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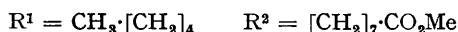
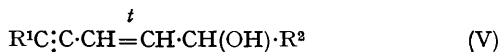
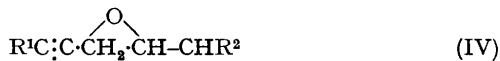
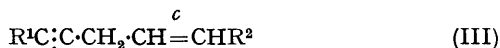
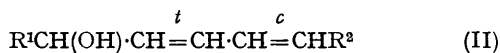
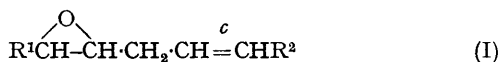
Base-catalysed Isomerisation of Epoxy-esters: The Partial Synthesis of Methyl Coriolate from Methyl Vernolate and of Racemic Methyl Helenynolate from Methyl Crepenynate

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WE have previously speculated on the biological relationship between linoleic acid, the epoxy-acids, vernolic and coronaric, the hydroxy-dienoic acids, coriolic and dimorphecolic, and the several conjugated octadecatrienoic acids.¹ We now report the successful base-catalysed conversion of two epoxy-esters into isomeric unsaturated hydroxy-esters.

Methyl vernolate (I) was treated with lithium diethylamide in anhydrous ether for 1 hr. at 0°. The major product, recovered in about 60% yield by preparative t.l.c., was a hydroxy-ester accompanied by other products including a diethylamide (~20%) with the same u.v. spectrum as the major ester.



The hydroxy-ester had a u.v. absorption band at 233 m μ ($E_{1\text{cm}}^{1\%}$, 850 MeOH) and i.r. bands at 3595, 945, and 980 cm.⁻¹, indicative of a hydroxy-ester with a conjugated (*cis, trans*) diene system. The n.m.r. spectrum contained a complex series of peaks in the region τ 3.3—4.9 (four olefinic protons) and a peak at τ 5.9 [C(OH)·H]. In all these respects the spectrum resembles that reported for methyl coriolate.³

Identity of structure was confirmed by the following: (a) The hydrogenated product gave dodecanedioic and tridecanedioic acids when oxidised with chromic acid.⁴ (b) von Rudloff oxidation⁵ of the unsaturated hydroxy-acid gave azelaic acid as the only dibasic acid. (c) The ester was readily dehydrated (1,2 and 1,6) by heating with 0.1N-methanolic hydrogen chloride;⁶ the product was a mixture of conjugated trienes (8,10,12- and 9,11,13-) from its u.v. spectrum and its oxidation to suberic and azelaic acids. (d) Partial reduction with potassium azodicarboxylate⁷ gave two hydroxy-monoene acids; the *cis*-isomer gave azelaic acid as the only dibasic acid when oxidised and the *trans*-isomer gave undecanedioic acid along with a small amount of the C₉-acid (probably from a little unchanged dienoic ester remaining in this fraction). This evidence is consistent with the product being methyl 13-hydroxyoctadeca-*cis*-9,*trans*-11-dienoate (methyl coriolate). Since vernolic acid⁸ and coriolic acid⁹ have the same absolute configuration at C(13) we

expect our product to be identical with the natural product.

Methyl crepenynate (III), isolated from *Afzelia cuanzensis* seed oil by preparative t.l.c. on silica impregnated with silver nitrate,⁹ was converted into its mono-epoxide (IV) by reaction with a 2M solution of monopero-phthalic acid in ether (12 hr.). This was isolated on thin layers of silica and isomerised with lithium diethylamide. The major product, isolated in 50% yield, was a hydroxy-ester with a *trans*-enyne chromophore (λ_{\max} 228 m μ [$E_{1\text{cm}}^{1\%}$ 600] and 238 m μ [$E_{1\text{cm}}^{1\%}$ 510], i.r. absorption

bands at 3590 and 950 cm.⁻¹). A second product with similar spectroscopic properties is probably the diethylamide of the same ester which we consider to be racemic methyl helenynolate (V).¹⁰

Other natural products such as the prostaglandins and several short chain poly-ynes contain the group *trans*-CH(OH)·CH=CH- which might arise, biologically, from the *cis*-olefin -CH=CH·CH₂- by epoxidation and rearrangement.

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