UDC 547.673.6.02 : 582.736

44. Michio Takido: Studies on the Constituents of the Seeds of *Cassia obtusifolia* L. II. The Structure of Obtusin, Chryso-obtusin, and Aurantio-obtusin.

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In the preceding paper,[1] the isolation of a new anthraquinone, obtusifolin (1-methoxy-2,8-dihydroxy-3-methylanthraquinone), accompanying chrysophanol and physcion, from the seeds of *Cassia obtusifolia* L. (Leguminosae) was reported. Subsequently from the extracts of above seeds, three new anthraquinone derivatives, obtusin, chryso-obtusin, and aurantio-obtusin, were isolated, with which the present paper is concerned.

Obtusin, yellow-brown long needles, m.p. 242~243°, whose analyses agreed with $C_{18}H_{16}O_7$ involving three methoxyl groups, is insoluble in water and 5% sodium hydrogencarbonate solution, but soluble in 5% sodium carbonte to give an orange solution. It gives a purple-blue color in conc. sulfuric acid, brown with ferric chloride, and orange in ethanolic magnesium acetate solution. The infrared spectrum of obtusin indicated the presence of a free hydroxyl group and both chelated and non-chelated carbonyls.

Obtusin forms a diacetate of m.p. 202~203°, a dimethyl ether of m.p. 132~133°, and a diethyl ether of m.p. 107°. It also forms a monomethyl ether of m.p. 173~174° or a monoethyl ether of m.p. 131~132°, whose infrared spectra show the absence of free hydroxyl group, and a monomethyl ether monoacetate of m.p. 143~144° and a monoethyl monomethyl ether of m.p. 129~130°. It is therefore suggested that obtusin is an anthraquinone derivative with two free hydroxyl groups in α- and β-positions.

Chryso-obtusin, yellow needles, m.p. 214~215°, whose analyses agreed with $C_{19}H_{18}O_7$ involving four methoxyl groups, is insoluble in water and 5% sodium hydrogencarbonate, but soluble in 5% sodium carbonate to form a red solution. It gives the same color reactions as obtusin when it is treated with conc. sulfuric acid, ethanolic magnesium acetate solution, but no color reaction with ferric chloride. The infrared spectrum of chryso-obtusin indicated the presence of a free hydroxyl group and showed that the carbonyl is non-chelated. Chryso-obtusin forms a monoacetate of m.p. 155°, a monomethyl ether of m.p. 132~133°, and a monoethyl ether of m.p. 128~130°. The last one was identified with obtusin monoethyl monomethyl ether by mixed fusion and infrared spectrum. It is therefore suggested that chryso-obtusin is a tetramethoxy-monohydroxy-anthraquinone derivative whose free hydroxyl group is in the β-position.

Aurantio-obtusin, orangne needles, m.p. 265~266°, whose analyses agreed with $C_{17}H_{14}O_7$ involving two methoxyl groups, is soluble in 5% sodium hydrogencarbonate to form an orange-red solution. It also gives the same color reactions as given by obtusin when it is treated with conc. sulfuric acid, ferric chloride, and ethanolic magnesium acetate solutions. Aurantio-obtusin affords a triacetate of m.p. 194~195°, a trimethyl ether of 132~133°, a dimethyl ether of m.p. 173~174°, and a dimethyl ether monoacetate of m.p. 143~144°. The latter two derivatives were identified respectively with obtusin monomethyl ether and its monoacetate by mixed fusion. On the other hand, chryso-obtusin monomethyl ether and aurantio-obtusin trimethyl ether were identified with obtusin dimethyl ether by mixed fusion and infrared spectral determination. It was, therefore, suggested that aurantio-obtusin is an anthraquinone derivative with two free hydroxyl groups in the β-position and one chelated hydroxyl group in the α-position. The

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1) M. Takido: This Bulletin, **6**, 398(1958).

demethylated derivatives (e.g. nor compound) of the above new pigments were obtained by treating them with hydrobromic acid or heating aurantio-obtusin with conc. sulfuric acid at 100°.

Nor compound, $C_{15}H_{10}O_7$, orange-red plates, m.p. 328~330°(decomp.), is soluble in 5% sodium hydrogencarbonate in dark violet, colors red-purple in conc. sulfuric acid, dark brown with ferric chloride, and dark purple with magnesium acetate. The infrared spectrum indicated the presence of free hydroxyl and chelated carbonyl. It forms a pentaacetate of m.p. 235~236° and a pentamethyl ether of m.p. 132~133°, which should be obtusin dimethyl ether.

