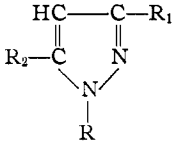
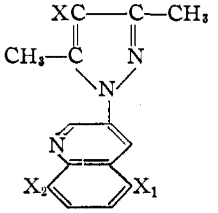
We have recently shown that both the 1-nitroguanyl[1] (I, R = —C(=NH)—$NHNO_2$) and the 1-guanylpyrazoles[2,3] (I, R = —C(=NH)—NH_2) resemble the 1-carbamyl type—being readily susceptible to fission. The 1-heterocyclic pyrazoles have been synthesized for the extension of this comparison. The 1-tetrazolyl compound (I, R = -CHN_4) has been described elsewhere.[4] The present communication deals with the prototype of the 1-(2′-quinolyl) class (I, R = C_9H_6N(2′)).


I


II

With this type of compound, however, at least three isomeric products may be obtained in reaction with cationoid reagents, *e.g.*, in halogenation, substitution may occur at the 4-, 5′- or 8′-position. No kinetic data are available for the accurate orientation of the monohalogenated compounds obtained.

The heterocyclic portion of the 1-quinoline substituent may be considered[5] as a deactivated nucleus toward such reagents; therefore, the competing centers in these halogenations are those of a benzene ring and a pyrazole ring. These centers[6] compete in the halogenation of 3,5-dimethyl-1-phenylpyrazole (I, R_1,R_2 = CH_3, R = C_6H_5) and 1-phenylpyrazole (I, R_1,R_2 = H, R = C_6H_5), and Balbiano[7] reports merely the formation of the 4-halopyrazole in these instances. With the latter compound trihalogenation may be effected to yield 1-phenyl-3,4,5-tribromopyrazole without substituting in the phenyl nucleus.

On the basis of present evidence then the products described below may be allotted the structure (II, X = Cl/Br/I, X_1, X_2 = H). Experiments are at present being undertaken to determine by degradation the unequivocal structure of these materials and, secondly, the proportion of the respective isomers (if any) formed. Irrespective of the final orientation, the experiments described below show that the 1-(2′-quinolyl) substituent approximates to the 1-aryl type in the stability of its attachment to the pyrazole ring.

Experimental[8]

3,5-Dimethyl-1-(2′-quinolyl)-pyrazole (A).—4.35 g. (0.03 mole) of 2-quinolylhydrazine was dissolved in 120 ml. of 95% ethanol and to the solution was added 3.06 ml. (0.03 mole) of acetylacetone. This mixture was refluxed for 3 hours and the dark colored solution obtained, was then evaporated to half-bulk, on a steam-bath. On cooling at 0°, crude A (4.7 g., m.p. 51–56°) separated; the filtrate was diluted with water and a further 1.02 g. of A was obtained. After recrystallization from petroleum ether (b.p. 40–60°) using a little animal charcoal, it was obtained as white needles of m.p. 57°.

Anal. Calcd. for $C_{14}H_{13}N_3$: C, 75.3; H, 5.8; N, 18.8. Found: C, 75.3; H, 6.2; N, 18.5.

It was characterized as its picrate, which after recrystallization from aqueous ethanol, was obtained as an orange micro-crystalline powder of m.p. 159°.

Anal. Calcd. for $C_{20}H_{16}N_6O_7$: C, 53.1; H, 3.5; N, 18.5. Found: C, 53.3; H, 3.6; N, 18.7.

Chlorination of A.—Through a solution of 0.5 g. (0.002 mole) of A, in 5 ml. of dry chloroform was bubbled an excess of dry chlorine. On evaporating the chloroform, after reaction had ceased, 0.48 g. of a yellow crystalline material of m.p. 46–49° was obtained. This was a mixture of the chloro derivative and unreacted A, and after fractional recrystallization from petroleum ether, it was obtained as a white amorphous solid of m.p. 72.5°.

Anal. Calcd. for $C_{14}H_{12}ClN$: C, 65.2; H, 4.7; Cl, 13.8; N, 16.3. Found: C, 64.8; H, 4.6; Cl, 14.1; N, 16.5.

