Studies on Pitch Problems Caused by Pulping and Bleaching of Tropical Woods. XIV.* Chemistry of the Aurone Derivatives at the Conventional Bleaching Stages

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Rengasin (*1*), which is responsible for the colored specks on a sheet of bleached sulfate pulp from the woods of rengas (*Anacardiaceae*), was converted into R_1 *7* having a novel carbon skeleton. A closely related analogue, S_1 *8*, prepared from sulfuretin (*2*) was used as a model to investigate further conversions under bleaching conditions. Chlorination of S_1 *8* produced an equilibrium mixture involving compound *9* as a dominant compound. The latter was transformed by the treatment with chlorine dioxide into an ortho-quinone (*16*) via two pathways containing *10* in one and *15* in another. The monomeric quinone (*16*) immediately dimerized in acidic media to give *20* under the same conditions as above, and the further oligomerization by the process similar to that in dimerization of *16* finally afforded a mixture of colored oligomers *26*.

Some characteristic phenomena as regards the formation of brown pitch specks on sheets of bleached sulfate pulps (BKP) from rengas wood (*Gluta* or *Melanorrhoea* sp., *Anacardiaceae*) grown in Sarawak and their exclusion from the pulps were mentioned in our previous papers.^{1,2} Rengasin (*1*) responsible for the brown specks was chemically converted during the alkaline cooking and subsequent bleaching stages into the final colored specks, while the latter were effectively removed by application of a phase transfer catalyst to the alkaline extraction stage in the conventional multistage bleaching. This proves that all the conversion reactions of rengasin (*1*) proceeded in

the interior of the neutral hydrophobic membrane formed with the components of wood extractives. As for the chemical conversion of rengasin (*1*) during the cooking stage, 4-methoxy-6-hydroxy-coumaranone (*3*), protocatechualdehyde (*5*), and an intermediate R_1 (*7*) were isolated from the pulp extractives but not from the wood extractives. This seems to indicate the presence of a thermal equilibrium³ among these compounds which is slightly different from the scheme shown in Fig. 1. Sulfuretin (*2*) is not only a closely related derivative of rengasin (*1*) but also responsible for colored pitch specks on sheets of BKP from the wood of sepetir paya (*Pseudosindora palustris*).⁴ Sulfuretin also affords intermediate S_1 *8*⁵ as a component of an equilibrium system similar to that involving R_1 *7* formed from rengasin (*1*). In the present paper, therefore, intermediate S_1 *8* was adopted as one of the aurones to elucidate the mechanism for the formation of colored specks during the bleaching stages, since S_1 can be synthesized more readily than R_1 . Although the colored specks can be produced by treatment with chlorine dioxide (ClO_2) alone, it has been suggested¹ that chlorination prior to the ClO_2 treatment plays an important role in making stable colored specks. The chlorination of S_1 will be discussed first under these considerations.

RESULTS AND DISCUSSION

Treatment of S_1 8 with chlorine. Although chlorination of *8* at 25 °C was found to be nearly completed within twenty minutes as confirmed by thin layer chromatography (TLC), the reaction was

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Fig. 1. Acid-catalyzed equilibria between aurones (1, 2 and 10) and coumaranone adducts (7, 8 and 9).

continued for a further twenty minutes. The resulting products were chromatographed on a silica-gel column to separate into seven fractions. The contributing yields and ratios¹ of the individual fractions to the total speck area are shown in Table 1. Fractions 2 and 3 were crystallized and identified as 6-hydroxy-coumaranone (4) and 5-chloro-protocatechualdehyde (6), respectively. In another experiment, the authentic sample of 6 for identification was synthesized by chlorination of protocatechualdehyde (5). Fraction 4, showing the highest yield as well as the highest contributing ratio, also gave crystalline compound 9 whose mass spectrum and elemental analysis are consistent with molecular formula $\text{C}_{23}\text{H}_{15}\text{O}_8\text{Cl}$. Its mass fragmentation pattern was quite similar to that of S_1 8 and R_1 7³ and, therefore, suggested the presence of a chlorine atom in the B-ring of the same carbon

skeleton as that of S_1 8. Spectral data obtained by ^{13}C nuclear magnetic resonance (CMR) of acetates 11, 13, 12 and 14, all of which have been prepared by acetylation of 2, 8, 5'-chloro-sulfuretin (10), and 9, respectively, are summarized in Table 2 and their numbering system is given in Fig. 2. Assignments of

Table 2. Comparison of ^{13}C NMR spectral data (ppm from TMS) of the acetates 11, 12, 13, and 14 in $\text{DMSO}-d_6$.

