Calibration curves were prepared for ferric iron by means of a Unicam SP 600 spectrophotometer and in the Table are given E_{495} ± standard deviation (S.D.) for 3 sets of curves in 0.4% (Column I) and 0.1% (Column II) SDEP solutions.

These readings were made 30 min after preparation of the solutions. The colours were stable for at least 24 h. At the higher concentrations of Fe^{+++}, E values were somewhat greater in 0.1% than in 0.4% SDEP reagent.

Behaviour of ferrous iron in 0.1% SDEP. Aliquots of a freshly prepared solution of ferrous alum (analytical reagent grade: 0.3263 g in 100 ml of deionized water) were added to 5 ml portions of 0.1% SDEP. No colour was detected in any tube 30 min after preparation (Table, column III). To each tube was added 0.01 ml of 30% hydrogen peroxide and the colours read at 495 nm after 30 min. Results for 3 sets of experiments are given in the Table, column IV. They are practically identical with those obtained in the direct reaction of SDEP with ferric iron (Column II).

Determination of ferric and ferrous iron in the same solution. A stock solution (100 ml) of 0.2006 g of ferric alum and 0.1632 g of ferrous alum was prepared and aliquots of the fresh solution which contained equal parts of ferric and ferrous iron, were added to 5 ml portions of 0.1% SDEP to give final concentrations of 1.9–15.1 µg of iron/ml. Colours were read after 30 min (Table, column V) and again (Table, column VI) 30 min after addition of 0.01 ml of 30% hydrogen peroxide to each tube. E_{495} for each peroxide-treated solution was approximately twice that of the untreated solution and the final readings were the same as those given by solutions containing Fe^{+++} only (Table, column II). Thus the direct reaction with SDEP is capable of determining ferric iron in a mixture of ferric and ferrous iron, and after peroxide addition, the increase in E_{495} permits determination of the ferrous iron content of the mixture.

Discussion. SDEP solutions are clear and colourless and seem to be stable indefinitely at room temperature. In this respect, the reagent is superior to a similar compound ethylenediaminedi(*o*-hydroxyphenylacetic acid) o–$HOC_6H_4CH(COOH)NH(CH_2)_2NHCH(COOH)C_6H_4OH$–o which was investigated by UNDERWOOD[4] as a possible reagent for ferric iron.

None of the common metal ions such as Cu^{++}, Mn^{++} and Ni^{++} gave a colour with SDEP reagent, but a pale green colour was given by K^{+4}.

Résumé. Nous avons préparé un nouveau produit par réaction entre le N, N'-salicylidène-1, 2-diaminoéthane et l'acide hypophosphoreux. Ce composé donne un complexe coloré avec l'ion ferrique et il semble convenir au dosage colorimétrique du fer.

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[4] A. L. UNDERWOOD, Anal. Chem. *30*, 44 (1958).

[5] Our thanks are due to Miss M. A. MCKINNON, Department of Chemistry, University of Sheffield, who carried out the microanalyses.

Synthesis of (±)-Isoelliptone

Isoelliptone[1] (erosone)[2], $C_{20}H_{16}O_6$, has been isolated along with some rotenoids (rotenone, pachyrrhizone etc.) from yam beans (*Pachyrrhizus erosus*). Its structure was shown to be an isomer of elliptone (I)[3] by NORTON and HANSBERRY[2], and lately was recognized as II on the basis of spectral studies by OLLIS et al.[1,4]. In previous papers[5,6], the authors have reported a convenient synthetic method of rotenoids (munduserone and elliptone) from corresponding 2'-hydroxyisoflavone derivatives[7,8]. The present paper will describe the synthesis of II from 2'-hydroxy-4', 5'-dimethoxyfurano [3'', 2'': 6, 7] isoflavone

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[1] W. D. OLLIS, *Symposium on Phytochemistry* (Ed. H. R. ARTHUR, Hong Kong Univ. Press, Hong Kong 1964), p. 128.

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[3] S. H. HARPER, J. chem. Soc. *1099*, 1424 (1939); *587*, 593 (1942).

