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Chemical Studies on the Oriental Plant Drugs. XX.[1] The Constituents of *Cassia tora* L. (1). The Structure of Torachrysone

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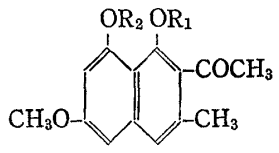
A new yellow pigment named torachrysone was isolated from the seeds of *Cassia tora* L. (Leguminosae). The structure of torachrysone was established as I.

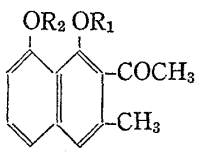
The seeds of *Cassia tora* L. (Leguminosae), a wild plant in tropical Asian countries, Taiwan and Rhukyu islands, are being used along with the seeds of *Cassia obtusifolia* L. as a purgative under the name of Juenmingzi (in Chinese), or Ketsumeishi (in Japanese) (決明子).

The presence of rubrofusarin and nor-rubrofusarin in the seeds of this plant has been reported by Rangaswami[3], and the isolation of chrysophanol, physcion, obtusin and aurantio-obtusin by Kimura, *et al.*[4] In the present paper we described on the structure of a new yellow pigment, named torachrysone (I), isolated from the benzene extract of the seeds of *Cassia tora*. L. Torachrysone, mp 214—215° (decomp.), $C_{14}H_{14}O_4$, is a phenolic compound which is soluble in alkali and gives a wine red colour with ferric chloride, an orange colour with diazo reagent, and a blue colour with Gibbs' reagent. The IR spectrum of I in chloroform shows absorptions at 1635 cm^{-1} (chelated C=O), 1607 and 1585 cm^{-1} (aromatic ring). Torachrysone (I) afforded diacetate (II), mp 181—182°, and dimethyl ether (III), mp 63—64°, both of which revealed an IR absorption of an aromatic acetyl at 1704 cm^{-1}.

Table I. UV Spectra of Acetates of Torachrysone and Musizin

Compounds	λ_{max} (log ε) in EtOH		
II	233 (4.65)	295 (3.70)	333 (3.36)
V	225 (4.82)	286 (3.80)	324 (3.13)





I: $R_1=R_2=H$ II: $R_1=R_2=COCH_3$ IV: $R_1=R_2=H$ V: $R_1=R_2=COCH_3$
III: $R_1=R_2=CH_3$ VI: $R_1=CH_3$, $R_2=H$ XI: $R_1=CH_3$, $R_2=H$ XII: $R_1=H$, $R_2=CH_3$
VII: $R_1=H$, $R_2=CH_3$

Chart 1

The UV spectrum of II resembled that of musizin diacetate[5] (V), suggesting that I would be a derivative of 2-acetyl-3-methylnaphthalene.

1) Part XIX: S. Shibata and T. Saitoh, *Chem. Pharm. Bull.* (Tokyo), **16**, 1932 (1968).
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3) S. Rangaswami, *Proc. Indian. Acad. Sci.*, A **57**, 88 (1963).
4) Y. Kimura, M. Takido and S. Takahashi, *Shoyakugaku Zasshi*, **18**, 28 (1964).
5) C.J. Covell, F.E. King and J.W.W. Morgan, *J. Chem. Soc.*, **1961**, 702.

The NMR spectra of II and III gave the signals of protons as shown in Table II. The acetate and the methyl ether of torachrysone revealed three aromatic ring protons, two of which were indicated by the coupling constant (J=2.5 cps) to be located in *meta* position. Only one methoxyl signal is given by II, whereas three in III. The acetate (II) shows 4 CH_3 (aromatic methyl or acetyl), whereas III gives only 2 CH_3. These results therefore indicate that two hydroxyls and one methoxyl are present in I.

Table II. NMR Spectra of Torachrysone Diacetate (II) and Dimethyl Ether (III) (τ in $CDCl_3$)

	II	III
arom. H	2.56 (H, s) 3.03 (H, d, J=2.5 cps) 3.23 (H, d, J=2.5 cps)	2.71 (H, s) 3.33 (H, d, J=2.5 cps) 3.47 (H, d, J=2.5 cps)
arom. OCH_3	6.14 (3H, s)	6.02 (3H, s) 6.06 (3H, s) 6.20 (3H, s)
arom. CH_3 and $COCH_3$	7.50 (3H, s) 7.64 (6H, s) 7.70 (3H, s)	7.41 (3H, s) 7.68 (3H, s)

On methylation with diazomethane in a short time, I afforded monomethyl ether A (VI), mp 64—65°, and monomethyl ether B (VII), mp 98—99°, in a yield of 59% and 22%, respectively.

