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 Ⅸ. 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 λ_{max}^{EtOH} mμ (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 resistent 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.

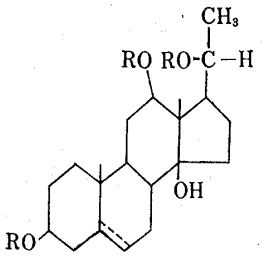
The neutral fraction holds two closely related components; boucerin, $C_{21}H_{34}O_4$*[1] (Ⅰ), m.p. 239~241°, $[\alpha]_D$ −3.7° (c=0.26, MeOH), IR ν_{max}^{Nujol} cm^{-1}: 3356, 1063, 848, NMR τ (in pyridine): 8.93 (singlet, 3H), 8.53 (doublet, 3H, J=6 c.p.s.), 8.33 (singlet, 3H), 4.51 (multiplet, 1H), and dihydroboucerin, $C_{21}H_{36}O_4$ (Ⅱ), m.p. 143°/205°, $[\alpha]_D$ +3.9° (c=0.29, MeOH). IR ν_{max}^{Nujol} cm^{-1}: 3380, 3320, 1043, NMR τ (in pyridine): 8.81 (singlet, 3H), 8.57 (doublet, 3H, J=6c.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 ν_{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

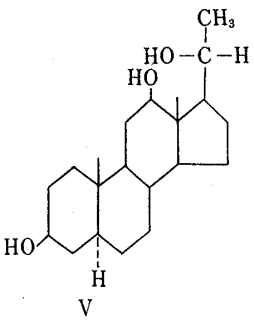
*1 Satisfactory analytical results were obtained for all compounds described in this communication.

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

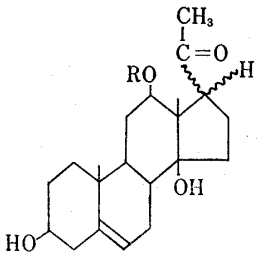
(multiplet, 1H), and (IV) $C_{27}H_{42}O_7$, m.p. 191.5~193°, IR ν_{max}^{Nujol} cm^{-1}: 3560, 1750, 1730, 1710, 1263, 1253, 1240, NMR τ (in $CDCl_3$): 9.21 (singlet, 3H), 9.04 (singlet, 3H), 8.86 (doublet, 3H, J=6 c.p.s.), 8.01 (6H), 7.94 (singlet, 3H), respectively. Both acetates still show the presence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



I : R=H, Δ^5
II : R=H, 5α-H
III : R=Ac, Δ^5
IV : R=Ac, 5α-H



V



VI : R=Benzoyl, 17α-H
VII : R=H, 17β-H

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[2] 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 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 3β,12β,14β-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 repects. This conclude unequivocally boucerin (I) is 3β,12β,14β,20β-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 : Tetrahdron 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).