

The Synthesis of Three Resin Acid Degradation Products

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WE report the synthesis of methyl (\pm)-13-oxopodocarp-8(14)-en-15-oate (XII), (\pm)-1-methoxycarbonyl-1,4 α -dimethyl-6-oxo-5-decahydronaphthalene-3'-propionic acid (XIII) and (\pm)-1-methoxycarbonyl-1,4 α -dimethyl-6-oxo-5 β -decahydronaphthaleneacetic acid (XVII), important resin-acid degradation products which are useful for the synthesis of diterpenes having the abietic acid-type stereochemistry.¹

Annelation² of 6-methoxy-1-methyl-2-tetralone^{3,4} with ethyl vinyl ketone and aqueous potassium hydroxide afforded the tricyclic enone (I), m.p. 95°, in 76% yield. Alkylation of (I) by the Stork procedure^{5,6} with ethyl bromoacetate and potassium t-butoxide gave the ethyl keto-ester (II). The latter was converted into (IV), m.p. 145—146°, by treatment of the thioketal (III) with Raney nickel followed by saponification and hydrogenation in acetic acid over palladium/charcoal. The yield from (I) to (IV) was 35%.

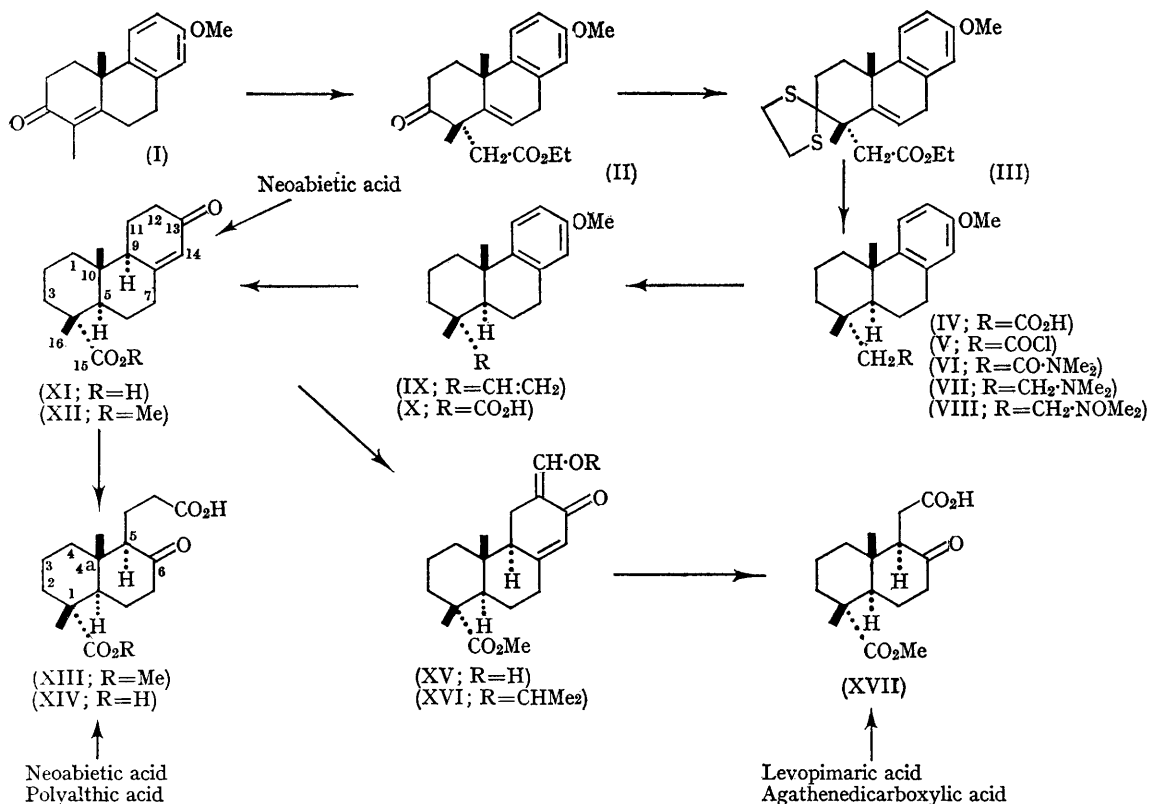
Degradation of (IV) to the nor-carboxylic acid (X) was effected by the method of Ireland and

Kierstead.⁷ The acid chloride (V) was converted into the dimethylamide (VI) which was in turn reduced with lithium aluminium hydride to the dimethylamine (VII). Oxidation of (VII) with hydrogen peroxide, followed by pyrolysis⁸ of the *N*-oxide (VIII) at 150—155° gave the ethylene derivative (IX), m.p. 60—61°. Oxidation of (IX) with sodium metaperiodate–permanganate⁹ gave the nor-carboxylic acid (X), m.p. 152—155°. The conversion of (IV) into (X) was effected in a yield of 52%.

Birch reduction of (X) followed by acid treatment afforded the enone acid (XI) which was methylated with diazomethane to give the (\pm)-enone ester (XII),¹⁰ m.p. 98—99° in 76% yield. The u.v., n.m.r., and infrared spectra (CHCl₃) of (XII) were identical with those of an authentic sample of (XII) prepared by degradation of methyl neoabietate.¹¹

Oxidative cleavage of (XII) with sodium metaperiodate and potassium permanganate under very carefully defined conditions gave (\pm)-(XIII),

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m.p. 112—114° in 85% yield, with an infrared spectrum in chloroform identical with that of a product from the degradation of methyl neoabietate.¹² Treatment of (XIII) with potassium hydroxide in boiling ethylene glycol gave the diacid (XIV) which was identical with the ozonization product from neoabietic acid¹³ and polyalthic acid.¹⁴

Application of the oxidation conditions cited to

the isopropyl ether (XVI), prepared from (XII) by hydroxymethylation followed by treatment with 2-iodopropane, gave the (±)-keto-acid (XVII), m.p. 171—173°. The infrared spectrum of synthetic (XVII) in chloroform was identical with that of the degradation product of methyl levopimarate¹² and dimethyl agathenedicarboxylate.¹⁵

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¹ The accompanying Communication, p. 96, describes the conversion of (XVII) into antipodal polyalthic acid.

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