1965).

[13] K. Crowshaw, R. C. Newstead and N. A. J. Rogers, *Tetrahedron Letters* No. 33, 2307 (1964).

could be applied to the synthesis of steroids has been carried out[14], this involving degradation of O-methylpodocarpinol (III) to the 4-oxoderivative, 12-methoxy-16-norpodocarpa-8,11,13-trien-4-one (IV) by essentially the same procedure as used[6] for the corresponding degradation of dehydroabietic acid, *viz.* dehydration of the alcohol grouping of III with concomittant rearrangement, followed by ozonolysis of the resulting alkene V.[*] Hoehn and Bible[14] did not state the yield, assign the stereochemistry of, or further elaborate their product, except for the preparation of derivatives of physiological activity. The recent interest in the use of lead tetra-acetate for the oxidative decarboxylation of diterpenoid acids possessing C_4-equatorial carboxyl groups[15] led us to apply the method to podocarpic acid as an alternative means of preparing the 4-oxoderivative (IV). A report[11] during the course of our work, of the formation of 4-oxo-16-norabieta-8,11,13-triene (VI) in 72% overall yield from dehydroabietic acid by reaction with lead tetra-acetate followed by ozonolysis added impetus to our investigation, for this represents a considerable improvement over all other preparations of this ketone.[6, 9]



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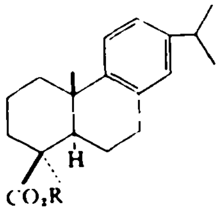

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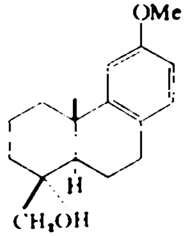

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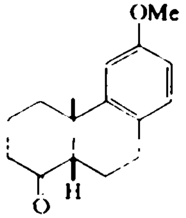

IV

For the present study O-methylpodocarpic acid (I, R = Me) was chosen as a suitable starting material. This acid was prepared in 92% yield by the halolytic cleavage of the hindered ester grouping of the fully methylated derivative methyl-O-methylpodocarpate (VII, R = Me) with lithium iodide in refluxing collidine,[16] or as

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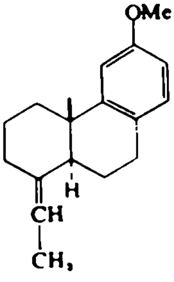
[*] In order to focus attention on the formation and/or reactions of a double bond the term "alkene" is used throughout this paper to denote compounds such as V, VIII, IX, and X which are not hydrocarbons as the name implies, but possess an oxygenated function at C_{16}."

[14] W. M. Hoehn and R. H. Bible, U.S. Pat. 2,764,616 (1956), *Chem. Abstr.* **51**, 4435 (1957).

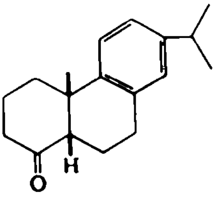
[15] W. A. Ayer, C. E. McDonald and J. B. Stothers, *Canad. J. Chem.* **41**, 1113 (1963); W. A. Ayer and C. E. McDonald, *Canad. J. Chem.* **43**, 1429 (1965); L. H. Zalkow and D. R. Brannon, *J. Chem. Soc.* 5497 (1964).

[16] E. Taschner and B. Liberek, *Rocz. Chem.* **30**, 232 (1956), *Chem. Abstr.* **51**, 1039 (1957); F. Elsinger, J. Schreiber and A. Eschenmoser, *Helv. Chim. Acta* **43**, 113 (1960); J. Schreiber, W. Leimgruber, M. Pesaro, P. Schudel, T. Threlfall and A. Eschenmoser, *Ibid.* **44**, 540 (1961).

podocarpic acid was available in plentiful supply, more conveniently by methylation of the crude acid with an excess of approximately equimolecular amounts of dimethylsulphate and sodium hydroxide at 35° which formed the insoluble sodium salt of O-methylpodocarpic acid in 65–75% yield.* The preparation of the latter acid has hitherto been carried out in unstated yield by vigorous hydrolysis (4 hr at 150°) of methyl-O-methylpodocarpate with strong alkali.[17] Neither this nor application of the method for the hydrolysis of hindered esters with lithium in liquid ammonia[18] was found to be suitable for the ready preparation of large quantities of the acid I ($R = Me$).

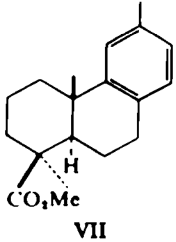


V



VI

When O-methylpodocarpic acid was reacted with lead tetra-acetate in the presence or absence of pyridine[19] a vigorous evolution of carbon dioxide occurred and four products were isolated after chromatography on alumina. The least polar material (76% yield), recovered from the column with light petroleum, was a mixture of three isomeric alkenes, $C_{17}H_{22}O$, in which GLC and the NMR spectrum indicated the presence of 63% of the $\Delta^{4(5)}$-isomer VIII, 28% of the $\Delta^{4(15)}$-isomer IX and 9% of the Δ^{5}-isomer X. This ratio and the identification of products was confirmed by the subsequent isolation of pure samples of the alkenes VIII and IX from other reactions (*vide infra*). That the pure exocyclic alkene IX was not isomerized under the GLC conditions to the thermodynamically more stable[20] endocyclic isomers VIII and X justifies the application of this method for determining product ratios in the alkene mixture.



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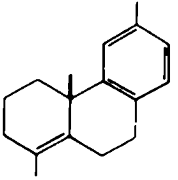

VIII

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* In a recent paper[19] the preliminary account without details of the preparation of O-methylpodocarpic acid by a similar method was reported.

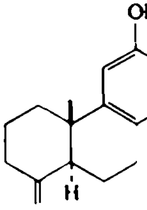
[17] I. R. Sherwood and W. F. Short, *J. Chem. Soc.* 1006 (1938).

[18] E. Wenkert and B. G. Jackson, *J. Amer. Chem. Soc.* **80**, 217 (1958).

[19] E. J. Corey and J. Casanova, *J. Amer. Chem. Soc.* **85**, 165 (1963).

[20] R. B. Turner and R. H. Garner, *J. Amer. Chem. Soc.* **80**, 1424 (1958); A. C. Cope, D. Ambros, E. Ciganek, C. F. Howell and Z. Jacura, *J. Amer. Chem. Soc.* **81**, 3153 (1959).

