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NEW NAPHTHOQUINONE DERIVATIVES FROM *LITHOSPERMUM ERYTHRORHIZON*

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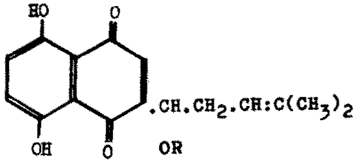
The roots of *Lithospermum erythrorhizon* Sib. et Zucc. (Japanese name: Shikon) have been widely used as a dye or a drug in Japan. In the previous paper(1), the authors have reported two new reddish violet pigments which were isolated from the benzene extracts of the root. Two additional naphthoquinone derivatives were further isolated from the benzene extracts of the roots of *Lithospermum erythrorhizon* and *Lithospermum euchromum* Royle(Japanese name: Nan-shikon). One of these is β-hydroxy-isovaleryl-shikonin(I), and the other is teracryl-shikonin (II) from the following evidence.



$R:CO.CH_2.(OH)C(CH_3)_2$ (I)
$:CO.CH_2.C(CH_3):C(CH_3)_2$(II)
$:H$ (III)

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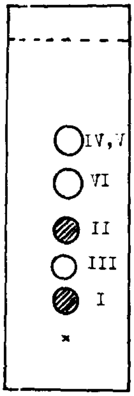

Fig. 1. Thin-layer chromatogram of the benzene extracts of Shikon on Silica gel G. Mobile phase: chloroform. Development: ascending, once. IV=isobutyl-shikonin; V=ββ-dimethylacryl-shikonin; VI=acetyl-shikonin; III=shikonin.

β-Hydroxy-isovaleryl-shikonin(I), m.p. 90-92°, reddish violet needles $[\alpha]^{15}_{600}$ -108°(ethanol), was assigned the formula $C_{21}H_{24}O_7$(Anal. Calcd.: C, 64.93; H, 6.23; Found: C, 65.27; H, 6.07). The molecular formula of I was confirmed by mass spectrometry with a molecular ion peak at m/e 388(Calcd., 388.403)(2), and by the infrared (ν^{KBr}_{max} 3496 cm^{-1}/OH/, 1705 cm^{-1}/C=O(ester)/, 1608 cm^{-1},1445 cm^{-1}, 778 cm^{-1}), ultraviolet ($\lambda^{ethanol}_{max}$ 273 mμ, logε 4.13) and n.m.r. spectrum: a sharp singlet (6H) at 1.30 ppm (methyl protons, $\underset{OH}{-C}(CH_3)_2$),two signals (6H) at 1.60-1.70 ppm(methyl protons, $-\underset{H}{C}=C(CH_3)_2$, a singlet (2H) at 2.61 ppm (allyl methylene protons), a broad singlet at 3.30 ppm (hydroxyl proton), a broad triplet (1H) at 5.15 ppm (vinyl proton), a triplet (1H) at 6.11 ppm (methine proton),a singlet (1H) at 7.05 ppm (proton on the quinon ring), a sharp singlet (2H) at 7.20 ppm (proton on the benzene ring), respectively.

Further confirmation was obtained by alkaline hydrolysis of I

Melting points were not corrected.

(2% NaOH, room temperature) affording shikonin (III) $C_{16}H_{16}O_5$(m.p. 147-149°, Anal. Calcd.:C, 66.66; H, 5.59; Found: C, 65.89; H, 5.51) and β-hydroxy-isovaleric acid. The acid was identified by paper chromatography using a mixture of butanol-2.5% aqueous ammonia (1:1) as the solvent. The acid gave the same Rf value (0.28) with that of an authentic sample prepared by the reaction of ethyl acetate with acetone in the presence of potassium hydroxide(3). From these experimental evidences I was identified as β-hydroxyisovaleryl-shikonin.

II was isolated from the benzene extracts of the root of Lithospermum euchromum Royle(Japanese name: Nan-shikon), reddish violet amorphous substance,$[\alpha]^{17}_{600}$ - 92°(ethanol), with infrared (ν^{Nujol}_{max} 1738 cm^{-1}/C=O(ester)/, 1612 cm^{-1}, 1453 cm^{-1}, 1112 cm^{-1}, 780 cm^{-1}), and ultraviolet spectra($\lambda^{ethanol}_{max}$ 273 mμ, logε4.66). The n.m.r. spectrum of II: two signals (6H) at 1.51-1.55 ppm (methyl protons, $-C=C(CH_3)_2$), two signals (6H) at 1.60-1.65 ppm (methyl protons, $-\underset{H}{C}-C(CH_3)_2$), a sharp singlet (3H) at 2.02 ppm (methyl protons), a broad quartet (2H) at 2.50 ppm (allyl methylene protons), a quartet (2H) at 2.95 ppm (methylene protons)a broad triplet (1H) at 5.10 ppm (vinyl proton), a triplet (1H) at 6.00 ppm (methine proton), a singlet (1H) at 6.90 ppm (proton on the quinon ring), a sharp singlet (2H) at 7.10 ppm (protons on the benzene ring), two signals (2H) at 12.30-12.50 ppm (protons of phenyl-OH).

Further confirmation was obtained by alkaline hydrolysis of II(2% NaOH, room temperature) affording shikonin $C_{16}H_{16}O_5$(m.p. 145-147°) and teracrylic acid which gave the same Rf value(0.23) with that of an authentic sample(4). From these evidences II was identified as teracrylshikonin.

REFERENCES

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5. The n.m.r. spectra were taken in deutrochloroform with tetramethylsilane as internal standared.