

structure VIII is supported from these facts.

A similar experiment has been carried out on a phenoxy radical instead of V in order to prove the free radical process more definitely. In this case, the normal coupling product (XII) was obtained at 0~5° accompanied by the disulfide K. XII showed m.p. 197° (from MeOH). *Anal.* Calcd. for $C_{27}H_{40}O_3N_4S$: C, 64.80; H, 8.00; N, 11.20; S, 6.40. Found: C, 64.52; H, 8.04; N, 10.98; S, 6.26. UV $\lambda_{\max}^{EtOH}$ m μ (log ϵ): 234.5 (4.22); 276.5 (4.03). Further XII was negative to the thiochrome test and turned out to be positive after the reduction with cysteine. From these facts, XII is confirmed to have normal coupling structure and S-alkyl structure should be excluded for XII.

Therefore, it has been shown that the reaction of thiamine in thiol form with $K_3(Fe(CN)_6)$ involves a free radical intermediate, since the typical coupling products have been isolated, and that syntheses of new types of thiamine derivatives are accomplished by these methods.

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Components of *Boucerosia aucheriana* DECNE

Boucerosia aucheriana DECNE (Asclepiadaceae) is a plant indigenous to Pakistan and known to have a very bitter taste. A dried collection of whole plants from the vicinity of Peshawar, Pakistan, furnished a mixture of glycosides after usual isolation procedure.¹⁾ The mixture consists of various glycosides and, after mild acid hydrolysis, cymarose, sarmentose, oleandrose and digitoxose were detected as the sugar components.

The aglycone part is also a noncrystalline mixture of diversified esters and resistant to further purification. After alkaline hydrolysis, however, it was partitioned into a crystalline neutral fraction and various acids, *i.e.* benzoic acid, acetic acid, propionic acid, *n*-butyric acid, isovaleric acid and *n*-valeric acid.

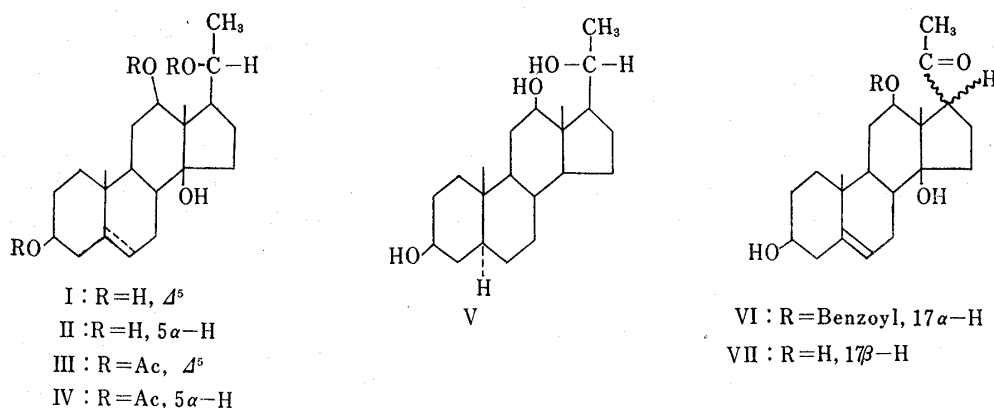
The neutral fraction holds two closely related components; boucerin, $C_{21}H_{34}O_4$ *¹ (I), m.p. 239~241°, $[\alpha]_D -3.7^\circ$ ($c=0.26$, MeOH), IR $\nu_{\max}^{Nujol}$ cm^{-1} : 3356, 1063, 848, NMR τ (in pyridine): 8.93 (singlet, 3H), 8.53 (doublet, 3H, $J=6$ c.p.s.), 8.33 (singlet, 3H), 4.51 (multiplet, 1H), and dihydroboucerin, $C_{21}H_{36}O_4$ (II), m.p. 143°/205°, $[\alpha]_D +3.9^\circ$ ($c=0.29$, MeOH). IR $\nu_{\max}^{Nujol}$ cm^{-1} : 3380, 3320, 1043, NMR τ (in pyridine): 8.81 (singlet, 3H), 8.57 (doublet, 3H, $J=6$ c.p.s.), 8.36 (singlet, 3H). The difference between both compounds lies only in one double bond, thus I was transformed to II by catalytic hydrogenation. The absence of a carbonyl function is evident from the IR spectra and a normal C_{21} steroidal structure with a hydroxyl function at C-20 was anticipated from the NMR data.