Following the alkene mixture a further product (14·5% yield) was isolated from later light petroleum eluates during the chromatography. This compound, a liquid, b.p. 168–171°/0·3 mm, had formula $C_{19}H_{28}O_3$ and was assigned the tertiary acetate structure XI (R = Ac). The IR spectrum showed bands of an acetate carbonyl group at 1735 and 1255 cm^{-1} while the NMR spectrum showed the features expected for the structure XI (R = Ac). Hydrolysis of the acetate gave the tertiary alcohol XI (R = H), m.p. 108–109°, whose IR spectrum showed OH absorption at 3560 cm^{-1} and a band at 1125 cm^{-1} attributed to tertiary OH stretching. Assignment of an α-configuration to the C_4-acetoxyl group of XI (R = Ac) follows from the NMR spectrum which showed a strongly deshielded C_{10}-methyl signal at 1·47 δ. In the spectrum of the alcohol XI (R = H) the corresponding signal appeared in the normal position[21] at 1·15 δ [cf. 12-methoxypodocarpa-8,11,13-triene (XII), 1·18 δ, totarol (XIII, R = H), 1·15 δ,[22] and totaryl methyl ether (XIII, R = Me), 1·19 δ[23]]. According to a report[24] methyl proton resonances are shifted to higher field when an alcoholic group having a 1,3-diaxial spatial relationship to that methyl group, is acetylated. In the present case the reverse effect is observed, a paramagnetic shift of 19 c/s on acetylation of XI (R = H) supporting the assignment of an equatorial conformation and hence an α-configuration for the OH group. This assignment is also in agreement with mechanistic considerations regarding the formation of the acetate XI (R = Ac) during the oxidation (*vide infra*).



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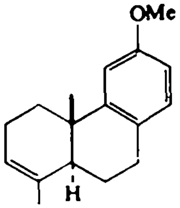

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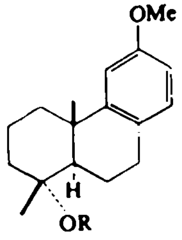
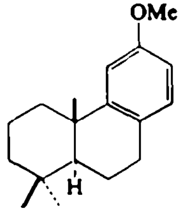


XI



XII

Also isolated by chromatography of the hydrolysis products of the tertiary acetate XI (R = Ac) was a homogeneous (GLC) sample of 12-methoxy-16-norpodocarpa-4(15),8,11,13-tetraene (IX) formed by selective elimination of the hydrogen atoms of

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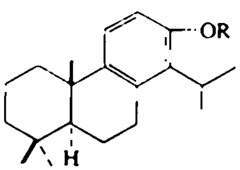
[21] E. Wenkert, A. Afonso, P. Beak, R. W. J. Carney, P. W. Jeffs and J. D. McChesney, *J. Org. Chem.* **30**, 713 (1965); C. H. Brieskorn, A. Fuchs, J. B-son. Bredenberg, J. D. McChesney and E. Wenkert, *J. Org. Chem.* **29**, 2293 (1964).

[22] R. C. Cambie and L. N. Mander, *Tetrahedron* **18**, 465 (1962).

[23] R. C. Cambie, W. R. J. Simpson and L. D. Colebrook, *Tetrahedron* **19**, 209 (1963).

[24] T. Okamoto and Y. Kawazoe, *Chem. Pharm. Bull. Japan* **11**, 643 (1963); Y. Kawazoe, Y. Sato, T. Okamoto and K. Tsuda, *Chem. Pharm. Bull. Japan* **11**, 328 (1963).

the C_{15}-methyl group. Dreiding models indicate that of the hydrogens on carbon atoms β to the alcohol group of XI ($R = H$) only those on the C_{15}-methyl group can adopt a favourable conformation for ready E_2 elimination. The IR spectrum of the alkene, b.p. 100–102°/0·2 mm, showed strong absorption at 893 cm^{-1} diagnostic of an exocyclic methylene group while the NMR spectrum displayed two broad signals at 4·56 and 4·80 δ characteristic of non-equivalent exocyclic vinyl protons [cf. 16-norabieta-4(15),8,11,13-tetraene (XIV), 4·59 and 4·83 δ[25]]. A Dreiding model of the alkene IX indicates that the C_{10}-angular methyl group lies in the cone of shielding of the double bond and hence its signal should occur at higher field than normal (1·18–1·22 δ[21]). This was indeed the case, the peak appearing at 0·98 δ. It has been established[21] that in the A/B-*cis* analogues of the dehydroabietic and podocarpic acid series the C_{10}-methyl group is approximately within the same ring C environment as that which it occupies in the *trans*-A/B series and therefore shows similar chemical shifts. The possibility that the alkene IX possessed a *cis*-A/B ring fusion is thus eliminated, for models indicate that regardless of the actual conformation, the C_{10}-methyl group in this case would be deshielded by the exocyclic double bond and would therefore show a downfield shift rather than the upfield shift observed.



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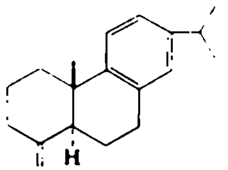

XIV

A further product, m.p. 173–174·5° (6·5% yield), of the lead tetra-acetate oxidation of O-methylpodocarpic acid, was eluted from the column with benzene and was identified as the acetoxy-lactone XV from the following evidence. Analytical data indicated the formula $C_{20}H_{24}O_5$, and bands in the IR spectrum showed the presence of γ-lactone (1783 cm^{-1}) and ester (1755 cm^{-1}) functions, while a further band in the spectrum at 1238 cm^{-1} showed the ester function was that of an acetate. This was confirmed by the NMR spectrum which showed three-proton signals at 1·06 δ (C_4-Me), 1·20 δ (C_{10}-Me), 2·24 δ (OAc), 3·78 δ (OMe), and a multiplet between 6·6 and 7·2 δ ($C_{11,13,14}$-aromatic protons). The spectrum also showed a C_5-proton doublet at 2·32 δ ($J = 7·0$ c/s), a C_6-proton quartet at 4·80 δ ($J_{5,6} = 7·0$ c/s, $J_{6,7} = 4·0$ c/s), and a broadened C_7-proton doublet at 6·24 δ ($J = 4·0$ c/s), the coupling constants of which are consistent with the structure XV($R = Ac$) [cf. Ref. 26 for the analysis of a related structure XVI]. Assignment of an α-configuration for the acetoxyl group is also supported by the absence of deshielding effects on the chemical shift of the C_{10}-angular methyl group which would be expected if a 7β-substituent was present.[21] Verification that the lactone ring of XV ($R = Ac$) assumes a β-configuration and that the compound retains a *trans*-A/B ring fusion was obtained by its conversion to the known keto-lactone XVII.[27,28] Alkaline hydrolysis gave the hydroxy-lactone XV ($R = H$; ν_{max} 3515 cm^{-1},

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[25] C. R. Bennett and R. C. Cambie, unpublished results.

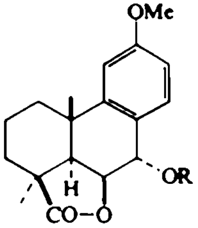
[26] E. Wenkert and B. L. Mylari, *J. Org. Chem.* **30**, 4387 (1965).

[27] E. Wenkert, P. Beak, R. W. J. Carney, J. W. Chamberlin, D. B. R. Johnston, C. D. Roth and A. Tahara, *Canad. J. Chem.* **41**, 1924 (1963).