Bromination of A.—To 0.5 g. (0.002 mole) of A, dissolved in 10 ml. of carbon tetrachloride was added 0.115 ml. (0.002 mole) of bromine, with stirring. Some yellow oil separated and on evaporating off the carbon tetrachloride in a stream of air, 0.81 g. of a substance, of m.p. 189–191° was obtained. This bromo-compound (which contained excess bromine) was recrystallized from glacial acetic acid as small feathery needles, of m.p. 108°.

Anal. Calcd. for $C_{14}H_{12}BrN_3$: C, 55.6; H, 3.9; Br, 26.5; N, 13.9. Found: C, 55.6; H, 3.8; Br, 26.6; N, 13.5.

Iodination of A.—To 0.5 g. (0.002 mole) of A, in 50 ml. of glacial acetic acid were added 0.23 g. (0.0014 mole) of potassium iodine and 0.48 g. (0.007 mole) of potassium iodate and an additional 5 ml. of acetic acid. The mixture was refluxed until the very dark color developed initially had lightened to a pale orange-yellow—this took 11 minutes. The inorganic, undissolved solid was then filtered off, and the solution allowed to stand for 24 hours at room temperature. 0.54 g. of material of m.p. 125° separated and a further 0.14 g. was precipitated from the filtrate on the addition of water. *Anal.* Calcd. for $C_{14}H_{12}N_3I$: C, 48.1; H, 3.4; N, 12.1; I, 36.4. Found: C, 48.9; H, 3.5; N, 12.7. I, 35.4.

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(1) F. L. Scott, M. T. Kennedy and J. Reilly, *Nature*, **169**, 72 (1952).

(2) F. L. Scott and J. Reilly, Pyrazoles I, This Journal, **74**, in press (1952).

(3) F. L. Scott, C. M. B. Murphy and J. Reilly, *Nature*, **167**, 1037 (1951).

(4) F. L. Scott, D. G. O'Donovan and J. Reilly, *J. App. Chem.*, in press.

(5) Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, 1949, p. 185. See also Remick, "Electronic Interpretations of Organic Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1949, p. 371.

(6) A closer analogy would have been the halogenation of 3,5-dimethyl-1(2′-(1′-nitro)-naphthyl)-pyrazole or allied substances, Such data are not available.

(7) Balbiano, *Ber.*, **23**, 1452 (1890); Balviano, *Gazz. chim. ital.*, **19**, 128, 133 (1889); see also Severini, *Atti Accad. Lincei* **5**, 1, II, 393 (1892).

(8) Analyses are by Drs. Weiler and Strauss, Oxford, England. All melting points are uncorrected.

Chemistry Department
University College
Cork, Ireland

Synthesis of Lignin Model Compounds

By Biswanath Sen

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The work of Kratzl and co-workers[1,2] on the sulfonation of chalcones and other α,β-unsaturated ketones shows that these compounds are readily sulfonated. However, it is not yet known whether pyran or furan ring formation of the three-carbon side chain would change the reactivity of the α,β-unsaturated ketonic grouping toward bisulfite. With this end in view, the present work describes

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(1) K. Kratzl and H. Daubner, *Ber.*, **77**, 519 (1944).

(2) K. Kratzl, H. Daubner and U. Siegens, *Monatsh.*, **77**, 146 (1947).

model compounds with α,β-unsaturated ketonic groups linking two aromatic nuclei, the three-carbon side chain being open in some but forming part of a heterocyclic ring in others.

The presence of differently substituted benzopyran groups in lignin has been postulated from time to time. Several model compounds containing substituted benzopyran groups have been studied in the past as to their behavior toward bisulfite, but more work in this direction is desirable. The present work also describes the syntheses of several similar model compounds, whose behavior toward bisulfite may be significant.

The following model compounds have been synthesized in order to compare their behavior with that of lignin: 2-vanilloylbenzofuran, 2-vanillylidene-3-coumaranone, 3-methoxy-2′,4-dihydroxychalcone, 3′-methoxy-4′-hydroxyflavone, 3′-methoxy-2,4′-dihydroxychalcone, 3′-methoxy-4′-hydroxyflavylium chloride, 3′-methoxy-4′-hydroxyflavanone and 3′-methoxy-4,4′-dihydroxyflavan.