On heating with hydriodic acid and phosphorus in glacial acetic acid, obtusin gives a reduction product which is converted into emodin on oxidation. Thus, the nor compound should be a dihydroxylated emodin.

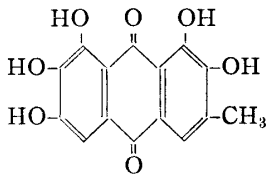
On heating with conc. sulfuric acid at 100°, obtusin, chryso-obtusin, and trimethyl-aurantio-obtusin give monomethyl-nor compound, but aurantio-obtusin gives the nor compound under the same condition.

The monomethyl-nor compound, $C_{16}H_{12}O_7$, orange-red needles, m.p. 273~274°, is soluble in 5% sodium hydrogencarbonate in dark green, colors red-purple in conc. sulfuric acid, dark brown with ferric chloride, and bluish purple with magnesium acetate. The infrared spectrum indicated the presence of a free hydroxyl, and both chelated and non-chelated carbonyls. It forms a tetraacetate of m.p. 252~253° and a tetramethyl ether of m.p. 132~133°, the latter of which should be obtusin dimethyl ether.

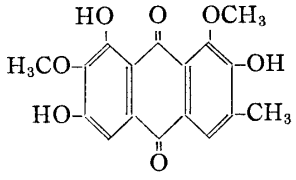
The nor compound and the monomethyl-nor compound are strong mordant dyes, showing that they are the derivatives of alizarin.

Recently, Tanaka[2] and Briggs, *et al.*[3] reported the infrared spectra of hydroxyanthraquinones and their data indicated that the non-chelated carbonyl in polyhydroxyanthraquinone derivatives is hardly identified in infrared spectrum. Birkinshow[4] and Ikeda, *et al.*[5] reported that hydroxyanthraquinone derivatives possessing 1,4-dihydroxyls in the molecule exhibit a shift of absorption band in the visible region and an absorption maximum appears at above 480 mμ. Perkin,[6] Graebe,[7] and Briggs, *et al.*[8] reported that on treating α,β-methoxyanthraquinone derivatives with sulfuric acid demethylation occurs first in the α-position. Thus, the infrared and ultraviolet spectra of the nor compound and the monomethyl-nor compound suggested that the two hydroxyls in the nor compound are not in 4- and 5-positions but in 3- and 7-positions.

Accordingly, structure (I) would be proposed for the nor compounds derived from three new anthraquinones of *Cassia obtusifolia*.



(I)



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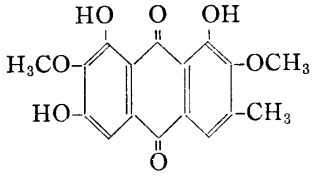


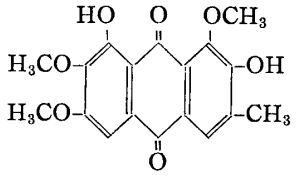
(III)

Obtusin, chryso-obtusin, and aurantio-obtusin are not mordant dyes, and they give orange-red or red colors in ethanolic magnesium acetate solution, brown in ferric chlor-

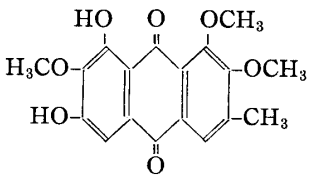
2) O. Tanaka : This Bulletin, **6**, 18(1958).
3) H. Bloom, L. H. Briggs, B. Cleverley : J. Chem. Soc., **1959**, 178.
4) J. H. Birkinshow : Biochem. J., **59**, 485(1955).
5) T. Ikeda, *et al.* : Yakugaku Zasshi, **76**, 217(1956).
6) A. G. Perkin : J. Chem. Soc., **1907**, 2066.
7) C. Graebe, C. Thode : Ann., **349**, 211(1906).
8) L. H. Briggs, G. A. Nicolls, R. M. L. Paterson : J. Chem. Soc., **1952**, 1719.

ide, and orange or orange-red in aqueous barium hydroxide solution. Their color reactions suggest that none of them possess vicinal hydroxyl groups in their molecules. Consequently, alternative possible structures, (II) and (III), could be forwarded to represent aurantio-obtusin. Aurantio-obtusin is soluble in 5% sodium hydrogencarbonate, as are 1,3,6,8-tetrahydroxyanthraquinone and 2,6- or 2,7-dihydroxyanthraquinone, suggesting the presence of at least two free hydroxyls in β-position. Aurantio-obtusin dimethyl ether was identical with obtusin monomethyl ether in which one free hydroxyl group is present in the α-position.

