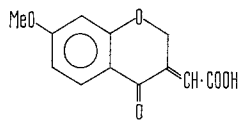

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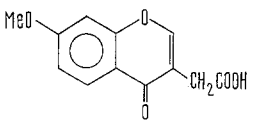
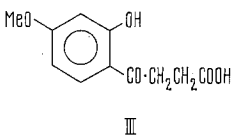
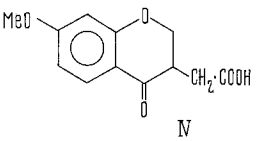


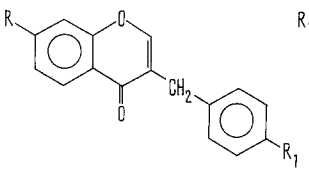
II

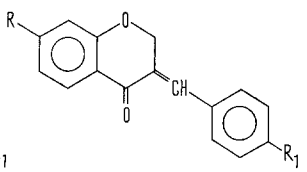


III



IV





(V)	$R = R_1 = H$	(X)	$R = R_1 = H$
(VI)	$R = OMe$, $R_1 = H$	(XI)	$R = OMe$, $R_1 = H$
(VII)	$R = H$, $R_1 = Me$	(XII)	$R = H$, $R_1 = Me$
(VIII)	$R = R_1 = OMe$	(XIII)	$R = R_1 = OMe$
(IX)	$R = H$, $R_1 = OMe$	(XIV)	$R = H$, $R_1 = OMe$

Similarly the homoisoflavones (VI, mp 130–131°; ν CO 1640 cm^{-1}), (VII, mp 90–91°; ν CO 1640 cm^{-1}), (VIII, mp 97–98°; ν CO 1639 cm^{-1}), (IX, mp 94–95°; ν CO 1640 cm^{-1}) were prepared respectively from the related arylidene derivatives (X[4], mp 113°; ν CO 1664 cm^{-1}) (XI, mp 98–99°; ν CO 1667 cm^{-1}), (XII, mp 118–119°; ν CO 1662 cm^{-1}), (XIII, mp 129–130°; ν CO 1660 cm^{-1}) and (XIV[5], mp 133–134°; ν CO 1660 cm^{-1}).

Zusammenfassung. Eine neue Synthese von Anhydrobrazilinsäure wird beschrieben. Es wird gezeigt, dass Arylidenchroman-on-4 zu Homoisoflavon isomerisiert werden kann.

J. N. Chatterjea, S. C. Shaw and J. N. Singh

Department of Chemistry, Patna University, Patna (India), 30 April 1970.

[5] P. Pfeiffer, K. Grimm and H. Schmidt, Justus Liebigs Annln. Chem. *564*, 208 (1949).

A New Ester Glucoside from the Bark of *Tecomella undulata*

Tecomella undulata[1] (G. Don) Seem. (*Bignoniaceae*; *Rakta-Rohitaka*) is a small tree which grows in Punjab, Sind, Waziristan, Baluchistan, Rajasthan, Kathiawar, Gujrat and the Deccan. In the indigenous systems of medicine, the plant is said to be useful in urinary discharges, enlargement of spleen, leucorrhoea, leucoderma and liver diseases. The bark of young branches is often employed as a remedy for syphilis. From the heartwood Seshadri et al.[2] isolated lapachol, a quinonoid compound, which gives toxic, termite and fungus resisting properties[3] to the wood.

In a preliminary pharmacological study, Bhattacharya[4] observed that the watersoluble portion of the alcoholic extract of the bark possessed smooth muscle relaxant, mild cardiotonic and choleretic activity. Further screening showed that the watersoluble portion of the chloroform extract of the bark also, after being extracted successively with petroleum ether and benzene, exhibited the same pharmacological action as the alcoholic extract. These observations prompted us to undertake chemical investigation of the bark for isolation of the active principles.