[28] R. H. Bible, U.S. Pat. 2,753,357 (1956), *Chem. Abstr.* **51**, 2869 (1957).

bonded OH) which on oxidation with chromic acid afforded the keto-lactone XVII, identical with an authentic sample prepared by dehydrobromination of 6α-bromo-7-oxo-methyl-O-methylpodocarpate (XVIII, R = Me, R′ = Br), or during bromination of 7-oxo-O-methylpodocarpic acid (XVIII, R = H, R′ = H).[29] The keto-lactone was also found to be a product (4·5% yield) of the lead tetra-acetate oxidation of O-methylpodocarpic acid where it was contained in the ether eluate from chromatography.

While oxidative decarboxylation of carboxylic acids with lead tetra-acetate undoubtedly involves carbonium ion intermediates[29,30] and while the relative ease of decarboxylation follows the order of stability of the carbonium ion formed by loss of carbon dioxide, *viz.* tertiary > secondary > primary, few studies have been concerned with the oxidative decarboxylation of tertiary acids.[11,15,31] Most workers have favoured an ionic mechanism involving direct formation of lead diacetate and an acyloxonium intermediate, RCO_2^+, which undergoes subsequent decarboxylation. However, on the basis of inhibition of the reaction by oxygen and the catalysis by copper salts as well as from rate studies, a free-radical chain mechanism has recently been put forward[32] and is supported by evidence from other workers.[33,34] According to Kochi[32] the initial step is a preequilibration to form the triacetyl-lead ester of the acid followed by the initiation step which involves homolysis of the ester to a triacetyl-lead radical, carbon dioxide, and an alkyl radical. In the propagation step either the



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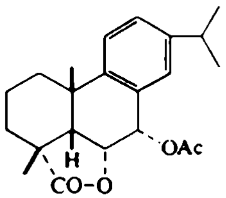
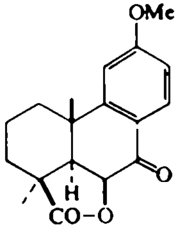


XVI



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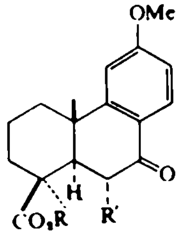

XVIII

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[29] A. K. Bose, M. S. Manhas and R. C. Cambie, *J. Org. Chem.* **30**, 501 (1965).

[30] W. A. Mosher and C. L. Kehr, *J. Amer. Chem. Soc.* **75**, 3172 (1953); **82**, 5342 (1960); W. A. Mosher, C. L. Kehr and L. W. Wright, *J. Org. Chem.* **26**, 1044 (1961).

[31] G. Büchi, R. E. Erickson and N. Wakabayashi, *J. Amer. Chem. Soc.* **83**, 927 (1961). See also A. J. Birch, *J. Chem. Soc.* 1551 (1950), and H. Plieninger and G. Ege, *Chem. Ber.* **94**, 2095 (1961).

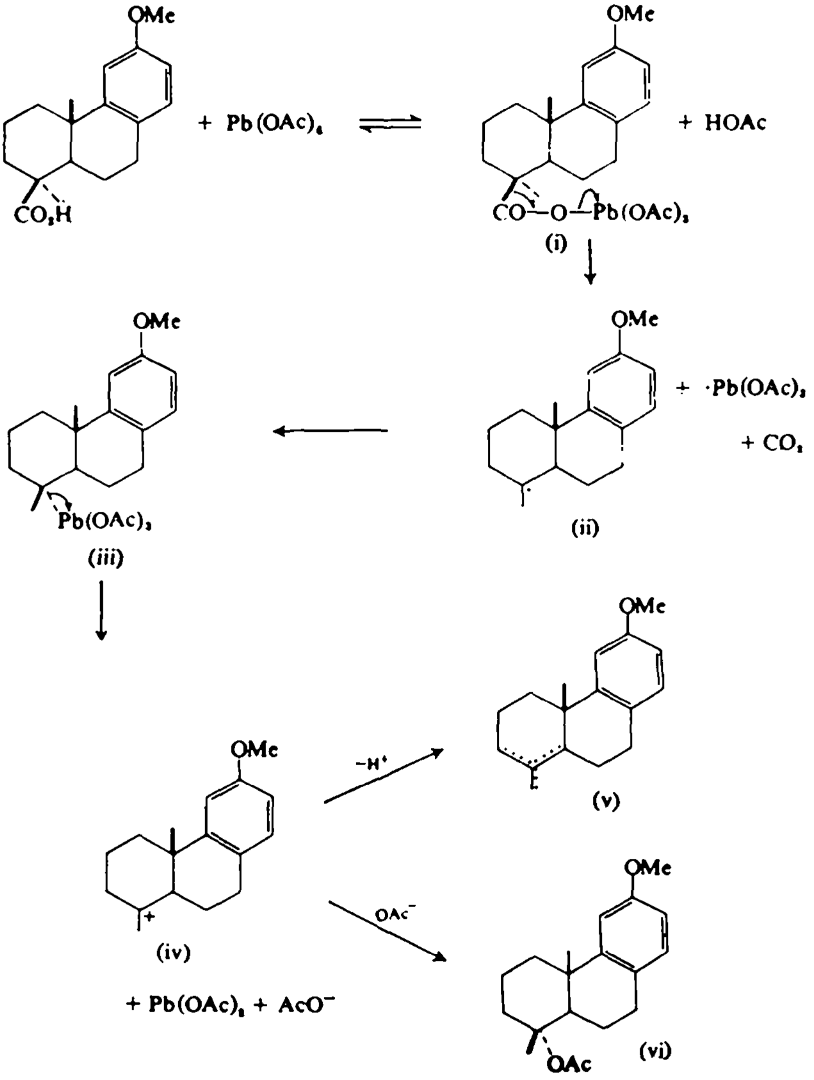
[32] J. K. Kochi, *J. Amer. Chem. Soc.* **87**, 3609 (1965).

[33] D. I. Davies and C. Waring, *Chem. Comm.* No 12, 263 (1965). See also M. S. Kharasch, H. N. Friedlander and W. H. Urry, *J. Org. Chem.* **16**, 533 (1951) for other radical mechanisms.

[34] M. Lj. Mihailović, Ž. Čeković, Z. Maksimović, D. Jeremić, Lj. Lorenc and R. I. Mamuzić, *Tetrahedron* **21**, 2799 (1965).

