

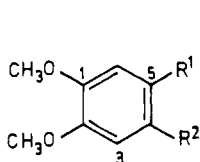
# CONSTITUENTS OF *ACORUS CALAMUS*: STRUCTURE OF ACORAMONE. CARBON-13 NMR SPECTRA OF *CIS*- AND *TRANS*-ASARONE

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**ABSTRACT.**—The phenylpropane derivatives isoeugenol methyl ether (1),  $\gamma$ -asarone (2), *cis*-asarone (3), *trans*-asarone (4) and the new natural product acoramone (5) have been isolated along with asarylaldehyde (6) from the oil of *Acorus calamus* Linn. The carbon-13 nmr signal assignments of 3, 4 and their dihydroderivative 7 are also reported.

In a previous communication (1) we reported the isolation of 2,4,5-trimethoxybenzaldehyde, 2,5-dimethoxybenzoquinone, galangin and sitosterol along with the new cyclobutanolignan acoradin from the rhizomes of *Acorus calamus* Linn. Further investigation has resulted in the isolation of isoeugenol methyl ether (1),  $\gamma$ -asarone [1,2,4-trimethoxy-5(2-propenyl)benzene] (2), *cis*-asarone [ $\beta$ -asarone or *cis*-1,2,4-trimethoxy-5(1-propenyl)benzene] (3), *trans*-asarone [ $\alpha$ -asarone or *trans*-1,2,4-trimethoxy-5(1-propenyl)benzene] (4) and acoramone [1,2,4-trimethoxy-5(2-propanonyl)benzene or 1(2,4,5-trimethoxyphenyl)-propan-2-one] (5) along with asarylaldehyde [2,4,5-trimethoxybenzaldehyde] (6) from the oil of the same



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|---|---|----|
|   | 1'  | 3' |
| 1 | R <sup>1</sup> = -CH = CH-CH <sub>3</sub> ( <i>trans</i> ), R <sup>2</sup> = H                        |    |
| 2 | R <sup>1</sup> = -CH <sub>2</sub> -CH = CH <sub>2</sub> , R <sup>2</sup> = OCH <sub>3</sub>           |    |
| 3 | R <sup>1</sup> = -CH = CH-CH <sub>3</sub> ( <i>cis</i> ), R <sup>2</sup> = OCH <sub>3</sub>           |    |
| 4 | R <sup>1</sup> = -CH = CH-CH <sub>3</sub> ( <i>trans</i> ), R <sup>2</sup> = OCH <sub>3</sub>         |    |
| 5 | R <sup>1</sup> = -CH <sub>2</sub> COCH <sub>3</sub> , R <sup>2</sup> = OCH <sub>3</sub>               |    |
| 6 | R <sup>1</sup> = -CHO, R <sup>2</sup> = OCH <sub>3</sub>  |    |
| 7 | R <sup>1</sup> = -CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> , R <sup>2</sup> = OCH <sub>3</sub> |    |

specimen. Their structures have been established mainly from their various spectral characteristics. This is the first report of the occurrence of 5 from a natural source. Probably 3 or 4 is the precursor of the congener lignan acoradin.

## EXPERIMENTAL

**EXTRACTION AND CHROMATOGRAPHY.**—Chloroform extract of the air-dried, milled rhizomes of *A. calamus* afforded an abundance of essential oil which was chromatographed over silica gel. The residue (0.5 g) from the benzene eluates was separated into its constituents by the use of preparative gas chromatography over SE-30 (4.5 m x 0.8 mm). Isoeugenol methyl ether (1),  $\gamma$ -asarone (2), *cis*-asarone (3), *trans*-asarone (4), asarylaldehyde (6) and acoramone (5) were eluted successively. Distillation of the essential oils of *A. calamus* under reduced pressure afforded a major fraction, b.p. ~135° at 0.35 mm which consisted mainly of 2, 3 and 4.