On the other hand, chryso-obtusin monoethyl ether was identified with obtusin monoethyl monomethyl ether as described above. Thus, structure (II) was deduced for aurantio-obtusin, the alternative structures (IV) and (V) for obtusin, and the structures (VI) and (VII) for chryso-obtusin.



(IV)



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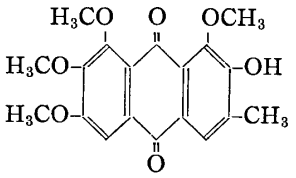

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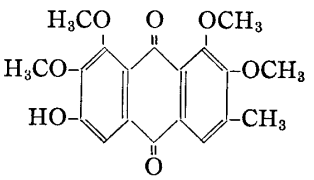
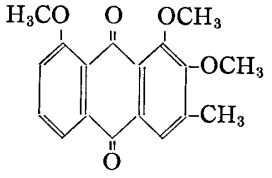
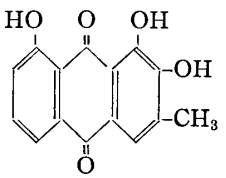


(VII)

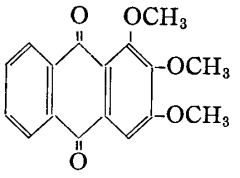
Nor-obtusifolin (VIII) and 3-O-methylanthragallol (IX) were respectively obtained from trimethylobtusifolin (X) and trimethylanthragallol (XI) by demethylation with conc. sulfuric acid at 100°, indicating that the methoxyl in the 3-position resists demethylation.



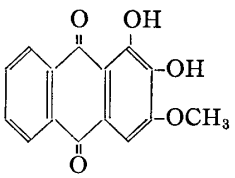
(X)



(VIII)



(XI)



(IX)

These experimental results and the fact that obtusin and chryso-obtusin retain their β-methoxyl on treating with sulfuric acid at 100° suggested the structures (IV) and (VI) for obtusin and chryso-obtusin, respectively.

Thus the structures of obtusin, chryso-obtusin, and aurantio-obtusin have been established as 1,6,7-trimethoxy-2,8-dihydoxy-3-methylanthraquinone, 1,6,7,8-tetramethoxy-2-hydroxy-3-methylanthraquinone, and 1,7-dimethoxy-2,6,8-trihydroxy-3-methylanthraquinone, respectively.

Experimental

Extraction of the Seeds of *Cassia obtusifolia* L. (Isolation of Obtusin, Chryso-obtusin, and Aurantio-obtusin)—The materials used for the present work were mostly collected in the Medicinal Plant Garden of Nihon University and some purchased in the market.

The seeds (1.0 kg.) were extracted three times with $CHCl_3$ (2 L.) or $CHCl_3$ (2 L.) and 20% H_2SO_4 (250 cc.). The concentrated $CHCl_3$ extract was chromatographed on a $CaHPO_4$-column and developed with benzene.

The first developed band, chrysophanol and physcion, and second band, obtusifolin, were isolated as described in Part I of this work.[1)]

The third developed yellowish brown band separated yellowish brown long needles, m.p. 242~243°, by recrystallization from EtOH, which was named obtusin. Yield, 100 mg. *Anal.* Calcd. for $C_{15}H_7O_4(OCH_3)_3$ (Obtusin) : C, 62.76; H, 4.65; OCH_3, 27.04; mol. wt., 344. Found : C, 62.88, 62.54; H, 5.02, 4.96; OCH_3, 27.89; mol. wt. (Rast), 334, 361. IR ν_{max}^{KBr} cm^{-1}: 3318 (OH), 1653 (non-chelated C=O), 1628 (chelated C=O). It gives an orange color in aq. $Ba(OH)_2$ solution.

The fourth developed yellow band separated yellow needles, m.p. 214~215°, by recrystallization from MeOH, which was named chryso-obtusin. Yield, 100 mg. *Anal.* Calcd. for $C_{15}H_6O_3(OCH_3)_4$ (Chryso-obtusin) : C, 63.66; H, 5.03; OCH_3, 34.64; mol. wt., 358. Found : C, 63.81; H, 5.03; OCH_3, 35.26; mol. wt. (Rast), 316, 358. IR ν_{max}^{Nujol} cm^{-1} : 3325 (OH), 1676 (non-chelated C=O), 1582 (phenyl band). It gives an orange-red color in aq. $Ba(OH)_2$ solution.