Carbon	11	12	13	14
2	146.80	147.77	151.67	151.71
3	182.18	182.18	143.20	143.19
3a	124.20	127.71	120.42	120.41
4	125.24	125.66	130.96	131.22
5	110.50	107.47	119.27	119.47
6	166.00	166.26	148.38	148.53
7	107.21	104.66	117.93	118.06
7a	167.88	166.96	148.40	148.54
α	118.35	118.00	106.05	106.09
1'	142.17	142.17	134.62	135.62
2'	125.85	124.38	123.90	122.05
3'	143.08	143.08	141.50	143.72
4'	157.40	157.78	141.99	139.61
5'	129.75	148.30	123.90	142.61
6'	130.41	130.46	112.76	127.34
2''	—	—	151.67	151.71
3''	—	—	143.20	143.19
3a''	—	—	120.42	120.41
4''	—	—	130.96	131.22
5''	—	—	119.27	119.47
6''	—	—	148.38	148.53
7''	—	—	117.93	118.06
7a''	—	—	148.40	148.54

Table 1. Yields and contribution ratios of each fraction separated from the chlorinated mixture of 8 to the total speck areas.

Fraction number	Compound	A ^a	B
1		8.6	5.8
2	4	19.7	17.1
3	6	13.7	15.3
4	9	29.2	35.8
5		3.3	3.5
6		8.7	10.1
7		11.6	12.4

^aA, Yield (weight percent to the total chlorinated mixture). B, Contribution ratio to the total speck areas (percent).

Fig. 2. The acetates of the compounds 2, 10, 8 and 9.

the signals were carefully made in reference to the CMR spectral data with those of aurone derivatives⁶ and flavone derivatives.⁷ All of the signals due to 23 carbons of 14 show δ -values almost identical with those of 13 but one due to 5'-carbon. The latter signal demonstrates a remarkable down-field shift compared to the corresponding signal for 13, which is nearly in accordance with a difference in resonance field between the 5'-carbon signals of 11 and 12. However, the unusually high down-field shift caused by the substituted chlorine atom is known as a characteristic feature of a tri-substituted B-ring.⁸ The above results are, therefore, consistent with structure 14. A further evidence for structure 9 was provided by the alkaline fission of the compound to afford 6-hydroxy-coumaranone (4) and 5'-chloro-sulfuretin (10). The fission mode is in good agreement with those of R₁ 7³ and S₁ 8.⁵ The authentic sample of 5'-chloro-sulfuretin (10) for identification was synthesized independently by condensation of 6-hydroxy-coumaranone (4) with 5-chloro-protocatechualdehyde (6) in the usual manner. In the light of the accumulated spectral and chemical evidence, structure 9 was assigned to the major chlorination product from S₁ 7.

Since the chlorination mixture at 25 °C was confirmed to contain 4 and 6 together with 9, an equilibrium shown in Fig. 1 must be established. In this case, however, 5'-chloro-sulfuretin (10) was not detected in spite of our expectation. As has been

already mentioned,³ a methanolic solution of 4 and 5, which was adjusted to pH 2.5 by adding hydrochloric acid at room temperature, gave S₁ 8 in a 15% yield. When a methanolic solution of 6-hydroxy-coumaranone (4) and 5-chloro-protocatechualdehyde (6) was treated in the manner as mentioned above, it afforded 10 and 9 in 13.4 and 9.1% yields, respectively. These findings actually indicate the presence of an equilibrium during the chlorination as shown in Fig. 1, and allow one to propose that 10 produced in a low yield on chlorination of S₁ 8 immediately undergoes the addition of chlorine to its double bond, followed by an oxidative cleavage. As shown in Fig. 1, however, the equilibrium system in acidic media at the present low temperature must involve some other reaction pathway different from that in neutral media at 170 °C shown in our previous paper.⁵ In any case, occurrence of the equilibrium may be primarily attributed to the somewhat sterically unstable nature of bonds around the tertiary carbon atoms placed at the center of the molecules, 8, 7 and 9.

