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STUDIES ON THE CONSTITUENTS OF THE SEEDS OF *CASSIA OBTUSIFOLIA*: THE STRUCTURES OF TWO NEW LACTONES, ISOTORALACTONE AND CASSIALACTONE*

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Key Word Index—*Cassia obtusifolia*; Leguminosae; torosachrysone; naphthalenic lactone; isotoralactone; cassialactone.

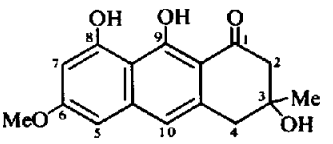
Abstract—Torosachrysone and two new naphthalenic lactones, isotoralactone and cassialactone, were isolated from the seeds of *Cassia obtusifolia*. Their structures were established as 9,10-dihydroxy-7-methoxy-3-methylene-1*H*-naphtho(2,3-*c*)dihydropyrone-1-one and 8-methoxy-4-methyl-1-oxo-4,10,11-trihydroxy-naphtho(2,3-*c*)oxepin, respectively.

INTRODUCTION

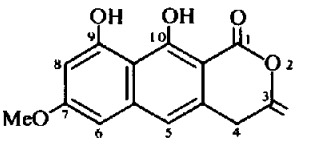
The seeds of *Cassia obtusifolia* L. and *C. tora* L. are called Ketsumeishi in Japan and are used as a laxative, tonic and diuretic. In previous investigations, some of which were carried out by the present authors, several anthraquinones and naphthopyrone derivatives were isolated from the seeds [1–8]. In the present paper, we report the isolation of torosachrysone (**1**) and the isolation and structural determination of two naphthalenic lactones, isotoralactone (**2**) and cassialactone (**3**).

RESULTS AND DISCUSSION

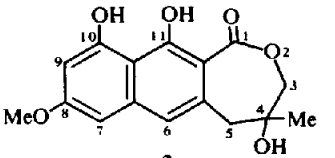
The crushed seeds were treated as described in the Experimental to yield chrysophanol, physcion, rubrofusarin, obtusifolin, emodin, obtusin, chryso-obtusin, aurantio-obtusin, **1**, **2** and **3**. **1**, yellow prisms, mp 196–200°, $C_{16}H_{16}O_5$, was identified as torosachrysone [9] by direct comparison with an authentic sample. **2**, isotoralactone, pale yellow needles, mp 233–235° (dec.), $C_{15}H_{12}O_5$, gave a positive $FeCl_3$ reaction and with Gibbs reagent gave a fluorescent light blue under UV radiation. Its UV and IR spectra suggested the presence of a hydroxynaphthalene skeleton having a chelated carbonyl group. Its ^1H NMR spectrum showed the presence of a $-CH_2-$ group, a $=CH_2$ group, an OMe group, three aromatic protons and two chelated phenolic OH groups (Table 1). The assignments of two methylene groups were confirmed by spin-decoupling experiments. Thus irradiation of a doublet-like $-CH_2-$ signal ($J = 1$ Hz) at δ3.78 changed each quartet-like $=CH_2$ signal ($J = 1$ Hz) at 4.62 and 4.93 to a doublet ($J = 2$ Hz) and the triplet aromatic proton signal ($J = 1$ Hz) at 6.91 to a singlet. Therefore, the $=CH_2$ group and the aromatic proton were adjacent to the $-CH_2-$ group. On acetylation with Ac_2O and pyridine, **2** afforded a diacetate (**5**), mp 244–245°, $C_{19}H_{16}O_7$, with the characteristic UV spectrum of a naphtho-α-pyrone



1



2



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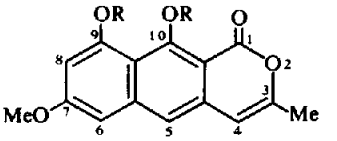

4 R = H
5 R = Ac

* Part 11 in the series "Studies of the Constituents of Purgative Crude Drugs". For Part 10 see Takahashi, S., Kitanaka, S., Takido, M., Sankawa, U. and Shibata, S. (1977) *Phytochemistry* **16**, 999.