The powdered bark of *T. undulata*[5] was extracted in a Soxhlet extractor successively with petroleum ether (b.p. 60–80°), benzene and then chloroform. The chloroform extract responded to tests for glycosides, and on thin layer chromatography showed the presence of 3 components, Rf 0.31, 0.48, 0.61 (SiO_2; solvent, $CHCl_3$: EtOH, 8:2; developer, $Ac_2O:H_2SO_4$:EtOH, 5:5:90). The residue from the chloroform extract on crystallization from alcohol after treatment with activated charcoal yielded a glucoside, mp 218–220°, $[\alpha]_D^{20}$-178 (Pyridine), Rf 0.48. Analysis[6] Found: C, 52.62, 52.94, 53.22, 52.96; H, 5.99, 5.86, 6.22, 6.10. Calcd. for $C_{15}H_{20}O_9$: C, 52.32; H, 5.86. On acetylation with acetic anhydride in presence of anhydrous sodium acetate, the glucoside gave a tetraacetyl derivative, needles, mp 120–124° (CH_3OH), Rf 0.31 (SiO_2, solvent $CHCl_3$). Analysis[6] Found: C, 53.71, 54.80; H, 4.65, 5.96. Calcd. for $C_{23}H_{28}O_{13}$: C, 53.90; H, 5.46. In the mass spectrum[6], the glucoside did not give a molecular ion peak as it did not volatalize at low temperature. At higher temperature (260 °C) the sample probably decomposed. The NMR-spectrum[6] could not be scanned as the glucoside was sparingly soluble in water. The IR-spectrum[6] in Nujol showed many absorption bands including significant absorptions at 3400 ~3200 cm^{-1} (strong and broad due to polymeric OH) and 1720 cm^{-1} (Ar–CO–O–). The glucoside on hydrolysis with dilute alkali yielded glucose and an acid (liberates I_2 from KI-KIO_3 mixture), mp 180–182°. Analysis[6] Found: C, 60.2; H, 6.23. $C_9H_{10}O_4$ requires C, 59.3; H, 5.4. IR-spectrum (in Nujol) of the acid showed a strong peak at 1690 cm^{-1} (Ar-COOH), but no peak due to OH absorption. NMR-spectrum showed prominent peaks at 3.95 δ (Ar-OMe), 6.85 and 6.95 δ (Ar-H) only. Mass spectrum of the acid exhibited a molecular ion peak *m/e* 182 (M^+), together with intense fragment ion peaks

[1] K. R. Kirtikar and B. D. Basu, *Indian Medicinal Plants* (L. M. Basu, Allahabad 1933), vol. 3, p. 1841. – I. C. Chopra, K. K. Handa and L. D. Kapur, *Indigenous Drugs of India*, 2nd edn (U. N. Dhur and Sons Ltd., Calcutta 1958), p. 527.

[2] S. R. Gupta, K. K. Malik and T. R. Seshadri, Ind. J. Chem. *7*, 457 (1969).

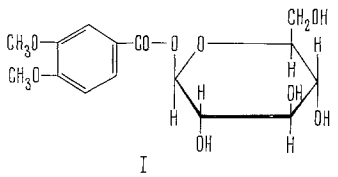
[3] W. Sandermann and H. H. Dietriches, Holz – Roh- u. Werkstoff *15*, 281 (1957).

[4] S. K. Bhattacharya, personal communication.

[5] The bark of *T. undulata* was received from Dr. L. D. Kapoor, National Botanic Gardens, Lucknow.

[6] Microanalyses were carried out by Dr. F. B. Strauss, Microanalytical Laboratory, Oxford (England) and by Central Drug Research Institute Lucknow (India). All IR-, NMR- and Mass-spectra were scanned by National Chemical Laboratory, Poona (India).

at *m/e* 167 (M-Me), 139 (*m/e* 167-CO), 165 (M-OH), 137 ($M\text{-}\overset{+}{O} \equiv$ C-OH), 122 (*m/e* 167-COOH), 121 and 45 ($\overset{+}{O} \equiv$ C-OH). An analysis of the spectral data indicated the presence of -COOH and -OMe groups only in the acid, which was subsequently identified as veratric acid by comparison of mp, mixture mp, and superimposable IR-spectrum with an authentic sample. The glucoside does not contain any free reducing group, is sparingly soluble in water (due to ester linkage), is easily hydrolyzed by emulsin, and exhibits a high negative specific optical rotation. On the basis of this evidence, the glucoside is assigned the structure (I), veratroyl β-D-glucoside and is named as *Tecomin*, as it appears to be new[7].



I

Zusammenfassung. Isolierung und Strukturaufklärung eines neuen Esterglukosides aus der Rinde von *Tecomella undulata*.

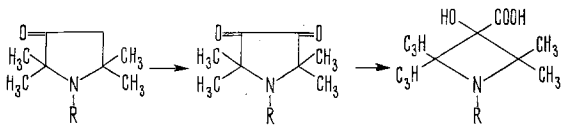
V. B. PANDEY and B. DASGUPTA

Department of Medicinal Chemistry, Research and Post Graduate Institute of Indian Medicine, Banaras Hindu University, Varanasi-5 (India), 27 April 1970.

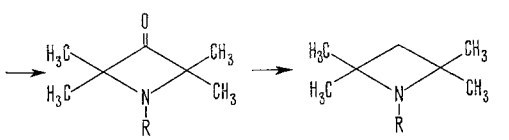
[7] This work was carried out under the Composite Drug Research Scheme, I.C.M.R., New Delhi, and the authors gratefully acknowledge the financial assistance.