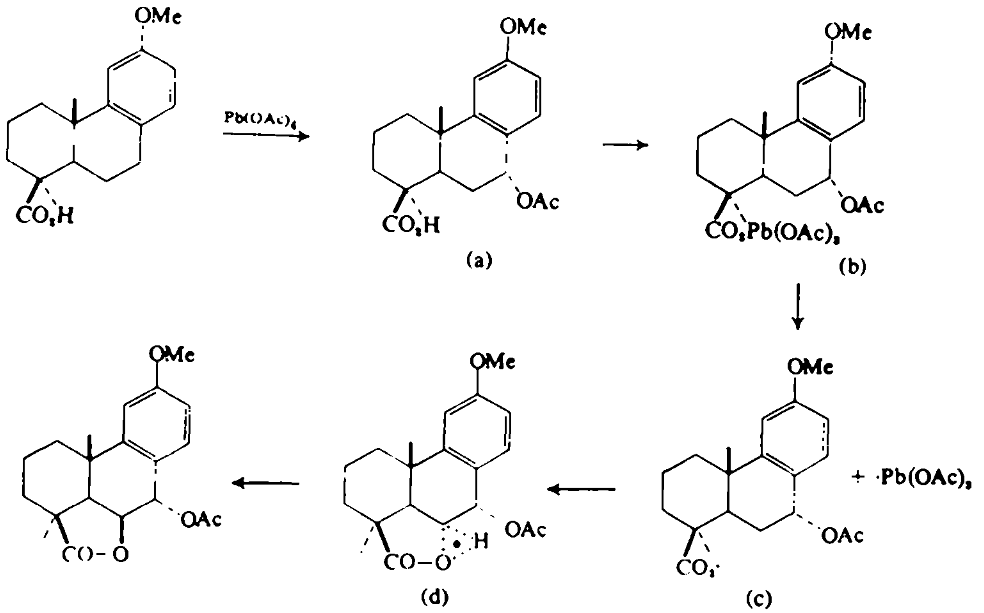
metastable Pb(III) ester of the parent acid decomposes to further alkyl radical, carbon dioxide, and stable Pb(II) diacetate, or the alkyl radical combines with lead tetraacetate to form the corresponding carbonium ion of the alkyl radical and a metastable Pb(III) intermediate. Termination occurs by combination of radicals or by reaction of the alkyl radical with the Pb(III) species to form a carbonium ion plus lead diacetate.

Although the present work adds no further evidence, similar initiation and termination steps can be envisaged for the formation of the alkenes VIII, IX, and X, and the acetate XI (R = Ac) during the oxidation of O-methylpodocarpic acid, according to the following scheme.



Homolytic fission of the ester (i) would give the alkyl radical (ii), carbon dioxide, and the bulky lead triacetate radical, attack by which on (ii) from the less hindered α-face would furnish the unstable organo-lead compound (iii). Fragmentation of the latter or of the radical (ii) by oxidation[34] would then yield the tertiary carbonium ion (iv), lead diacetate, and acetate anion. Elimination of a proton from either C_3, C_5 or C_{15} would then give rise to the alkene mixture (v) while attack by acetate anion from the less-hindered α-face would afford the tertiary acetate (vi). In accord with the formation of a stable tertiary carbonium ion at C_4 during the above process the tetrasubstituted $\Delta^{4(5)}$-alkene VIII is the predominant product but the formation of a larger amount of the exocyclic alkene IX than of the Δ^3-alkene X is contrary to normal expectation.

Lactone formation during lead tetra-acetate oxidations has usually occurred during reactions with dicarboxylic acids.[15,35] However, the ready formation of γ-lactones from 7-oxopodocarpic acid derivatives during oxidative processes is known[28,29] and a plausible route to the lactone XV (R = Ac) during the lead tetra-acetate oxidation of O-methylpodocarpic acid can be postulated *viz.*



Here oxidation at the activated C_7-position either by a radical-chain mechanism,[36] concerted mechanism,[37] or by direct carbonium ion formation from a benzylic radical[34] would provide the α-acetate (a) by attack from the least hindered face. The triacetyl-lead ester (b) formed by attack of lead tetra-acetate on (a) could then give the carboxy radical (c) by homolytic fission of the Pb—O bond, instead of eliminating carbon dioxide. A six-membered transition state (d) is now proposed to facilitate hydrogen abstraction from the unactivated C_6-position[34] to give the acetoxy-lactone (e). A direct analogy for the formation of the acetate (a) is provided by the

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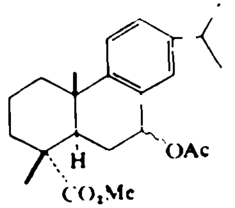
[35] L. L. McCoy and A. Zagalo, *J. Org. Chem.* 25, 824 (1960); W. R. Moore and H. Arzoumanian, *J. Org. Chem.* 27, 4667 (1962); K. Kitahonoki and Y. Takano, *Tetrahedron Letters* No 24, 1597 (1963).

[36] M. J. S. Dewar, *The Electronic Theory of Organic Chemistry* p. 276. Oxford Univ. Press, London (1949); G. W. K. Cavill and D. H. Solomon, *J. Chem. Soc.* 3943 (1954).

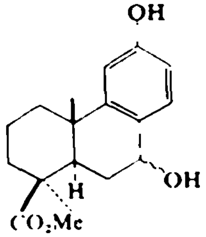
[37] D. I. Davies, *J. Chem. Soc.* 2351 (1963).

lead tetra-acetate oxidation of methyldehydroabietate (II, R = Me) to the 7-acetoxy derivative XIX,[38] while the conversion of (c) to (d) is similar to a mechanism proposed for the cyclization of alcohols to ethers.[34,39]

For the case of the lactone XVII it is assumed that direct oxidation at the C_7-position produces an alcohol or alkoxide since the production of ketones[40] from lead tetra-acetate oxidations involves the participation of lead alkoxides, ROPb(OAc)$_3$.[41] It is not clear how the alcohol is formed in the present case but evidence for its participation follows from the fact that when methylpodocarpate (VII, R = H) was treated with lead tetra-acetate in glacial acetic acid only a single product was isolated whose structure was shown to be that of the 7-hydroxyderivative XX.[42] Formation of the lactone ring of XVII would then follow a similar pathway to that given above for the formation of the acetoxy-lactone XV (R = Ac).



XIX



XX

An indication that benzylic attack is a secondary reaction during the lead tetra-acetate oxidation of O-methylpodocarpic acid and is probably independent of the primary process of oxidative decarboxylation, was obtained when methyl-O-methylpodocarpate (VII, R = Me) was oxidized under the same conditions. In this case no visible reaction occurred and a large amount of starting material was recovered together with a small amount of the known $\alpha\beta$-unsaturated ketone, methyl-5,6-dehydro-7-oxo-O-methylpodocarpate (XXII),[37] identified by comparison with a sample prepared from methyl-6α-bromo-7-oxo-O-methylpodocarpate.[39] Its formation is thought to arise *via* the enol form of a 7-oxoderivative whose oxo-group is derived in a similar manner to that of the lactone XVII. Formation of an $\alpha\beta$-unsaturated ketone could then occur by an ionic process similar to that given[43] for the formation of flavones from flavanones or alternatively by a radical mechanism.[44]

In order to find the most suitable route to the C_4-ketone IV a number of oxidative fissions of the alkene mixture obtained from the lead tetra-acetate oxidation of O-methylpodocarpic acid were examined. TLC showed that ozonolysis of the alkenes

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[38] G. Dupont, R. Dulou, G. Ourisson and C. Thibault, *Bull. Soc. Chim. Fr.* 708 (1955).