Experimental

2-Vanilloylbenzofuran.—To a solution of 12.2 g. of salicylaldehyde and 276 g. of ω-bromoacetovanillone acetate[3] in 100 ml. of absolute ethanol was added 14 g. of anhydrous potassium carbonate, and the mixture was boiled for one hour on the steam-bath. The mixture was poured into excess water and the precipitated oil extracted with ether. The ether solution, after drying with anhydrous sodium sulfate, was evaporated to a viscous residue which distilled with partial decomposition at 250° and 7–10 mm.; on repeated recrystallization from dilute ethanol it gave 3.2 g. of pure 2-vanilloylbenzofuran acetate, m.p. 126–127°. *Anal.* Calcd. for $C_{18}H_{14}O_5$: C, 69.7; H, 4.5; MeO, 10.0. Found: C, 69.7; H, 4.6; MeO, 10.6. Refluxing 2 g. of 2-vanilloylbenzofuran acetate in 50 ml. of ethanol with 5 ml. of concd. hydrochloric acid for 12 hours on a steam-bath, evaporating the solution to half its volume and diluting it with water gave 1 g. of 2-vanilloylbenzofuran; white crystals from dilute ethanol, m.p. 137.5–138.5°. *Anal.* Calcd. for $C_{16}H_{12}O_4$: C, 71.6; H, 4.5; MeO, 11.6. Found: C, 71.7; H, 4.6; MeO, 11.6.

Because of the low over-all yield, an alternative procedure was developed starting from ω-bromoacetovanillone benzyl ether, which was prepared by benzylation of acetovanillone and bromination of the resulting acetovanillone benzyl ether. After this synthesis was completed, Leopold[4] reported a similar preparation of ω-bromoacetovanillone benzyl ether. To a solution of 4 g. of ω-bromoacetovanillone benzyl ether and 3 g. of salicylaldehyde in 50 ml. of absolute ethanol, 1.5 g. of anhydrous potassium carbonate was added and the reaction mixture was refluxed for two hours on the water-bath. The reaction mixture was poured into excess water, extracted with ether, and the ether extract washed with dilute sodium hydroxide solution and water and dried over anhydrous sodium sulfate. Evaporation of the ether yielded a residue which, when recrystallized from dilute ethanol, gave 3.8 g. of white crystals, m.p. 119–120°. *Anal.* Calcd. for 2-vanilloylbenzofuran benzyl ether, $C_{23}H_{18}O_4$: C, 77.1; H, 5.0; MeO, 8.7. Found: C, 77.1; H, 5.2; MeO, 9.0. A solution of 1.4 g. of 2-vanilloylbenzofuran benzyl ether in 100 ml. of ethyl acetate was shaken with 1 g. of 10% palladium-on-activated charcoal under hydrogen at 26° and 50 pounds pressure for 15 minutes. The catalyst was filtered and the solution was extracted with dilute sodium hydroxide solution. The alkaline extract was cooled with crushed ice and acidified with hydrochloric acid, giving 0.7 g. of 2-vanilloylbenzofuran, m.p. 137.5–138.5°.

2-Vanillylidene-3-coumaranone.—To a solution of 14.2 g. of 3-coumaranone[5] and 15.8 g. of vanillin in the minimum amount of absolute ethanol at 50–60°, 10 ml. of concd. hydrochloric acid was added dropwise, whereby an orange-yellow crystalline product separated. This was filtered, washed with dilute alcohol, and recrystallized from chloroform–methanol mixture and then from dioxane to give 15.5 g. of 2-vanillylidene-3-coumaranone; orange needles, m.p. 206–207°. *Anal.* Calcd. for $C_{16}H_{12}O_4$: C, 71.6; H, 4.5; MeO, 11.6. Found: C, 71.6; H, 4.6; MeO, 11.5. The methyl derivative, prepared with dimethyl sulfate and alkali, melted at 158–160°. 2-Veratrylidene-3-coumaranone was also prepared according to Freudenberg and co-workers,[6] who reported the m.p. to be 150°, by condensing veratraldehyde with 3-coumaranone. It mixed m.p. with the above methyl derivative was 158–160°.