Chlorine dioxide treatment of 9. Chlorine dioxide prepared as a bleaching agent in the laboratory as well as in the bleach plant generally contains a few percent of chlorine⁹ which lowers the pH of bleaching liquor to about 4.0–4.5, and the reaction temperature is usually maintained at 60 °C.

When a methanolic solution of 9 (1.0 mmol) was adjusted by dilute hydrochloric acid to pH 4.0 and kept at 60 °C for ten to ninety minutes, the resulting mixture afforded *ca.* 0.5 mmol of 10, 0.4 mmol of 9, and 0.4 mmol of 4 regardless of duration of the reaction. The constant yields of the above compounds, therefore, prove that a certain equilibrium is achieved immediately at that temperature. However, the equilibrium thus attained is in favor of the formation of 10 relative to the case when S₁ 8 is chlorinated at such a low temperature and pH. As mentioned in the previous section, 5'-chloro-sulfuretin (10) cannot be obtained by direct chlorination of sulfuretin (2) but only by a splitting reaction from 9 at the stage of ClO₂ treatment.

When 9 was treated with ClO₂ in *t*-butanol–water for ten minutes at 60 °C, the reddish quinoid compound (15) was furnished in a yield of 18.2%. Its IR¹⁰ and UV spectra¹¹ indicate an ortho-quinone structure. Reduction of 15 with sodium borohydride (NaBH₄) afforded 9 as a sole product. The quinoid compound is, therefore, formulated as 15. When 15 was further treated at

Fig. 3. Transformation of 9 to 16 in the reaction media with ClO_2 .

60 °C in weakly-acidic media, it underwent a fission to give 6-hydroxy-coumaranone (4) along with the formation of another reddish product. The latter was also confirmed to be an ortho-quinone by spectral data and reduced with NaBH_4 to afford 10. Accordingly, the second quinone must have structure 16.

On the other hand, compound 16 was also obtained in a relatively high yield by oxidation of 10 with ClO_2 . After all, a major fraction of 9, the dominant product on chlorination of S_1 , can be transformed into 16 by the treatment with ClO_2 via the two different pathways as shown in Fig. 3. In other words, as a result of the complete chemical conversion of 2 caused by cooking during the bleaching process, an important intermediate (16) was produced in a comparatively high yield. While 16 is stabilized by the chlorine substituent¹² at 5'-position, it can be subjected further to an acid-catalyzed oligomerization by treatment with ClO_2 . However, the intermediate (16) used for the experiments in later sections was prepared by oxidation of 10 with sodium metaperiodate (NaIO_4),¹³ because ClO_2 oxidation of 10 was accompanied by some undesirable reactions.

Reaction of 16 in weakly-acidic media. A further reaction of 16 in weakly-acidic media at 60 °C afforded four products as confirmed by TLC of the reaction mixture. Quantitative analysis of these products at various lengths of reaction time was performed by using a chromato-scanner. The products were designated as I–IV on the basis of the magnitude of R_F values on TLC in a decreasing order, IV being zero. The changes in yields of these components are shown in Fig. 4. While the starting material (16) rapidly decreases within five minutes,

III appeared instantaneously and increased until the elapse of thirty minutes, and decreased gradually thereafter. In contrast, the reddish product (IV) increased slowly. In fact, the direct conversion of III to the final product (IV) was achieved under the same conditions as above and this proves that the former is one of the major precursors for the latter. The chemical structure for III is to be discussed in the next section. Component II, which appeared fifteen minutes after the initiation of reaction, was obtained but in a low yield and identified as 10. This suggests the occurrence of some intermolecular oxidation-reduction, though the detail is still unknown.

Fig. 4. Change in the yields of I, III and IV obtained from the reaction mixture of 16.

Fig. 5. The dimer III 20 and the derivatives.

