o-hydroxyacetophenone and benzaldehyde in alkaline medium.

This new procedure affords a convenient route to the 3-substituted chromanones and it has been experimented successfully on some *o*-hydroxyarylalkylketones, such as *o*-hydroxypropiophenone, quoted above, and its 5-bromo and 5-methyl derivatives, *o*-hydroxybutyrophenone and the *o*-hydroxyphenylbenzylketone.

In the case of *o*-hydroxyacetophenone, we have obtained only a polymeric material and, with the *o*-hydroxyisobutyrophenone, the 5-hydroxymethyl derivative. Evidently the presence or the absence of a substituent on the active methylene group is sufficient to orient the reaction in another direction.

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Riassunto

Viene descritta una semplice sintesi di cromanoni 3-sostituiti, da *o*-idrossiarilalchilchetoni e formaldeide in ambiente alcalino.

Alkaloids of Apocynaceae V
Hunterine, a New Alkaloid from *Hunteria eburnea* Pichon[1]

Recently, BARTLETT, TAYLOR, and RAYMOND-HAMET have described four new alkaloids from the bark of *Hunteria eburnea* Pichon[2] and have shown that they represent a new class of indole alkaloids[3]. We wish to report the isolation and characterization of another new alkaloid, hunterine, from the root bark of *Hunteria eburnea* Pichon[4].

A careful chromatography of the alkaloidal fraction on deactivated alumina using benzene-chloroform mixtures (1:3) and chloroform as eluents yielded the crude base. Crystallization from methanol or methanol-chloroform mixture afforded hunterine in colorless plates, m. p. 264–265°C (dec. uncorr.), $[\alpha]_D^{27} = -205{\cdot}1$ ($CHCl_3$, C = 1).

Calc. for $C_{42}H_{52}O_4N_4$: C, 74·52; H, 7·74; O, 9·46; N, 8·28; OCH_3 (1), 4·59; $N(CH_3)$ (1), 2·22. Found: C, 74·60; H, 7·49; O, 9·38; N, 8·57; OCH_3, 4·96; $N(CH_3)$, 2·40.

The hydrochloride was prepared in the conventional manner and recrystallized from acetone, m. p. > 270°C (dec.).

Calc. for $C_{42}H_{52}O_4N_4 \cdot 2\,HCl$: C, 67·27; H, 7·26; Cl, 9·46; OCH_3 (1), 4·11. Found: C, 67·01; H, 7·49; Cl, 9·60; OCH_3, 4·18.

Electrometric titration of hunterine in 66% aqueous dimethyl formamide indicates the molecular weight of 685 ± 25 (Calc. for $C_{42}H_{52}O_4N_4$: 678·8) with two basic groups, pK'_a 7·0 and 7·4 as well as one acidic group, pK'_a 12·6. The ultraviolet spectrum is characterized by the following bands: λ_{max}^{EtOH} 228 mμ, $a_M = 38{,}500$; 293 mμ, $a_M = 11{,}300$, and 250 mμ, $a_M = 9{,}500$ (shoulder).

The band at 293 mμ shifts to a broader band at 305 mμ in the alkaline solution (phenolic group, pK'_a 12·6, *vide supra*). This spectrum is tentatively interpreted as resulting from the additive effect of dihydroindole and 5-hydroxyindole chromophores[5].

The infrared spectrum of hunterine in chloroform solution shows a band at 5·75 μ, $a_M = 375$ (M. W. 685) and indicates the presence of one unconjugated ester per molecule[5]. The band envelope with maxima at 6·16 and 6·20 μ is also consistent both in wave length and intensity with the presence of 5-hydroxyindole and dihydroindole moieties as was shown by comparison with the spectra of appropriate models[6]. While the band of free indole NH is missing at 2·90 μ, there is a band at 2·77 μ and an intense underlying absorption from 2·9 to 4·5 μ indicative of free and hydrogen bonded hydroxyl.

These as yet preliminary data suggest that hunterine represents another example of dimeric indole-indoline alkaloids[7]. Hunterine was shown to exhibit hypotension of short duration in anesthetized animals at 1 mg/kg[8].

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N. NEUSS and NANCY J. CONE

Lilly Research Laboratories, Indianapolis (Indiana), December 11, 1959.

Zusammenfassung

Hunterin wird als ein neues Alkaloid aus der Wurzelrinde von *Hunteria eburnea* Pichon beschrieben. Die analytischen und physikalischen Eigenschaften dieser Verbindung weisen darauf hin, dass Hunterin ein dimeres Alkaloid vom Indol-Indolin-Typus darstellt.

[1] Paper IV in this series see Exper. *15*, 414 (1959).

[2] Another *Hunteria* species, *H. corymbosa* Roxb. was investigated by M. GRESHOFF and a crystalline alkaloid isolated; however, no data on the compound were given. Ber. deutsch. chem. Ges. *23*, 3537 (1890).

[3] F. BARTLETT, W. I. TAYLOR, and RAYMOND-HAMET, C. R. Acad. Sci., Paris *249*, 1259 (1959). The appearance of this work has prompted the presentation of this preliminary communication. The physical properties and formulae of these alkaloids are in good agreement with the data obtained on alkaloids isolated in our laboratories and tentatively named huntericine, hunteridine, and hunteriline. Therefore, we assume that these compounds are identical with eburnamonine, isoeburnamine, and eburnamine respectively, and refrain from repeating our analytical and physical data as well as from the usage of our names for these alkaloids. We should like to thank Dr. TAYLOR for calling his work to our attention.

[4] Commercial sample from S. B. Penick & Co., New York, N. Y., U.S.A.

[5] For comparison, see the spectrum of sarpagine and ajmaline in N. NEUSS, *Physical Data of Indole and Dihydroindole Alkaloids* (Lilly Research Laboratories, Indianapolis, Indiana, July 1959).

[6] The model substances were: bufotenine, $\lambda_{max}^{CHCl_3}$ 6·15 and 6·30 μ, and ajmaline, $\lambda_{max}^{CHCl_3}$ 6·23 μ. The spectra were recorded on a Beckman, Model IR 7, Infrared Spectrophotometer using a 2·0 mm cell.

[7] M. GORMAN, N. NEUSS, and G. H. SVOBODA, J. Amer. chem. Soc. *81*, 4745 (1959).

[8] Hypotensive effects of extracts of *Hunteria eburnea* were first reported by RAYMOND-HAMET, C. R. Acad. Sci., Paris *240*, 1470 (1955) and subsequently by ENGELHARD and GELBRECHT, Naturwissenschaften *45*, 547 (1958).