3-Methoxy-2′,4-dihydroxychalcone.—The method of Russell and Todd[7] for the preparation of this compound was modified as follows: To a solution of 15.2 g. of vanillin and 13.6 g. of *o*-hydroxyacetophenone in 50 ml. of ethanol, cooled to 0°, was added with stirring 75 ml. of a 60% potassium hydroxide solution, also cooled to 0°. The mixture was kept for seven days at room temperature with occasional shaking. Crushed ice was added to the bright orange mixture, which was then acidified (congo red) with 6 *N* hydrochloric acid. The oily precipitate was extracted with ether, washed with a saturated solution of sodium bisulfite, and subjected to a steam distillation. The residue was recrystallized from dilute ethanol to give 12 g. of 3-methoxy-2′,4-dihydroxychalcone, whose m.p. and mixed m.p. with an authentic sample prepared by Russell and Todd's method was 129°.

3′-Methoxy-4′-hydroxyflavone.—To a solution of 2 g. of 3-methoxy-2′,4-dihydroxychalcone in 15 ml. of anhydrous pyridine, 8 ml. of acetic anhydride was added, and the mixture kept overnight at room temperature. On pouring the reaction mixture into excess of ice-water, a precipitate was obtained, which was washed with dilute hydrochloric acid and with water. Recrystallization from 95% ethanol gave 2.35 g. of 3-methoxy-2′,4-diacetoxychalcone, pale yellow crystals, m.p. 133°. *Anal.* Calcd. for $C_{20}H_{18}O_6$: C, 67.8; H, 5.1; MeO, 8.8. Found: C, 67.9; H, 5.1; MeO, 9.0.

A solution of 1.1 g. of bromine in 10 ml. of dry chloroform was added dropwise to 2.35 g. of 3-methoxy-2′,4-diacetoxychalcone dissolved in 20 ml. of dry chloroform at room temperature. The solvent was completely evaporated on the steam-bath giving a solid residue which, when recrystallized several times from dilute acetone, yielded 3-methoxy-2′,4-diacetoxychalcone dibromide; white crystals, m.p. 170–171°. *Anal.* Calcd. for $C_{20}H_{18}O_6Br_2$: C, 46.7; H, 3.5; Br, 31.1. Found: C, 46.9; H, 3.7; Br, 31.0.

3-Methoxy-2′,4-diacetoxychalcone dibromide (1 g.) in 20 ml. of ethanol was heated on the steam-bath and 10 ml. of 60% aqueous potassium hydroxide was gradually added. After heating on the steam-bath for 15 minutes, the solution was cooled, acidified with dilute hydrochloric acid, and kept in the refrigerator; the yellow crystals which separated were recrystallized twice from dilute ethanol, giving 3′-methoxy-4′-hydroxyflavone, m.p. 194–195°. *Anal.* Calcd. for $C_{16}H_{12}O_4$: C, 71.6; H, 4.5; MeO, 11.6. Found: C, 71.5; H, 4.6; MeO, 11.6.

3′-Methoxy-2,4′-dihydroxychalcone.—To a solution of 12.2 g. of salicylaldehyde and 16.6 g. of acetovanillone, cooled to 0°, was added with stirring 75 ml. of 60% potassium hydroxide (also cooled to 0°) and the mixture was kept for five days at room temperature. It was then poured into an excess of ice water, acidified with 6 *N* hydrochloric acid, and the precipitate was extracted with ether. The ether solution was washed with sodium bisulfite solution, dried over anhydrous sodium sulfate, and evaporated to a sirupy residue. This was triturated with a little ethanol to yield brownish crystals, which were filtered and recrystallized repeatedly from dilute ethanol. The product had no sharp m.p., and on slow heating it gradually intensified in color and finally melted to a deep blue liquid at 152–157°. The benzoyl derivative was prepared by the Schotten–Baumann method and was purified by recrystallization from ethanol to yield 3′-methoxy-2,4′-dibenzoxychalcone; white crystals, m.p. 146.5–147.5°. *Anal.* Calcd. for $C_{30}H_{22}O_6$: C, 75.3; H, 4.7. Found: C, 75.4; H, 4.8.