The chemical structure for III. The reddish crystalline compound (III) obtained by reaction of 16 in weakly-acidic media, is taken as the direct precursor for the final product (IV). However, III is unfortunately too labile in the free form to be purified. The compound (III) was, therefore, reduced with NaBH_4 , and then acetylated with acetic anhydride and pyridine to afford 17. Its FD and CMR spectra indicated that the product has a carbon skeleton of 5'-chloro-sulfuretin (10). On the basis of its ^1H NMR spectrum (PMR), which revealed signals due to two vicinal methine protons, chemical structure 17 was assigned to the acetate. To confirm this, reduction product 18 from III was methylated with dimethyl sulfate and potassium carbonate in acetone, and the resulting methyl ether 19 (420 mg) was ozonized. This was followed by decomposition of the ozonide with hydrogen peroxide and acetic acid to afford 38 mg of 4-

methoxy-salicylic acid (23), 23 mg of 2,4-dimethoxybenzoic acid (24), and 135 mg of an unknown mixture. The latter mixture was, therefore, oxidized further with alkaline permanganate and yielded solely 10 mg of 5-chloro-veratric acid (25). As shown in Fig. 5, 23, 24 and 25 must originate from rings A, A' and B' of 19, respectively. The extent of yields and that of procurement of the acids under the experimental conditions may allow structure 19 to be satisfactorily assigned to the methyl ether, and hence, structure 18 to the reduction product from III. This leads to confine possible chemical structures for III, an ortho-quinonoid compound, to 20 and 20'. It is conceivable that structure 20' accounts better than 20 for the ready reduction to 17, but it may not for the stable feature toward an oxidant, ClO_2 . However, III afforded a phenylenediamine adduct 21 under mild conditions and the latter produced a stable crystalline acetate

Fig. 6. Degradation of the methyl ether 19.

Fig. 7. Condensation of 16 via the dimer 20 to the final oligomers 26.

(22). The PMR spectrum of the crystalline acetate revealed proton signals due to two acetoxyl groups and one methine proton, as a singlet, fully corresponding to structure 22. The elemental analysis was also consistent with 22. Based on the findings mentioned above, structure 20 for III is preferred to 20'.

It has been generally realized that the ortho-quinone undergoes two types of condensation reactions, one is the diene addition^{13,14} between two quinone rings through the Diels-Alder process, and another is the formation of benzodioxene derivatives.¹⁵⁻¹⁷ However, the third type of intermolecular condensation through acid-catalyzed oxidation-reduction between a quinone and a phenolic moiety has been reported very recently from our laboratory.¹⁸ Therefore, the formation of the dimer (20) apparently belongs to the second type which is also an acid-catalyzed condensation as shown in Fig. 7. Nevertheless, the PMR spectrum of impure dimer III disclosed signals corresponding to those of methine protons,¹⁴ which may be derived from the products furnished by the first type of reaction. Therefore, dimer III, having difficulty in purification, may be contaminated by a small amount of dimers produced by the Diels-Alder process.

The colored oligomers, IV. The elemental and chlorine analyses of the final product (IV) separated by column chromatography proved that the elemental composition was in good agreement with that of 16. The UV and IR spectra of IV are quite similar to those of 20. Reduction of IV with NaBH₄ followed by acetylation gave the product, whose CMR spectrum is almost identical with that of 17 and particularly indicates signals referred to β , γ , and δ carbons. The numbering system for the skeletal carbon atoms of 17 is shown in Fig. 5. The

colored substance (IV) apparently consists of a mixture of oligomers of 16. The oligomerization seems to proceed by the same process as dimerization of 16 to give 20. This leads us to postulate structure 26 for IV as shown in Fig. 7. However, the gel-permeation chromatogram of 26 indicated the molecular weights of the predominant fractions to be about 1500–2000, corresponding to the pentamer or hexamer of 16. Accordingly, the color of IV is developed only from the terminal ortho-quinone in 26.

It must be emphasized again that the complete chemical conversions mentioned above proceed in the interior of the neutral hydrophobic membrane, through which chlorine and ClO₂ penetrate.¹⁹ The final oligomers (26) are almost insoluble in many organic solvents, in a manner similar to that observed for the colored specks which appeared on sheets of BKP from the wood of rengas as well as sepetir paya.⁴ The oligomers (26) and conceivable analogues 27 originated from rengasin 1 are, therefore, suggested to constitute one of the major parts of the colored specks in the pulps from sepetir paya and rengas, respectively.