Table 1. ^{1}H NMR spectral data 1–5 (100 Mz, $CDCl_3$, TMS as internal standard, J in Hz)

Position of H	1	2	4	5	3
2	2.83 *s* (*br*)				
3					3.66 *d* 3.84 *d* (*J* = 12.2)
3-Me	1.45 *s*		2.24 *d* (*J* = 0.7)	2.21 *d* (*J* = 0.7)	
3-CH_2		4.62 *q*-like 4.93 *q*-like (*J* = 2)			
3-OH	1.68 *s* (*br*)				
4	3.04 *s* (*br*)	3.78 *d*-like (*J* = 1)	6.23 *q* (*J* = 0.7)	6.18 *q* (*J* = 0.7)	
4-Me					1.41 *s*
4-OH					2.08 *s* (*br*)
5	6.54 *d* (*J* = 2.4)	6.91 *t* (*J* = 1)	6.97 *s*	7.41 *s*	2.71 *d* 3.44 *d*. (*J* = 16.6)
6		6.59 *d* (*J* = 2.4)	6.61 *d* (*J* = 2.4)	6.93 *d* (*J* = 2.4)	6.93 *s*
6-OMe	3.88 *s*				
7	6.48 *d* (*J* = 2.4)				6.57 *d* (*J* = 2.4)
7-OMe		3.90 *s*	3.90 *s*	3.91 *s*	
8		6.54 *d* (*J* = 2.4)	6.53 *d* (*J* = 2.4)	6.80 *d* (*J* = 2.4)	19%
8-OH	9.79 *s*				
8-OMe					3.89 *s*
9					6.54 *d* (*J* = 2.4) 35%
9-OH	16.10 *s*	9.38 *s*	9.41 *s*		
9-OAc				2.42 *s*	
10	6.86 *s* (*br*)				
10-OH		13.30 *s*	13.54 *s*		9.45 *s*
10-OAc				2.53 *s*	
1-OH					13.70 *s*

Arrows and figures in % indicate enhancement in NOE experiment.

homologue. The diacetate was identified as toralactone diacetate (**5**) by ^{1}H NMR and by direct comparison with an authentic sample [8]. A similar isomerization of isotoralactone (**2**) to toralactone (**4**) was effected with HCl–Me_2CO. Thus, the structure of **2** was shown to be 9,10-dihydroxy-7-methoxy-3-methylene-1*H*-naphtho-(2,3-*c*)dihydropyrone-1-one.

3, cassialactone, very pale yellow needles, mp 196–197.5°, $C_{16}H_{16}O_6$, was light pink under UV radiation, and gave positive $FeCl_3$ and Gibbs tests. Its UV and IR spectra suggested the presence of a hydroxy-naphthalene skeleton having a chelated carbonyl group. Its ^{1}H NMR spectrum showed the presence of a Me group, two —CH_2— groups, an OMe group, three aromatic protons, an alcoholic OH group and two chelated phenolic OH groups. The positions of the functional groups were confirmed by spin-decoupling experiments. A NOE experiment showed that irradiation of the OMe protons at δ 3.89 increased the area of the H-9 (δ 6.54, 35%) and H-7 (δ 6.57, 19%) signals, respectively. Irradiation of H-6 at δ 6.93 caused an increase of peak height of H-5 at δ 2.77 by long range coupling. Therefore, it was considered that **3** had a naphthalene skeleton similar to isotoralactone. The structure of the third ring was deduced from the ^{13}C NMR spectra, which showed signals from a Me group (δ 21.7), a —CH_2— group (δ 33.6), a —OCH_2— group (δ 66.4), a quaternary carbon (δ 84.7) and a CO group (δ 170.2). Thus, the structure of **3** was established as 8-methoxy-4-methyl-1-oxo-4,10,11-trihydroxy-naphtho(2,3-*c*)oxepin.

Biogenetically cassialactone may be derived from torosachrysone by a Baeyer–Villiger-type oxidation.

EXPERIMENTAL

Plant material was obtained from the Drug Plant Garden of the College of Science and Technology, Nihon University.

Extraction and purification of torosachrysone (**1**). Crushed *Cassia obtusifolia* L. seeds (1 kg) were mixed with H_2O (1 l.), and extracted with C_6H_6 (3 × 8 l.). The extract was chromatographed over silicic acid (Mallinckrodt) using C_6H_6–EtOAc (9:1) and subsequently C_6H_6–EtOAc (4:1) to afford a mixture of **1** and

aurantio-obtusin. The mixture was then chromatographed through a Sephadex LH-20 column in MeOH to give **1** (5 mg).