3′-Methoxy-4′-hydroxyflavylium Chloride.—A solution of 1.5 g. of a fairly pure 3′-methoxy-2,4′-dihydroxychalcone in

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[3] L. Brickman, W. Hawkins and H. Hibbert, *Can. J. Research*, **19B**, 24 (1941).

[4] Leopold, *Acta Chem. Scand.*, **4**, 1523 (1950).

[5] K. Fries and W. Pfaffendorf, *Ber.*, **43**, 212 (1910).

[6] K. Freudenberg, H. Fikentscher and M. Harder, *Ann.*, **441**, 157 (1925).

[7] A. Russell and J. Todd, *J. Chem. Soc.*, 421 (1937).

15 ml. of glacial acetic acid was cooled in an ice-bath and dry hydrogen chloride was passed through the solution for ten minutes. The intense red solid which separated was filtered by suction, and recrystallized from 70% ethanol saturated with hydrogen chloride. Addition of a 7.5% ferric chloride solution in glacial acetic acid to 3′-methoxy-4′-hydroxyflavylium chloride in the same solvent gave 3′-methoxy-4′-hydroxyflavylium ferrichloride, glistening crystals from glacial acetic acid. *Anal.* Calcd. for $C_{16}H_{13}O_3Cl \cdot FeCl_3$: Fe, 12.4. Found: Fe, 12.6.

3′-Methoxy-4′-hydroxyflavanone.—To a solution of 5 g. of 3′-methoxy-2′,4-dihydroxychalcone in 150 ml. of ethanol, heated on the steam-bath, a 3% hydrochloric acid solution was added slowly until a permanent turbidity appeared. The solution was refluxed for 24 hours and cooled, causing the separation of pale yellow crystals. These were filtered, decolorized with charcoal, and recrystallized several times from absolute ethanol, and finally from dry ethyl acetate to give 3′-methoxy-4′-hydroxyflavanone; white crystals, m.p. 171–172°. *Anal.* Calcd. for $C_{16}H_{14}O_4$: C, 71.1; H, 5.2; MeO, 11.5. Found: C, 71.2; H, 5.3; MeO, 11.8.

3′-Methoxy-4,4′-dihydroxyflavan.—3′-Methoxy-4′-hydroxyflavanone (20 g.) and 5 g. of aluminum isopropoxide were covered with 150 ml. of absolute isopropyl alcohol in a round-bottom flask fitted with a short reflux condenser to which was attached another small condenser set for distillation. The solution was refluxed on the steam-bath with no water passing through the reflux condenser. The rate of distillation was 5 drops per minute. A positive test for acetone in the distillate given by 2,4-dinitrophenylhydrazine reagent showed that the reduction of the carbonyl group to the secondary alcoholic group was proceeding. The distillation was continued for about 30 hours, until the distillate, after refluxing for five minutes with water passing through the reflux condenser, gave a negative test for acetone. Most of the isopropyl alcohol was then removed under reduced pressure, and the cooled residue was hydrolyzed with cold dilute hydrochloric acid solution. The yellow crystalline product which separated was filtered, dried, and leached with hot petroleum ether (b.p. 60–110°), giving a white residue. Repeated recrystallizations from dilute ethanol gave 3′-methoxy-4,4′-dihydroxyflavan monohydrate; white needles, m.p. 160–161°. This m.p. was obtained when the temperature of the melting point bath was raised very gradually but, if the rate of heating was fast, the compound melted at a much lower temperature. Analytical values show that the compound retains water of crystallization unless dried under special conditions. *Anal.* Calcd. for $C_{16}H_{16}O_4 \cdot H_2O$: C, 66.2; H, 6.2; MeO, 10.7. Found after drying the compound over phosphorus pentoxide for three hours at 60° and 2 mm. pressure: C, 67.1; H, 6.3; MeO, 11.1. Calcd. for $C_{16}H_{16}O_4$: C, 70.6; H, 5.9. Found after drying the compound for eight hours over phosphorus pentoxide at 11° and 1 mm. pressure: C, 70.6; H, 6.0.