CONCLUSION

The chemical conversions of S₁ 8 to the final colored oligomers (26) occurred through bleaching reactions were discussed. The dominant product (9) at the chlorination stage is transformed *via* two pathways into 5'-chloro-sulfuretin quinone (16) as the major product at the early stage of ClO₂ treatment. However, the monomeric quinone (16) readily undergoes condensation in acidic media to the dimer (20) and then gradually to the final colored oligomers (26) at the later stage of ClO₂ treatment.

The latter (26) and its plausible analogues 27 are suggested to be one of the major constituents of the colored specks in BKP's from the woods of *sepetir paya* and *rengas*, respectively.

EXPERIMENTAL

Synthesis of S_1 8. This was prepared by the method used for the synthesis of R_1 7.³ The product obtained by the treatment of the compounds (4) and (5) with 0.5 N HCl-methanol (MeOH) was chromatographed on silica-gel column (benzene – ethyl acetate – formic acid = 10:4:1, designated as solvent A) to afford the fraction, recrystallization of which from MeOH furnished S_1 8. (Yield 11.0%, m.p. (d.p.) 275 °C.

Chlorination of S_1 8. S_1 8 (2.0 g) was dissolved in 200 ml of *t*-butanol (*t*-BuOH), to which 200 ml of aqueous chlorine solution (24 mmol) was added under stirring. After 40 min the solution was neutralized and evaporated to small volume under reduced pressure and the residual solution was extracted with ethyl acetate (EtOAc). The EtOAc solution was washed sufficiently with water and then evaporated to dryness. The residue (2.4 g) was separated on a silica-gel column (solvent A) into seven fractions. Each fraction was subjected to determination of the contributing ratio to the total speck area according to the previous method.¹ Among them Fraction 2 was recrystallized from MeOH to afford orange plates (260 mg), having m.p. 245–247 °C. This was identified as 6-hydroxy-coumaranone (4) by comparing the m.p. mixed m.p., and IR spectra with those of the authentic sample. Fraction 3 was recrystallized from MeOH – H_2O to afford white powder (150 mg), m.p. 228–230 °C. MS: 172 (M). Found: C 48.46; H 3.12. Calc. for $C_7H_5O_3Cl$: C 48.52; H 2.91. UV [abs. MeOH (log ϵ)]: 240 (3.18), 291 (3.12), 328 (2.88) nm. IR (KBr): 1640, 1590, 770 cm^{-1} . 1H NMR ($CDCl_3$): δ 9.73 (1H, s, CHO), 7.37 (1H, d, *J* 2.0 Hz), 7.28 (1H, d, *J* 2.0 Hz). The results and direct comparison to the authentic sample confirmed the identity with 5-chloro-protocatechualdehyde (6).²⁰ The authentic sample (6) was prepared by direct chlorination of the compound (5) in *t*-BuOH – H_2O followed by chromatography on silica-gel column (solvent A) (yield 12%). Fraction 4 was recrystallized from MeOH to afford white powder 9 (550 mg), m.p. over 270 °C. MS: 454 (M), 304, 269, 168, 150, 121. Found: C 59.12; H 3.21. Calc. for $C_{23}H_{15}O_8Cl \cdot 1/2 H_2O$: C 59.55; H 3.48. UV [abs. MeOH (log ϵ)]: 230 (4.27), 276 (4.15), 317 (3.95) nm. IR (KBr): 1680, 1590, 1420, 800 cm^{-1} . 1H NMR ($DMSO-d_6$): δ 3.42 (1H, q, *J* 8 Hz, H_α), 5.08 (2H, d, *J* 8 Hz, $H_{2,2'}$), 6.30 (2H, d, *J* 2 Hz, $H_{7,7'}$), 6.46 (1H, d, *J* 2 Hz, H_2), 6.52 (2H, dd, *J* 8

Hz, $H_{5,5'}$), 7.06 (1H, d, *J* 2 Hz, H_6), 7.40 (2H, s, *J* 8 Hz, $H_{5,5'}$).

