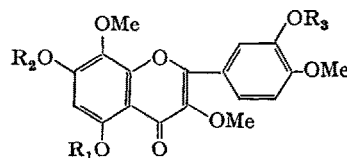
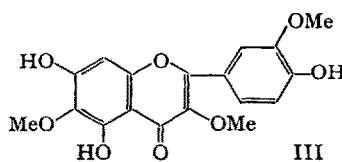
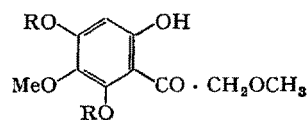


- I $R_1 = R_3 = H$
 $R_2 = \beta\text{-D-glucosyl}$
 II $R_1 = R_2 = R_3 = H$
 VI $R_1 = R_2 = H$ $R_3 = C_6H_5CH_2$
 VIII $R_1 = R_2 = R_3 = Et$



- IV $R_1 = R_2 = R_3 = H$
 VII $R_1 = R_2 = H$ $R_3 = C_6H_5CH_2$



- V $R = H$
 IX $R = Et$

trimethoxyflavone (VIII) [m.p. 104.5–105.5°, UV λ_{max}^{EtOH} nm (log ϵ): 242 (4.32), 335 (4.36). Found: C, 64.77; H, 6.24. $C_{24}H_{28}O_8$ requires: C, 64.85; H, 6.35%], which was also prepared from 4,6-diethoxy-5, ω -dimethoxy-2-hydroxyacetophenone (IX)⁵ and *O*-ethylisovanillic anhydride by an unambiguous method. IR- and UV-spectral data of the synthetic II was in full accord with that of the natural product². Partial synthesis of the glucoside I had been carried out earlier², so the total synthesis of I is now accomplished.

Debenzylation of VII afforded 5,7,3'-trihydroxy-3,8,4'-trimethoxyflavone (IV) [m.p. 213.5–214.5°, UV λ_{max}^{EtOH} nm (log ϵ): 260 (4.44), 275.5 (4.47), 360 (4.33).

Found: C, 59.91; H, 4.37. $C_{18}H_{16}O_8$ requires: C, 60.00; H, 4.48%. Its triacetate (m.p. 144–145°) and triethyl ether (m.p. 152.5–153°) were also prepared.

Zusammenfassung. Die Synthese von Centaureidin (5,7,3'-Trihydroxy-3,6,4'-trimethoxyflavon) aus 2,4,6-Trihydroxy-3, ω -dimethoxyacetophenon wird beschrieben.

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⁷ The author wishes to express his gratitude to Prof. K. FUKUI, Hiroshima University, for his kind encouragement.

A New Partial Synthesis of Holaphyllamine

Holaphyllamine (3 β -amino- Δ^5 -pregnen-20-one) (III) was isolated in 1959 from *Holarrhena floribunda* by a French research group¹. Shortly thereafter, a partial synthesis of this alkaloid starting with Δ^5 -pregnen-3 β -ol-20-one was reported².

Our earlier studies³ on the conversion of 3 α ,6 α -ditosyloxy-5 β -steroids into the corresponding 3 β -substituted Δ^5 -compounds led us to the conclusion that an improved partial synthesis of III can be developed employing 5 β -pregnane-3 α ,6 α -diol-20-one (I) as the starting substance. This assumption was confirmed by a preliminary experiment carried out on methyl 3 α ,6 α -ditosyloxy-5 β -cholanate which by azidolysis and concomitant dehydro-sylation gave methyl 3 β -azido- Δ^5 -cholenate (m.p. 95–97° from MeOH) in 58% yield. Similarly 3 α ,6 α -ditosyloxy-5 β -pregnan-20-one (Ia) could be converted into 3 β -azido- Δ^5 -pregnen-20-one (IIa) (m.p. 87–89° from MeOH).

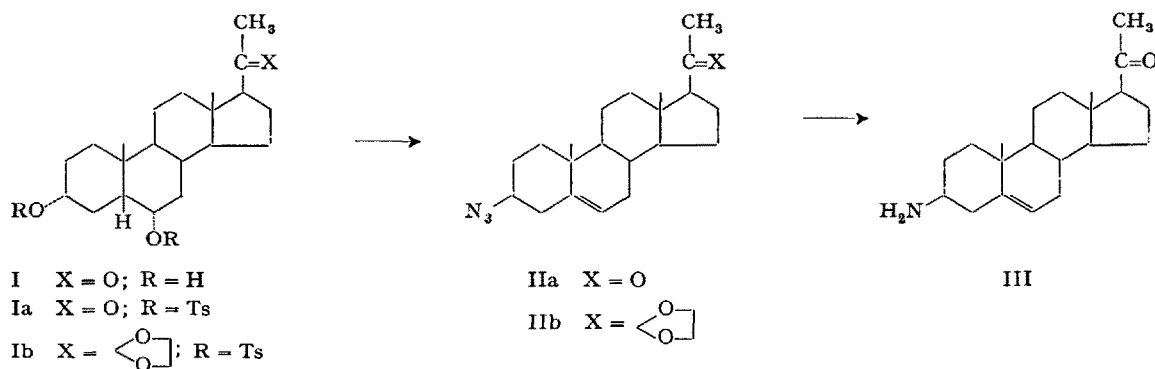
The azidolyses with concomitant dehydro-sylation were performed on heating 1 part of 3 α ,6 α -ditosyloxy-5 β -steroid for 5 h at 85–90° in N₂ atmosphere with 3 parts of NaN₃ in 15 parts of DMSO.