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[5] K. FUKUI, M. NAKAYAMA and T. HARANO, Experientia *23*, 613 (1967).

[6] T. HARANO, J. Sci. Hiroshima Univ. Series A-II, in press.

[7] V. CHANDRASHKAR, M. KRISHNAMURTI and T. R. SESHADRI, Tetrahedron *23*, 2505 (1967).

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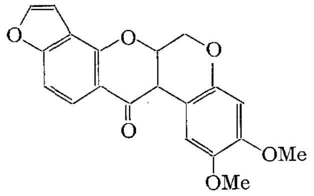
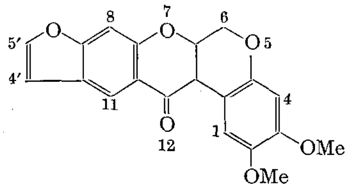
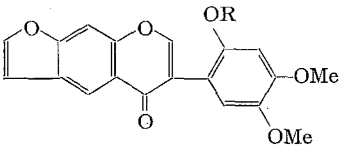


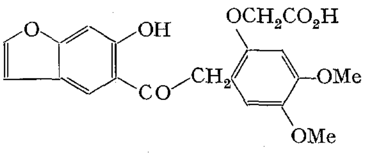
I



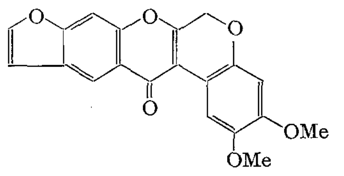
II



III R = H
IV R = $CH_2CO_2C_2H_5$



V



VI

(III)[9,10] according to a modification of a procedure reported earlier[5,6,8].

Reaction of the 2′-hydroxyisoflavone (III) with ethyl bromoacetate in the presence of potassium carbonate gave the 2′-phenoxyacetate derivative (IV, mp 180–181°, IR 1725, 1653 cm^{-1} (C=O) (Nujol), UVλ_{max}^{EtOH} nm (log ε); 237 (4.54), 297 (4.10). Found: C, 65.02; H, 4.70. $C_{23}H_{20}O_8$ requires: C, 65.09; H, 4.75%). Treatment of IV with dilute alkali gave isoelliptic acid (V, mp 216–217°, IR 3250 (OH), 1730, 1640 cm^{-1} (C=O) (Nujol), UVλ_{max}^{EtOH} nm (log ε); 233 (4.56), 278 (4.02), 340 (3.81). Found: C, 62.04; H, 4.83. $C_{20}H_{18}O_8$ requires: C, 62.17; H, 4.70%) (lit. mp 204°[2], mp 193–194°[9]). By intramolecular cyclization with acetic anhydride and anhydrous sodium acetate, the acid (V) afforded dehydroisoelliptone (VI, mp 286–288°, IR 1633 cm^{-1} (C=O) (Nujol), UVλ_{max}^{EtOH} nm (log ε); 237.5 (4.51), 273 (4.39), 307 (4.30). Found: C, 68.40; H, 4.09. $C_{20}H_{14}O_6$ requires: C, 68.57; H, 4.03%). According to the MIYANO and MATSUI's method[11], VI was reduced with sodium borohydride in dioxane and subsequently, without any purification, followed by Oppenauer oxidation to give (±)-isoelliptone (II, mp 215–216°, IR 1680 cm^{-1} (C=O) (Nujol), UVλ_{max}^{EtOH} nm (log ε); 236 (4.59), 254.5 (4.09), 276 (4.01), 300sh (3.80), 335 (3.55). NMR[12]: 3.78_s, 3.82_s (each 3H, CH_3O), $3.9–5.2_m$ (4H, C-6, 6_a, 12_a), 6.54_s (1H, C-4), 6.80_q (1H, J = 2.0, 1.0 Hz, C-4′), 6.83_s (1H, C-1), 7.11_{bd} (1H, J = 1.0 Hz, C-8), 7.61_d (1H, J = 2.0 Hz, C-5′), 8.32_s (1H, C-11). Found: C, 68.14; H, 4.73. $C_{20}H_{16}O_6$ requires: C, 68.18; H, 4.58%). The mass spectrum data of II[13] (m/e: 352, 192, 191, 177, 161, 160, 149, 134, 131, 121, 106) is identical with that of natural isoelliptone which was reported by REED and WILSON[4].