The compound (9) was acetylated with acetic anhydride and pyridine to produce the acetate, which was recrystallized from isopropyl ether to afford white crystalline powder 14, m.p. 168–170 °C. MS: 706 (M). Found: C 54.23; H 3.98. Calc. for $C_{23}H_{19}O_2Cl(OCOCH_3)_6$: C 54.54; H 3.85. UV [abs. MeOH (log ϵ)]: 254 (4.15), 311 (4.12), 371 (3.94) nm. IR (KBr): 1760, 1610, 1480, 890, 810 cm^{-1} . 1H NMR ($CDCl_3$): δ 2.06 (6H, s, OAc $\times$ 2), 2.31 (12H, s, OAc $\times$ 4), 6.34 (1H, s, H_α), 6.96 (2H, dd, *J* 8 Hz, $H_{5,5'}$), 7.18 (2H, d, *J* 2 Hz, $H_{7,7'}$), 7.24 (1H, d, *J* 2 Hz, H_6), 7.30 (2H, d, *J* 8 Hz, $H_{4,4'}$), 7.35 (1H, d, *J* 2 Hz, H_2). The chemical shifts of its ^{13}C NMR spectrum were shown in Table 2, and all ^{13}C NMR spectra were measured in $DMSO-d_6$ with tetramethylsilane as an internal standard.

The compound (9) (230 mg) was dissolved in 15% KOH-MeOH and refluxed for an hour. The solution was acidified and extracted with EtOAc. The extracts evaporated were chromatographed on silica-gel column (solvent A) to afford two compounds. The one (45 mg) was identified as 6-hydroxy-coumaranone (4) and the other was recrystallized from MeOH – H_2O to afford yellow powder (58 mg), m.p. over 270 °C. MS 305 (M), 270 (M – 35), 150. Found: C 54.36; H 3.59. Calc. for $C_{15}H_9O_5Cl \cdot 3/2 H_2O$: C 54.31; H 3.64. UV [abs. MeOH (log ϵ)]: 259 (3.82), 390 (4.01) nm. IR (KBr): 1680, 1580, 810 cm^{-1} . 1H NMR ($DMSO-d_6$): δ 6.72 (1H, dd, *J* 8 Hz, H_5), 6.73 (1H, d, *J* 2 Hz, H_7), 6.90 (1H, d, *J* 2 Hz, H_6), 6.92 (1H, s, H_α), 7.64 (1H, d, *J* 8 Hz, H_4), 7.80 (1H, d, *J* 2 Hz, H_2). This was identified as 5'-chloro-sulfuretin (10) through direct comparison of spectral data with those of the authentic sample, which was obtained by condensation²¹ of 4 with 6.

The methanolic solution (100 ml) of 240 mg of 4 and 140 mg of 6 was adjusted with HCl to pH 2.5 and stood for 40 min under stirring. To the equilibrium mixture a large volume of water was added and this was extracted with EtOAc. After evaporation of the solvent the residue (374 mg) was chromatographed on a silica-gel column (solvent A) to afford 50 mg of 10 and 34 mg of 9.

ClO_2 treatment of 9. Quantitative determination of the individual component in the reaction mixture was made by Iatron-chromatoscanner using the developing solvents (benzene – ethyl acetate – formic acid = 20:4:1).

The compound (9) (400 mg) was dissolved in 60 ml of *t*-BuOH, to which 50 ml of ClO_2 solution (4.4 mmol) was added under stirring. After standing for five minutes at 60 °C the reaction mixture was diluted with a large volume of water and this was extracted with ethyl ether (Et_2O). After evaporation of the solvent the residue (426 mg) was subjected to the preparative TLC (PLC: solvent A) for isolation

and further purification of the reddish compound (15). (Yield 22%). MS: 454 (M + 2), 452 (M). Found: C 57.25; H 3.60. Calc. $C_{23}H_{13}O_8Cl \cdot 3/2H_2O$: C 57.56; H 3.36. UV [abs. MeOH (log ϵ)]: 260 (3.71), 373 (3.69), 415 (sh, 241) nm. IR (KBr): 1680, 1640, 1600 cm^{-1} . On reduction with $NaBH_4$ by the usual manner this afforded 9.

The methanolic solution (20 ml) of 15 (80 mg) was adjusted with dilute HCl to pH 4.0 and stood for 10 min at 60 °C under stirring. After dilution with a large volume of water the resulting solution was extracted with Et_2O , and the solvent was evaporated to dryness. The residue was subjected to PLC (solvent A) and this yielded 15 mg of 6-hydroxy-coumaranone (4) and 28 mg of the reddish powder (16), which newly appeared, m.p. (d.p.) 250 °C. MS: 304 (M + 2), 302 (M). Found: C 55.88; H 3.08; Cl 11.82. Calc. for $C_{15}H_7O_5Cl \cdot H_2O$: C 56.17; H 2.83; Cl 11.73. UV [abs. MeOH (log ϵ)]: 268 (3.32), 370 (3.67), 445 (sh, 2.90) nm. IR (KBr): 1685, 1660, 1590 cm^{-1} .