**TRANS-ISOEUGENOL METHYL ETHER (2, 3) (1).**—The compound was liquid (5 mg), C<sub>11</sub>H<sub>14</sub>O<sub>2</sub> (M<sup>+</sup> 178). It displayed 80 MHz pmr signals (CDCl<sub>3</sub>) at  $\delta$  1.88 (3H, d,  $J$  = 5.6 Hz, -CH = CH-CH<sub>3</sub>), 3.87 and 3.89 (each 3H, s, two OCH<sub>3</sub>), 6.02 (1H, dq,  $J$  = 16 Hz & 5.6 Hz, H-2'), 6.37 (1H, d,  $J$  = 16 Hz, H-1') and 6.7-7.0 ppm (3H, m, H-3, H-4 & H-6) and ion peaks in the mass spectrum at  $m/e$  178 (M<sup>+</sup>, 100%), 163 (M<sup>+</sup>-CH<sub>3</sub>, 42%) and 135 (M<sup>+</sup>-CH<sub>3</sub>-CO, 30%).

**$\gamma$ -ASARONE (SEKISHONE) (2-4) (2).**—The constituent was a liquid (5 mg), C<sub>12</sub>H<sub>16</sub>O<sub>3</sub> (M<sup>+</sup> 208.1124, ca. 208.1099). It displayed the following spectral characteristics: 80 MHz pmr (CDCl<sub>3</sub>):  $\delta$  3.32 (2H, dd,  $J$  = 6.4 Hz & 1.2 Hz, -CH<sub>2</sub>-), 3.80, 3.83, and 3.88 (each 3H, s, three OCH<sub>3</sub>), 5.01 (2H, m, =CH<sub>2</sub>), 5.90 (1H, m, -CH=), 6.53 (1H, s, H-3) and 6.69 ppm (1H, s, H-6); high resolution mass: ion peaks at  $m/e$  208.1124 (C<sub>12</sub>H<sub>16</sub>O<sub>3</sub>, M<sup>+</sup>, 100%), 193.0888 (C<sub>11</sub>H<sub>14</sub>O<sub>3</sub>, M<sup>+</sup>-CH<sub>3</sub>, 98%), 181.0884 (C<sub>10</sub>H<sub>12</sub>O<sub>3</sub>, M<sup>+</sup>-C<sub>2</sub>H<sub>3</sub>, 19%), 165.0936 (C<sub>10</sub>H<sub>12</sub>O<sub>2</sub>, M<sup>+</sup>-CH<sub>3</sub>-CO, 69%), 162.0731 (C<sub>10</sub>H<sub>10</sub>O<sub>2</sub>, M<sup>+</sup>-CH<sub>3</sub>-H-OCH<sub>2</sub>, 21%), 150.0642 (C<sub>9</sub>H<sub>10</sub>O<sub>2</sub>, M<sup>+</sup>-CH<sub>3</sub>-CO-CH<sub>3</sub>, 19%) and 133.0086 (C<sub>8</sub>H<sub>8</sub>O, M<sup>+</sup>-CH<sub>3</sub>-OCH<sub>2</sub>-OCH<sub>2</sub>, 42%).

***CIS*-ASARONE (5) (3).**—The constituent identified as *cis*-asarone was a liquid (68 mg), C<sub>12</sub>H<sub>16</sub>O<sub>3</sub> (M<sup>+</sup> 208.1123). It exhibited ir bands at 1605, 1580 & 1500 cm<sup>-1</sup> (aromatic) and 855 cm<sup>-1</sup> (*cis*-double bond) and 80 MHz pmr signals (CDCl<sub>3</sub>) at  $\delta$  1.84 (3H, dd,  $J$  = 7 Hz & 2 Hz, -CH = CH-CH<sub>3</sub>), 3.74, 3.79 and 3.83 (each 3H, s, three OCH<sub>3</sub>), 5.69 (1H, dq,  $J$  = 12 Hz & 7 Hz,

H-2'), 6.45 (1H, dq,  $J=12$  Hz & 2 Hz, H-1'), 6.47 (1H, s, H-3) and 6.79 ppm (1H, s, H-6) and ion peaks in its mass spectrum at  $m/e$  208.1123 ( $C_{12}H_{16}O_3$ ,  $M^+$ , 100%), 193.089 ( $C_{11}H_{13}O_3$ ,  $M^+-CH_3$ , 47%), 165.0939 ( $C_{10}H_{13}O_2$ ,  $M^+-CH_3-CO$ , 24%) and 162.0733 ( $C_{10}H_{13}O_2$ ,  $M^+-CH_3-H-OCH_2$ , 11%). These data are in good agreement with its assigned structure, which was also supported by its C-13 nmr spectrum (table 1).

