Intramolecular Functionalisation of the Isopropyl Group of Dehydroabietic Acid

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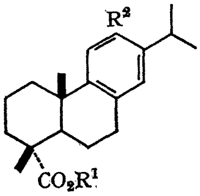
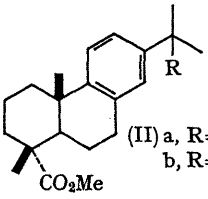
Summary Functionalisation of the isopropyl group of dehydroabietic acid (Ia) has been achieved by intramolecular cyclisations of the 12-carboxy-derivative (Ic) with lead tetra-acetate and by thermolysis of the diazomethyl ketone (Ie).

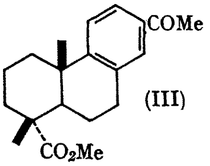
ATTEMPTS to functionalise the isopropyl group of abieta-8,11,13-trien-18-oic acid (Ia; dehydroabietic acid) have met with varied success. Oxygenation of its methyl ester (Ib) gives only a 9% yield of the 15-hydroperoxide (IIa), oxidation occurring mainly at the C-7 benzylic position as is also the case during chromium trioxide oxidation which leads to moderate to low yields of the 15-acetate (IIb) and the 13-acetyl derivative (III).[2] Other attempts involving vigorous oxidation of the 12-nitro- and 12,14-dinitro-derivatives gave products from rupture of ring B.[3] More recently Dev *et al.*[4] have devised a high-yield intermolecular process whereby the isopropyl group is oxidised by tetrachloro-*o*-benzoquinone to give a quinol ether which, on thermolysis, affords a compound with a 13-isopropenyl group.



	R^1	R^2
(I) a	H	H
b	Me	H
c	Me	CO$_2$H
d	Me	COCl
e	Me	CO·CHN$_2$



(II) a, R=O$_2$H
b, R=OAc



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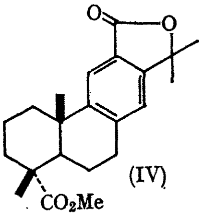

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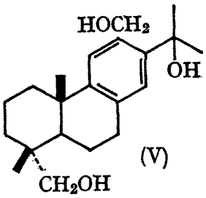

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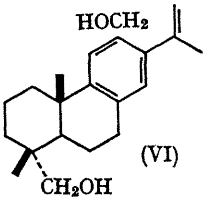

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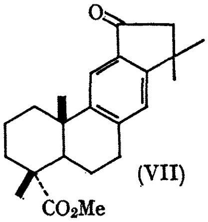
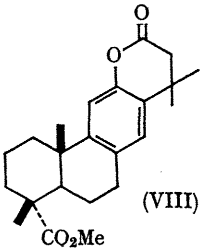


(VII)



(VIII)

During a programme utilizing abieta-8,11,13-trien-18-oic acid as an intermediate for synthesis[5] we have examined the possibility of intramolecular functionalisation of the isopropyl group. The methyl ester (Ib) was converted into methyl 12-carboxyabieta-8,11,13-trien-18-oate (Ic)[6] which was oxidised with lead tetra-acetate.[7] This gave a high yield (93%) of the γ-lactone (IV), which resisted hydrolysis but which was reduced quantitatively with lithium aluminium hydride to the triol (V). Dehydration of the triol with phosphorus oxychloride–pyridine gave the unsaturated diol (VI) in 75% yield, corresponding to a 44% overall yield from the ester (Ib).

We have also used a method involving the copper-catalysed decomposition of a C-12 diazomethyl ketone to effect an intramolecular cyclisation to C-15 of the isopropyl group. Reaction of the carboxy-ester (Ic) with oxalyl chloride gave a quantitative yield of the acyl chloride (Id) which on treatment with diazomethane gave the diazomethyl ketone (Ie). Slow thermolysis of a cyclohexane solution of the diazomethyl ketone using copper(I) oxide as the catalyst[8] gave mainly the ketone (VII) which on Baeyer–Villiger oxidation gave the δ-lactone (VIII).

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