Zusammenfassung. Die Synthese von Isoellipton aus 2′-Hydroxy-4′,5′-dimethoxyfurano[3″,2″:6,7]isoflavon wird beschrieben.

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[9] V. CHANDRASHKAR, M. KRISHNAMURTI and T. R. SESHADRI, Curr. Sci. *36*, 623 (1967); Chem. Abstr. *68*, 59402q (1968).

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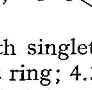
[11] M. MIYANO and M. MATSUI, Bull. agric. chem. Soc. Japan *22*, 128 (1958); Chem. Ber. *91*, 2044 (1959).

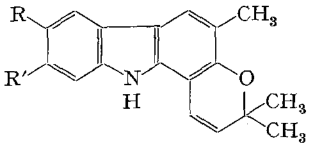
[12] The NMR-spectrum was measured with a Hitachi R-20 (60 MHz) spectrometer, using tetramethylsilane as the internal standard (δ-value in $CDCl_3$; *s*, singlet; *d*, doublet; *bd*, broad doublet; *q*, quartet).

[13] The mass spectrum measured by a Hitachi RMU-6D Mass Spectrometer.

New Alkaloids from *Murraya koenigii* Spreng.[1]

Current interest in the biosynthesis of alkaloids and the publication of 2 recent communications[2,3] prompt us to report our results on the structures of 2 of the new bases isolated by us from the leaves of *Murraya koenigii* Spreng.

The first new alkaloid, koenigicine, $C_{20}H_{21}NO_3$ (mol. wt. 323 by mass spectrum), mp 224–225°, is optically inactive. Its UV-spectrum, $\lambda_{max.}^{EtOH}$ 239, 300, and 361 nm (log ε 4.56, 4.52, and 3.97 respectively) indicated the presence of a carbazole nucleus already established in its congeners. This was supported by its IR-spectrum which showed peaks at 3420 (–NH), 1635, 1620, and 1600 cm^{-1} (unsaturation and aromatic system). The NMR-spectrum[4] showed the following signals (τ, multiplicity, number of protons under the peak, and assignment given): 8.5, singlet, 6,  $-O-C\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$; 7.67, singlet, 3, $\gt C-CH_3$; 6.14 and 6.04, both singlets, 3 each, 2 methoxyls attached to an aromatic ring; 4.37 and 3.42, both doublets (J = 10 cps), 1 each, olefinic protons. In addition, the spectrum showed 3 aromatic protons – all singlets at τ 3.17, 2.60, and 2.50 respectively as well as a broad signal for a single proton, exchangeable with D_2O at 2.19 τ (>N–H). The mass-spectrum showed, apart from the M$^+$ peak at 323, abundant ions at m/e 308, 293, 292, 264, 250 and 154. Supporting evidence for the M$^+$ peak at 323 and for some of the important ions was provided by the appearance of doubly charged ions at 161.5, 146.5 and 132.5. All this evidence could be summarized in the structure (I):



(I) R = R′ = OMe
(V) R = OMe; R′ = H
(VI) R = H; R′ = OMe

On catalytic hydrogenation over Raney Ni in ethanol, or over Pt in glacial acetic acid, koenigicine yielded the dihydro-derivative (II), $C_{20}H_{23}NO_3$, mp 232° (M$^+$ 325, by mass-spectrum); $\lambda_{max.}^{EtOH}$ 238, 267, and 325 nm (log ε 4.58, 4.25, and 4.21 respectively). The NMR-spectrum of this compound showed replacement of olefinic protons by

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[1] Communicating No. 1353 from the Central Drug Research Institute, Lucknow.

[2] D. P. CHAKRABORTY and K. C. DAS, Chem. Comm. *967* (1968).

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[4] All spectra were taken in $CDCl_3$ on a Varian A-60D machine using TMS as internal standard.