Synthesis of 2,2,4,4-Tetramethyl-Azetidine

For a number of years we have been working on the synthesis and pharmacological activities of compounds containing tetramethylated heterocyclic amines, like 2, 2, 6, 6-tetramethyl-piperidine, 1, 2, 5, 6-tetrahydro-2, 2, 6, 6-tetramethyl-pyridine, 2, 2, 5, 5-tetramethyl-pirrolidine and 2, 2, 5, 5-tetramethyl-pyrroline[1,a-f]. In order to complete these lines of research, it was found interesting to have also the unknown 2, 2, 4, 4-tetramethyl-azetidine (XI). As starting compound 1-acetyl-3-hydroxy-2, 2, 4, 4-tetramethyl-3-azetidincarboxylic acid (IV)[2,3], was used in preliminary experiments.



I R = H
II R = COC_6H_5
III R = COC_6H_5
IV R = $COCH_3$
V R = COC_6H_5



VI R = $COCH_3$
VII R = COC_6H_5
VIII R = $COCH_3$
IX R = COC_6H_5
X R = $CH_2C_6H_5$
XI R = H

Compound (VI) was obtained by oxidative decarboxylation of (IV); by reducing the ketogroup a compound identified as (VIII) was obtained. This compound readily underwent hydrolysis under alkaline conditions, but the desired 2, 2, 4, 4-tetramethyl-azetidine was not obtained. Ring opening with development of NH_3, acetic acid and a branched unsaturated hydrocarbon occurred. Since it was necessary to avoid the final hydrolysis of the compound, we protected the cyclic nitrogen by a benzoyl group, which, by reduction, becomes a benzilic group and can thus easily be removed by catalytic hydrogenation. Using this method it was possible to obtain 2, 2, 4, 4-tetramethyl-azetidine. All the compounds were isolated, purified, and their structure assigned by IR- and NMR-spectra (Table).

1-acetyl-2, 2, 4, 4-tetramethyl-3-azetidinone (VI) was obtained according to CHEN et al.[3], by boiling for 5 h the 1-acetyl-3-hydroxy-2, 2, 4, 4-tetramethyl-3-azetidincarboxylic acid (IV)[2,3] with $Pb(CH_3COO)_4$ in CCl_4 (Yield 82%[4], b.p. 106–108 °C/16 mm Hg, mp 41–42 °C; Anal. Calc. for $C_9H_{15}NO_2$ (169.2) C 63.88 H 8.94 *N* 8.28, Found C 62.76 H 8.88 *N* 8.29).

$$\nu_{CO\ ketone} = 1820\ cm^{-1};\quad \nu_{CO\ amide} = 1648\ cm^{-1}.$$

1-acetyl-2, 2, 4, 4-tetramethyl-azetidine (VIII) was obtained by heating the compound (VI) with hydrazine hydrate and KOH in triethylenglicol at 160 °C[5], and subsequently distillation (Yield 65%, b.p. 95–97 °C/16 mm Hg; Anal. Calc. for $C_9H_{17}NO$ (155.2) C 69.65 H 11.04 *N* 9.02, Found C 69.98 H 10.97 *N* 9.03).

$$\nu_{CO\ amide} = 1640\ cm^{-1}.$$

In order to obtain 2, 2, 4, 4-tetramethyl-azetidine by hydrolysis of (VIII), the following experiments were performed: a) acid hydrolysis by boiling with HCl 6*N*: no modifications took place. b) Alkaline hydrolysis by boiling 5 h with KOH 30%[6]. Under these conditions the unmodified compound, together with potassium acetate and molecular fragments not further identified (during the reaction there is development of NH_3) were obtained. c) Alkaline hydrolysis, by heating with anhydrous KOH at 220 °C followed by distillation, gave NH_3, CH_3COOK

[1] a) Belg. Pat. 697,242; b) Belg. Pat. 702,780; c) Belg. Pat. 702,535; d) Belg. Pat. 702,778; e) Belg. Pat. 702,781 (To ERASME); f) Belg. Pat. 724,007 (To CIRM).
[2] C. SANDRIS and G. OURISSON, Bull. Soc. chim. Fr. (*1958*), 354.
[3] T. CHEN, T. SANNJIKI, H. KATO and N. M. OHTA, Bull. chem. Soc. Japan *40*, 2398 (1967).
[4] In [2] there were obtained only small quantities of (VI), in [3] with a Yield of 37%.
[5] US 3020288 (May-Baker Ltd) – CA *57*, 3416g (1962).
[6] In [2] hydrolysis experiments of 2,2,5,5 tetramethyl-3-pirrolidinone were made but without success.