Summary

I. Dancing bees indicate to their hive-mates the direction towards a goal by tail-wagging dances. In dancing, they orient themselves according to the position of the sun in the sky or, when the sun is covered, according to the polarized light visible in the sky. A small spot of blue sky suffices for the bee to be able to indicate the direction correctly. Experiments with polaroid have proved that it is the direction of vibration of the polarized light which is the determining factor in this case. Polarized light can also be used as a substitute for the missing sun during their free flight through the landscape.

Orientation by means of polarized light has also been found to exist in many other Arthropods. Certain species of insects, custaceans and even spiders are able, with the help of their memories, to maintain *any* angle with the direction of vibration of polarized light, just as bees are (Menotaxis), while others again, from the outset, will orient themselves so as to form a definite fairly constant angle—usually a right angle—with the plane of vibration (Tropotaxis).

II. Electrophysiological, polarization-optical, and electron-microscopical studies have indicated unanimously that polarized light is analyzed within the compound eyes of insects, in the rhabdomeres of the visual cells (radial analyzers Fig. 2).

III. Several views contradictory to this have been put forward:

1. The analyzer is situated within the dioptric apparatus. – This assumption has been proved wrong for insects, their optical system having been more closely investigated. It appears to be improbable for other Arthropods as well – having no foundation whatsoever.

2. The reactions of bees are not based on direct analysis of the plane of polarisation, but on their recognition of the pattern of brightness produced by it in the surroundings or on the substratum, as a secondary effect. – Such an assumption, however, cannot explain the orientation of bees according to the polarization of the sky's light, for under natural conditions, the prerequisites for the production of clear reflection patterns are not met. And even if such a reflection pattern should once be produced, the dancing bees would be unable to recognize it, since dancing in the throng of their companions they can have no view of the background.

IV. Since the assumption of an indirect recognition of the plane of polarization has nevertheless found some acceptance, we have checked it by performing some new experiments.

1. It is clear that for a direct analysis of the polarized sky's light during the dance on a horizontal comb, the *upper parts* of the eyes would be needed, while, on the other hand, the *lower parts* of the eyes would be essential for the recognition of a reflection pattern. Now, whenever a sector of the upper eye has been masked, the orientation of the dances was heavily impaired (Fig. 5), whereas even extensive masking of the lower part of the eye did not impair orientation at all (Fig. 6).

2. When bees are forced to walk, they can be trained to walk in a certain direction of the compass. Although their only means of orientation was polarized sky's light, their orientation was just as good on a white substratum (which even under the most favourable conditions does not give a clear reflection pattern) as on a black, glossy substratum (which gives a very obvious reflection pattern under favourable conditions), Fig. 9. On a white substratum, many dances could be observed: all, without exception, were correctly oriented.

3. Under the natural conditions prevailing in the experiments performed in the open, the reflection pattern of the polarized sky's light was obliterated or altered by secondary influences exerted by the surroundings (shading, position of the observer, cloud formation), without the orientation of the bees being in the least impaired.

Thus it has been proved that, in our experiments, the bees oriented themselves through a direct analysis of the blue sky's light, and not according to a reflection pattern.

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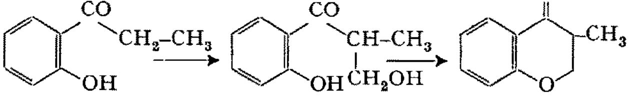
A New Synthesis of 3-Substituted Chromanones

In the course of our researches into the chromone group, we have examined some possibilities of synthesis offered by the fundamental intermediates of this class of compounds, i.e. the *o*-hydroxyarylalkylketones.

We showed recently[1] that the Marasse modification of the Kolbe-Schmitt synthesis[2], when applied to *o*-hydroxyarylalkylketones, gives rise to the corresponding benzotetronic acids. We have now found that from the reaction between formaldehyde and an *o*-hydroxyarylalkylketone it is possible to obtain a 3-substituted chromanone. For instance, the sodium salt of *o*-hydroxypropiophenone, in aqueous medium, at 50°C, reacts with an equivalent quantity of formaldehyde with separation, after some time, of an oleous layer, consisting of the 3-methylchromanone.

The reaction probably runs through a β-ketoalcohol formed by the electrophilic attack of formaldehyde on the α-carbon of the carbonyl group, followed by cyclodehydration:



This course recalls that postulated by Reichel and Müller[3] for the synthesis of the flavanone, starting from

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[1] P. Da Re and E. Sandri, Ber. deutsch. chem. Ges. *93* (1960), in press.

[2] A. S. Lindsey and H. Jeskey, Chem. Rev. *57*, 583 (1957).

[3] L. Reichel and K. Müller, Ber. deutsch. chem. Ges. *74*, 1741 (1941).

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.

P. Da Re and L. Verlicchi

Research Department of Recordati-Laboratorio Farmacologico S. p. A., Milano (Italy), April 21, 1960.

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.), $[\alpha]_D^{27} = -205\cdot1$ ($CHCl_3$, $C = 1$).

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].

Acknowledgment. The authors are grateful to Dr. H. E. Boaz for the infrared data, Mr. L. G. Howard for the ultraviolet data, Messrs. W. L. Brown, R. Hughes, H. L. Hunter, and G. M. Maciak for microanalyses, and Dr. F. G. Henderson for pharmacological testing.

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.

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[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).