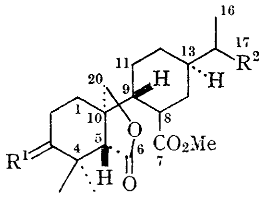
Acyloin Condensation with Some γ-Lactone Esters

By EIICHI FUJITA, TETSURO FUJITA, HAJIME KATAYAMA, and SONOKO KUNISHIMA
(*Institute for Chemical Research, Kyoto University, Takatsuki, Osaka-fu, Japan*)

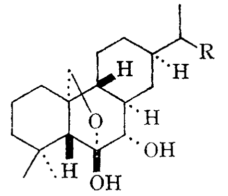
THE reaction of lactone ester (I)[1] derived from enmein, a diterpene of *Isodon* species, with sodium in liquid ammonia gave an oily 6-hemiketal-7-ol derivative (II) [ν_{max}($CHCl_3$) 3500, 1028, and 1006 cm.$^{-1}$, δ 0·88 (6H, doublet, J = 5·0 c./sec.), 1·15, 1·30 (each 3H, singlet), 3·12 (1H, doublet, J = 8·0 c./sec., C-7–*H*), 3·68 (2H, AB type, J = 8·0 c./sec.), and 4·41 p.p.m. ($CDCl_3$) (1H, singlet, O*H*)] as a major product, but the use of a large excess of sodium resulted in an increase of the yield of triol (III) and diol (IV). A by-product (V), in which the methoxycarbonyl group of the starting material (I) was reduced to hydroxymethyl, was also obtained.

The major product (II) on acetylation afforded diacetate (VI). Sodium borohydride reduction of (II) gave a triol (VII), which is a C-6 epimer of the foregoing triol (III). Triol (VII) on acetylation yielded diacetate (VIII), which on further acetylation under more vigorous conditions afforded triacetate (IX), while triol (III) on acetylation easily gave triacetate (X).

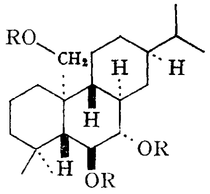
Subsequently, a new lactone diester (XIII), $C_{22}H_{34}O_6$, m.p. 155—156°, was prepared by desulphurization with Raney nickel of the thioketal (XII), $C_{24}H_{36}O_6S_2$, m.p. 118—120°, of the known keto-lactone diester (XI).[2] It was allowed to react with sodium in liquid ammonia to give two acyloin products (XIV) [ν_{max}($CHCl_3$) 3500, 3450—3300, and 1725 cm.$^{-1}$, δ 3·14 (1H, doublet, J = 8·0 c./sec., C-7–*H*), 3·65 (2H, AB type, J = 8·0 c./sec.), and 3·66 p.p.m. ($CDCl_3$) (3H, singlet)] and (XV)



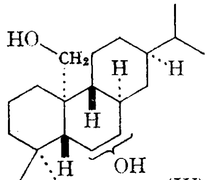
(I; R^1=H_2, R^2=Me)
(XI; R^1=O, R^2=CO_2Me)
(XII; R^1=$[^S_S$, R^2=CO_2Me)
(XIII; R^1=H_2, R^2=CO_2Me)



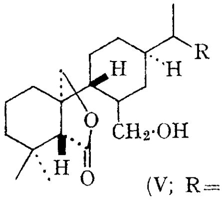
(II; R=Me)
(XIV; R=CO_2Me)
(XV; R=CH_2OH)



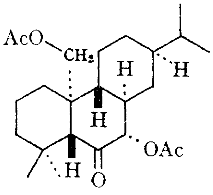
(III; R=H)
(X; R=Ac)



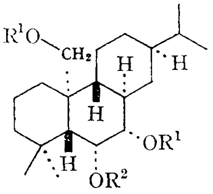
(IV)



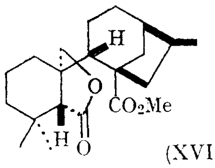
(V; R=Me)
(XVI; R=CH_2OH)



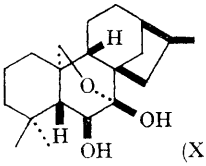
(VI)



(VII; R^1=R^2=H)
(VIII; R^1=Ac, R^2=H)
(IX; R^1=R^2=Ac)



(XVII)



(XVIII)

[$C_{20}H_{34}O_4$, m.p. 79—82°, $\nu_{max}(CHCl_3)$ 3380 cm.$^{-1}$, δ 3·12 (1H, doublet, J = 9·0 c./sec., C-7-H), 3·54 (2H, multiplet, $>CH-CH_2-OH$), and 3·65 p.p.m. ($CDCl_3$) (2H, AB type, J = 8·5 c./sec.)], accompanied by a by-product (XVI).

The major product in the acyloin reaction with lactone ester (XVII) was the 7-hemiketal (XVIII),[1] whereas the acyloin products of abietane type are 6-hemiketals; in either case, the major product was found to be the thermodynamically more stable hemiketal, in agreement with a study of stereomodels.

(*Received, January* 13*th*, 1967; *Com.* 042.)

---

[1] E. Fujita, T. Fujita, K. Fuji, and N. Ito, *Tetrahedron*, 1966, **22**, 3423.

[2] T. Kubota, T. Matsuura, T. Tsutsui, S. Uyeo, H. Irie, A. Numata, T. Fujita, and T. Suzuki, *Tetrahedron*, 1966, **22**, 1659.