

## Crotonin, a Furanoid Norditerpene from *Croton lucidus* L.

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EXTRACTION of the leaves and twigs of *Croton lucidus* L. (Euphorbiaceae) has yielded the new furanoid norditerpene crotonin (I),  $C_{19}H_{24}O_4$ ,\* m.p. 146–148°,  $[\alpha]_D -1.4^\circ$ ,  $\nu_{max}$  3100, 1504, 877 (furan), 1761 ( $\gamma$ -lactone), and 1709  $cm^{-1}$  (ketone),  $\lambda_{max}$  207  $m\mu$  ( $\epsilon$  5700). The n.m.r. spectrum† shows two secondary methyls (1.03 and 1.25,  $J = 7$  c./sec.), a  $\beta$ -substituted furan (7.42,  $\alpha$ -protons, and 6.46,  $\beta$ -proton) and H-12 as the X part of an ABX system (5.30, quartet,  $J_{AX} + J_{BX}$  16 c./sec.).

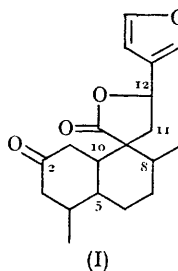
Hydrogenation of (I) gave the acid, hexahydrocrotonin (II), m.p. 78–80°, and tetrahydrocrotonin (I; furan saturated), m.p. 99–101°, in the ratio of 2 : 1. This result defines the relation of the furan ring to the lactone. The acid (II) was converted into the keto-alcohol (VI) *via* (III), (IV), and (V) in the usual way. Oxidation of (VI) gave a mixture of (II), and (VII) (characterised as its bis-2,4-dinitrophenylhydrazone, m.p. 125–127°) whose n.m.r. spectrum shows the aldehydic proton as a singlet at 9.40.

Selenium dioxide oxidation of (I) yielded the amorphous phenol (VIII),  $\lambda_{max}$  280 ( $\epsilon$  2300) and 287  $m\mu$  ( $\epsilon$  2300), shifting in base to 304  $m\mu$  ( $\epsilon$  2900). The methyl ether (IX), m.p. 139–142°,  $\lambda_{max}$  277 ( $\epsilon$  2300) and 286  $m\mu$  ( $\epsilon$  2400), had n.m.r. bands at 1.15 ( $J = 6$  c./sec. (secondary methyl), 2.22 (aromatic methyl), 3.68 (methoxyl), and 6.47 and 6.67 (doublets,  $J = 2$  c./sec., *meta*-coupled aromatic protons). Chromium trioxide in acetic acid oxidation of (IX) gave (X) whose ultraviolet spectrum,  $\lambda_{max}$  225 ( $\epsilon$  23,600) and 274  $m\mu$  ( $\epsilon$  15,400), is that of a substituted *p*-methoxyacetophenone.<sup>1</sup> The n.m.r. spectrum, which shows the aromatic methyl shifted downfield to 2.63, confirms the position of the methyl at C-4.

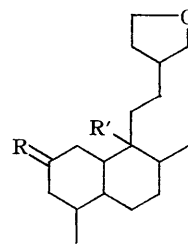
The furfurylidene (XI), m.p. 183–184°, has  $\lambda_{max}$  235 ( $\epsilon$  11,200) and 348  $m\mu$  ( $\epsilon$  24,600), in good agreement with the furfurylidene derivative of *p*-methoxyacetophenone, m.p. 79–80°,  $\lambda_{max}$  230 ( $\epsilon$  9800) and 342  $m\mu$  ( $\epsilon$  30,000). The C-8 proton in (XI) appears as a quartet at 4.30 ( $J = 7$  c./sec.) and the methyl at C-8 as an unperturbed doublet at

1.27 ( $J = 7$  c./sec.). This spectrum further revealed the ABX system<sup>2</sup> (C-11 and C-12 protons) [A at 2.91, B at 2.28, and X at 5.55. ( $J_{AB} = -13.5$ ,  $J_{AX} = 6.25$ , and  $J_{BX} = 10.0$  c./sec.)].

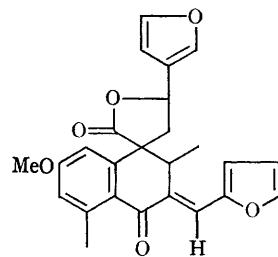
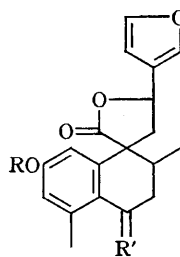
The evidence cited establishes the gross structure (I) for crotonin, which is structurally related to the cascarillins<sup>3</sup> isolated from *Croton eluteria*.



(I)



- (II) R = O; R' = CO<sub>2</sub>H  
 (III) R = O; R' = CO<sub>2</sub>Me  
 (IV) R = ·O·CH<sub>2</sub>·CH<sub>2</sub>·O·;  
           R' = CO<sub>2</sub>Me  
 (V) R = ·O·CH<sub>2</sub>·CH<sub>2</sub>·O·;  
           R' = CH<sub>2</sub>OH  
 (VI) R = O; R' = CH<sub>2</sub>OH  
 (VII) R = O; R' = CHO



(XI)

- (VIII) R = H; R' = H<sub>2</sub>  
 (IX) R = Me; R' = H<sub>2</sub>  
 (X) R = Me; R' = O

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\* Analysis and mass-spectral data. The mass spectrum was obtained by Dr. A. G. Loudon on an A.E.I. MS 9 spectrometer.

† N.m.r. spectra are for deuteriochloroform solutions and are in p.p.m. from tetramethylsilane.

<sup>1</sup> *cf.*, R. A. Morton and A. L. Stubbs, *J. Chem. Soc.*, 1940, 1347; E. Wenkert, P. Beak, R. W. J. Carney, J. W. Chamberlin, D. B. R. Johnston, C. D. Roth, and A. Tahara, *Canad. J. Chem.*, 1963, 41, 1924.

<sup>2</sup> H. J. Bernstein, J. A. Pople, and W. G. Schneider, *Canad. J. Chem.*, 1957, 35, 65.

<sup>3</sup> T. G. Halsall, A. W. Oxford, and W. Rigby, *Chem. Comm.*, 1965, 218, and references cited therein.