The melting point and the UV absorption maxima of the monomethyl ether B (VII) agreed with those of 2-acetyl-6,8-dimethoxy-3-methyl-1-naphthol (X) appearing in literature, which was derived from eleutherinol dimethyl ether (IX)[6] by alkaline degradation. The structure of VII was confirmed to lead to IX, mp 186—186.5° (*cf.* lit. mp 186—187°) by Claisen condensation with ethyl acetate followed by cyclization using conc. HCl. The structure of IX was proved by the NMR spectrum.

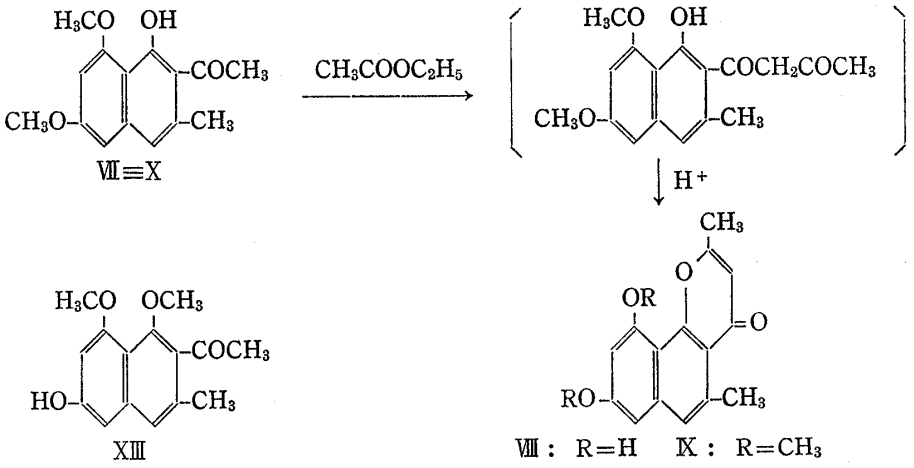
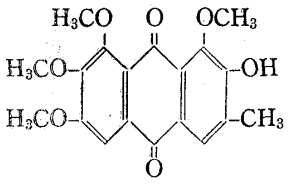


Chart 2

The monomethyl ethers A (VI) and B (VII) show positive Gibbs' reaction (blue: λ_{max} 610 mμ, 607 mμ, respectively), and give an IR absorption at 3400 cm^{-1} of a weak hydrogen bonding hydroxyl (in CCl_4).

6) A. Ebnöther, Th. M. Meijer and H. Schmid, *Helv. Chim. Acta*, **35**, 910 (1952); H. Frei and H. Schmid, *Ann. Chem.*, **603**, 169 (1957).



XIV

Chart 3

In analogy to this, musizin (IV) afforded by methylation with diazomethane 1-O-methylmusizin (XI) and 8-O-methylmusizin (XII) in a yield of 31% and 14%, respectively and also show an IR absorption at 3360 cm^{-1} of an intramolecularly hydrogen bonded hydroxyl.[5] The above results rejected the possibility of XIII for the monomethyl ether A, and it has been formulated as 2-acetyl-1,6-dimethoxy-3-methyl-8-naphthol (VI).

Consequently, torachrysone has finally been represented by 2-acetyl-6-methoxy-3-methyl-1,8-naphthalenediol (I).

On silica gel column chromatography of the benzene extracts of the seeds of *Cassia tora* L., a golden yellow pigment, mp 219—220°, was isolated from the elution running out after torachrysone. This pigment was identified by a mixed fusion, and comparison of IR spectra and thin-layer chromatograms with chryso-obtusin (XIV), which was isolated first by Takido[7] from the seeds of *Cassia obtusifolia* L.