The fifth developed brown band separated orange needles, m.p. 265~266°, by recrystallization from EtOH or $CHCl_3$ which were sublimed at 200~210°/1 mm. Hg, and named aurantio-obtusin. Yield, 10 mg. *Anal.* Calcd. for $C_{15}H_8O_5(OCH_3)_2$ (Aurantio-obtusin) : C, 61.82; H, 4.24; OCH_3, 18.79; mol. wt., 332. Found : C, 62.12; H, 4.22; OCH_3, 19.44; mol. wt. (Rast), 335. IR ν_{max}^{Nujol} cm^{-1} : 3325 (OH), 1663 (non-chelated C=O), 1629 (chelated C=O). It gives an orange color in aq. $Ba(OH)_2$ solution.

Diacetylobtusin—A mixture of obtusin (100 mg.) with Ac_2O and a drop of conc. H_2SO_4 was allowed to stand over night at room temperature. The product was recrystallized from EtOH to light yellow needles, m.p. 202~203° (100 mg.). It is insoluble in 5% Na_2CO_3, gives no color reaction with $FeCl_3$ or on addition of $Mg(OAc)_2$ in EtOH. *Anal.* Calcd. for $C_{18}H_{14}O_5(OCOCH_3)_2$: C, 61.68; H, 4.67; CH_3CO, 20.09. Found : C, 61.81; H, 4.63; CH_3CO, 20.42. IR ν_{max}^{KBr} cm^{-1} : 1760 (phenolic acetate C=O), 1663 (C=O), 1583 (phenyl band).

Di-O-methylobtusin—A mixture of obtusin (100 mg.), Me_2CO (50 cc.), Me_2SO_4 (2.0 cc.), and anhyd. K_2CO_3 (1.5 g.), was refluxed for 8 hr. The solvent was evaporated and the residue was heated on a water bath with ethanolic 5% KOH to decompose Me_2SO_4. The yellow crystals which separated were recrystallized from petr. ether to pale yellow needles, m.p. 132~133° (ca. 80 mg.). It is insoluble in 5% NaOH and gives no $FeCl_3$ color reaction in EtOH. *Anal.* Calcd. for $C_{15}H_5O_2(OCH_3)_5$: C, 64.52; H, 5.40; OCH_3, 41.67. Found : C, 64.31; H, 5.33; OCH_3, 42.26. IR ν_{max}^{Nujol} cm^{-1} : 1673, 1662 (C=O), 1591 (phenyl band).

Di-O-ethylobtusin—A mixture of obtusin (100 mg.), Me_2CO (50 cc.), Et_2SO_4 (2.0 cc.), and anhyd. K_2CO_3 (1.5 g.) was refluxed for 10 hr. The solvent was evaporated and the residue was heated on a water bath with ethanolic 5% KOH to decompose Et_2SO_4. The yellow crystals which separated were recrystallized from petr. ether to light yellow needles, m.p. 107° (ca. 90 mg.). It is insoluble in 5% NaOH and gives no $FeCl_3$ color reaction in EtOH. *Anal.* Calcd. for $C_{22}H_{24}O_7$: C, 66.00; H, 6.00; Found : C, 65.63; H, 6.11.

Mono-O-methylobtusin—Obtusin (100 mg.) was methylated with CH_2N_2 (from 1.0 g. of nitrosomethylurea) in Et_2O (20 cc.) and Me_2CO (20 cc.) by standing over night at room temperature. The solvent was evaporated, extracted with Et_2O, and the Et_2O extract was freed from raw material by shaking with 5% Na_2CO_3. The solvent was evaporated and the residue was extracted with benzene. The concentrated benzene extract was chromatographed on a $CaHPO_4$-column and developing with benzene. The lowest main part of the yellow-orange band formed yellowish orange, long needles by recrystallization from MeOH, m.p. 173~174° (ca. 60 mg.), which is insoluble in 5% Na_2CO_3, but soluble in 5% NaOH to give an orange solution, and gives a brown color with $FeCl_3$. *Anal.* Calcd. for $C_{19}H_{18}O_7$: C, 63.66; H, 5.03. Found : C, 63.57; H, 4.95. IR ν_{max}^{Nujol} cm^{-1} : 1670 (non-chelated C=O), 1623 (chelated C=O), 1588 (phenyl band).

