structure $\text{III}$ is supported from these facts.

A similar experiment has been carried out on a phenoxy radical instead of $\text{V}$ in order to prove the free radical process more definitely. In this case, the normal coupling product ($\text{II}$) was obtained at $0^\circ$-5$^\circ$ accompanied by the disulfide $\text{X}$. $\text{II}$ showed m.p. 197$^\circ$ (from MeOH). *Anal.* Caled. for $\text{C}_{27}\text{H}_{32}\text{O}_{4}\text{N}_{4}\text{S}$: 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 $\lambda_{\text{max}}$ m$\mu$ (log e) : 234.5 (4.22); 276.5 (4.03). Further $\text{II}$ was negative to the thiocromene test and turned out to be positive after the reduction with cysteine. From these facts, $\text{II}$ is confirmed to have normal coupling structure and $S$-alkyl structure should be excluded for $\text{II}$.

Therefore, it has been shown that the reaction of thiamine in thiol form with $K_2(\text{Fe(CN)}_4)$ 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, $\text{C}_{21}\text{H}_{26}\text{O}_{4}$ (I), m.p. 239$^\circ$-241$^\circ$, $[\alpha]_D -3.7^\circ$ (c=0.26, MeOH), IR $\nu_{\text{max}}$ cm$^{-1}$ : 3356, 1063, 848, NMR $\tau$ (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, $\text{C}_{31}\text{H}_{30}\text{O}_{4}$ (II), m.p. 143$^\circ$-205$^\circ$, $[\alpha]_D +3.9^\circ$ (c=0.29, MeOH). IR $\nu_{\text{max}}$ cm$^{-1}$ : 3380, 3320, 1043, NMR $\tau$ (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 $\text{C}_1$ 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), $\text{C}_{29}\text{H}_{32}\text{O}_{4}$, m.p. 147$^\circ$-149$^\circ$, IR $\nu_{\text{max}}$ cm$^{-1}$ : 3520, 3430, 1737, 1723, 1260, 1242, NMR $\tau$ (in CDCl$_3$): 8.98 (6H), 8.81 (doublet, 3H, J=6 c.p.s.), 7.96 (6H), 7.87 (3H), 4.60

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$^{*1}$ Satisfactory analytical results were obtained for all compounds described in this communication.

(multiplet, 1H), and (V) C₇H₄O₇, m.p. 191.5~193°, IR ν_{max}^{max} cm⁻¹ : 3560, 1750, 1730, 1710, 1263, 1253, 1240, NMR τ (in CDCl₃) : 9.21 (singlet, 3H), 9.04 (singlet, 3H), 8.86 (doublet, 3H, J=6 c.p.s.), 8.01 (6H), 7.74 (singlet, 3H), respectively. Both acetates still show the presence of a hydroxyl group and its tertiary nature was confirmed by ineptness of N 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 3β,12β,20β-trihydroxy-5α-pregnane by direct comparison. This led to the conclusion that II has a partial structure of 3β,12β,20β-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 C₃₅ steroids originated from the same family favored 14β-hydroxy-Δ⁴-structure. In 1962, Mitsuhashi and Nomura reported the isolation of "benzoylranamone"² (VI) from Metaplexis japonica Makino,³ which, upon alkaline hydrolysis, afforded ramanone (VII) that was later identified with isodigipurungenin-II.⁴ The structure of VII was firmly established as 3β,12β,14β,17β-tetrahydroxy-Δ⁴-17β-hydroxy-Δ⁴-pregnene-20-one by synthetic way.⁵ In order to settle the whole problem by correlation, VII was reduced with LiAlH₄. The sole product obtained was proved to be boucerin (I) in all respects. This conclude unequivocally boucerin (I) is 3β,12β,14β,20β-tetrahydroxy-Δ⁴-pregnene. At the same time, it was also shown that VII 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 isodigipurungenin-II = ramanone with stable 17α-orientation. The optical rotatory dispersion data favors the possible inversion and VII should be designated as "benzoylisoranamone" as proved (vide infra).