[39] D. Hauser, K. Schaffner and O. Jeger, *Helv. Chim. Acta* 47, 1883 (1964); D. Hauser, K. Heusler, J. Kalvoda, K. Schaffner and O. Jeger, *Ibid.* 47, 1961 (1964); K. Heusler and J. Kalvoda, *Angew. Chem.* (Intern. English Ed) 3, 525 (1964).

[40] R. Criegee, *Oxidation in Organic Chemistry* (Edited by K. B. Wiberg) Chap. V; p. 287. Academic Press, New York (1965).

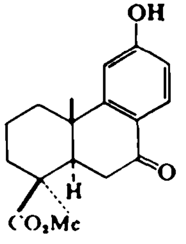
[41] See also M. Lj. Mihailović, Z. Maksimović, D. Jeremić, Ž. Čeković, A. Milovanović and Lj. Lorenc, *Tetrahedron* 21, 1395 (1965).

[42] G. F. Birkinshaw, M.Sc. Thesis, University of Auckland, 1965.

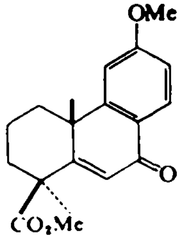
[43] Ref. 40, p. 308.

[44] G. W. K. Cavill, F. M. Dean, A. McGookin, B. M. Marshall and A. Robertson, *J. Chem. Soc.* 4573 (1954).

and decomposition of the ozonides with potassium iodide[11] gave a complex mixture of products, the two major constituents of which were isolated by chromatography on alumina. From the benzene eluate a crystalline ketone, m.p. 77–78°, was obtained

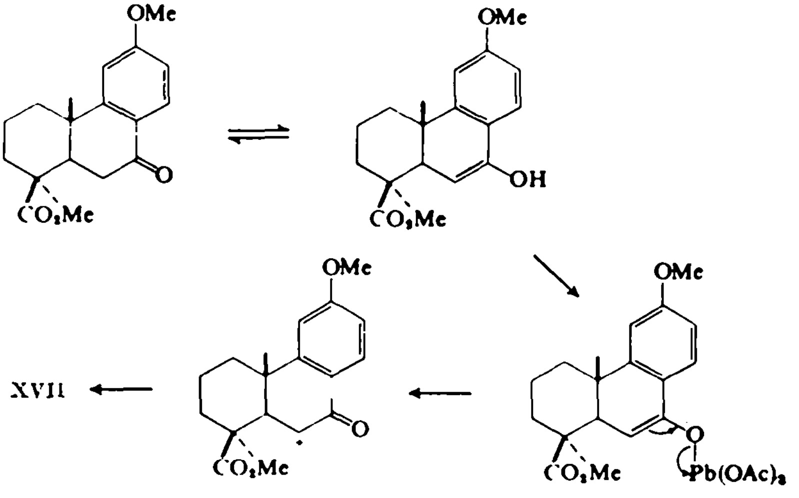


XXI



XXII

(30% yield based on the appropriate alkene in the mixture) which was identified as the desired product, 12-methoxy-15,16-dinorpodocarpa-8,11,13-trien-4-one (IV) from IR and NMR spectral evidence. The ketone has previously been obtained from ozonolysis of the dehydration product V of O-methylpodocarpinol only as an oil[44]



and it possibly existed there as a mixture of *cis*- and *trans*-A/B forms. The IR spectrum of the crystalline material showed six-membered ring carbonyl absorption at 1709 cm^{-1} and a single methyl signal in the NMR spectrum at 1·03 δ assigned to the C_{10}-angular methyl group. The molecular formula and other spectral features were also in agreement with the proposed structure. The presence of a C_4-carbonyl group should permit easy epimerization at the C_5-carbon atom to give the sterically favoured isomer, and indeed, it has been shown that epimerization of a 4- or a 6-oxo-octahydrophenanthrene occurs readily to give the thermodynamically more stable A/B-*cis* compound.[9,45] Compounds possessing a keto-function adjacent to an epimerisable hydrogen atom

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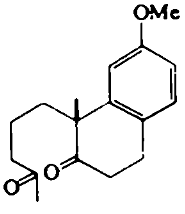
[44] C. D. Gutsche and W. S. Johnson, *J. Amer. Chem. Soc.* 68, 2239 (1946); W. E. Parham, E. L. Wheeler and R. M. Dodson, *J. Amer. Chem. Soc.* 77, 1166 (1955); N. N. Saha, B. K. Ganguly and P. C. Dutta, *Chem. & Ind.* 412 (1956); J. A. Barltrop and N. A. J. Rogers, *J. Chem. Soc.* 2566 (1958).

at a ring junction undergo ready equilibration when adsorbed on alumina[9,46] and thus the 12-methoxy-15,16-dinorpodocarpa-8,11,13-trien-4-one should possess an A/B-*cis* ring junction. This was confirmed from the ORD curve of the ketone which showed a strong positive Cotton effect. Application of the octant rule[47] clearly shows that a *trans*-A/B ring ketone would exhibit a negative Cotton effect curve.

The major product (79% yield based on the appropriate alkene) was a diketone XXIII, arising from the degradation of the more abundant $\Delta^{4(5)}$-isomer VIII in the alkene mixture. Bands in the IR spectrum at 1723 (straight-chain ketone) and 1713 cm^{-1} (six-membered ring ketone) showed the presence of two carbonyl groups one of which was a methyl ketone since the compound gave a positive iodoform test and its NMR spectrum showed a three-proton signal at 1·92 δ due to a methyl group adjacent to a carbonyl group.



XXIII

Osmic acid–sodium metaperiodate oxidation of the alkene mixture also gave, after chromatography, the ketone IV in 25% yield based on the amount of the alkene IX in the mixture. From earlier light petroleum eluates was obtained the unreactive tetrasubstituted alkene VIII, b.p. 121–122°/0·15 mm, in a pure state. Its IR spectrum showed no alkene absorption in the bending region but the presence of a tetrasubstituted double bond was indicated by the formation of a strong red coloration with tetranitromethane. No signals were present in the NMR spectrum which could be ascribed to vinylic protons, the only low field signals being those in the region 6·70 δ due to the three aromatic protons. Of the remaining three-proton signals that due to the methoxyl protons appeared at 3·68 δ, that of the allylic C_{10}-angular methyl group occurred downfield from the normal position at 1·33 δ as a result of the deshielding influence of the $\Delta^{4(5)}$-double bond, while that of the C_{15}-methyl group attached to the double bond, occurred at 1·64 δ in the expected position. The alkene has previously been isolated by Barltrop and his co-workers as a by-product during the preparation of the corresponding nitrile by treatment of the sodium salt of O-methylpodocarpic acid with cyanogen chloride.[48] However, the recorded analytical figures indicate that their material was impure.

