

SYNTHESIS OF ERIOSTOIC ACID AND ERIOSTEMOIC ACID

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A linear-type carboxyethyl pyronochromanone derivative (V), after being converted into methyl ester-methyl ether (VI), was reduced with sodium borohydride to give methyl eriostate (VII). Hydrolysis of the ester (VII) with alkali afforded eriostoic acid (I). Eriostemoic acid (II) was also synthesized from an angular-type pyronochromanone derivative (IV) in a similar manner.

Eriostoic acid has been isolated from Eriostemon difformis and the structure has been elucidated to be a linear-type benzodipyrane (I) on the basis of degradative and spectral data.¹⁾ On the other hand, eriostemoic acid isolated from Eriostemon tomentellus has been shown to be an angular benzodipyrane derivative (II) which was closely related to I.²⁾ In the present paper, we wish to report the synthesis of I and II, which confirms the proposed structures of natural eriostoic acid and eriostemoic acid.

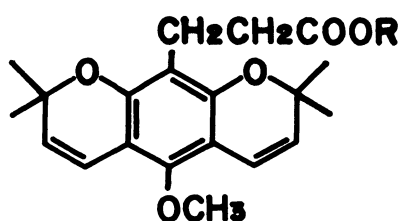
The condensation of a linear pyronochromanone (III)³⁾ with acrylic acid in the presence of polyphosphoric acid at 80-85 °C for 2 hr gave easily the linear carboxyethyl pyronochromanone (V) [mp 190-191 °C; IR ν_{\max}^{KBr} 1610, 1675, 1735 cm^{-1} ; NMR $\delta_{\text{ppm}}^{\text{CDCl}_3}$ 1.46_s (12H) (CH₃ x 4), 2.37-2.92_m (4H) (CH₂CH₂), 2.66_s (4H) (CH₂CO x 2), 13.76_s (OH)]. The exhaustive methylation of V with dimethyl sulfate afforded the corresponding methyl ester-methyl ether (VI) [mp 121.5-122.5 °C; IR ν_{\max}^{KBr} 1693, 1730 cm^{-1} ; NMR $\delta_{\text{ppm}}^{\text{CDCl}_3}$ 3.67_s (3H) (OCH₃), 3.87_s (3H) (OCH₃)]. The reduction of VI with an excess of sodium borohydride⁴⁾ in dry methanol containing a small amount of pyridine gave methyl eriostate (VII) [liquid; IR ν_{\max} 1630, 1735 cm^{-1} ; NMR $\delta_{\text{ppm}}^{\text{CDCl}_3}$ 3.66_s (3H) (OCH₃), 3.70_s (3H) (OCH₃), 5.45_d, 6.48_d (each J=10 Hz and 2H) (CH=CH)]. The hydrolysis of VII with 4% aqueous methanolic sodium hydroxide gave easily the desired acid (I) [mp 173-174 °C; IR ν_{\max}^{KBr} 1630, 1718 cm^{-1} ; NMR $\delta_{\text{ppm}}^{\text{CDCl}_3}$ 1.40_s (12H) (CH₃ x 4), 2.43-2.97_m (4H) (CH₂CH₂), 3.70_s (3H) (OCH₃), 5.45_d, 6.48_d (each J=10 Hz and 2H) (CH=CH); UV $\lambda_{\max}^{\text{EtOH}}$ nm (log ϵ) 259(4.60), 268(4.59), 340(3.52); Found: C, 69.87; H, 7.18%, Calcd for C₂₀H₂₄O₅: C, 69.74; H, 7.02%] (lit.¹⁾ mp 173-174 °C).

By a method similar to that described above, methyl eriostemate (X) [liquid; IR ν_{\max} 1635, 1735 cm^{-1} ; NMR $\delta_{\text{ppm}}^{\text{CCl}_4}$ 3.60_s (3H) (OCH₃), 3.67_s (3H) (OCH₃), 5.33_d (J=10 Hz and 2H) (CH=CH), 6.38_d, 6.48_d (each J=10 Hz and 1H) (CH=CH)], which was obtained from

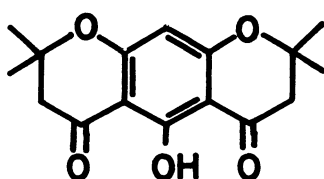
an angular pyronochromanone (IV)³⁾ via three steps, was hydrolyzed with dilute alkali to give the desired acid (II) [mp 100-101.5 °C; IR $\nu_{\text{max}}^{\text{KBr}}$ 1640, 1708 cm^{-1} ; NMR δ^{CDCl_3} 1.39_s (12H) (CH₃ x 4), 2.43-2.93_m (4H) (CH₂CH₂), 3.69_s (3H) (OCH₃), 5.45_d (J=10 Hz and 2H) (CH=CH), 6.46_d, 6.59_d (each J=10 Hz and 1H) (CH=CH); UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ) 206(4.29), 254(4.33), 258(4.33), 280(4.13), 331(3.39), 347(3.29); Found: C, 70.03; H, 7.09%, Calcd for C₂₀H₂₄O₅: C, 69.74; H, 7.02%] (lit.²⁾ mp 101 °C).

The synthetic acid (I) and (II) were, respectively, shown to be identical with natural eriostoic acid and eriostemoic acid on the basis of a mixed-melting-point determination and by NMR, IR and UV spectral comparisons.

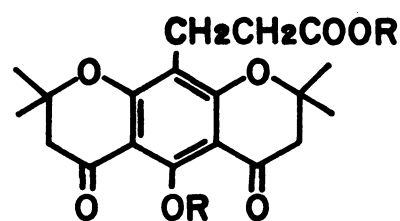
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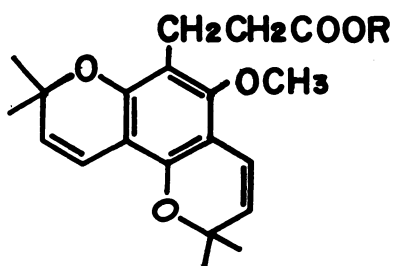
I R=H
VII R=CH₃



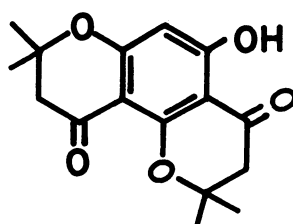
III



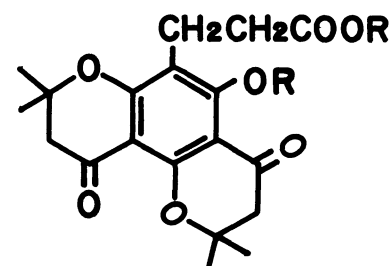
V R=H
VI R=CH₃



II R=H
X R=CH₃



IV



VIII R=H
IX R=CH₃

References

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