Mono-O-methylobtusin Monoacetate—The acetate was obtained by the usual method, as for diacetylobtusin, as light yellow needles, m.p. 143~144° (from MeOH). It is insoluble in 5% Na_2CO_3, gives no color with $FeCl_3$ in EtOH, and also by the addition of $Mg(OAc)_2$ in EtOH. *Anal.* Calcd. for $C_{21}H_{20}O_8$: C, 63.00; H, 5.00. Found : C, 63.27; H, 5.09.

Mono-O-ethylobtusin—A mixture of obtusin (200 mg.), Me_2CO (20 cc.), Et_2SO_4 (4.0 cc.), and anhyd. K_2CO_3 (3.0 g.) was refluxed for 1.5 hr. The solvent was evaporated and the residue was heated on a water bath with 5% aq. KOH and MeOH to decompose Et_2SO_4, acidified with dil. HCl, and extracted with benzene. The concentrated benzene extract was chromatographed on a $CaHPO_4$-column and

developed with benzene. From the second main part of bands separated yellowish orange needles, m.p. 131~132° (from petr. ether). Yield, 150 mg. It is insoluble in 5% Na_2CO_3, but soluble in 5% NaOH to give an orange solution, and a brown color with $FeCl_3$. *Anal.* Calcd. for $C_{20}H_{20}O_7$: C, 64.52; H, 5.40. Found: C, 64.91; H, 5.49. IR ν_{max}^{Nujol} cm^{-1}: 1665 (non-chelated C=O), 1630 (chelated C=O), 1591 (phenyl band).

Mono-O-ethylobtusin Monomethyl Ether—The methyl ether was obtained by the usual method as yellow needles, m.p. 129~130° (from MeOH). It is insoluble in 5% NaOH, gives no $FeCl_3$ color reaction in EtOH. *Anal.* Calcd. for $C_{23}H_{26}O_7$: C, 65.28; H, 5.70. Found: C, 65.17; H, 5.68. IR ν_{max}^{Nujol} cm^{-1}: 1676 (C=O), 1583 (phenyl band).

Acetylchryso-obtusin—The acetate was obtained by the usual method as yellow needles, m.p. 155° (from MeOH or petr. ether). It is insoluble in 5% Na_2CO_3, gives no color with $FeCl_3$ in EtOH, and also by the addition of $Mg(OAc)_2$ in EtOH. *Anal.* Calcd. for $C_{19}H_{17}O_6(OCOCH_3)$: C, 63.00; H, 5.00; CH_3CO, 10.75. Found: C, 63.00; H, 5.01; CH_3CO, 11.56. IR ν_{max}^{Nujol} cm^{-1}: 1772 (phenolic acetate C=O), 1680 (C=O), 1587 (phenyl band).

Chryso-obtusin Methyl Ether—The methyl ether was obtained by the usual method of methylation with CH_2N_2 in Et_2O as pale yellow long needles, m.p. 132~133°, alone and on admixture with dimethylobtusin, m.p. 132~133°.

Chryso-obtusin Ethyl Ether—The ethyl ether was obtained by the usual method as yellow needles, m.p. 128~130° (from MeOH), alone and on admixture with mono-O-ethyl-O-methylobtusin, m.p. 128~130°.

Triacetylaurantio-obtusin—The acetate was obtained by the usual method as pale yellow needles, m.p. 195~196° (from MeOH). It is insoluble in 5% Na_2CO_3, gives no color with $FeCl_3$ in EtOH, and also by the addition of $Mg(OAc)_2$ in EtOH. *Anal.* Calcd. for $C_{17}H_{14}O_7(OCOCH_3)_3$: C, 60.53; H, 4.39; $COCH_3$, 28.29. Found: C, 60.44; H, 4.40; $COCH_3$, 29.10. IR ν_{max}^{Nujol} cm^{-1}: 1769 (phenolic acetate C=O), 1680 (C=O), 1590 (phenyl band).

Tri-O-methylaurantio-obtusin—The methyl ether was obtained by the usual method as pale yellow long needles, m.p. 132~133° (from petr. ether), alone and on admixture with dimethylobtusin, m.p. 132~133°.