The alkene VIII and the ketone IV (60% yield based on the amount of IX in the mixture), were again obtained from potassium permanganate–sodium metaperiodate oxidation of the alkene mixture along with other products which were not further investigated. Although the yield of ketone IV from this last reaction was superior

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[46] R. E. Ireland and P. W. Schiess, *J. Org. Chem.* **28**, 6 (1963); R. E. Ireland and J. Newbould, *J. Org. Chem.* **28**, 23 (1963).

[47] C. Djerassi, *Optical Rotatory Dispersion* p. 181. McGraw-Hill, New York (1960); W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne and C. Djerassi, *J. Amer. Chem. Soc.* **83**, 4013 (1961).

[48] J. A. Barltrop, A. C. Day and D. B. Bigley, *J. Chem. Soc.* 3185 (1961).

to those obtained from ozonolysis or the osmic acid–sodium metaperiodate reactions the presence of traces of persistent impurities inhibited crystallisation of the product.

EXPERIMENTAL

Microanalyses were by Dr. A. D. Campbell and his associates, University of Otago, New Zealand. IR spectra were measured with a Perkin–Elmer 237 instrument and UV spectra were determined for EtOH solutions with a Perkin–Elmer 137 UV spectrophotometer. ORD curves and optical rotations were determined with a Jasco ORD/UV-5 spectrophotometer at 25° and, unless otherwise stated, are for solns in MeOH. NMR spectra were determined in $CDCl_3$ with a Varian A60 spectrometer, using TMS as internal reference.

Light petroleum b.p. 50–60° and alumina used for column chromatography was P. Spence Type H material. GLC of alkene fractions: a Wilkens Autoprep instrument, Model A-700 with a 20′ SE30 column operating at 270°.

M.ps on a Kofler block were uncorrected.

O-Methylpodocarpic acid (I, R = Me)

(a) A soln of methyl-O-methylpodocarpate (6·2 g), in 2,4,6-collidine (100 ml) containing LiI (20·1 g) was heated under reflux in anhydrous conditions for 4 hr. The cooled soln was poured onto crushed ice and acidified with HCl. Extraction with ether and treatment of the conc ether soln with 30% NaOHaq gave the insoluble Na salt of I (R = Me). The salt was collected, suspended in water, and acidified with 10% HCl. Crystallization of the product from aqueous EtOH gave plates (5·44 g) of the free acid, m.p. 158° (lit.[17] m.p. 158°), $[\alpha]_D$ +135° (*c* 1·0), $\nu_{max}(CCl_4)$ 3300–2500 (bonded acid OH), 1712 (CO_2H), 1212 (acid C—O), and 1050 cm^{-1} (OMe). NMR (CCl_4) 1·13 (C_4-axial Me), 1·32 (C_{10}-angular Me), 3·71 (ArOMe), 6·45–6·95 ($C_{11,13,14}$-aromatic protons), and 13·30 δ (CO_2H).

(b) In a typical experiment Me_2SO_4 (35 ml, 0·36 mole) was added dropwise to a stirred soln of crude podocarpic acid (25 g, 0·09 mole) in NaOH (15 g, 0·37 mole) and water (75 ml) while the temp was maintained at ca. 35°. The pale yellow ppt which formed was filtered off and dried to give a powder which was heated under reflux with light petroleum (2 × 500 ml) for 1 hr. Concentration of the light petroleum extracts gave methyl-O-methylpodocarpate (1·5 g), m.p. and mixed m.p. 127–128° (identical IR spectrum).

Working up of the Na salt as in (a) gave I (R = Me) (18·5 g), m.p. and mixed m.p. 157–158° (identical IR spectrum).

Lead tetra-acetate oxidation of O-*methylpodocarpic acid* (I, R = Me)

A mixture of I (R = Me) (14·0 g), dry benzene (100 ml), dry pyridine (6 ml), and lead tetra-acetate (23·5 g) was stirred under N_2 at 20° for 1 hr, and then heated under reflux for a further 3 hr. The cooled mixture was filtered and the filtrate concentrated to yield a pale yellow oil which was chromatographed on acid-washed alumina (500 g). Elution with light petroleum gave a viscous alkene fraction (8·89 g), b.p. 121–122°/0·15 mm. (Found: C, 83·95; H, 9·2. $C_{17}H_{22}O$ requires: C, 84·25; H, 9·15%.) GLC showed 3 peaks with retention volumes 9·1 L, 9·75 L, and 8·15 L in a ratio of ca. 63 (VIII), to 28 (IX), to 9 (X), the first 2 peaks possessing retention volumes identical to those of the respective homogeneous alkenes. ν_{max}(film) 1660 (w, trisubstituted C=C), 1640 (terminal C=C), 1613, 1570 (aromatic C=C), 1045 (OMe), 893 (terminal C=C), 847 (w, trisubstituted C=C), 868 and 803 cm^{-1} (1,2,4-aromatic trisubstitution). NMR 0·98 (C_{10}-angular Me of IX), 1·00 (C_{10}-angular Me of X), 1·33 (C_{10}-angular Me of VIII), 1·64 (C_4-methyls of VIII and X), 3·68 (ArOMe), 4·68 (d, J = 14·0 c/s, terminal methylene of IX), 5·40 (broad s, C_3-proton of X), and 6·67 δ (m, $C_{11,13,14}$-aromatic protons)

The alkene mixture was reactive towards monoperphthalic acid at 20° while oxidation with H_2O_2 and formic acid[40] followed by saponification with methanolic NaOH gave a mixture of non-crystalline diols as determined from the IR spectrum.

Concentration of later light petroleum eluates gave 12-*methoxy*-16-*norpodocarpa*-8,11,13-*trien*-4α-*yl acetate* (XI, R = Ac) as a viscous oil (2·03 g), b.p. 168–171°/0·3 mm, $[\alpha]_D$ +185° (*c* 1·0). (Found: C, 75·5; H, 8·9. $C_{19}H_{26}O_3$ requires: C, 75·5; H, 8·7%.) ν_{max}(film) 1735 (alkyl acetate), 1610, 1580 (aromatic stretching), 1255 (acetate), 1045 (OMe), 865 and 810 cm^{-1} (1,2,4-aromatic trisubstitution). NMR 1·14 (C_4-axial Me), 1·47 (C_{10}-angular Me), 1·88 (acetate), 3·68 (ArOMe), and 6·69 δ (m, $C_{11,13,14}$-aromatic protons).

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[40] L. F. Fieser and S. Rajagopalan, *J. Amer. Chem. Soc.* 71, 3938 (1949).