Ketalization of the azido compound IIa with ethylene glycol afforded 3 β -azido-20,20-ethylenedioxy- Δ^5 -pregnene

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(IIb) (m.p. 127–130° from MeOH) which by reduction with LiAlH_4 and subsequent treatment with aqueous HCl gave III isolated as chlorohydrate (m.p. > 300°, $[\alpha]_D^{25} + 19.6^\circ$ in MeOH)⁴.

These 3 steps could be carried out without the purification of the intermediary products in an overall yield of 50%.

In an alternative route we converted the ditosylate Ia into the corresponding 20, 20-ethylenedioxy derivative Ib⁵ and then, following the general procedure indicated above, into the azido compound IIb in 80% yield.

The elemental analyses data as well as the IR-spectra are in perfect agreement with the formulae assigned to the described compounds.

Résumé. L'holaphyllamine peut être aisément préparée à partir du 3 α , 6 α -ditosyloxy-5 β -pregnan-20-one par réaction avec NaN_3 .

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⁴ The authors are indebted to Dr. R. GOUTAREL (Institut de Chimie des Substances Naturelles, Gif-sur-Yvette) under whose leadership the comparison of this substance with an authentic sample of holaphyllamine chlorohydrate was performed.

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Chemical Investigation of *Pluchea lanceolata* II. Identity of Pluchine with Betaine Hydrochloride

In a recent communication¹, the isolation of a quaternary base chloride named pluchine, m.p. 243–244° (decomposition and volatilization with evolution of gas), $[\alpha]_D^{20} - 29.51$ (H_2O) was reported from the whole plant of *Pluchea lanceolata*, Linn. (N.O. Compositae). Pluchine has since been identified as betaine hydrochloride by comparison of its paper chromatographic behaviour, m.p. and mixed m.p. with an authentic specimen.

Analysis found for pluchine: C, 38.74, 38.59, 39.12, 39.09; H, 7.79, 7.67, 7.78, 7.81; N, 8.64, 8.30, 7.49, 7.68; Cl, 23.55, 23.80, 22.85, 22.80. Analysis required for betaine hydrochloride, Cl^- , $\text{N}^+(\text{CH}_3)_3 \cdot \text{CH}_2 \cdot \text{COOH}$: C, 39.08; H, 7.81; N, 9.12; Cl, 23.12.

Both pluchine picrate and the picrate prepared from betaine hydrochloride melted at 181–182°, and there was no depression in their mixed m.p. Analysis found for pluchine picrate: C, 38.46, 38.58; H, 3.87, 4.08; N, 16.09, 15.86. Analysis required for betaine picrate, $(\text{NO}_2)_3 \text{C}_6\text{H}_5\text{O}^- \text{N}^+(\text{CH}_3)_3 \cdot \text{CH}_2 \cdot \text{COOH}$: C, 38.15; H, 4.04; N, 16.18.

Thus, the analyses of pluchine and its picrate agree well with those for betaine hydrochloride and its picrate.

PRASAD et al.² found pluchine to have anti-inflammatory and anti-arthritis activity in experimental animals (albino rats) with inflammation produced by both immunological and non-immunological methods. Pluchine was found not only to suppress the acute inflammation induced by carrageenin, histamine and formaldehyde in comparison with betamethasone, a known anti-inflammatory agent, but also effectively to suppress both primary and secondary phases of adjuvant arthritis (induced by

a suspension of dead tubercle bacilli, human DT strain, in liquid paraffin) like metamethasone. Pluchine significantly suppressed acute sensitivity reaction produced by purified tuberculin, and was less toxic than betamethasone in albino rats. These interesting properties of pluchine or betaine hydrochloride can account for the use of the drug, *Pluchea lanceolata*, for the treatment of rheumatism in clinical cases in the ayurvedic system of medicine.

Zusammenfassung. Die Struktur von Pluchin, einer quaternären Base aus *Pluchea lanceolata*, wurde als die des Betainhydrochlorids aufgeklärt. Damit sind auch die mit Pluchin beobachteten biologischen Wirkungen verständlich.

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Department of Medicinal Chemistry, Research and Post Graduate Institute of Indian Medicine, Banaras Hindu University, Varanasi-5 (India), 18 March 1968.

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