Experimental

Isolation of Torachrysone (I)——The pulverized seeds of *Cassia tora* L. (2 kg) were extracted first with *n*-hexane to remove fat and oil (50 g), and then extracted with benzene on a water bath. The addition of petroleum ether (300 ml) to the benzene extract (55 g) gave dark yellow precipitates (6.0 g), which were chromatographed in $CHCl_3$ on silicagel. The second yellow band from the bottom was eluted and evaporated to give yellow solid, which was recrystallized from benzene to obtain yellow needles of torachrysone (I) (0.4 g), mp 214—215° (decomp.). It is soluble in 5% NaOH to form an orange solution and shows a wine red colour with 1% $FeCl_3$ and a blue colour with Gibbs' reagent. *Anal.* Calcd. for $C_{14}H_{14}O_4$: C, 68.32; H, 5.71; mol. wt. 246. Found: C, 68.05, 68.58; H, 5.75, 5.75; mol.wt. 246 (mass spectrometric). UV λ_{max}^{EtOH} mμ (log ε): 232 (4.45), 267 (4.43), 315 (3.69), 383 (3.75). IR ν_{max}^{KBr} cm^{-1}: 1634 (chelated C=O), 1588 (aromatic); $\nu_{max}^{CHCl_3}$ cm^{-1}: 1635 (chelated C=O), 1607, 1585 (aromatic).

Torachrysone Diacetate (II)——On acetylation with pyridine (1.2 ml) and Ac_2O (5 ml), standing overnight at room temperature, torachrysone (I) (100 mg) afforded colourless plates of torachrysone diacetate (from EtOH) (89 mg), mp 181—182°. *Anal.* Calcd. for $C_{18}H_{18}O_6$: C, 65.51; H, 5.50. Found: C, 65.74; H, 5.74. UV λ_{max}^{EtOH} mμ (log ε): 233 (4.65), 295 (3.70), 333 (3.36). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1775 (OAc), 1704 (non-chelated C=O), 1637, 1615, 1575.

Torachrysone Dimethyl Ether (III)——A mixture of I (50 mg), Me_2SO_4 (0.5 ml), K_2CO_3 (500 mg) and dry acetone (20 ml) was refluxed for 3 hr under stirring. The solution was then filtered, concentrated, and treated with conc. ammonia to decompose Me_2SO_4 and the product was extracted with $CHCl_3$. The $CHCl_3$ solution was washed with water, dried, and concentrated to give yellow oily syrup, which was purified by chromatography on silica gel column using $CHCl_3$ as the solvent. The first, white green fluorescent band was eluted and evaporated to yield colourless syrup, which was crystallized from aqueous MeOH as colourless tiny plates of torachrysone dimethyl ether (25 mg), mp 63—64°. *Anal.* Calcd. for $C_{16}H_{18}O_4$; C, 70.13; H, 6.62; mol. wt. 274. Found: C, 70.37; H, 6.69; mol. wt. (Mass) 274. UV λ_{max}^{EtOH} mμ (log ε): 237 (4.62), 303 (3.71), 334 (infl.) (3.62). IR $\gamma_{max}^{CCl_4}$ cm^{-1}: 1704 (non-chelated C=O), 1627, 1608, 1579 (arom.).

Torachrysone Monomethyl Ethers A (VI) and B (VII)——To a solution of I (100 mg) in dry ether was gradually added an ethereal CH_2N_2 (prepared from 1 g of N-nitrosomethylurea) under stirring at 0°. After standing at room temperature for 1 hr, the solvent was removed and the yellow oily syrup obtained was chromatographed on silica gel using $CHCl_3$ as the solvent. The greenish yellow fluorescent bottom band was eluted and recrystallized from aqueous MeOH affording colourless plates (63 mg, 59%), mp 64—65° (torachrysone monomethyl ether A). *Anal.* Calcd. for $C_{15}H_{16}O_4$: C, 69.29; H, 6.20. Found: C, 69.09; H, 6.13. UV λ_{max}^{EtOH} mμ (log ε): 231 (4.51), 242 (4.51), 337 (3.59). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3400 (intramolecularly hydrogen bonded OH), 1702 (non-chelated C=O). NMR $\tau_{Me_4Si}^{CDCl_3}$: 0.80 (H, s), [O<u>H</u>]; 2.75 (H, s), 3.40 (H, d, J=2.5 cps), 3.46 (H, d, J=2.5 cps) [arom. H]; 6.08 (3H, s), 6.14 (3H, s) [OC<u>H</u>$_3$]; 7.39 (3H, s), 7.67 (3H, s) [COC<u>H</u>$_3$, C-C<u>H</u>$_3$].