The solution of 16 (20 mg) in pyridine (1 ml) was mixed with a solution of *o*-phenylenediamine (15 mg) in the same solvent (0.2 ml). After standing for 1 h at room temperature a part of the solvent was removed under reduced pressure. On addition of water it gave a crystalline precipitate which was recrystallized from MeOH– H_2O . Red crystalline powder, m.p. over 270 °C. MS: 374 (M). Found: C 66.88; H 3.12; N 7.21. Calc. for $C_{21}H_{11}O_3N_2Cl$: C 67.29; H 2.96; N 7.47. UV [abs. MeOH (log ϵ)]: 256 (3.63), 352 (3.62), 415 (sh, 3.28) nm. IR (KBr): 1680, 1600, 840, 760 cm^{-1} . Reduction of 16 with $NaBH_4$ yielded 10.

Reaction of 16 in weakly-acidic solution at 60 °C. The compound (16) (2.15 g), prepared by the treatment of 10 with $NaIO_4$,¹³ was dissolved in 100 ml of MeOH and the methanolic solution was adjusted with dilute HCl to pH 4.0 and stood for 30 min at 60 °C. The solution was evaporated to small volume and extracted with Et_2O . The etherial solution was washed sufficiently with water and dried over Na_2SO_4 and then evaporated to dryness. The extracts (2.11 g) were chromatographed on silica-gel column (solvent A) to afford 133 mg of I, 80 mg of II, and 485 mg of III. Recrystallization of II from MeOH– H_2O gave yellow powder, m.p. over 270 °C. This was identified as 5'-chloro-sulfuretin (10) by comparing the mass and IR spectra with those of an authentic sample.

The product III (20) was purified by the repeated PLCs (solvent A). Found: C 57.44; H 2.85. Calc. for $C_{30}H_{14}O_{10}Cl_2 \cdot H_2O$: C 57.79; H 2.59. UV [abs. MeOH (log ϵ)]: 271 (3.91), 348 (4.11), 410 (sh, 3.16) nm. IR (KBr): 1700, 1660, 1640, 1600, 1420 (dioxene C–O band²²).

The solution of 20 (50 mg) in pyridine (3 ml) was mixed with the solution of *o*-phenylenediamine (30

mg) in the same solvent (0.5 ml). After standing for 1 h at room temperature the solvent was evaporated to dryness under reduced pressure. Recrystallization of the residue from MeOH gave reddish crystalline powder, m.p. over 270 °C. MS: 676 (M). Found: C 63.45; H 2.87; N 3.98. Calc. for $C_{36}H_{18}O_8N_2Cl_2$: C 63.82; H 2.68; N 4.13. This adduct (21) was acetylated with acetic anhydride and pyridine to afford the acetate (22), which was recrystallized from MeOH to yield brown powder, m.p. 167–170 °C. MS: 718 (M). Found: C 62.76; H 3.18; N 3.50. Calc. for $C_{40}H_{22}O_{10}N_2Cl_2$: C 63.08; H 2.91; N 3.68. 1H NMR ($CDCl_3$): δ 2.31 (6H, s, OAc $\times$ 2), 5.81 (1H, s, H_8), 6.70–7.10 (6H, m), 7.10–7.38 (4H, m), 7.42–8.20 (6H, m).