The diacetyl derivative of the above compound was prepared by adding 2 ml. of acetic anhydride to a solution of 0.1 g. of 3′-methoxy-4,4′-dihydroxyflavan in 5 ml. of anhydrous pyridine and keeping the solution overnight at room temperature. On dilution with 50 ml. of ice-water, crystals separated which washed with dilute hydrochloric acid and water and recrystallized from ethanol, gave 3′-methoxy-4,4′-diacetoxyflavan, white crystals, m.p. 121.5–123°. *Anal.* Calcd. for $C_{20}H_{20}O_6$: MeO, 8.9. Found: MeO, 8.7.

THE INSTITUTE OF PAPER CHEMISTRY
APPLETON, WISCONSIN

Investigations on Lignin and Lignification. X. The Isolation and Characterization of the Native Lignin from *Kiri* Wood

BY GEORGE DE STEVENS AND F. F. NORD

RECEIVED FEBRUARY 28, 1952

Previous work from this Laboratory[1,2] has established that the native lignin isolated from some woods by the method of Brauns[3] is representative of all the lignin present therein. Furthermore, our investigations have revealed that lignins differ not only from species to species, but also within the same species.[4] As an extension to our studies, we have selected to study the lignin from the Japanese tree, *Paulownia tomentosa*, otherwise known as "kiri" wood. To date, nothing has been reported in the literature on the nature of this lignin. Kiri native lignin was isolated in 0.2% yield with ethyl alcohol at room temperature. This lignin was obtained as a white amorphous powder, and the results of its characterization are recorded in Table I.

TABLE I

CHEMICAL COMPOSITION OF KIRI NATIVE LIGNIN

C, %	60.1
H, %	6.2
OCH_3, %	16.6
Acetate, OCH_3, %	13.5
Phenylhydrazone, OCH_3, %	15.2

Kiri native lignin was found to be soluble in methanol, ethanol, dioxane, 1% sodium hydroxide, pyridine, acetone and glacial acetic acid, but was insoluble in petroleum ether, benzene, ether and water. It reduced Fehling solution and gave positive color tests with phloroglucinol–hydrochloric acid and with the phenol reagent.

In Fig. 1 is presented the infrared absorption spectrum of kiri native lignin. It can be readily seen that it exhibits a marked similarity to the infrared spectra of other native lignins isolated in this Laboratory.[1–3,5]

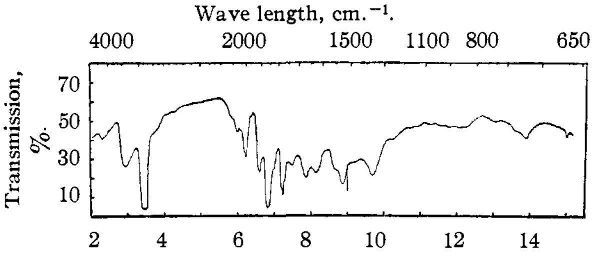

Fig. 1.—Spectrum of kiri native lignin.

Its ultraviolet absorption spectrum is shown in Fig. 2. It is similar to the absorption curves of other native lignins in that it gives an absorption peak at 282 mμ. However, the plateau from 295 to 320 mμ is quite unique.

Finally, kiri native lignin was compared with kiri lignins isolated with the aid of 10% alkali and 72% sulfuric acid. The data of this comparison are listed in Table II.

TABLE II

COMPARISON OF THE NATIVE AND CHEMICAL LIGNINS FROM KIRI WOOD

Lignin	C, %	H, %	OCH_3, %
Native	60.1	6.2	16.6
72% H_2SO_4	61.2	5.6	18.0
10% NaOH	60.9	5.7	17.4

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[1] W. J. Schubert and F. F. Nord, THIS JOURNAL, **72**, 977, 3835 (1950).

[2] G. de Stevens and F. F. Nord, *ibid.*, **73**, 4622 (1951).

[3] F. E. Brauns, *ibid.*, **61**, 2120 (1939).

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[5] S. F. Kudzin and F. F. Nord, *ibid.*, **73**, 4619 (1951).