Di-O-methylaurantio-obtusin—Aurantio-obtusin (50 mg.) was methylated with CH_2N_2 (from 1.0 g. of nitrosomethylurea) in Et_2O (20 cc.) and Me_2CO (10 cc.) by standing over night at room temperature. The solvent was evaporated, the residue was extracted with Et_2O, and Et_2O extract was freed from raw material by shaking with 5% Na_2CO_3. The solvent was evaporated, the residue was extracted with benzene, and concentrated benzene extract was chromatographed on a $CaHPO_4$-column, developing with benzene. From main brown part of the bands separated yellowish orange long needles (from MeOH), m.p. 173~174° (ca. 35 mg.), alone and on admixture with mono-O-methylobtusin, m.p. 173~174°.

Di-O-methylaurantio-obtusin Acetate—The acetate was obtained by the usual method as light yellow needles, m.p. 143° (from MeOH), alone and mixed with mono-O-methylobtusin acetate, m.p. 143~144°.

Nor Compound (1,2,6,7,8-Pentahydroxy-3-methylanthraquinone)—A mixture of obtusin (100 mg.), glacial AcOH (20 cc.), and HBr (20 cc., 48%) was refluxed for 5 hr. at 160~180°. The reaction mixture was poured into water, the separated orange-red precipitate (ca. 85 mg.) was collected, and recrystallized from MeOH to red plates, which was sublimed, m.p. 328~330° (decomp.) (ca. 50 mg.). It is soluble in 5% $NaHCO_3$ to give a dark violet solution and colors red-purple in conc. H_2SO_4. It gives a dark brown color with $FeCl_3$ and dark purple with $Mg(OAc)_2$. *Anal.* Calcd. for $C_{15}H_{10}O_7$: C, 59.60; H, 3.31. Found: C, 59.20; H, 3.34. IR ν_{max}^{Nujol} cm^{-1}: 3466 (OH), 1620 (chelated C=O), 1585 (phenyl band). UV λ_{max}^{EtOH} $m\mu$ ($\log \varepsilon$): 234 (3.94), 290 (4.32), 325 (3.76), 420 (3.89).

The nor compound was also obtained by the same method from chryso-obtusin, aurantio-obtusin, and their permethyl ether, and also by heating aurantio-obtusin with conc. H_2SO_4 at 100° for 1.5 hr.

Penta-O-acetylated Nor Compound—The acetate was obtained by the usual method as pale yellow needles, m.p. 235~236° (from MeOH). It is insoluble in 5% Na_2CO_3, gives no color with $FeCl_3$ in EtOH. *Anal.* Calcd. for $C_{15}H_5O_2(OCOCH_3)_5$: C, 58.59; H, 3.91; CH_3CO, 41.99. Found: C, 58.48; H, 3.98; CH_3CO, 42.77. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1775 (phenolic acetate C=O), 1681 (C=O), 1599 (phenyl band).

Penta-O-methylated Nor Compound—The methyl ether was obtained by the usual method as pale yellow long needles, m.p. 132~133° (from petr. ether), alone and on admixture with dimethylobtusin, m.p. 132~133°.

Reduction of Obtusin (Formation of Emodin)—A mixture of obtusin (ca. 390 mg.), red P (400 mg.), glacial AcOH (12 cc.), and HI (2.4 cc., sp. gr. 1.7) was refluxed for 5 hr. The brown mixture was cooled, poured into water, and decolorized with addition of a small amount of $NaHSO_3$. The resulting brown precipitate was collected, washed with water, and dried. This substance gave a color reaction of anthrone (soluble in conc. H_2SO_4 in yellowish brown color and separates Se from SeO_2 in conc. H_2SO_4). The crude anthrone dissolved in glacial AcOH (20 cc.) was added with a solution of CrO_3 (0.3 g.) in

glacial AcOH (15 cc.). After standing for 30 min. at a room temperature, the brown mixture was diluted with water and extracted with Et_2O. The yellowish orange extract freed from AcOH was shaken repeatedly with 5% $NaHCO_3$, washed with water, and evaporated to dryness. The residue was crystallized from MeOH and sublimed to orange needles, m.p. 255° (ca. 30 mg.), alone and on admixture with authentic emodin, m.p. 255°. For further confirmation, a portion of the product was converted into the acetate, which was recrystallized from MeOH to light yellow needles, m.p. 198~200°. It showed no m.p. depression on admixture with authentic tri-O-acetylemodin, m.p. 199~200°.