TABLE 1. Carbon-13 chemical shifts<sup>a</sup> of *cis*-asarone (3), *trans*-asarone (4) and their dihydroderivative (7).

	3	4	7
C-1.....	141.8	142.6	142.4
C-2.....	148.0	148.0	147.2
C-3.....	97.2	97.3	97.7
C-4.....	150.9	149.9	151.1
C-5.....	117.6	118.3	122.3
C-6.....	113.7	109.2	114.2
C-1'	125.1	124.4	31.1
C-2'	124.3	123.4	22.8
C-3'	14.6	18.7	13.3
OCH <sub>3</sub> .....	55.8	55.1	55.6
	56.2	55.7	55.6
	56.4	56.1	56.1

<sup>a</sup>The chemical shifts are in  $\delta$  (ppm). The <sup>13</sup>C nmr spectra were recorded in CDCl<sub>3</sub>;  $\delta$  TMS =  $\delta$  CDCl<sub>3</sub> + 76.9 ppm.

*TRANS*-ASARONE (6) (4).—*Trans*-asarone (370 mg), mp 48° (EtOH-H<sub>2</sub>O),  $C_{12}H_{16}O_3$  ( $M^+$  208.1127) showed the following spectral characteristics:  $\lambda$  max (EtOH) at 258 nm (log  $\epsilon$  3.83) and 313 (4.15);  $\nu$  max (KBr) at 1600, 1585 & 1560 (aromatic) and 965  $cm^{-1}$  (*trans*-double bond); 80 MHz pmr signals (CDCl<sub>3</sub>) at  $\delta$  1.87 (3H, dd,  $J=6.2$  Hz & 1.5 Hz,  $-CH=CH-CH_3$ ), 3.77, 3.81 and 3.84 (each 3H, s, three OCH<sub>3</sub>), 6.02 (1H, dq,  $J=16$  Hz & 6.2 Hz, H-2'), 6.45 (1H, s, H-3), 6.64 (1H, dq,  $J=16$  Hz & 1.5 Hz, H-1') and 6.91 ppm (1H, s, H-6); ion peaks in the mass spectrum at  $m/e$  208.1127 ( $C_{12}H_{16}O_3$ ,  $M^+$ , 100%), 193.0886 ( $C_{11}H_{13}O_3$ ,  $M^+-CH_3$ , 45%), 165.0935 ( $C_{10}H_{13}O_2$ ,  $M^+-CH_3-CO$ , 24%) and 162.0736 ( $C_{10}H_{13}O_2$ ,  $M^+-CH_3-H-OCH_2$ , 11%). The assigned structure 4 also received support from its carbon-13 nmr spectrum (table 1).

ACORAMONE (5).—Acoramone,  $C_{12}H_{16}O_4$  ( $M^+$  224), was isolated as a liquid (5 mg). It exhibited ir bands at 1715 (C=O), 1605 & 1510  $cm^{-1}$  (aromatic); 80 MHz pmr signals (CDCl<sub>3</sub>) at  $\delta$  2.13 (3H, s,  $-COCH_3$ ), 3.61 (2H, s,  $ArCH_2CO-$ ), 3.79, 3.82 and 3.89 (each 3H, s, three OCH<sub>3</sub>), 6.58 (1H, s, H-3) and 6.66 ppm (1H, s, H-6); ion peaks in the mass spectrum at  $m/e$  224.1064 ( $C_{12}H_{16}O_4$ ,  $M^+$ , 33%), 182.0886 ( $C_{10}H_{14}O_3$ ,  $M^+-CH_2CO$ , 12%), 181.0865 ( $C_{10}H_{13}O_3$ ,  $M^+-CH_3CO$ , 100%), 151.0767 ( $C_9H_{11}O_2$ ,  $m/e$  181.0865  $-CH_2O$ , 35%) and 136.0489 ( $C_8H_9O_2$ ,  $m/e$  151.0767  $-CH_3$ , 11%).

Catalytic hydrogenation of *cis*-asarone or *trans*-asarone in the presence of 10% Pd-C in ethanol afforded the dihydroderivative 7, the structure of which was established from its <sup>13</sup>C nmr spectrum (table 1).

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