From the benzene eluate was obtained the *γ-lactone of 6β-hydroxy-7α-acetoxy-O-methylpodocarpic acid* (XV, R = Ac) which crystallized from chf–light petroleum as prisms (0·95 g), m.p. 173–174·5°, $[\alpha]_D$ +64° (c 1·3 chf). (Found: C, 70·2; H, 7·1; O, 23·2. $C_{20}H_{24}O_5$ requires: C, 69·75; H, 7·0; O, 23·2%.) λ_{max} 236 (log ε 4·55), 273 (4·43), and 280 mμ (4·41), $\nu_{max}(CS_2)$ 1785 (γ-lactone), 1755 (alkyl acetate), 1605 (aromatic stretching), 1228 (acetate) and 1045 cm^{-1} (OMe). NMR 1·06 (C_4-equatorial Me), 1·20 (C_{10}-angular Me), 2·24 (acetate), 2·32 (d, J = 7·0 c/s, C_5-methine proton), 3·78 (ArOMe), 4·80 (quartet, $J_{5,6}$ = 7·0 c/s, $J_{6,7}$ = 4·0 c/s, C_6-methine proton), 6·24 (d, J = 4·0 c/s, C_7-methine proton) and 6·6–7·2 δ (m, $C_{11,13,14}$-aromatic protons).

Elution of the above column with ether gave the lactone XVII which crystallized from aqueous MeOH as needles (0·62 g), m.p. 201°, undepressed by a sample, m.p. 199–200° (lit.[37] m.p. 195–197·5°), prepared as reported,[37] or as recorded below. λ_{max} 231 (log ε 3·95) and 291 mμ (4·10), ν_{max}(chf) 1780 (γ-lactone), 1690 (aryl CO), 1600, 1570 (aromatic stretching), ν_{max}(KBr) 1775 (γ-lactone), 1690 (aryl CO), 1610, 1570 (aromatic stretching), 880 and 815 cm^{-1} (1,2,4-aromatic trisubstitution). The NMR spectrum was identical with that recorded.[44]

Lactone of 6β-hydroxy-7α-hydroxy-O-methylpodocarpic acid (XV, R = H)

The lactone XV (R = Ac, 1·56 g) was heated under reflux with 2N methanolic NaOH (80 ml) for 2½ hr, and the cooled mixture was acidified and extracted with ether. Chromatography of the product on alumina and elution of the column with ether gave the *γ-lactone of 6β-hydroxy-7α-hydroxy-O-methylpodocarpic acid* (1·54 g) as long needles, m.p. 190–192°, $[\alpha]_D$ +40° (c 1·2). (Found: C, 71·9; H, 7·7; O, 20·9. $C_{18}H_{22}O_4$ requires: C, 71·5; H, 7·3; O, 21·2%.) λ_{max} 236 (log ε 4·42), 274 (4·34), and 281 mμ (4·34), ν_{max}(KBr) 3515 (OH), 1768 (γ-lactone), 1620, 1580 (aromatic stretching), 1087 (secondary OH stretching), 1050 (OMe), 873 and 815 cm^{-1} (1,2,4-aromatic trisubstitution). NMR 0·95 (C_4-equatorial Me), 1·26 (C_{10}-angular Me), 2·31 (d, J = 8·0 c/s, C_5-methine proton), 4·62 (OH, exchanged with D_2O), 4·89 (quartet, $J_{5,6}$ = 8·0 c/s, $J_{6,7}$ = 4·0 c/s, C_6-methine proton), 5·10 (d, J = 4·0 c/s, C_7-methine proton).

Oxidation of the hydroxy-lactone (25 mg) with CrO_3 in AcOH for 15 hr at 20° followed by working-up and crystallization of the product from chf–ether gave the lactone of 6β-hydroxy-7-oxo-O-methylpodocarpic acid (19 mg) as needles, m.p. and mixed m.p. 201° (identical IR spectrum).

12-*Methoxy*-16-*norpodocarpa*-4(15),8,11,13-*tetraene* (IX) *and* 12-*methoxy*-16-*norpodocarpa*-8,11,13-*trien*-4α-*ol* (XI, R = H)

The acetate XI (R = Ac, 500 mg) was heated under reflux with 2N methanolic NaOH (100 ml) for 2½ hr. Water was added, the bulk of the MeOH was removed by distillation, and the remaining mixture was extracted with ether. Chromatography of the concentrate from the ethereal extracts on acid-washed alumina and elution of the column with light petroleum gave 12-*methoxy*-16-*norpodocarpa*-4(15),8,11,13-*tetraene* as a mobile oil (110 mg), b.p. 100–102°/0·2 mm, $[\alpha]_D$ +158° (c 0·9 chf). (Found: C, 84·0; H, 9·3; O, 6·55. $C_{17}H_{22}O$ requires: C, 84·25; H, 9·15; O, 6·6%.) $\nu_{max}(CCl_4)$ 3050, 1650, 1415 and 893 (terminal C=C), 1613, 1575 (aromatic stretching), and 1047 cm^{-1} (OMe). NMR 0·98 (C_{10}-angular Me), 3·68 (ArOMe), 4·68 (2 proton d, J = 14·0 c/s, C_4-terminal methylene) and 6·67 δ (m, $C_{11,13,14}$-aromatic protons). The alkene gave a strong red colour with tetranitromethane.

Concentration of the ether eluate from the column gave a solid (270 mg) which was recrystallized from chf–light petroleum to yield fine needles of 12-*methoxy*-16-*norpodocarpa*-8,11,13-*trien*-4α-*ol*, m.p. 108–109°, $[\alpha]_D$ +68° (c 0.9). (Found: C, 78·3; H, 9·4; O, 12·3. $C_{17}H_{24}O_2$ requires: C, 78·4; H, 9·3; O, 12·3%.) λ_{max} 233 (log ε 3·73), 280 (3·81), and 287·5 mμ (3·76), $\nu_{max}(CCl_4)$ 3560 (OH), 1605, 1570 (aromatic stretching), 1125 (tertiary OH stretching), and 1045 cm^{-1} (OMe). NMR 1·11 (C_4-axial Me), 1·15 (C_{10}-angular Me), 1·56 (OH exchanged with D_2O), 3·69 (ArOMe), and 6·62 δ (m, $C_{11,13,14}$-aromatic protons).

Ozonolysis of the alkene mixture VIII, IX *and* X

A stream of O_3 was passed through a soln of the above alkenes (5·26 g) in dichloromethane (150 ml) at −75° for 3 hr. The mixture was warmed to 20°, sat KIaq (200 ml) and AcOH (10 ml) were added, and the mixture was shaken vigorously and allowed to stand for 15 min. Sat $Na_2S_2O_3$aq was then added and the mixture was again shaken to remove I_2. The organic layer was washed with water and dried, and the concentrate was chromatographed on silica gel (200 g).

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[44] E. Wenkert, A. Fuchs and J. D. McChesney, *J. Org. Chem.* **30**, 2931 (1965).

Concentration of the benzene eluate gave plates (0·45 g) of 12-*methoxy*-15,16-*dinorpodocarpa*-8, 11,13-*trien-4-one* (IV) which on recrystallization from chf–light petroleum had m.p. 77–78°, $[\alpha]_D$ +146° (*c* 0·8). (Found: C, 78·4; H, 8·5; O, 13·1. $C_{16}H_{20}O_2$ requires: C, 78·65; H, 8·25; O, 13·1%.) ν_{max}(nujol) 1709 (6-membered ring CO), 1610, 1572 (aromatic stretching), 1225 (alkyl ketone), 1042 (OMe), 870 and 807 cm^{-1} (1,2,4-aromatic trisubstitution). NMR 1·03 (C_{10}-angular Me), 3·77 (ArOMe), 6·87 δ (m, $C_{11,13,14}$-aromatic protons). RD (*c* 0·211) $[\phi]_{589}$ +348°, $[\phi]_{400}$ +925°, $[\phi]_{323}$ + 3010°, $[\phi]_{340}$ + 1510°.