The second violet fluorescent band was eluted and recrystallized from aqueous MeOH to form colourless needles of torachrysone monomethyl ether B (23 mg, 22%), mp 98—99°. *Anal.* Calcd. for $C_{15}H_{16}O_4$: C, 69.29; H, 6.20. Found: C, 69.56; H, 6.45. UV λ_{max}^{EtOH} mμ (log ε): 233 (4.53), 260 (4.30), 338 (3.75). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3400 (intramolecularly hydrogen bonded OH), 1695 (non-chelated C=O). NMR $\tau_{Me_4Si}^{CDCl_3}$: 0.24 (H, s) [O<u>H</u>]; 3.10 (H, s), 3.46 (H, d, J=2.5 cps), 3.65 (H, d, J=2.5 cps) [arom. H]; 6.02 (3H, s), 6.15 (3H, s) [OC<u>H</u>$_3$];

7) M. Takido, *Chem. Pharm. Bull.* (Tokyo), **8**, 246 (1960).

7.40 (3H, s), 7.65 (3H, s), [COC$\underline{H}_3$, C–C$\underline{H}_3$]. The melting point and the UV absorption curve of this product are identical with those of the alkaline degradation product (X) derived from eleutherinol dimethyl ether (IX) by H. Schmid, *et al.*[6] Both VI and VII give a blue colour reaction with Gibbs' reagent (λ_{max} 610 mμ, 607 mμ, respectively), and an orange yellow colour reaction with diazo reagent.

Preparation of Eleutherinol Dimethyl Ether (IX) from Torachrysone Monomethyl Ether B (VII)——To a solution of VII (84 mg) in dry AcOEt (1 ml) was added dropwise at 0° a suspension of NaH (100 mg) in dry AcOEt (5 ml). The mixture was stirred, at 0° for 1/2 hr, at room temperature for 2 hr, and then refluxed for 2 hr. After standing overnight at room temperature, the reaction mixture was poured into ice water, acidified, and extracted with $CHCl_3$. The $CHCl_3$–layer was washed with 5% $NaHCO_3$ and water, dried, and evaporated to give almost colourless syrup, which solidified on cooling. The solution of the product as above obtained in MeOH (10 ml) containing conc. HCl (1 ml) was refluxed for 10 min. Concentration of the reaction mixture yielded yellow solid, which was washed and chromatographed on silica gel using a mixture of benzene–acetone (4:1) as the solvent. From the second blue fluorescent band was obtained almost colourless solid, which was recrystallized from EtOH to give almost colourless needles of eleutherinol dimethyl ether (IX) (36 mg, 39%), mp 186—186.5°, which showed the same melting point of the dimethyl ether derived from natural eleutherinol obtained from *Eleutherine bulbosa* by H. Schmid, *et al.*[6] *Anal.* Calcd. for $C_{17}H_{16}O_4$: C, 71.89; H, 5.68. Found: C, 71.81; H, 5.58. UV λ_{max}^{EtOH} mμ (log ε): 238 (4.60), 270 (4.57), 340 (infl.) (3.97), 353 (4.07). IR $\gamma_{max}^{CHCl_3}$ cm^{-1}: 1658 (γ-pyrone C=O), 1620, 1607, 1575 (aromatic). NMR $\tau_{Me_4Si}^{CDCl_3}$: 2.82 (H, s), 3.37 (H, d, J=3.0 cps), 3.49 (H, d, J=3.0 cps) [arom. H], 3.80(H, s) [olefinic H], 6.03 (3H, s), 6.07 (3H, s) [OC$\underline{H}_3$], 7.14, (3H,s), 7.60 (3H, s) [C–C$\underline{H}_3$].

Isolation and Identification of Chryso-obtusin (XIV)——A dark yellow solid (1 g) obtained from the benzene extracts by the addition of petr. ether, was chromatographed on silicagel using $CHCl_3$ as the solvent. The fifth dark yellow band was eluted and evaporated to give a brown solid, which was purified again by chromatography on silicagel column using benzene–acetone mixture (9:1) as the solvent. The second dark yellow fluorescent band afforded yellow needles (from MeOH) (10 mg), mp 219—220°. This compound was identified with the authentic sample of chryso-obtusin by a mixed fusion (the mixed mp 219—220°) and comparison of IR spectra and thin-layer chromatograms.

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