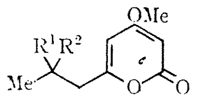
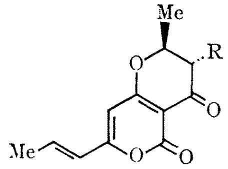
# The Synthesis of (±)-Radicinin

By KUNIKI KATO and YOSHIMASA HIRATA
(*Chemical Institute, Nagoya University, Chikusa, Nagoya, Japan*)
and SHOSUKE YAMAMURA*
(*Pharmaceutical Institute, Meijo University, Yagotourayama, Showa-ku, Nagoya, Japan*)

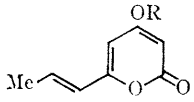
PREVIOUSLY[1] we reported the reaction of 6-carboxymethyl-4-methoxy-2-pyrone with acetic anhydride in pyridine to give the tetra-acetic lactone methyl ether (I), which was regarded as a precursor of radicinin (II).[2] We report here the synthesis of radicinin (II) from the methyl ether (I). Reaction of compound (I) with $NaBH_4$ in tetrahydrofuran (0°; 1 hr.), gave an oily compound [(III], 90%, *m/e* 184 ($M^+$)], which was heated with methanesulphonyl chloride in pyridine–dimethylformamide (80—85°; 1 hr.) and then refluxed for a further hour to give the dehydration product [(IV), 61%, m.p. 102—103°, δ($Me_4Si$) ($CDCl_3$) 1·90 (3H, q, $J_{AX}$ 1·5, $J_{BX}$ 7 c./sec.), 3·80 (3H, s), 5·43 (1H, d, $J$ 2·3 c./sec.), 5·75 (1H, d, $J$ 2·3 c./sec.), 5·97 (1H, oct, $J_{AB}$ 15·5, $J_{AX_3}$ 1·5 c./sec.), and 6·73 p.p.m. (1H, oct, $J_{AB}$ 15·5, $J_{BX_3}$ 7 c./sec ). Product (IV) was refluxed with $AlCl_3$ in carbon disulphide (3 hr.) to give the expected 4-hydroxy-6-propenyl-2-pyrone [(V), 60%, m.p. 191—195°]. In the presence of $TiCl_4$, the reaction of (V) with crotonoyl chloride in tetrachloroethane (100°; 3 hr.) gave 3,4-dihydro-2-methyl-7-propenyl-2*H*,5*H*-pyrano[4,3-*b*]pyran-4,5-dione [(VI), 70%, m.p. 183—184°, δ($Me_4Si$) ($CDCl_3$) 1·53 (3H, d, $J$ 6·5 c./sec.), 1·96 (3H, q, $J_{AX}$ 1·5, $J_{BX}$ 7 c./sec.), 2·63 (1H, d, $J$ 9 c./sec.), 2·64 (1H, d, $J$ 7 c./sec.), 4·78 (1H, m), 5·85 (1H, s), 6·02 (1H, oct, $J_{AB}$ 15·5, $J_{AX_3}$ 1·5 c./sec.), and 6·94 p.p.m. (1H, oct, $J_{AB}$ 15·5, $J_{BX_3}$ 7 c./sec.),† Finally, oxidation of (VI) with lead tetra-acetate in acetic acid (100°; 2 hr.) gave a mixture of an α-acetoxy-product [(VII), 13%, m.p. 202—203°] and (VIII), (15%, m.p. 205—206°).[3] The former was shown to be identical with an authentic sample of acetylradicinin, which was known to be reconverted with 50% $H_2SO_4$ into radicinin (II),[4] from i.r. (in $CDCl_3$), n.m.r. (in $CDCl_3$) and mass spectra and t.l.c. (in two solvent systems) evidence. All compounds gave satisfactory physical data.



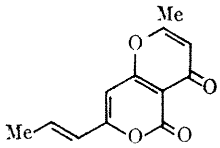
(I) $R^1, R^2=O$
(III) $R^1=H, R^2=OH$



(II) R=OH
(VI) R=H
(VII) R=OAc



(IV) R=Me
(V) R=H



(VIII)

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† Cyclization reactions of triacetic lactone or 4-hydroxycoumarin with αβ-unsaturated acyl chlorides were carried out in pyridine or in carbon disulphide (or tetrachloroethane) containing $TiCl_4$. These results will be reported soon.

[1] S. Yamamura, K. Kato, and Y. Hirata, *Chem. Comm.*, 1968, 1580.

[2] J. F. Grove, *J. Chem. Soc.*, 1964, 3234.

[3] K. Kato, Y. Hirata, and S. Yamamura, *Chem. Comm.*, 1968, 319.

[4] D. D. Clarke and F. F. Nord, *Arch. Biochem. Biophys.*, 1955, **59**, 269.