The 2,4-*dinitrophenylhydrazone* (83% yield) crystallized from chf–light petroleum as orange needles, m.p. 181–182°. (Found: C, 62·3; H, 5·9. $C_{22}H_{24}N_4O_5$ requires: C, 62·25; H, 5·7%.) Recorded m.p. 95–100°.[14]

Concentration of the ether eluate from chromatography of the ozonolysis product gave 2-*methoxy*-8-*methyl*-8-[4′-*oxopentyl*]*tetral*-7-*one* (XXIII) as a pale yellow viscous oil (2·97 g), b.p. 149–152°/0·2 mm, $[\alpha]_D$ +65·6° (*c* 0·38). (Found: C, 74·0; H, 8·2. $C_{17}H_{22}O_3$ requires: C, 74·4; H, 8·1%.) λ_{max} 234 (log ε 4·23), 280 (4·31), and 288 mμ (4.27), ν_{max}(CCl_4) 1723 (acyclic ketone), 1713 (6-membered ring ketone), 1610, 1576 (aromatic stretching), and 1043 cm^{-1} (OMe). NMR 1·27 (C_8-tertiary Me), 1·92 (COMe), 3.74 (ArOMe), and 6·77 δ (m, $C_{1,3,4}$-aromatic protons).

Osmium tetroxide–sodium periodate oxidation of the alkene mixture VIII, IX, and X

A soln of the alkene mixture (14.3 g) in dioxan (870 ml), water (190 ml), and glacial AcOH (175 ml) was stirred with OsO_4 (350 mg) for 15 min, and then sodium metaperiodate (24·1 g) was added over a period of 30 min. The mixture was stirred at 20° for 5 days and then extracted with ether. Concentration of the ethereal soln gave a dark oil which was chromatographed on acid-washed alumina.

Elution of the column with light petroleum gave 12-*methoxy*-16-*norpodocarpa*-4(5),8,11,13-*tetraene* as a viscous oil (4·49 g), b.p. 121–122°/0·15 mm, $[\alpha]_D$ +272° (*c* 1·8). (Found: C, 83·95; H, 9·2. $C_{17}H_{22}O$ requires: C, 84·25; H, 9·15%.) ν_{max}(film) 1613, 1580 (aromatic stretching), 1045 (OMe), 871 and 803 cm^{-1} (1,2,4-aromatic trisubstitution). NMR 1·33 (C_{10}-angular Me), 1·64 (C_4-Me), 3·68 (ArOMe), and 6·70 δ (m, $C_{11,13,14}$-aromatic protons).

Concentration of the benzene eluate from the column gave a crystalline mass (0·99 g) which afforded large plates of IV, m.p. and mixed m.p. 77–78° (identical IR and NMR spectra) when recrystallized from chf–light petroleum.

Potassium permanganate–sodium periodate oxidation of the alkene mixture VIII, IX, *and* X

The alkene mixture (7·1 g), anhyd K_2CO_3 (7·0 g), t-butanol (1·0 l.), and water (700 ml) were treated with an aqueous soln (200 ml) of sodium metaperiodate (42·9 g) and one (100 ml) of $KMnO_4$ (540 mg). The mixture was stirred at 20° for 4 hr, filtered, and the filtrate was concentrated to ca. 100 ml *in vacuo* and extracted with ether (4 × 100 ml). The ethereal soln was washed with water, dried, and concentrated to yield a pale yellow oil (5.0 g) which was chromatographed on acid-washed alumina. Elution of the column with light petroleum gave 12-methoxy-16-norpodocarpa-4(5),8,11,13-tetraene as a viscous oil (1·98 g) (identical IR spectrum and retention volume), while 12-methoxy-15,16-dinorpodocarpa-8,11,13-trien-4-one (1·20 g) (identical IR spectrum) was obtained from the benzene eluate.

Lead tetra-acetate oxidation of methyl-O-methylpodocarpate (VII, R = Me)

A mixture of methyl-O-methylpodocarpate (6·0 g), dry pyridine (2·2 ml), lead tetra-acetate (10·3 g), and dry benzene (70 ml) was treated as for O-methylpodocarpic acid. Chromatography of the product on alumina gave methyl-O-methylpodocarpate (5·53 g) from the benzene eluate. From the ether eluate was obtained methyl-5,6-dehydro-7-oxo-O-methylpodocarpate (45 mg), m.p. 169–170·5° with sublimation (lit.[27] m.p. 173–174°), undepressed by a sample prepared from methyl-6α-bromo-7-oxo-O-methylpodocarpate with MeONa.[27] ν_{max}(nujol) 1727 (ester CO), 1655 (aryl CO), 1603, 1570 (aromatic stretching), 828 cm^{-1} (trisubstituted C=C). NMR 1·32 (C_4-equatorial Me), 1·49 (C_{10}-angular Me), 3·65 (CO_2Me), 3·89 (ArOMe), 6·58 (C_6-proton), 6·80–8·40 δ (m, $C_{11,13,14}$ aromatic protons).

Lactone of 6β-*hydroxy*-7-*oxo*-O-*methylpodocarpic acid* (XVII)

7-Oxo-O-methylpodocarpic acid[27] (50 mg) was treated with Br_2 in AcOH with the addition of a drop of 48% HBr.[28] The mixture was kept at 20° for 2 hr and then poured into water. Crystallization of the product from aqueous MeOH gave needles of the lactone (38 mg), m.p. 197–199° (lit.[27] m.p. 195–197·5°). (Found: C, 72·1; H, 6·65. Calc. for $C_{18}H_{20}O_4$: C, 72·0; H, 6·7%.) λ_{max} 231 (log ε 3·95) and 291 mμ (4·10).

Lactone of 6β-hydroxy-7-oxo-O-acetylpodocarpic acid

Treatment of 7-oxo-O-acetylpodocarpic acid[41] (100 mg) with Br_2 in AcOH gave the lactone which crystallized from aqueous MeOH as needles (56 mg), m.p. 165–165·5° (lit.[27] 161–164°). (Found: C, 69·05; H, 6·2. Calc. for $C_{19}H_{20}O_5$: C, 69·5; H, 6·1%.) λ_{max} 260 mμ (log ε 4·02), ν_{max}(nujol) 1780 (γ-lactone), 1715 (OAc), and 1695 (aryl CO), 880 and 822 cm^{-1} (1,2,4-aromatic trisubstitution).

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[41] R. C. Cambie, L. N. Mander, A. K. Bose and M. S. Manhas, *Tetrahedron* **20**, 409 (1964).