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SHORT COMMUNICATION

STRUCTURE OF HAUTRIWAIC ACID

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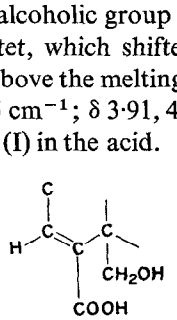
Abstract—The structure of a diterpene carboxylic acid, hautriwaic acid, isolated from *Dodonea viscosa*, has been confirmed by chemical and spectroscopic studies.

INTRODUCTION

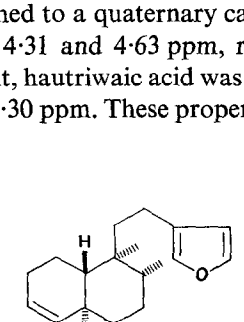
THE LEAVES of *Dodonea viscosa* (Japanese name, Hautiwa), distributed in Taiwan, exude a viscous resin. In 1936, Kotake and Kuwata[1] isolated a diterpenoid acid, hautriwaic acid, from the resin and characterized it as monohydroxycarboxylic acid, but the full structure was not then determined.

As a part of our studies on the constituent of Chinese drugs, we isolated hautriwaic acid and determined its structure as II.

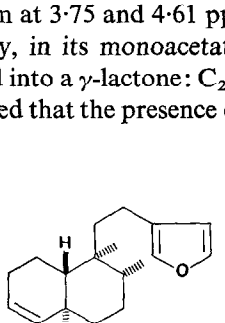
Hautriwaic acid, $C_{20}H_{28}O_4$, has an α,β-disubstituted acrylic acid group, because the acid showed absorptions at 1660 and 2700 cm^{-1} in the IR spectrum and one-proton triplet at 6·60 ppm in the NMR spectrum, the later signal shifted to 5·75 ppm by reduction of the carboxylic group with $LiAlH_4$. The NMR of hautriwaic acid showed the presence of a primary alcoholic group attached to a quaternary carbon atom at 3·75 and 4·61 ppm by an AB-quartet, which shifted to 4·31 and 4·63 ppm, respectively, in its monoacetate. Upon heating above the melting point, hautriwaic acid was converted into a γ-lactone: $C_{20}H_{26}O_3$; λ_{max} 1765 cm^{-1}; δ 3·91, 4·33, 6·30 ppm. These properties showed that the presence of partial structure (I) in the acid.



(I)



(II)



(III)

The presence of the furano-3-alkyl group in the acid was deduced from positive Ehrlich reaction, IR absorptions at 3180, 1590, 1540, 860 cm^{-1}; NMR peaks at δ 6·35, 7·34, 7·41

[1] M. KOTAKE and K. KUWATA, *J. Chem. Soc. Japan* **57**, 837 (1936).

ppm, characteristic of 3-substituted furans; and the fragments *m/e* 81 (C_5H_5O), and *m/e* 95 (C_6H_7O) in the high resolution mass spectrum. From these facts and biogenetic considerations, the structure (II) was deduced for hautriwaic acid.

Jefferies and Payne[2] have isolated a lactone having the structure (III), and they suggested that the acid (II) derived from the lactone III would be identical with hautriwaic acid. Indeed, hautriwaic acid has the structure (II) as shown by direct comparison with Jefferies acid by IR and NMR spectra, and mixed melting.

EXPERIMENTAL

Hautriwaic acid. Dried leaves of *Dodonea viscosa* were extracted with Et_2O, and the extract was evaporated to give crude crystals which were recrystallized from EtOH to give white needles: m.p. 179–179·5°. (Found C 72·26; H 8·49. Calcd. for $C_{20}H_{28}O_4$: C 71·99; H 8·49%.) ν^{KBr} 3180, 2700, 1660, 1590, 1540, 860 cm^{-1}; λ_{max}^{EtOH} 212 nm; NMR δ (acetone-d_6) 0·78 (3H, s), 0·84 (3H, d, J = 5 Hz), 3·75 (1H, d, J = 9·6 Hz), 4·16 (1H, d, J = 9·63), 6·35 (1H, m), 6·60 (1H, t), 7·34 (1H, m), 7·41 p.p.m. (1H, m); mass spectrum.

Found	Calcd. for	
332·1973 (M^+)	$C_{20}H_{28}O_4$	332·1988
302·1789	$C_{19}H_{26}O_3$	302·1882
284·1777	$C_{19}H_{24}O_2$	284·1777
219·1376	$C_{14}H_{19}O_2$	219·1385
207·1386	$C_{13}H_{19}O_2$	207·1385
189·1276	$C_{13}H_{17}O$	189·1279
81·0332	C_5H_5O	81·0341
95·0538	C_6H_7O	95·0499

Hautriwaic lactone. Hautriwaic acid was heated at 180–190° for 30 min. and the resulting solid was recrystallized from EtOH: m.p. 117·5–118°; ν^{KBr} 3140, 1765, 1660, 1590, 1540, 880 cm^{-1}; NMR $\delta(CDCl_3)$ 0·61 (3H, s), 0·86 (3H, d, J = 5 Hz), 3·91 (1H, d, J = 8 Hz), 4·33 (1H, d, J = 8 Hz), 6·29 (1H, m), 6·77 (1H, m), 7·31 (1H, m), 7·37 (1H, m); mass spectrum *m/e* 314, 220, 81, 95. (Found: C 76·09; H 8·50. Calcd. for $C_{20}H_{26}O_3$:C 76·40; H 8·34%).

Acetyl hautriwaic acid. Acetylation of hautriwaic acid with a mixture of Ac_2O and pyridine afforded a mixture (7:1) of acetyl hautriwaic acid and hautriwaic lactone. The acetate was recrystallized from hexane to afford white crystals: m.p. 91·5–93·5°; ν^{KBr} 1745, 1680, 860 cm^{-1}; NMR $\delta(CDCl_3)$ 0·97 (3H, s), 1·00 (3H, d, J = 5 Hz), 1·97 (3H, s), 4·31 (1H, d, J = 10 Hz), 4·63 (1H, d, J = 10 Hz), 6·25 (1H, m), 7·09 (1H, brt), 7·21 (1H, m), 7·28 (1H, m), 9·58 ppm (1H, br s); mass spectrum *m/e* 374(M^+), 314, 301, 279, 219, 95, 81. (Found: C 70·43; H 8·21. Calcd. for $C_{22}H_{30}O_5$: C 70·56; H 8·08%.)

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[2] P. R. JEFFERIES and T. G. PAYNE, *Tetrahedron Letters* 4777 (1967).