Demethylation of Obtusin (Formation of 1,2,7,8-Tetrahydroxy-6-methoxy-3-methylanthraquinone)—Obtusin (70 mg.) was partly demethylated by heating with conc. H_2SO_4 (5.0 cc.) for 1.5 hr. at 100°. The purple mixture was cooled and poured into water to obtain an orange precipitate which was collected, washed with water, and dried. The orange material was dissolved in $CHCl_3$ containing a little Me_2CO, chromatographed on a $CaHPO_4$-column, and developed with $CHCl_3$. From the second main part of bands separated orange needles, m.p. 273~274°. Yield, 40 mg. It is soluble to give a dark green solution in 5% $NaHCO_3$ and colors red-purple in conc. H_2SO_4, dark brown with $FeCl_3$, and blue-purple with $Mg(OAc)_2$. *Anal.* Calcd. for $C_{15}H_9O_6(OCH_3)$: C, 60.76; H, 3.79; OCH_3, 9.81. Found: C, 60.77; H, 3.81; OCH_3, 10.64. IR $\nu_{max}^{dioxane}$ cm^{-1}: 3250 (OH), 1657 (shoulder, non-chelated C=O), 1618 (chelated C=O).

It was also obtained by the same method from chryso-obtusin and aurantio-obtusin trimethyl ether.

Its tetramethyl ether was obtained by the usual method as pale yellow long needles, m.p. 132~133°, alone and on admixture with dimethylobtusin, m.p. 132~133°.

1,2,7,8-Tetraacetyl-6-methoxy-3-methylanthraquinone—It was obtained by the usual method as light yellow needles, m.p. 252~253° (from MeOH). It is insoluble in 5% Na_2CO_3 and gives no color with $FeCl_3$ in EtOH. *Anal.* Calcd. for $C_{24}H_{20}O_{11}$: C, 59.50; H, 4.13. Found: C, 59.40; H, 4.19.

Demethylation of Dimethylobtusifolin (Formation of Norobtusifolin)—Obtusifolin dimethyl ether (50 mg.) was demethylated by heating with conc. H_2SO_4 (5.0 cc.) for 1.5 hr. at 100°. The reaction mixture was poured into water to separate brown red precipitate which was collected and recrystallized from MeOH to orange-red needles, m.p. 255° (ca. 30 mg.), alone and on admixture with authentic norobtusifolin, m.p. 255°.

Demethylation of Trimethylanthragallol (Formation of 3-Methylanthragallol)—Trimethylanthragallol (50 mg.) was demethylated by heating with conc. H_2SO_4 (5.0 cc.) for 1.5 hr. at 100°. The reaction mixture was poured into water and orange precipitate was collected, which was dissolved in $CHCl_3$ and chromatographed on a $CaHPO_4$-column, developing with $CHCl_3$. From the second main part of bands separated orange needles (ca. 25 mg.), which were sublimed m.p. 239~241°. *Anal.* Calcd. for $C_{21}H_{20}O_8$: C, 66.66; H, 3.70. Found: C, 66.39; H, 3.81.

Diacetyl derivative, m.p. 200~201°, was obtained by the usual method.

The author is deeply grateful to Prof. S. Shibata of the University of Tokyo and Prof. Y. Kimura of this Institute for their kind encouragements and valuable advices. He is indebted to Mr. T. Kimura of the Medicinal Plant Garden attached to this Institute for the cultivation of plant materials. The measurement of infrared spectra were carried out at the Faculty of Pharmaceutical Sciences, University of Tokyo, microanalyses were made by the members of microanalytical laboratories of University of Tokyo, Hoshi College of Pharmacy, and the Daiichi Seiyaku Company, and Misses T. Kurosu and K. Fukaya cooperated in preparing materials, to all of whom the author's thanks are due.

Summary

From the seeds of *Cassia obtusifolia* L. (Leguminosae), three new anthraquinone pigments, obtusin (m.p. 242~243°), chryso-obtusin (m.p. 214~215°), and aurantio-obtusin (m.p. 265~266°), were isolated. The structures of these pigments were established respectively as 1,6,7-trimethoxy-2,8-dihyroxy-3-methylanthraquinone, 1,6,7,8-tetramethoxy-2-hydroxy-3-methylanthraquinone, and 1,7-dimethoxy-2,6,8-trihydroxy-3-methylanthraquinone.

(Received August 15, 1959)