Extraction and purification of isotoralactone (**2**) *and cassialactone* (**3**). Crushed seeds (5 kg) were extracted with 70% MeOH and the filtrates were evapd to syrup. The syrup was partitioned with C_6H_6 several times. The C_6H_6 extract was chromatographed over silicic acid using C_6H_6 to afford chrysophanol, physcion, **2** (200 mg), and rubrofusalin, and subsequently with C_6H_6–EtOAc (9:1) to afford obtusifolin, emodin and obtusin, and with C_6H_6–EtOAc (4:1) to afford chryso-obtusin, aurantio-obtusin and a mixture of aurantio-obtusin and **3**. The mixture gave **3** (60 mg) after chromatography on Sephadex LH-20 with MeOH.

Torosachrysone (**1**) was recrystallized from C_6H_6 to give yellow needles, mp 196–200°. High resolution MS: Found: 288.0998, calcd for $C_{16}H_{16}O_5$: 288.0997; UV $\lambda_{max}^{dioxane}$ nm: 271, 305, 314, 328, 390; IR ν_{max}^{KBr} cm^{-1}: 3300, 1640, 1580.

Isotoralactone (**2**) was recrystallized from C_6H_6 to give pale yellow needles, mp 233–235° (dec.). High resolution MS: Found: 272.0654, calc. for $C_{15}H_{12}O_5$: 272.0683; UV $\lambda_{max}^{dioxane}$ nm (log ε): 264 (4.78), 292 (3.75), 308 (3.64), 370 (4.05); IR ν_{max}^{KBr} cm^{-1}: 3400, 1675, 1645, 1630, 1580; MS 70 eV *m/z* (rel. int.): 272 (M^+, 100), 230 ($M^+ - CO{=}CH_2$, 53), 202 ($M^+ - CO{=}CH_2{-}CO$, 6). Acetylation of **2** (10 mg) with Ac_2O (1 ml) and pyridine (1 ml) gave pale yellow needles (**5**) (5 mg), mp 244–245° (from Me_2CO). High resolution MS: Found: 356.0873, calc. for $C_{19}H_{16}O_7$: 356.0894; UV $\lambda_{max}^{dioxane}$ nm (log ε): 272 (4.84), 284 (4.92), 310 (3.79), 323 (3.78), 340 (sh, 3.55), 374 (3.40); IR ν_{max}^{KBr} cm^{-1}: 1765, 1720, 1670, 1630, 1570. **5** was found to be identical with toralactone diacetate, by spectral comparison with an authentic sample.

Cassialactone (**3**) was recrystallized from MeOH to give very pale yellow needles, mp 196–197.5°, $[\alpha]_D^{22}$ − 17.2° (dioxane: *c* 0.41). High resolution MS: Found: 304.0907, calc. for $C_{16}H_{16}O_6$: 304.0945; UV $\lambda_{max}^{dioxane}$ nm (log ε): 260 (4.79), 298 (sh, 3.64), 307 (3.68), 364 (4.06), 374 (sh, 4.05); IR ν_{max}^{KBr} cm^{-1}: 3400, 2950, 1640, 1580; ^{13}C NMR (25.2 MHz, DMSO-d_6): δ 21.9 (*q*), 33.6 (*t*), 55.5 (*t*), 66.4 (*q*), 84.7 (*s*), 99.2 (*s*), 99.2 (*d*), 101.2 (*d*), 108.1 (*s*), 116.6 (*d*), 133.2 (*s*), 146.7 (*s*), 157.9 (*s*), 162.0 (*s*), 170.2 (*s*); MS 70 eV *m/z* (rel. int.): 304 (M^+, 100), 286 ($M^+ - H_2O$, 11), 258 ($M^+ - H_2O - CO$, 36), 257 ($M^+ - H_2O - CHO$, 25), 256 ($M^+ - H_2O - OCH_2$, 11), 243 ($M^+ - H_2O - CO - Me$, 13), 241 ($M^+ - H_2O - COOH$, 13), 240 ($M^+ - 2H_2O - CO$, 23).

Conversion of **2** *to toralactone* (**4**). A soln of **2** (10 mg) dissolved in 3% HCl–Me_2CO was left overnight. The soln was concd *in vacuo*, and the residue was recrystallized from C_6H_6 to give **4** (4 mg), which was identified by direct comparison with an authentic sample (mmp and IR).

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