Acetylation of I and II with pyridine-acetic anhydride gave corresponding triacetates: (III), $C_{27}H_{40}O_7$, m.p. 147~149°, IR $\nu_{\max}^{Nujol}$ cm^{-1} : 3520, 3430, 1737, 1723, 1260, 1242, NMR τ (in $CDCl_3$): 8.98 (6H), 8.81 (doublet, 3H, $J=6$ c.p.s.), 7.96 (6H), 7.87 (3H), 4.60

*¹ Satisfactory analytical results were obtained for all compounds described in this communication.

1) J. v. Euw, H. Hess, P. Speiser, T. Reichstein: *Helv. Chim. Acta*, **34**, 1821 (1951).

(multiplet, 1H), and (IV) $C_{27}H_{42}O_7$, m.p. 191.5~193°, IR $\nu_{\text{max}}^{\text{Nujol}}$ cm^{-1} : 3560, 1750, 1730, 1710, 1263, 1253, 1240, NMR τ (in CDCl_3): 9.21 (singlet, 3H), 9.04 (singlet, 3H), 8.86 (doublet, 3H, $J=6$ c.p.s.), 8.01 (6H), 7.94 (singlet, 3H), respectively. Both acetates still show the presence of a hydroxyl group and its tertiary nature was confirmed by inertness of IV to chromic acid oxidation.



The direct clue for the structure was obtained from the following reactions. When II was treated in hydrogen with Adams catalyst in acetic acid containing a small amount of hydrochloric acid, dehydration of the tertiary hydroxyl group and concomitant hydrogenation eventuated to afford a saturated triol (V) m.p. 256~257°, which proved to be $3\beta,12\beta,20\beta$ -trihydroxy- 5α -pregnane²⁾ by direct comparison. This led to the conclusion that II has a partial structure of $3\beta,12\beta,20\beta$ -trihydroxy- 5α -pregnane and the remaining problem rests upon the locations of the tertiary hydroxyl group and the double bond in I.

The analogy of other C_{21} steroids originated from the same family favored 14β -hydroxy- Δ^5 -structure. In 1962, Mitsuhashi and Nomura reported the isolation of "benzoylramanone" ^{*2} (VI) from *Metaplexis japonica* MAKINO,³⁾ which, upon alkaline hydrolysis, afforded ramanone (VII) that was later identified with isodigipurpurogenin-II.⁴⁾ The structure of VII was firmly established as $3\beta,12\beta,14\beta$ -trihydroxy- Δ^5 - 17β -H-pregnen-20-one by synthetic way.⁵⁾ In order to settle the whole problem by correlation, VI was reduced with LiAlH_4 . The sole product obtained was proved to be boucerin (I) in all respects. This conclude unequivocally boucerin (I) is $3\beta,12\beta,14\beta,20\beta$ -tetrahydroxy- Δ^5 -pregnene. At the same time, it was also shown that VI has the 17β -side chain (17α -H) as had been expected from the optical rotatory dispersion data.⁶⁾

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^{*2} This name was given negligently, because the inversion of the side-chain could happen during base treatment to give isodigipurpurogenin-II=ramanone with stable 17α -orientation. The optical rotatory dispersion data favors the possible inversion and VI should be designated as "benzoylisoramanone" as proved (*vide infra*).

2) H. Mitsuhashi, Y. Shimizu : Tetrahedron Letters, **1962**, 909.

3) H. Mitsuhashi, T. Nomura, Y. Shimizu, I. Takemori, E. Yamada : This Bulletin, **10**, 811 (1962).

4) R. Tschesche, G. Grimmer : Ber., **88**, 1569 (1955).

5) H. Mitsuhashi, T. Nomura : This Bulletin, **13**, 1332 (1965).

6) *Idem* : Steroids, **3**, 271 (1964).