Reduction of III (420 mg) gave the yellow compound 18, which was acetylated with acetic anhydride and pyridine to yield the acetate. The latter was recrystallized from MeOH to afford yellow crystalline powder 17 (310 mg), m.p. 163–165 °C. FD-Mass: 820 (M). Found: C 58.54; H 3.18. Calc. for $C_{30}H_{13}O_5Cl_2(OCOCH_3)_5$: C 58.61; H 3.44. UV [abs. MeOH (log ϵ)]: 266 (4.20), 330 (4.07), 365 (4.00), 381 (4.03) nm. IR (KBr): 1780, 1735, 1710, 1650, 1440, 1416 cm^{-1} . 1H NMR ($CDCl_3$): δ 2.30 (15H, s, OAc $\times$ 5), 5.88 (1H, d, J 8 Hz, H_7), 5.93 (1H, d, J 8 Hz, H_8), 6.79 (1H, d, J 2 Hz, $H_{3''}$), 6.90 (1H, d, J 2 Hz, $H_{2''}$), 6.96 (1H, dd, J 8 Hz, H_6), 7.20 (1H, d, J 2 Hz, H_8), 7.24 (1H, s, H_{α}), 7.26 (1H, d, J 2 Hz, H_2), 7.54 (1H, dd, J 8 Hz, $H_{5''}$), 7.59 (1H, d, J 8 Hz, $H_{6''}$), 7.80 (1H, d, J 8 Hz, H_5), 7.81 (1H, d, J 2 Hz, $H_{6''}$), 8.12 (1H, d, J 2 Hz, H_6). ^{13}C NMR (carbon number): δ 71.55 (γ), 97.87 (δ), 104.25 ($3''$), 107.12 (7), 110.27 (5), 115.48 (6''), 118.06 (2''), 118.58 (α), 118.62 (6''), 119.87 (1''), 121.39 (5''), 124.78 (3a), 125.20 (4), 125.43 (2'), 126.25 (1''), 127.54 (5''), 128.24 (5'), 128.65 (6'), 137.83 (3''), 140.99 (1'), 141.52 (3'), 147.77 (2), 157.61 (4'), 159.56 (4''), 159.83 (2'), 166.09 (6), 166.61 (4''), 166.79 (7a), 170.01 (β), 182.06 (3).

The compound (18) (400 mg) was refluxed with dimethyl sulfate and potassium carbonate in acetone. The solution of the resulting methyl ether (19) (420 mg) in dichloromethane was cooled in ice and subjected to the treatment with ozonized oxygen (40 mmol of O_3). The resulting mixture was decomposed by addition of 10% H_2O_2 – CH_3COOH . After addition of water the solution was extracted with EtOAc. The extracts (353 mg) were chromatographed on silica-gel column (solvent A) to yield three products, 38, 23, and 135 mg. Each of the former two was recrystallized from MeOH– H_2O to yield colorless needles, m.p. 158–159 °C and m.p. 107–108 °C, respectively. The former was identified as 4-methoxy-salicylic acid (23) (lit. m.p. 159 °C²³), the latter as 2,4-dimethoxybenzoic acid (24) (lit. m.p. 107–108 °C²⁴) by comparing the mixed m.p. IR with those of authentic samples, respectively.

The third product (135 mg) dissolved in aqueous sodium hydroxide (100 ml) was mixed with 200 ml of potassium permanganate solution (5%) under stirring and stood overnight at room temperature. The solution was then acidified and extracted with Et₂O. The solvent was evaporated to dryness to afford a single compound (24 mg), which was recrystallized from MeOH to yield colorless powder, m.p. 189–190 °C. This was identified as 5-chloro-veratric acid²⁵ by comparing the mixed m.p. and IR with those of an authentic sample.

Analyses of IV, 26. After elution of I–III the residual column was washed well with solvent A to remove impurities. Subsequently IV was eluted with EtOAc–HCOOH (1:1) and the solvents were evaporated to dryness. The resulting compound (270 mg) was purified repeatedly by precipitation with CHCl₃ to yield 174 mg of 26. Found: C 58.77; H 2.62; Cl 12.01. Calc. for (C₁₅H₇O₅Cl)₅·H₂O: C 58.81; H 2.44; Cl 11.59. UV [abs. MeOH (log ϵ)] : 272 (3.10), 325 (sh, 3.00), 410 (sh, 2.62) nm. IR (KBr): 1700, 1655, 1640, 1600, 1450, 1440 cm⁻¹. IV was subjected to gel-permeation chromatography (Sephadex LH-20) using MeOH–CHCl₃ (1:1).

IV 26 was reduced and subsequently acetylated by the same manner as mentioned in the preparation of 17 from III, and the resulting acetate was subjected to the ¹³C NMR spectroscopy. ¹³C NMR (carbon number): δ 71.11 (γ), 97.31 (δ), 169.92 (β).

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