to produce the di-potassium salt, $K_2B_{12}H_{12}$ (II). Similarly, treatment of I with aqueous triphenylmethylphosphonium chloride solution precipitated the corresponding triphenylmethylphosphonium salt (III). Ebullioscopic molecular weight determinations of III in acetonitrile indicated an apparent molecular weight of 241 at infinite dilution (calcd. 231.9).

The infrared spectrum of II contained a terminal B-H stretching band at 3.97 μ and five additional bands between 4 and 25 μ (8.95 μ (w), 9.30 μ (s), 13.25 μ (w), 13.40 μ (w) and 14.0 μ (s). The simplicity of this infrared spectrum suggests a highly symmetrical anion.

Examination of the B^{11} nuclear magnetic resonance spectra of I in acetonitrile and II in water revealed a single strong doublet. In the case of I the doublet was centered at 419 cycles higher field than methyl borate and separated by 115 cycles. This result is in agreement with an icosahedral arrangement of boron atoms.

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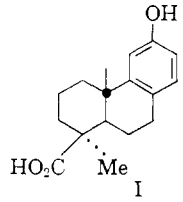
TOTAL SYNTHESIS OF *d*-PODOCARPIC ACID[1]

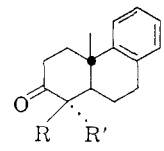
Sir:

We wish to report the total synthesis of *d*-podocarpic acid (*d*-I).[2] This completes the first phase of our studies of the synthesis of diterpenic natural products.[3]



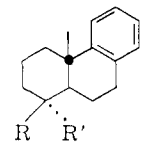
I

Methylation of the ketoester IIa[3d] with methyl iodide and potassium *t*-butoxide in *t*-butyl alcohol gave two alkylation products in 2.4:1 ratio, ketoesters IIb, m.p. 103-104° (found: C, 75.44; H, 7.93), and IIc, m.p. 111.5-113° (found: C, 75.72; H, 7.93), respectively.[4] Clemmensen reduction of the former yielded methyl *d,l*-deisopropyldehydroabietate (IIIb),[2d,5] m.p. 110-112° (found: C, 79.51; H, 8.81), whose infrared spectrum was identical with that of the *d*-antipode of IIIb.[6] Similar reduction of IIc led to methyl *d,l*-deoxypodocarpate (IIIc),[2d,7] m.p. 130-131° (found: C, 79.62; H, 9.13), whose infrared spectrum was the same as that of the *d*-enantiomer of IIIc.[8]



II

a, R = H, R′ = CO_2Me
b, R = Me, R′ = CO_2Me
c, R = CO_2Me, R′ = Me



III

d, R = CN, R′ = Me
e, R = CHO, R′ = Me
f, R = CO_2H, R′ = Me

Further proof of the structure of IIIc and a further supply of the compound were obtained by mixing *d*-IIIc, m.p. 141-142°, $[\alpha]_D$ +138.2° (ethanol)[3c] and *l*-IIIc, m.p. 141-142°, $[\alpha]_D$ −149.4° (ethanol) (found: C, 79.46; H, 8.93). The latter could be produced by the lithium aluminum hydride reduction of *l*-desoxypodocarponitrile (IIId)[8] to *l*-desoxypodocarpinal (IIIe), m.p. 90-93°, $[\alpha]_D$ −86.1° (ethanol) (Found: C, 84.18; H, 8.59), permanganate oxidation to *l*-desoxypodocarpic acid (IIIf), m.p. 194-195.5°, $[\alpha]_D$ −141.0° (ethanol) (Found: C, 79.33; H, 8.62), and diazomethane treatment. Basic hydrolysis of *d,l*-IIIc, as well as a synthetic 1:1 mixture of the aforementioned *l*-acid IIIf and its *d*-enantiomer, m.p. 197-198°, $[\alpha]_D$ +140.8° (ethanol),[3c] yielded *d,l*-desoxypodocarpic acid (IIIf), m.p. 232-233° (Found: C, 79.06; H, 8.53).[2d,7] Exposure of the latter to cinchonine and crystallization of the mixture from aqueous methanol yielded an insoluble salt, m.p. 197-201°, 210-215° (found: C, 78.49; H, 8.15; N, 5.10), identical with the salt formed from the *d*-acid IIIf. Mild hydrochloric acid metathesis liberated *d*-desoxypodocarpic acid (IIIf). Since this compound has been converted already to *d*-podocarpic acid (I),[3c] this completes the total synthesis of the natural product.

In view of the recent transformation of podocarpic acid to nimbiol[9] the present work represents a total synthesis of this compound also. Furthermore, it constitutes a formal total synthesis of ferruginol[10] and sugiol.[11]

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(1) The authors are indebted to the National Science Foundation for support of this research.

(2) For previous methods of synthesis of the racemic compound *cf.* (a) B. K. Bhattacharyya, *J. Ind. Chem. Soc.*, **22**, 165 (1945); (b) R. D. Haworth and B. P. Moore, *J. Chem. Soc.*, 633 (1946); (c) F. E. King, T. J. King and J. G. Topliss, *Chemistry and Industry*, 113 (1956); (d) U. R. Ghatak, THIS JOURNAL, **82**, 1728 (1960).

(3) (a), (b) E. Wenkert and T. E. Stevens, *ibid.*, **78**, 2318, 5627 (1956); (c) E. Wenkert and B. G. Jackson, *ibid.*, **80**, 217 (1958); (d) *ibid.*, **81**, 5601 (1959).

(4) The reason for the amazing lack of stereospecificity in this case and the general problem of the stereochemistry of alkylation of rigidly held β-ketoesters is under present study.

(5) *Cf.* J. A. Barltrop and A. C. Day, *Chemistry and Industry*, 1450 (1959).

(6) (a) M. Ohta and L. Ohmori, *Pharm. Bull. (Japan)*, **5**, 91 (1957); (b) E. Wenkert and J. W. Chamberlin, THIS JOURNAL, **81**, 688 (1959).

(7) *Cf.* R. D. Haworth and R. L. Barker, *J. Chem. Soc.*, 1299 (1939).

(8) E. Wenkert and B. G. Jackson, THIS JOURNAL, **80**, 211 (1958).

(9) E. Wenkert and V. I. Stenberg, Abstracts of the 137th Meeting of the American Chemical Society, April 5-14, 1960, p. 36-O.

(10) W. P. Campbell and D. Todd, THIS JOURNAL, **64**, 928 (1942).

(11) C. W. Brandt and B. R. Thomas, *J. Chem. Soc.*, 2442 (1952).